Appendix 3A
Software documentation

Acute-to-Chronic Estimation (ACE v 2.0)
BurrliOZ Help, Licensing, Readme file
Level I Fugacity Model License, Description, Update
Level II Fugacity Model Licence, Description, Update
Level III Fugacity Model Licence, Description, Update
ETX 1.3
ETX 2.0
EXAMS
Interspecies Correlation Estimations (ICE v 1.0)

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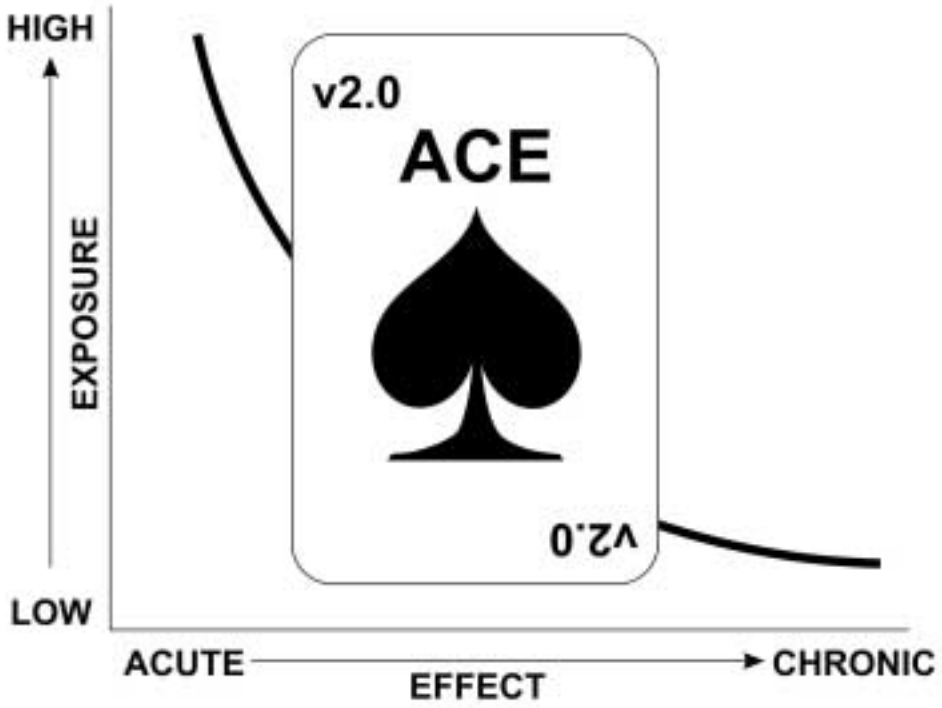
December 2003

Acute-to-Chronic Estimation (Ace v 2.0) with Time - Concentration - Effect Models

User Manual and Software



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Acute-to-Chronic Estimation (ACE v 2.0) with Time-Concentration-Effect Models

User Manual and Software

By

Mark R. Ellersieck, Amha Asfaw, Foster L. Mayer*, Gary F. Krause, Kai Sun, and Gunhee Lee

University of Missouri-Columbia
College of Agriculture, Food and Natural Resources
Agricultural Experiment Station-Statistics
Columbia, MO 65211

*U.S. Environmental Protection Agency
Office of Research and Development
National Health and Environmental Effects Research Laboratory
Gulf Ecology Division
Gulf Breeze, FL 32561-5299

U.S. Environmental Protection Agency
Office of Research Development
1200 Pennsylvania Avenue, NW
Washington, DC 20460

Notice

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Abstract

Predictive toxicological models, including estimates of uncertainty, are necessary to address probability-based ecological risk assessments. Methods and software (ACE) were developed for estimating chronic toxicity from raw acute toxicity data (all response observations at all times and exposures). Three methods were developed - - Accelerated Life Testing (ALT), Multifactor Probit Analysis (MPA), and two-stage Linear Regression Analysis (LRA). Of the three, the method of choice is ALT, in that time to failure (death) of each experimental unit is independent. It requires three partial responses over the time period of acute testing, but will function with one. The MPA is a two dimensional probit analysis using both time and concentration to produce a multiple regression equation, however, each experimental unit is not independent. Also, the MPA requires more partial responses than the ALT. The LRA calculates LC values for each time period and then regresses the LC values as the Y axis and the reciprocal of time as the X axis. The Y intercept is the chronic no-effect concentration. The LRA will function when ALT and MPA fail; no partial responses are required. All methods provide confidence limits for the point estimates. The methods have previously been shown to estimate chronic no-effect concentrations very well when validated against actual paired acute and chronic test results with fishes.

Introduction

Both understanding and evaluating chronic toxicity of chemicals are essential to assessing their ecological hazards and making environmentally sound management decisions. Because of the large number and variety of industrial, agricultural and home-use chemicals released in the U.S. annually and the high cost and effort required for chronic tests, resources are often insufficient to obtain experimental information about long-term environmental impacts for all potentially hazardous chemicals. In comparison, acute tests are less costly and time consuming and, for these reasons, an abundance of acute toxicity data exists for numerous chemicals and organisms. Also, procedures have been developed for extrapolating effects data within classes of chemicals sharing similar chemical structures (Lipnick 1995). Thus, there is a strong rationale to relate acute and chronic toxicities of chemicals and to develop statistical and mathematical techniques to predict chronic toxicity based on data from acute experiments.

Use of short-term tests as a basis for linkage of exposure and time to response with chronic effects for ecological risk assessments is significant. The ability to accurately and precisely associate chronic effects from acute time-concentration-effect data is a powerful approach that integrates various aspects of toxicokinetics and directly addresses a variety of uncertainties in terms of chronicity. Three models were developed (Lee et al. 1995; Mayer et al. 1994, 2002; Sun et al. 1995b), tying together classical methods (e.g., probit regression) (Finney 1978) and time to event methods (Newman 1994) to provide models that predict chronic toxicity from acute toxicity data.

- Accelerated Life Testing (ALT) – A survival analysis and population-based approach (Weibull distribution) using accelerated life testing theory (Mayer et al. 2002, Sun et al. 1995b). The method was originally used for mechanical and electrical devices placed under short-term or "acute" stress (e.g., generator running constantly at full power and high heat) to predict long-term or "chronic" time to failure. In the ACE software, the model is applied to organisms placed under acute stress (i.e., toxicant), and the variable measured is time to failure or death. The model assumes that both exposure concentrations and duration affect survival probability, and hence, has the ability to summarize the entire concentration-time-response data of a toxicity test. Actual proportion responses are used; probit transformations are not applied. ALT also takes into account the spontaneous survival probability and is suitable to describe both acute and chronic lethality data. The survival function includes competing risks, with contaminant exposure being one.

- Multifactor Probit Analysis (MPA) – Multiple regression models that simultaneously evaluate the relationship among exposure concentration, time, and probit % mortality to predict chronic response (Mayer et al. 2002, Lee et al. 1995). This model is appropriate when different experimental units are present for concentration-time combinations (i.e., one complete replicate is removed at one or more time intervals for a measurement different than survival; only the remaining replicates are used for the remainder of the toxicity test). ALT and LRA models are more appropriate for predicting chronicity from standard acute toxicity data; however, multiple regression models, such as MPA, are necessary when estimating chronicity under changing conditions (e.g., varying exposure scenarios in effluents).

- Linear Regression Analysis (LRA) – A two-step linear regression analysis (Mayer et al. 1994, Mayer et al. 2002). This model combines two linear regressions: 1) estimates low lethal concentrations at each observation time period and 2) regresses those concentrations (dependent variable) against the reciprocal of time (independent variable), with the intercept being the chronic no-effect concentration. Probit transformations of percent response are used.

The software program, Acute-to-Chronic Estimation (ACE), described herein, allows the user to estimate chronic toxicity for a species from raw acute toxicity data with accuracy and precision. ACE will, therefore, greatly enhance the use of probability-based risk assessments for chemicals having minimal data sets. However, if a chronic test is to be conducted, ACE can be used to more accurately identify the range of exposure concentrations required. ACE is based on the Windows platform and is specifically designed

for estimating chronic toxicity and providing graphical and tabular presentation of results. ACE v 2.0 is an upgrade of the former DOS version (Mayer et al. 1999).

Background

Using acute mortality data to estimate chronic toxicity (survival, growth, reproduction) to aquatic organisms customarily involves deriving an application factor (Mount and Stephan 1967) or an acute-to-chronic ratio (Kenaga 1982), both of which require acute and chronic toxicity testing. Kenaga (1979) reviewed the principal measurements of the acute LC50, the maximum acceptable toxicant concentration (MATC), and the application factor (AF) used in determining chronic NOECs (highest concentration causing 0% or no statistically significant effect) for many chemicals. The AF is derived by dividing the MATC for a compound, as determined in a chronic toxicity test with a given species, by the acute LC50 for the same compound tested with the same species. The acute-to-chronic ratio (ACR) is the inverse of the AF. The AF or ACR is then used to estimate chronic NOECs for other species for which only acute toxicity data (EC or LC50s) exist (Buikema et al. 1982). These approaches have limitations.

One limitation is that the biological endpoints and degrees of responses are often not comparable between acute and chronic toxicity data. When either the AF or ACR is used, the acute median lethal concentration (EC or LC50) is compared with the MATC, often derived from an endpoint other than mortality. Although different degrees of response (acute 50% vs. chronic no-effect) could be used when response slopes are similar, the slopes may be different. Additionally, use of the AF or ACR method does not take into consideration the progression of mortality through time that is derived in acute toxicity tests. The concentration-time-response interaction has been addressed by Shirazi and Lowrie (1988), but they directed their efforts toward better defining the LC50. The acute toxicity value represents only one point in time (e.g., 96-h LC50), and the relationship of degree of response with duration of exposure should be essential when chronic toxicity is predicted from acute toxicity data.

Lethality and other toxic effects are dependent on both concentration of a chemical to which an organism is exposed and length of exposure time. It is a common practice to investigate the toxicity of new and existing chemicals and effluents using acute toxicity tests. This is done by observing mortality resulting from exposure to a series of chemical concentrations, usually at 24, 48, 72, and 96 h. Time course distinguishes acute from chronic toxicity and also relates them as an integrated and progressive process. A time to response approach gives a better understanding of the progression of toxic effects over time, and survival time modeling has shown great applicability in toxicological studies (Crane et al. 2002, Dixon and Newman 1991, Newman and Aplin 1992).

The models included here are more comprehensive approaches to predicting chronicity, both toxicologically and statistically. Simultaneous consideration is given to exposure concentration, degree of response, and time course of effect, all of which are usually included in describing the results of an acute toxicity test, but are seldom used in hazard assessment. A consistent endpoint (mortality) and degree of response (~0%) are used to predict long-term (chronic) lethality from acute toxicity test data. These calculations are based solely on raw acute toxicity test data and do not require conducting a chronic toxicity test. Estimated long-term (chronic) lethality values have previously been validated for accuracy with actual chronic no-effect values derived for 28 chemical-fish species combinations (Mayer et al. 2002).

Software Language

The ACE software is based on a Windows® platform and written in Visual Basic (Microsoft® Visual Basic 6.0 1987-2000). Subroutines (Fortran programs) in Visual Basic and Visual Fortran are required to call Fortran IMSL Routines necessary in certain calculations (Compaq Fortran 1999, Visual Numeric 1999).

Installing ACE

System Requirements

- Operates on Microsoft Windows 95, 98, 2000, NT and XP (Windows® 98 or later is suggested).
- Minimum 16 MB RAM (64 MB or greater is suggested).
- CPU speed of over 200 MHz is suggested; ACE will work with less, but is very slow.
- 6MB hard disk space.
- Mouse or pointing device.
- Printer (optional).

Remove any existing versions of ACE before installing the new one or malfunctions may occur.

To remove old ACE software:

1. Double click **My Computer**.
2. Double click **Control Panel**.
3. Double click **Add/Remove Programs**.
4. Click **ACE**.
5. Click **Delete** or **Change/Remove**.

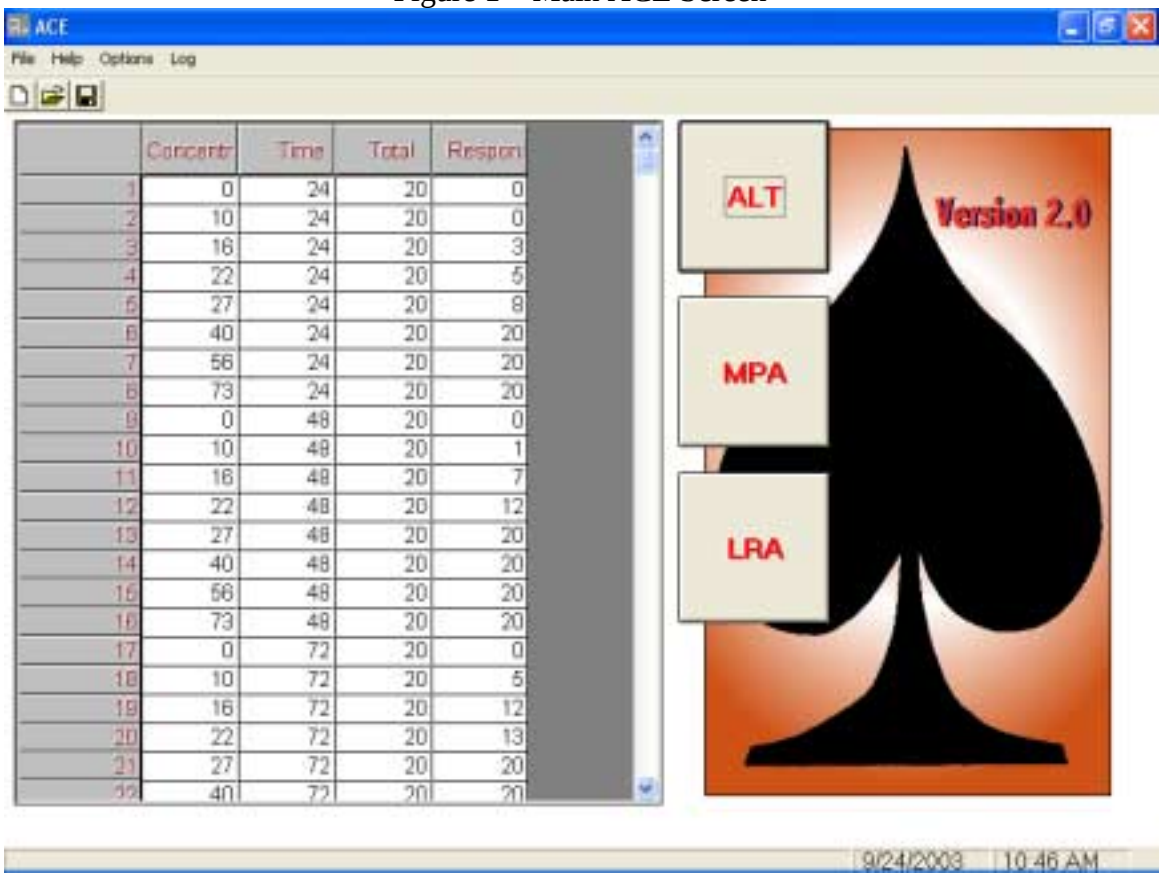
To install new ACE software:

1. Place the ACE CD in the CD ROM drive.
2. Click **Start** button.
3. Select **Run** from the menu.
4. Select **Browse** from the **Run** window.
5. Select drive letter associated with the CD drive from **Browse** window (or ACE 2003 [D:]).
6. Double-click **Setup** file or **D:\SETUP.EXE** file.
7. Click **OK**.
8. Windows now walks you through the installation process. If a "Yes" or "No" question is encountered, choose "Yes".
9. Following installation, the ACE program can be accessed by clicking **Start**, **Programs**, and then **ACE**. You can create an icon on the Desktop screen by placing the mouse pointer on the ACE icon, holding down on the control button, and dragging the icon to desired location on the screen.

Using ACE in Windows

Double click on the ACE icon in the Desktop screen and the main ACE screen will appear (Fig. 1). There are three main sections to the screen. The first section (left) is for data entry or for including data from other sources (e.g., Excel, Lotus 123, etc.). The second section (right center) represents the models available in ACE (ALT, accelerated life testing; MPA, multifactor probit analysis; LRA, linear regression analysis). The third section is the ACE logo, appearing in the background at right. Following data entry and conversion to ASCII files (see below), click on the box for the model of choice (ALT, MPA, LRA), and the analysis results and graphics will automatically be generated.

Figure 1 – Main ACE Screen



Menu Bar - Main Screen

File – Clicking on **File** provides the following drop down menu:

- **New** – Clears spreadsheet so new data can be entered.
- **Open** – Obtains a saved data set from an outside source (see **Obtaining Data from an Outside Source**).
- **Save** – Saves any changes back to the same file name.
- **Save As** – Saves a data set for the first time or saves an existing data set to a new file name.
- **Exit** – Clicking on **Exit** will end the ACE program; clicking on **X** in the upper right-hand corner of the main ACE window will perform the same function as **Exit**.
- Help – User manual.

Options – Option screen will appear; see **OPTIONS** for explanation.
Log – If the ACE program does not run, then an error list will appear; the screen will be empty if no problems occur.
Sheet icon – This is the same as **New** under the **File** drop down menu.
File icon – This is the same as **Open** under the **File** drop down menu.
Floppy disk icon – This is the same as **Save** under the **File** drop down menu.

Menu Bar - ALT, MPA, LRA

- **Print** – Allows printing of selected output (statistical output, graph, or log).
- **Save_on_file** – Saves the statistical output to a file; this is the same as **Save as** described previously.

- **Log** – Provides additional statistical output information.

Data Entry

Format

The following acute toxicity data set for Kepone (Buckler et al. 1981) is used to demonstrate data formatting. The data must be entered in column format as follows, except that columns may be in any order; each column is identified by column headers in the first window (Fig. 1). Data must be entered in the following format for rows:

Concentration	Time (h)	Total (# of Organisms Tested)	Response (# Dead)
0	24	20	0
10	24	20	0
16	24	20	3
22	24	20	5
27	24	20	8
40	24	20	20
56	24	20	20
73	24	20	20
0	48	20	0
10	48	20	1
16	48	20	7
22	48	20	12
27	48	20	20
40	48	20	20
56	48	20	20
73	48	20	20
0	72	20	0
10	72	20	5
16	72	20	12
22	72	20	13
27	72	20	20
40	72	20	20
56	72	20	20
73	72	20	20
0	96	20	0
10	96	20	5
16	96	20	12
22	96	20	13
27	96	20	20
40	96	20	20
56	96	20	20
73	96	20	20

Entering Data Directly

Acute toxicity data can be entered directly to ACE using the spreadsheet (Fig. 1) and keypad functions. The following keypad functions are operational in the spreadsheet: arrow keys, Delete key, Enter key

(functions the same as the down arrow key), and number keys. Each column has to be identified for the ACE program to function properly. Click on each of the column headers, click on arrow, and select appropriate descriptor for that column.

- ID – This is not necessary if a single data set is entered. If more than one data set is to be entered, see **Entering Data from Outside Source** below.
- Concentration – Exposure concentration or % effluent (for extremely large numbers, convert to next higher unit [e.g., µg to mg]).
- Time – Observation time in hours, usually 24, 48, 72, and 96 hours (maximum times are 12).
- Total – Number of organisms exposed per concentration.
- Response – Number of organisms dead or affected.

The ACE default order of column designation is the same as above.

Next, enter the data, click on **File** and then **Save as** and enter a data set name in the file name box. The data set will be saved as a tab delimited file unless an extension name of CSV is typed. An extension name of CSV will results in a comma delimited file. The Tab or Comma delimited file types are preferred. The data are brought back into ACE by clicking on the icon file, data set to be analyzed, and **Open**. Then click on the model of preference (ALT, MPA, LRA), and the analysis is automatically conducted. If data are not analyzed, recheck the column headers to make sure they are correct.

Entering Data from Outside Source

The software is not meant to be a sophisticated spreadsheet, and the best way to enter multiple data sets is from an outside source using softwares capable of producing ASCII text files (e.g., Excel, Word, etc.). If data sets are stacked, a fifth column (ID) must be added in order to identify the different acute data sets.

Once data have been entered, save them as an ASCII file. This is done by clicking on **File** in the upper left corner and then clicking on **Save as**. The **Save as** screen will appear with two boxes at the bottom; **File name** and **Save as type:**. Type in a name for the data set in the File name box. Click **Save as type:**, a list of file types will appear. The following file types are appropriate for the ACE software: **Space delimited, Tab delimited** and **Comma delimited (CSV).** The Tab delimited or CSV file types are preferred.

Obtaining Data from Outside Source

To obtain a data set from an outside source while in the ACE program, click on the File icon in the upper left-hand corner and the following drop down menu will appear:

New Ctrl N
Open
Save
Save As
Exit

Click **Open**; if the data set is not listed in the **Open** screen, click **Files of type:**. Click arrow and then **All(*.*)**. If the file is still not present, click on **Look in:**. This will list all of the disk drives in your computer. Once the data set has been found, double click on the data set and the data will be entered into the ACE program. Again, data sets must be converted to Tab, Comma or Space delimited file types, with Tab and CSV being preferred.

Once the data set is imported into the ACE program in the correct format, title or other descriptive lines must be removed. Click on the line number in the spreadsheet for the line that is to be deleted (left side of main ACE window) and press the Delete key on keyboard.

Each column needs to be identified by the ACE program. Check the column headers on the Main ACE Screen. If they are correct, the program is ready to run. If not, click on each of the column headers and correct (see **Entering Data Directly**).

Data Correction

If data need to be corrected, it can be done within ACE. Just click on the cell, delete the incorrect number with the Delete key, and then correct the entry. If columns are too narrow to fully observe identifiers or numbers, widen the columns by placing the cursor on the right border of the column header and, while holding down the left mouse button, drag to the right until the desired width is achieved. Reverse this process to narrow the columns. Changes are saved by clicking on **File**, selecting either **Save** or **Save as**, entering a name for the data set in **File name:**, and clicking on **Save**.

Model Selection

Brief guidelines for using ACE and selecting the appropriate models are:

1. Exposure Type - Historically, three test exposure techniques have been used to determine acute toxicity for aquatic organisms (static, static renewal, and flow-through). Acute toxicity data used in ACE should be based on static renewal or flow-through techniques, since static exposure may give erroneous results, except for chemicals that are water soluble (see fluridone, Mayer et al. 1994). Further research is needed to determine at what octanol/water or solubility values static test data begin resulting in erroneous chronic predictions.

2. Model Preference – ALT is the method of choice, followed by LRA and MPA, based on experimental designs commonly used in acute toxicity testing. MPA is a special case application and is seldom used.

3. Partial Responses – Dependability of chronicity estimates is generally enhanced with increasing numbers of partial responses (% mortality >0<100%). Recommended partial responses are: ALT $\geq$ 3, MPA $\geq$ 5, and LRA $\geq$ 1. However, ALT will generally function with one partial response; LRA will function with no partial responses as long as there is an exposure-response in time. It is not uncommon to conduct acceptable acute toxicity tests where no partial responses occur, only 0 and 100%; under these conditions, the LRA is the model of choice.

4. Percent Effect for Chronicity – Recommended percent values to be selected for estimated chronic toxicity are: ALT = 1.0%, MPA = 0.01%, and LRA = 0.01%. Use of 0.01% for the MPA and LRA represents a very close approximation to zero on the probit scale (Mayer et al. 1994, Mayer et al. 2002). ALT differs in that 1.0% is presently considered the smallest detectable difference due to the model being population-based (small numbers of organisms usually exposed in each concentration). These percentages correspond well to statistically-based chronic no-effect concentrations for mortality using hypothesis testing (i.e., analysis of variance; Mayer et al. 2002).

ACE Application Windows

Data Analysis

Download a data set to the main ACE screen and click on a model (ALT, MPA, or LRA); the data will automatically be analyzed. Click on the **X** in the upper right hand corner to return to the main screen; a different model can then be selected. When you click on a model on the main screen, a split screen will appear; statistical output on the left and graphics on the right. Double click on either to fill screen; double click again to return to split screen. Click on the **X** in the upper right-hand corner of the main screen to exit ACE.

Printing Output

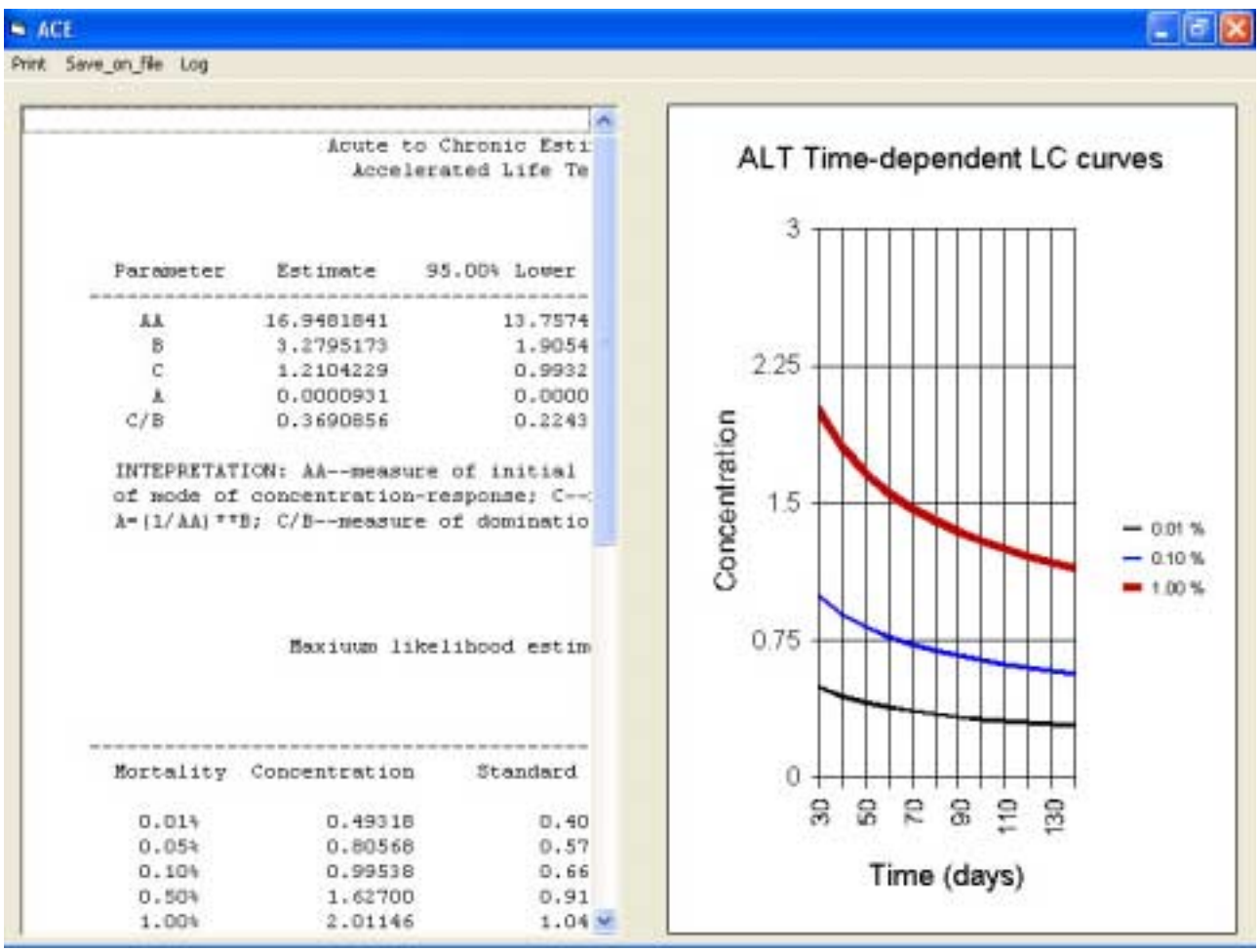
Printing of the statistical or graphics output is achieved by clicking **Print**, or the outputs can be saved by clicking **Save_on_file** (upper left-hand corner of screen). Additional statistical output can be obtained by clicking on **Log**. The output for **Log** includes the statistical output plus the additional information below and can also be printed or saved.

- ALT – Data input, iterations required to solve function estimates, variance-covariance matrix for function estimates to estimate confidence intervals, and data used in the analysis (the highest concentration having 0% response and the lowest concentration having 100% response are used for each observation time).
- MPA – Data used in the analysis as described in ALT.
- LRA – Statistical analyses for all six models including slope, estimated no-effect chronic concentration, confidence intervals, r^2, and data used in the analysis as described in ALT.

ALT- Accelerated Life Testing Model

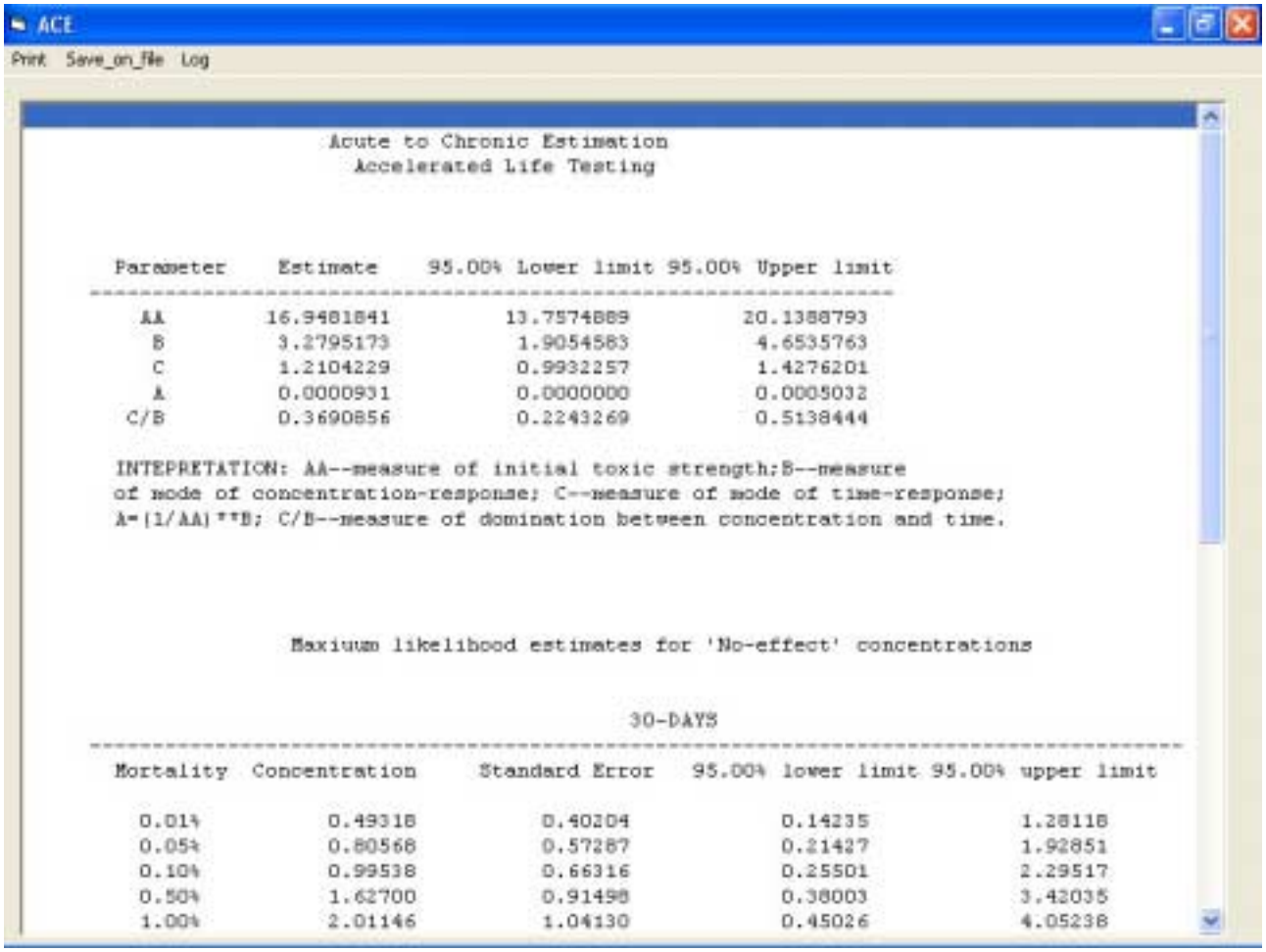
Click on the box **ALT** (Accelerated Life Testing) in the main ACE screen, and analysis of the downloaded acute toxicity data is performed (Fig. 2).

Figure 2 –Accelerated Life Testing (ALT) Screen



Double click on the statistical output screen (left side) in order to obtain the full screen (Fig. 3).

Figure 3 – ALT Full Screen



ACE

Print Save_on_file Log

Acute to Chronic Estimation
Accelerated Life Testing

Parameter	Estimate	95.00% Lower limit	95.00% Upper limit
AA	16.9481841	13.7574889	20.1388793
B	3.2795173	1.9054583	4.6535763
C	1.2104229	0.9932257	1.4276201
A	0.0000931	0.0000000	0.0005032
C/B	0.3690856	0.2243269	0.5138444

INTEPRETATION: AA--measure of initial toxic strength;B--measure of mode of concentration-response; C--measure of mode of time-response; A=(1/AA)**B; C/B--measure of domination between concentration and time.

Maxiuum likelihood estimates for 'No-effect' concentrations

30-DAYS

Mortality	Concentration	Standard Error	95.00% lower limit	95.00% upper limit
0.01%	0.49318	0.40204	0.14235	1.28118
0.05%	0.80568	0.57287	0.21427	1.92851
0.10%	0.99538	0.66316	0.25501	2.29517
0.50%	1.62700	0.91498	0.38003	3.42035
1.00%	2.01146	1.04130	0.45026	4.05238

There are two main parts to the statistical output. The first part contains statistical parameter estimates, along with confidence limits. Interpretation of these parameters follows the estimates. C/B provides an indication of the importance of exposure time (C) versus exposure concentration (B); if equal to one, both are equally important.

The second part of the statistical output is the maximum likelihood estimates of chronic no-effect concentrations. By default, analyses are performed for three different chronic times (30, 60 and 90 days). Within each time period are percent level of chronic mortality (0.01 – 10.0%; 1.0% is recommended for chronic survival with ALT), predicted toxicant concentration associated with each percentage, standard error of the predicted toxicant concentration, and confidence limits (default is 95% confidence limits).

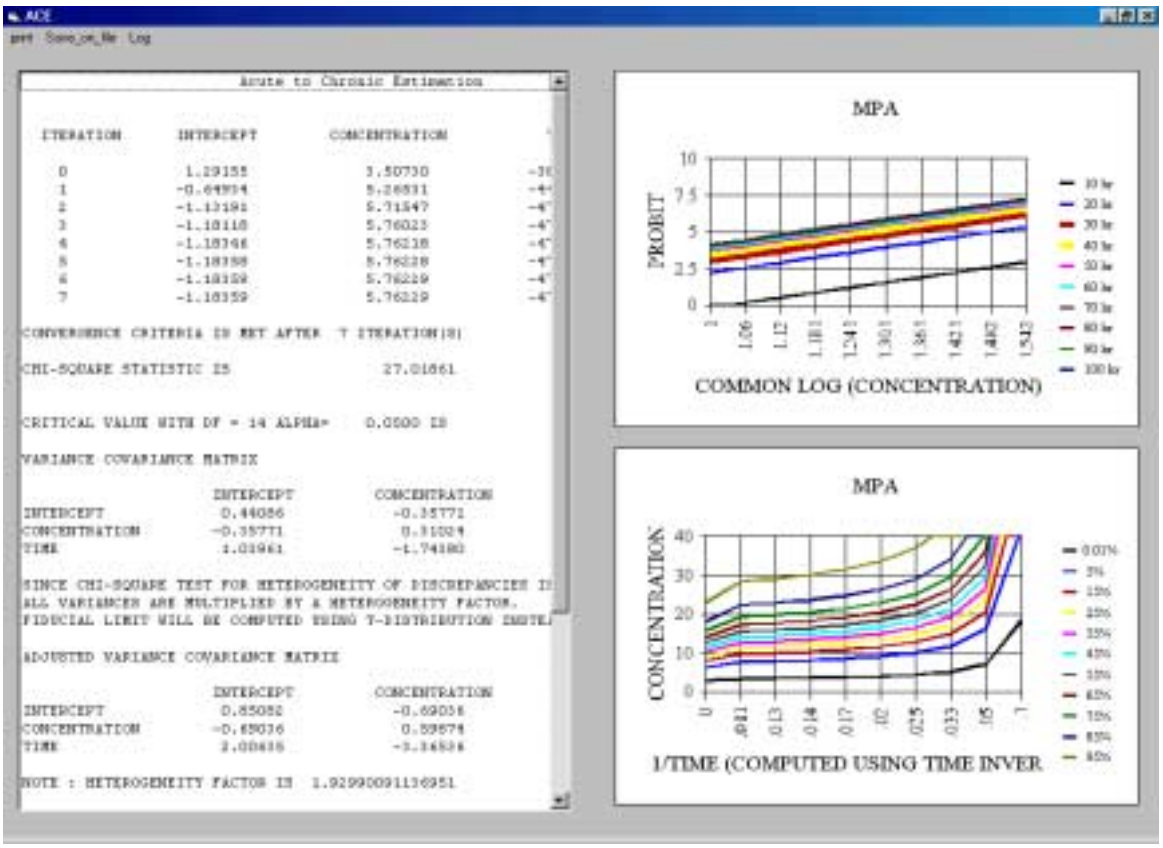
The ALT procedure will function even with a small number of partial responses in the raw acute toxicity data. However, the confidence limits may be large; an error message will appear and the ALT will fail if no partial responses are present in the data.

Additional chronic exposure times and the *alpha* level for confidence limits can be specified (see **Options**).

MPA – Multifactor Probit Analysis Model

Click on the box **MPA** (Multifactor Probit Analysis) in the main ACE screen, and analysis of the downloaded acute toxicity data is performed (Fig. 4).

Figure 4 – Multifactor Probit Analysis (MPA) Screen



Double click on the statistical output screen (left side) in order to obtain the full screen (Fig. 5).

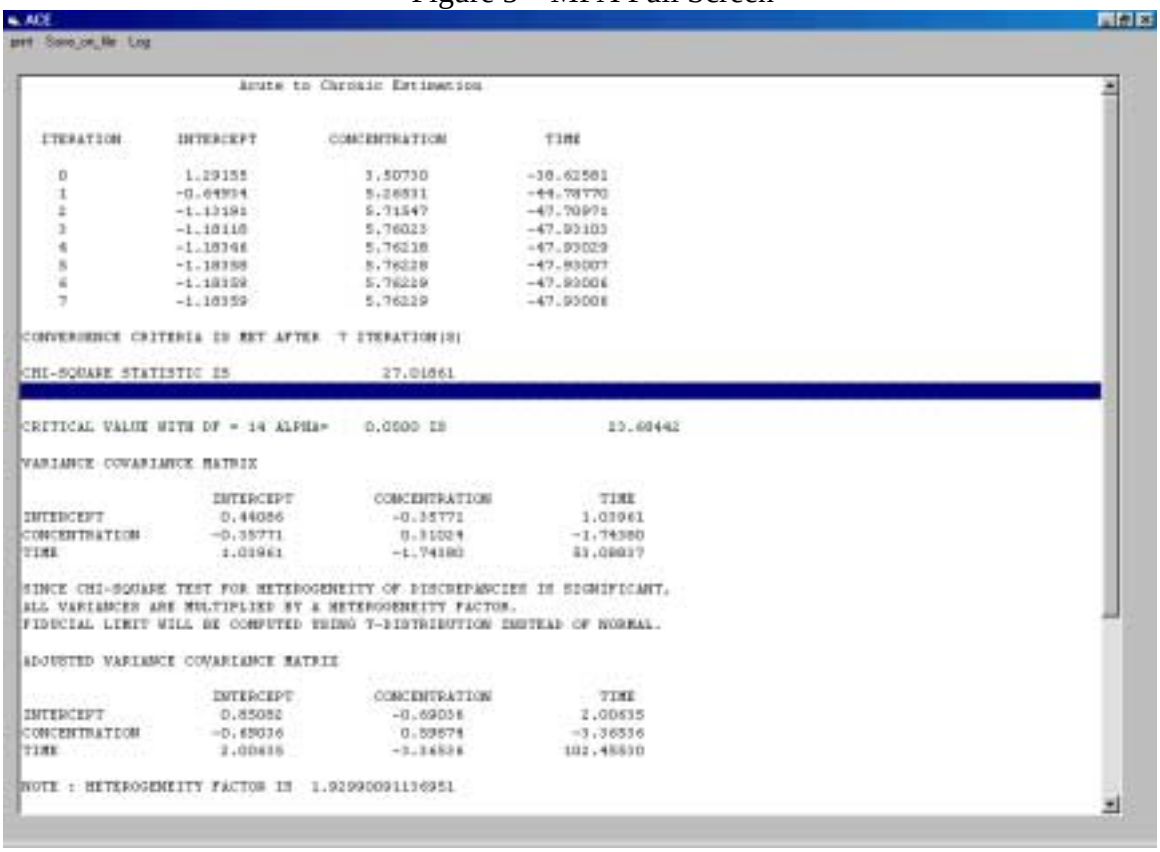
The output provides the number of iterations required to calculate factors for the MPA model, test statistics, variance-covariance matrix, and the predicted chronic no-effect concentrations along with 95% confidence limits.

The MPA includes four different models to choose from that may give different estimates of the MPA functions (see **Options**). The default model is Model 3 in **Options**:

$$\text{Probit}_p = \alpha + \beta(\text{Concentration}) + \Upsilon/\text{Time}$$

Chronic exposure time is specified and the assumption is that slopes change with a constant rate as observation times increase.

Figure 5 – MPA Full Screen



By default, there is one chronic time period (infinity). Within each time period are percent level of mortality (0.01 – 50%; 0.01% is recommended for MPA), predicted toxicant concentration associated with each percentage, and confidence limits (default = 95%). The data fit the model if the chi-square statistic is $\leq$ the critical chi-square value.

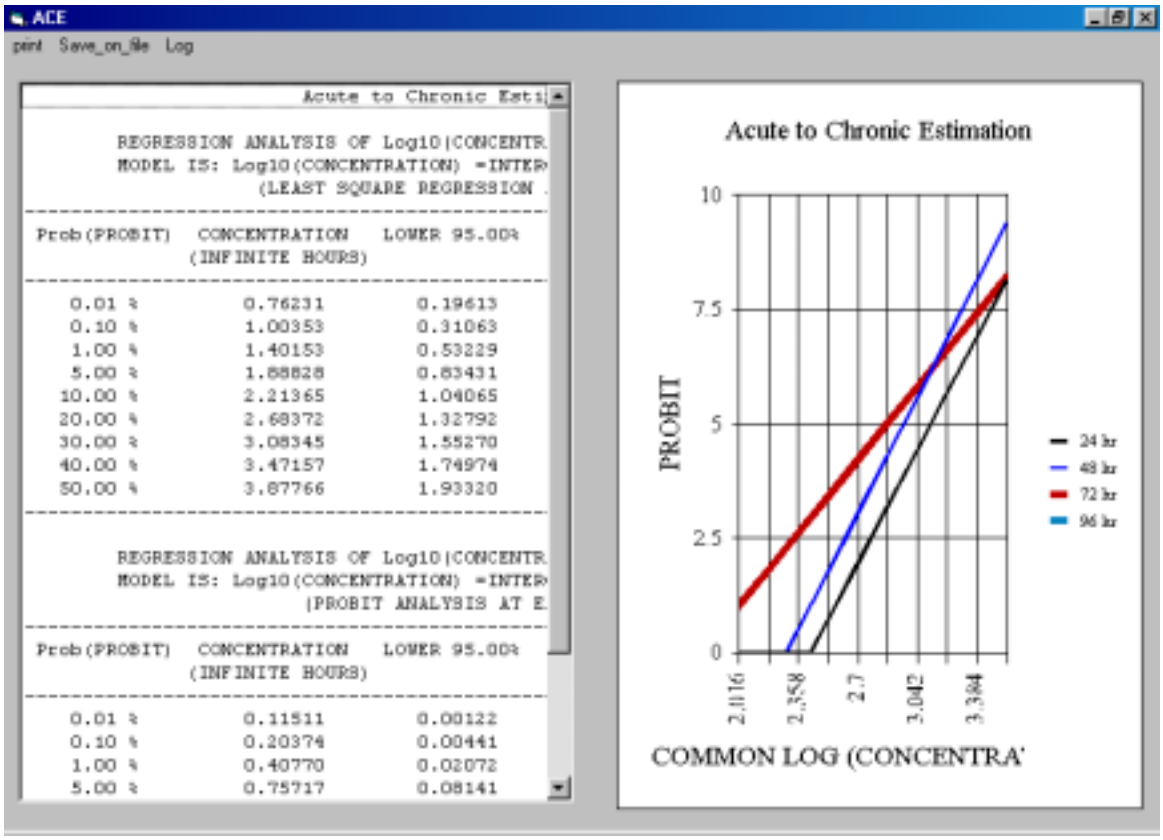
The MPA is the most sensitive to lack of partial mortalities (responses); at least five partial responses between 10 and 90% among all exposure concentrations and times are preferred. An error message will appear and MPA will fail if inadequate partial responses or an insufficient range of partial responses exist.

Additional chronic exposure times and the *alpha* level for confidence limits can be specified (see **Options**).

LRA - Linear Regression Analysis Model

Click on the box **LRA** (Linear Regression Analysis) in the main ACE screen, and analysis of the downloaded acute toxicity data is performed (Fig. 6).

Figure 6 – Linear Regression Analysis (LRA) Screen



Double click on the statistical output screen (left side) in order to obtain the full screen (Fig. 7).

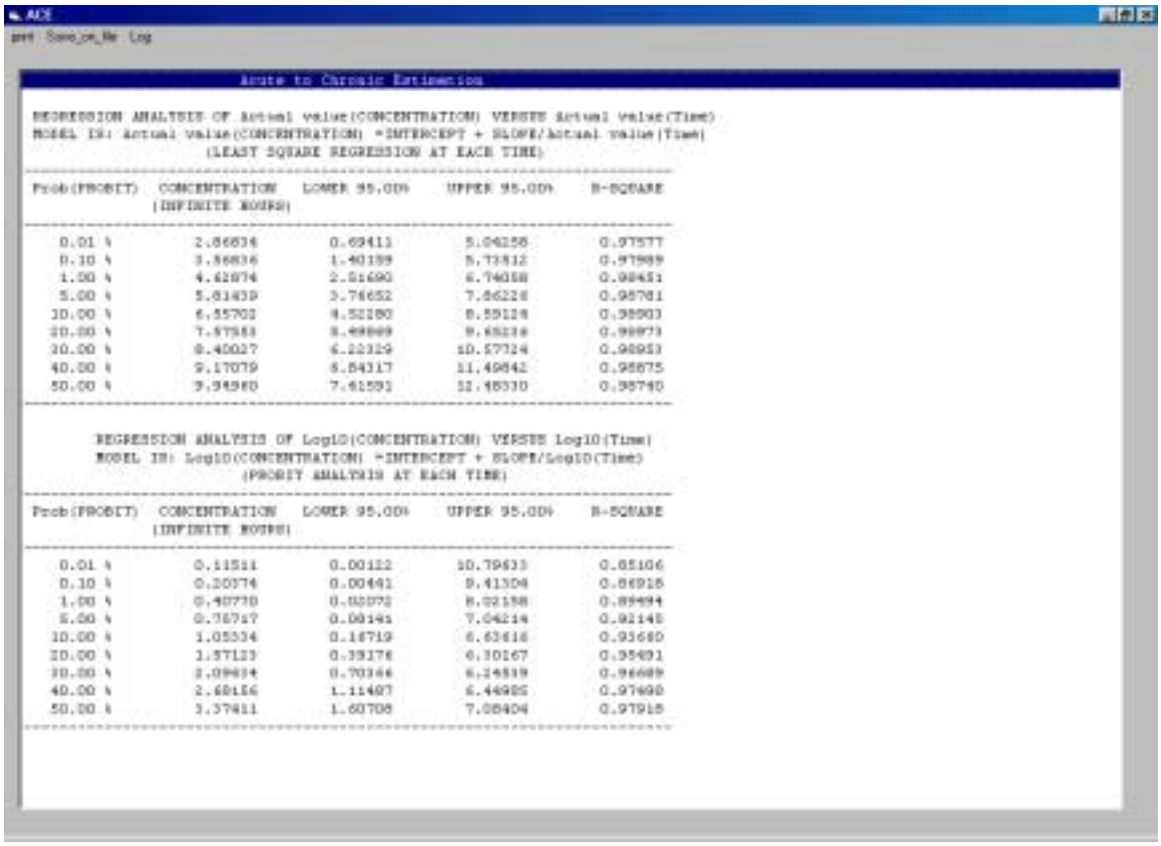
Calculations are based on a two-stage regression analysis, and two analyses will appear; one based on linear regression analysis and another based on probit analysis in stage 1. The following values are given: percent effect (0.01 – 50%; 0.01% is recommended for LRA), estimated chronic no-effect concentration at infinite hours, 95% confidence limits, and r^2. Select the chronic no-effect concentration for 0.01% with the largest r^2 value. Six models are used in the analyses, but only the best stage 1 linear regression and probit analyses (highest r^2) appear in Fig. 7. Click on **Log** to see analyses for all six models.

Note: If percent effects are selected above low percentages (0.01 – 1.0%), abberant values may be apparent when slopes among observation times in stage 1 are very unparallel.

LRA does not require partial responses. If no partial responses are present in the acute toxicity data, LRA uses the highest concentration having 0% (i.e., 0.01%) response at each time period for stage 1, and in stage 2, only the least square analysis is performed.

The only change that can be made for LRA is the *alpha* level for confidence limits (see **Options**); time in hours is set at infinity.

Figure 7 – LRA Full Screen



REGRESSION ANALYSIS OF Actual Value(CONCENTRATION) VERSUS Actual Value(Time)
MODEL IS: Actual Value(CONCENTRATION) =INTERCEPT + SLOPE/Actual Value(Time)
(LEAST SQUARE REGRESSION AT EACH TIME)

Prob(PROBIT)	CONCENTRATION (INFINITE ROOTS)	LOWER 95.0%	UPPER 95.0%	R-SQUARE
0.01 %	2.66834	0.69411	5.04258	0.97577
0.10 %	3.86836	1.40159	5.73512	0.97989
1.00 %	4.62874	2.51690	6.74058	0.98431
5.00 %	5.61439	3.76652	7.86228	0.98781
10.00 %	6.55703	4.52180	8.59124	0.98903
20.00 %	7.57583	5.49869	9.65218	0.98973
30.00 %	8.40027	6.22329	10.57724	0.98953
40.00 %	9.17079	6.84317	11.49842	0.98875
50.00 %	9.94960	7.41591	12.48330	0.98740

REGRESSION ANALYSIS OF Log10(CONCENTRATION) VERSUS Log10(Time)
MODEL IS: Log10(CONCENTRATION) =INTERCEPT + SLOPE/Log10(Time)
(PROBIT ANALYSIS AT EACH TIME)

Prob(PROBIT)	CONCENTRATION (INFINITE ROOTS)	LOWER 95.0%	UPPER 95.0%	R-SQUARE
0.01 %	0.11511	0.00122	10.79633	0.85106
0.10 %	0.20374	0.00441	9.41508	0.86918
1.00 %	0.40770	0.02072	8.02158	0.89494
5.00 %	0.78717	0.08141	7.04214	0.92148
10.00 %	1.05534	0.16719	6.63418	0.93680
20.00 %	1.57123	0.39176	6.30167	0.95491
30.00 %	2.09834	0.70344	6.24539	0.96689
40.00 %	2.68156	1.11487	6.44985	0.97490
50.00 %	3.37411	1.60708	7.08404	0.97915

Options

A number of options are available for controlling the output of each of the ACE models. The options screen is obtained from the main ACE screen. Click **Options** located in the upper left-hand corner of the main ACE window and the following screen will appear (Fig. 8). Once an *alpha* for confidence limits, chronic exposure time, MPA model, and/or statistical output title are changed, click **Save Options**. These changes will remain for present and future analyses. If **Save Options** is not selected, the changes will only remain for the current analysis and then return to default values the next time ACE is used. Click **Restore defaoul options** at the bottom right of the Options window to return to default values.

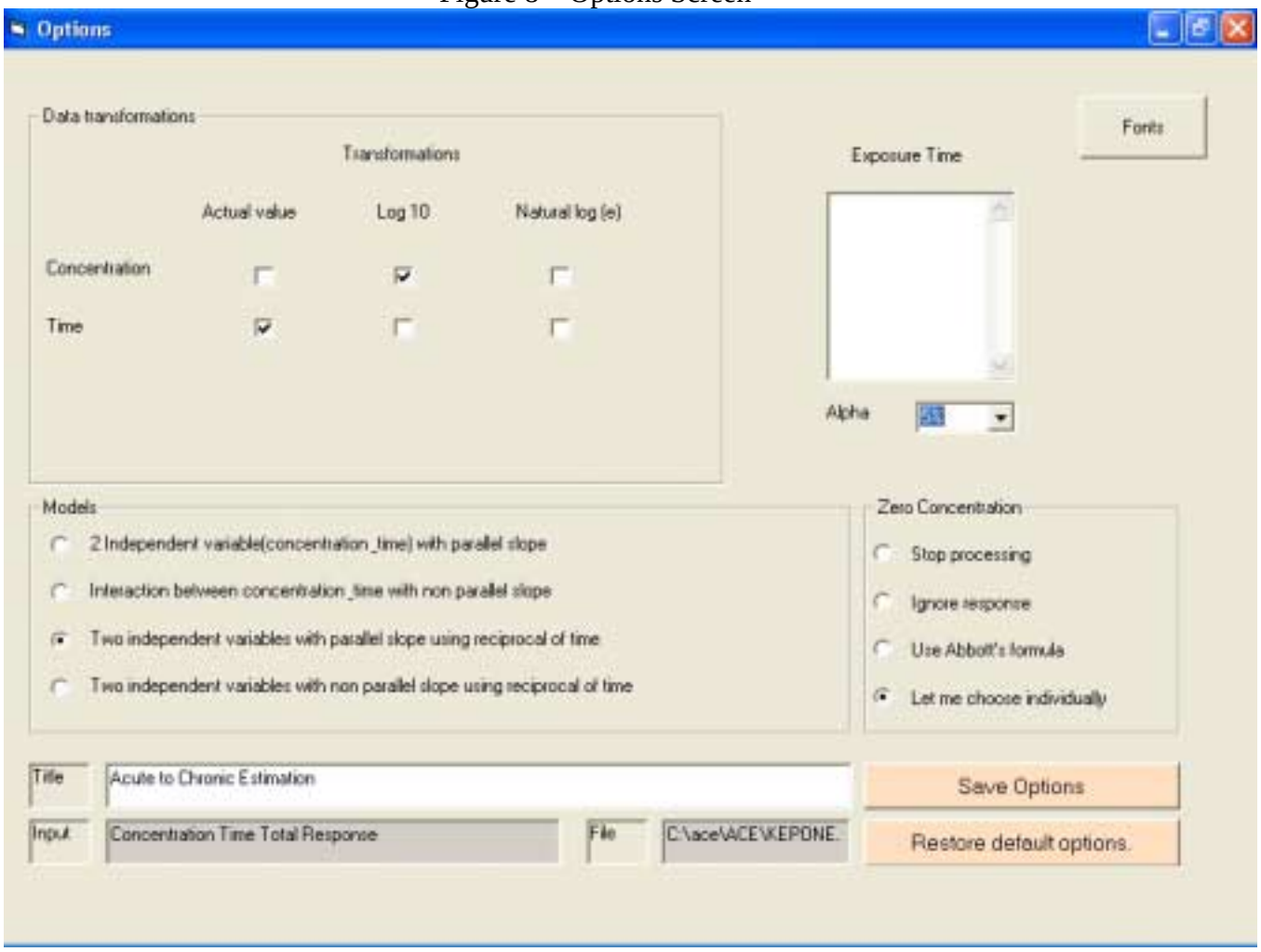
Font

Select **Font** (upper right-hand corner) to change font style of statistical output. Two font styles are presented; fixed font styles should be selected in the left-hand box. The font size may also be changed to fill the data output screen.

Alpha

To change *alpha* levels, click on the arrow associated with **Alpha** located on the upper right side of the **Options** screen; choose the desired *alpha* percent. The *alpha* controls the *t*, z, or chi-square values for producing confidence limits; the *alpha* default value is 5%.

Figure 8 – Options Screen



Exposure Time

In order to change to a different time, go to options window as described previously. To the right is a white box with the header **Exposure Time**. A time change can be accomplished in a number of ways. Type in a number (in hours) in the white box. If a number already exists in the box, write over it or add a number below the existing numbers. No time definition is needed if the number is in terms of hours. However, if one wants to enter days, just type the number of days desired and type "days" after the number and days will be converted to hours by the program. Weeks, months or years can be used as well, by typing in the appropriate time description. Two of these time descriptions (eg., days and months) cannot appear together on the same line. The default for the ALT is 30, 60 and 90 days. The default for MPA is infinite time if the model is based on the reciprocal of time. If the models are not based on the reciprocal of time, a number has to be placed in the **Exposure Time** box in order for the program to calculate NOEC values. The LRA procedure only calculates for infinite time.

Zero Concentration

This section applies only to the MPA and LRA. Abbott's formula (Finney 1978) is used to adjust data if control mortality (zero concentration) exists when probit analysis is performed. The default is **Let me**

choose individually. If control mortality exists, the MPA or LRA will present a message box that allows the user to choose Abbott"s correction. If only one control mortality is present, the message box will appear only once. If control mortality appears more than once, the message box will appear for each one. If **Stop processing** is selected, MPA and LRA will not run if control mortality is present. The **Ignore response** option does not apply Abbott's correction. The **Use Abbott's formula** applies Abbott's correction to all control mortalities.

Title

The title of the statistical output can be changed; click on **Title** and type in a new title. The default title is "Acute to Chronic Estimation".

Selecting MPA Models

The basic Multifactor Probit Analysis equation has a general form in which LC% = Intercept + b_1(Exposure Concentration) + b_2(Time) where b_1 and b_2 are partial regressions for exposure concentration and time, respectively. An additional b_3 [interaction of (exposure concentration)(time)] is added if the slopes among probits are not parallel (see Lee et al. 1995, Mayer et al. 2002).

A number of statistics require evaluation to determine the MPA model of choice. If the chi-square statistic is $\leq$ the critical chi-square value, the data fit the model adequately. Should the other models provide a smaller chi-square statistic, that model is preferred.

To change to one of the other three basic MPA models, exit the MPA program by clicking the **X** in the upper right corner, and then click on **Options** in the upper left-hand corner of the main ACE screen; select **Models** and the four models listed below will appear. The model parameters can be changed to actual values or log values of time and concentration within **Data Transformation** located in the upper left portion of the **Options** screen. This procedure takes much more manipulation to determine the best model. The combination of model choice and actual or log values of concentration and time that gives the lowest chi-square statistics is the best model.

The four models are as follow (1.281 = probit value for 0.01%):

Model 1: Chronic exposure time is specified and equal slopes among observation times are assumed.

Exposure Concentration – Time – Response relationship is defined as:

$$\text{Probit}_P = \alpha + \beta(\text{Concentration}) + \Upsilon(\text{Time})$$

Chronic no-effect concentration (NOEC) at specified T hours is:

$$NOEC_T = \frac{1.281 - \alpha - \gamma * T}{\beta}$$

Model 2: Chronic exposure time is unknown and equal slopes among observation times are assumed.

Exposure Concentration – Time – Response relationship is defined as:

$$\text{Probit}_p = \alpha + \beta(\text{Concentration}) + \Upsilon/\text{Time}$$

NOEC at infinite time is:

$$NOEC_T = \frac{1.281 - \alpha - \gamma * T}{\beta + \delta + T}$$

Model 3: Chronic exposure time is specified and it is assumed that the slope changes with constant rate as observation times increase.

Exposure Concentration – Time - Response relationship is defined as:

$$\text{Probit}_p = \alpha + \beta(\text{Concentration}) + \Upsilon(\text{Time}) + \delta(\text{Concentration})(\text{Time})$$

NOEC at T hours is:

$$NOEC = \frac{1.281 - \alpha}{\beta}$$

Note: This is the default model in ACE; actual value of time and the log10 of concentration.

Model 4: Chronic exposure time is unknown and and it is assumed that the slope changes with constant rate as observation times increase.

Exposure Concentration – Time – Response relationship is defined as:

$$\text{Probit}_p = \alpha + \beta(\text{Concentration}) + \Upsilon/\text{Time} + \delta\ (\text{Concentration})/(\text{Time})$$

NOEC at infinite time is:

$$NOEC = \frac{1.281 - \alpha}{\beta}$$

Note: Chronic times are necessary for Models 1 and 2; default chronic time is infinity for Models 3 and 4, but additional chronic times may be added.

Estimating Sublethal Effects

Raw data for sublethal endpoints are seldom available under acute exposure conditions for modeling chronic no-effect concentrations. Sublethal endpoints are also difficult to estimate from chronic lethality data. Conservative chronic no-effect concentrations for sublethal endpoints may be estimated by multiplying the predicted NOEC for lethality by 0.2 for growth and other sublethal endpoints and 0.1 for reproductive endpoints. This is based on the analysis of differences among endpoints in chronic toxicity tests (Table 1). However, it must be understood that these estimates of chronic sublethal effects are extremely conservative; note that the median values (that value where 50% of the observations are above or below it) are approximately 1.0 for growth and reproduction and only slightly below 1.0 for "other" sublethal endpoints. In addition, the NOECs for lethality were exactly the same or less than those for weight, length, reproduction, and "other" endpoints 59, 58, 56, and 41% of the time, respectively. Based on the extreme variation of ratios, and the fact that no central tendency exists within the distribution of ratios, **the authors do not recommend using factors to estimate sublethal endpoints at this time**. The data (see table below) are based on hypothesis testing, and using regression analysis to estimate no-effect concentrations for lethal and sublethal endpoints might provide an improved comparison and deserves further investigation.

Univariate analyses for the ratios of growth, reproduction, or other sublethal endpoint chronic no-effect concentrations (NOEC) to that for survival (sublethal NOEC/survival NOEC)[1].

Univariate parameter	Growth		Reproduction	Other[2]
	Weight	Length		
n	46	62	18	22
Mean	0.96	0.90	1.13	0.76
Median	1.0	1.0	1.0	0.6
Range	0.10-4.4	0.16-2.3	0.12-4.5	0.06-2.0
95% CL	0.7-1.2	0.8-1.1	0.6-1.7	0.5-1.0
$\pm$1 SD	0.2-1.8	0.3-1.5	0.1-2.2	0.2-1.3
95th percentile	2.3	2.2	4.5	2.0
Median	1.0	1.0	1.0	0.6
5th Percentile	0.1	0.2	0.1	0.2

[1]Data are from Mayer et al. (1986) and the USEPA Gulf Ecology Division (ORD/NHEERL), Gulf Breeze, FL.
[2]Sublethal endpoints deemed detrimental to survival and/or ability to contribute to population success were cataracts, disease susceptibility, severe fin erosion, severe organ pathology, and spinal curvature.

Additional Model Documentation

Details regarding each model and validation of those models using paired acute and chronic toxicity data are published (Lee et al. 1992, Lee et al. 1995, Mayer 1990, Mayer 1991, Mayer et al. 1992a, Mayer et al. 1992b, Mayer et al. 1994, Mayer et al. 1999, Mayer et al. 2002, Sun et al. 1992, Sun et al. 1994, Sun et al. 1995a, Sun et al. 1995b).

ALT

The ALT procedure uses a Quasi-Newton method to find the maximum likelihood estimates of parameters. Confidence limits for parameters are based on Normal approximations to distributions of the maximum likelihood estimates. The parameter estimates given in Fig. 3 are used in the following model to obtain predicted chronic no-effect concentrations for a particular percent effect and exposure time in days.

$$\text{No-effect concentration} = \text{Exp}[(\ln(-\ln(1-p))-\ln(A) - C*\ln(\text{days}*0.24))/B]$$

A, B, and C are parameter estimates and p is the percent effect, ranging from 0.01 to 10% (see **ALT – Accelerated Life Testing Model**).

MPA

The MPA method uses all time and concentration data simultaneously to produce a multiple regression probit equation to predict chronic no-effect values for specified times.

If the chi-square statistic is ≤ the critical chi-square value, a variance-covariance matrix is produced and is necessary to calculate confidence limits. If the chi-square statistic is not ≤ the critical chi-square value, the variance-covariance matrix is adjusted by a heterogeneity factor to produce an adjusted variance-covariance matrix. The heterogeneity factor (HF) is given in the statistical output and is equal to the chi-square statistic divided by the degrees of freedom (n – 1 of data used; Finney 1978).

The assumptions of independence may be violated with typical acute toxicity data using MPA. The procedure is appropriate if observations at one time are not the same experimental units at another time. Regardless of the issue of independence, MPA does provide acceptable acute and predicted no-effect chronic concentrations when adequate partial responses are present in the acute data.

LRA

Calculations are based on a two-stage regression analysis. Stage 1 performs two types of analyses. The first type is a simple linear regression at each observation time in which the X axis is log10 concentration and the Y axis is the probit transformation of proportion responding (dead). The second type is a probit analysis at each observation time (Finney 1978). Following these two types of analyses, no-effect concentration values are estimated at different percent response levels. The concentrations are transferred to the stage 2 simple linear regression in which the X axis is the reciprocal of time (1/t) and the Y axis is the concentration at each observation time for a specific percentage value. The equation is:

$c = a + b/t$ where c = chronic no-effect concentration
a = Y intercept
b = regression coefficient
t = time

There are three possible transformations that are made in the stage 2 regression: 1) actual values of concentration and time, 2) log10 of concentration and actual value of time, and 3) log10 of both concentration and time. Thus, six analyses occur due to two types of analyses in stage 1 and three transformations of data in stage 2. As time goes to infinity, the term b/t goes to zero; thus, the concentration at infinite time is the intercept (a), or the chronic no-effect concentration for lethality.

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BurrliOZ Help

1 Usage

The BurrliOZ software is designed to estimate the protecting concentrations of chemicals such that a given percentage of species will survive. Before the software can be run, data on the relevant chemicals must be available in ascii files. The software can be run on PCs running Windows NT 4.0, Windows 98 or Windows 2000.

The estimations of the protecting concentrations are computed by fitting a certain distribution to the input data. The distribution, called the Burr III distribution, is that required by the Environment Protection Authority. There are other distributions fitted to the data, the normal and the log-logistic distributions, as these are distributions that the users of this software may be familiar with. However, these two latter distributions are provided only as a reference guide and are not used for the estimation of the protecting concentrations. For further details on the distributions that are fitted and the estimation techniques used see the end of this document.

1.1 Opening a data file for reading

The relevant data file must be opened for reading before the concentration estimation can be done. From the **File** menu select **Open**. A browser window will appear and you can select the desired file. The file should be a readable ascii file, with more than 3 data points listed in it. If this is not the case an error message will appear. In the data file each data point must be on a new line.

1.2 Opening an output file for writing

A file for saving the output must be specified before the protecting concentration can be estimated. From the **File** menu select **Save Output As**. A browser window will appear and you can select an existing file or name a new file in which to save the output. If you select an existing file it will be overwritten.

1.3 Setting percentiles

The percentile is the percentage of species that the estimated concentration should protect. The default is 95%. Accompanied with the percentile is a confidence interval for the estimated concentration. The default for the confidence interval is 50%, which corresponds to no confidence interval being estimated.

To change the percentile and confidence interval select **Set Percentiles** from the **Settings** menu. There are several already specified settings available, which are in the form of ``PC 99 50". This refers to the protecting concentration such that 99% of species survive, with a 50% confidence interval. If **other** is selected from the dialog box by single clicking with the left mouse button, two data entry boxes will appear giving you opportunity to enter a percentile and confidence interval of your choosing. The percentile and the confidence interval should be whole numbers between 0 and 100. If this is not the case an error message will appear. Except for a value of 50%, if the entered confidence interval is less than 80 a warning message will appear. It is conventional to choose a confidence interval of 80%, 85%, 90% or 95%.

1.4 Setting the number of bootstrap samples

If a confidence interval other than 50% is selected, the software must simulate new data in order to estimate the lower confidence limit. The procedure of simulating the data and estimating the confidence

limit from the new data is known as *bootstrapping*. The number of bootstrap samples is the number of data sets simulated to allow for the estimation. The default number is 501, and this should not need to be altered. If changes to this number are required, select **Set number of bootstrap samples** from the **Settings** menu. A sliding bar will appear and a number from 200 to 1000 can be selected. The higher the number, the more accurate the confidence interval estimate will be (but the longer the software will take to run). If the number selected is less than 500, then a warning window will appear when the protecting concentration is estimated, although the estimation procedure will still be allowed to proceed.

1.5 Setting the concentration divisor

The concentration divisor is used to adjust the estimated protecting concentration to give a more conservative level. The choices are *chronic* or *acute*, which give a divisor of 1 or a manually selected value, respectively. Chronic is the default setting. To manually set the divisor select **Set concentration divisor** from the **Settings** menu. If **Acute** is selected in the new dialog box, there will be a choice of dividing by 10 or manually entering an ACR (acute chronic ratio). By default the ACR is 10. Click **OK** when you are happy with your selection.

1.6 Performing the estimation

To compute the protecting concentration for the percentile selected and to estimate the corresponding confidence interval select **Run** from the **File** menu. When this is done a distribution is fitted to the data and the protecting concentration is estimated according to the fitted distribution. A new window will appear with the results displayed and the data and fitted distribution plotted in the window. At the same time as the new window is displayed, the numerical results are saved to the ascii output file that was previously selected.

1.7 Using the results window

The results window shows a plot of the fitted Burr III distribution, along with fits of the normal and log-logistic distributions. Lines are marked on the plot to indicate the estimated protecting concentration (as computed from the Burr III distribution fit).

There are several features of the results window that may be useful in the selection of protecting concentrations that are appropriate for your application. These features are described below.

1.7.1 Highlighting parts of the plot

In the results window a legend appears in the top right hand corner. As the mouse is moved over the legend, a single click on part of the legend will highlight the corresponding part of the plot. More than one part of the plot can be highlighted at one time. The highlighting works as a toggle, so a second click of the left mouse button will revert the corresponding part of the graph back to its original state.

1.7.2 Changing the concentration scale

The scale of the horizontal axis can be on the natural or the log scale. The default is the natural scale. If the log scale is selected, the low end of the horizontal axis will be stretched and the high end will be squashed.

1.7.3 Selecting different percentiles

There is a data entry box in the results window where a different percentile can be typed in. When the

return/enter button is hit the protecting concentration corresponding to the entered percentile is computed. The newly estimated protecting concentration is also marked on the plot. The percentile can only be between 0 and 100.

1.7.4 Selecting concentrations

There is a data entry box in the results window where a protecting concentration can be typed in. When the return/enter button is hit the percentile corresponding to the entered concentration is computed. It is also marked on the plot. The concentration can only be between 0 and the highest concentration shown on the plot.

1.7.5 Zooming

To zoom into part of the plot, click and hold the left mouse button down on the top-left of the desired zoom area. While holding the button down move the mouse to the bottom-right of the desired area and release the button. A single left button mouse click will now complete the zoom. A single right button mouse click will undo the last zoom that was done. This zoom tool may be useful to see the estimated protecting concentration, which can sometimes be too low to see on the original plot.

1.8 Saving results

The results of the estimation procedure are written to the selected output file when **Run** is selected from the **File** menu. To save the results plot simply click the **Save** button on the results window and a Windows metafile will be created and saved to the clipboard. This file can then be pasted into a Word document for future use.

1.9 Printing results

The results plot can be printed by selecting **Print** from the **File** menu in the original BurrliOZ window. A standard Windows printer dialog box will appear and the usual settings can be selected.

1.9.1 Page setup

Some settings for the printing of results can be made in the dialog box that appears by selecting **Page Setup** from the **File** menu in the original BurrliOZ window.

2 Statistical methodology

As outlined at the beginning of this document, the estimations of the protecting concentrations are computed by fitting a certain distribution to the input data. The distribution is called the Burr III distribution, and is the distribution that is required by the Environment Protection Authority. There are other distributions fitted to the data, the normal distribution and the log-logistic distribution, as these are distributions that the users of this software may be familiar with. However, these latter two distributions are provided only as a reference guide and are not used for the estimation of the protecting concentrations.

After the Burr III distribution has been fitted to the data, the protecting concentration (for preserving, for example, 90% of the species) is estimated using the estimated distribution parameters to compute the concentration such that the probability of there being a greater concentration (according to the fitted distribution) is 90%.

After the Burr III distribution has been fitted to the data, the protecting concentration (for preserving, for example, 90% of the species) is estimated using the estimated distribution parameters to compute the concentration such that the probability of there being a greater concentration (according to the fitted distribution) is 90%.

Once the protecting concentration has been computed, an estimate for the lower confidence limit (of a specified percent, say 95%) can be computed. This value can be used as a very conservative (lower) estimate for the protecting concentration.

Further details on how these estimations are done are given below. Some statistical knowledge is required to understand the estimation techniques outlined.

2.1 Fitting the distributions

2.1.1 Burr III fitting

The Burr III distribution is a very flexible 3-parameter distribution, which can provide good approximations to many commonly used distributions such as the log-normal, log-triangular and Weibull. The cumulative distribution function (CDF) for the Burr III distribution is

$$F_{\text{Burr III}}(x) = \frac{1}{\left[1 + \left(\frac{b}{x}\right)^{c}\right]^{k}}$$

The 3 parameters of the Burr III distribution, b, c, and k are estimated by maximising the log-likelihood function (which is based on the probability distribution function). This maximisation is performed using the simplex algorithm, an optimisation technique that is not reliant on derivative information.

A complication of the Burr III distribution is that at limits of some of the parameters the Burr III distribution tends to a limiting distribution. As $k \rightarrow \infty$ the Burr III distribution tends to the reciprocal Weibull distribution. As $c \rightarrow \infty$ the Burr III distribution tends to the reciprocal Pareto distribution. In practical terms, if the Burr III distribution is fitted and k is estimated to be greater than 100, the estimation procedure is carried out again with a reciprocal Weibull distribution fitted. Similarly for the reciprocal Pareto distribution, if c is greater than 80.

Once the parameters are estimated they can be used to compute the CDF of the appropriate distribution (Burr III or one of the limiting distributions), which is plotted with the input dataset in the results window.

2.1.2 Log-logistic fitting

The log-logistic distribution is a commonly used distribution, which happens to be a special case of the Burr III distribution. Because of its possible familiarity with the software user, it has been included as one of the distributions that is fitted to the data and plotted on the results window for comparison against the Burr III fit.

The CDF for the log-logistic distribution is

$$F_{\text{log-logistic}}(x) = \frac{1}{1 + \exp(-[\ln(x) - \mu]/\sigma)}$$

The parameters of the log-logistic distribution, μ and σ, are estimated in the same way as the parameters for the Burr III distribution, by using the simplex algorithm to maximise the log-likelihood function.

2.1.3 Normal fitting

Because the normal (or Gaussian) distribution is a commonly used and well known distribution it has also been included as one of the distributions that is fitted to the data, to allow the user to compare the fit with that of the Burr III distribution. The CDF for the normal distribution is

$$F_{\text{normal}}(x) = \int_{-\infty}^{x} \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(u-\mu)^2}{2\sigma^2}\right) du$$

For a dataset of n samples, the mean and standard deviation are estimated, respectively, with the maximum likelihood estimators

$$\hat{\mu} = \frac{\sum_{i=1}^{n} x_i}{n}$$

and

$$\hat{\sigma} = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}}.$$

As with the log-logistic distribution, the estimated best fit to the data of the normal distribution is also plotted on the results window.

2.2 Estimating the protecting concentration

The protecting concentration is only calculated from the Burr III distribution (or an associated limiting distribution) fit to the data. This is a requirement set out by the Environment Protection Authority. The software user will require the computation of the concentration corresponding to the statement that ``q% of the species should be protected if the concentration of the chemical is less than the estimated concentration". The value of q should be between 0 and 100 and, for the expected use of the BurrliOZ software, will be somewhere close to 100, such as 80, 85, 90 or 95.

For a given value for q, the protecting concentration is estimated from the Burr III distribution fit as

$$PC(q) = \frac{b}{[(1/(1-q))^{1/k} - 1]^{1/c}} .$$

If the limiting distribution of reciprocal Weibull is used then the protecting concentration is estimated as

$$PC(q) = (-\alpha/\ln(1-q))^{1/\beta}$$

where α and β are the two parameters of the reciprocal Weibull distribution that were estimated in the fitting step. Similarly, if the reciprocal Pareto distribution has been necessarily fitted, the protecting concentration is estimated as

$$PC(q) = x_0 (1-q)^{1/\theta}$$

where x_0 and θ are the two parameters of the reciprocal Pareto distribution that were estimated in the fitting step.

2.3 Estimating a confidence interval for the protecting concentration

Unlike the estimation of the protecting concentration (PC), there is no theoretically derived equation for estimating the lower bound of a confidence interval (CI) about the protecting concentration estimate. Instead, a technique known as bootstrapping is used to estimate the lower bound of the CI.

To perform the bootstrapping, a new dataset of the same size as the original dataset is created by selecting values from the original set at random with replacement. With the new dataset, the PC is estimated using the steps outlined above. This process is repeated many times (the default being 501). This gives a large set of estimates for the PC. In essence, this is a representation of the distribution of the PC. The lower bound of a 90% confidence interval (for example) for the PC can then be estimated by ordering all the PC values and selecting the value that is 5% in from the lowest value.

It should be noted that the estimated lower bound to the CI is based on a random sampling method and will not be the same when the bootstrap is repeated.

File translated from T_EX by T_TH, version 2.60.
On 25 May 2000, 15:16.

Environmetrics

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Skills and Research

- Hybrid Climate Modelling: Physical Statistical Models

Current Projects

Team

BurrliOZ

A Flexible Approach to Species Protection

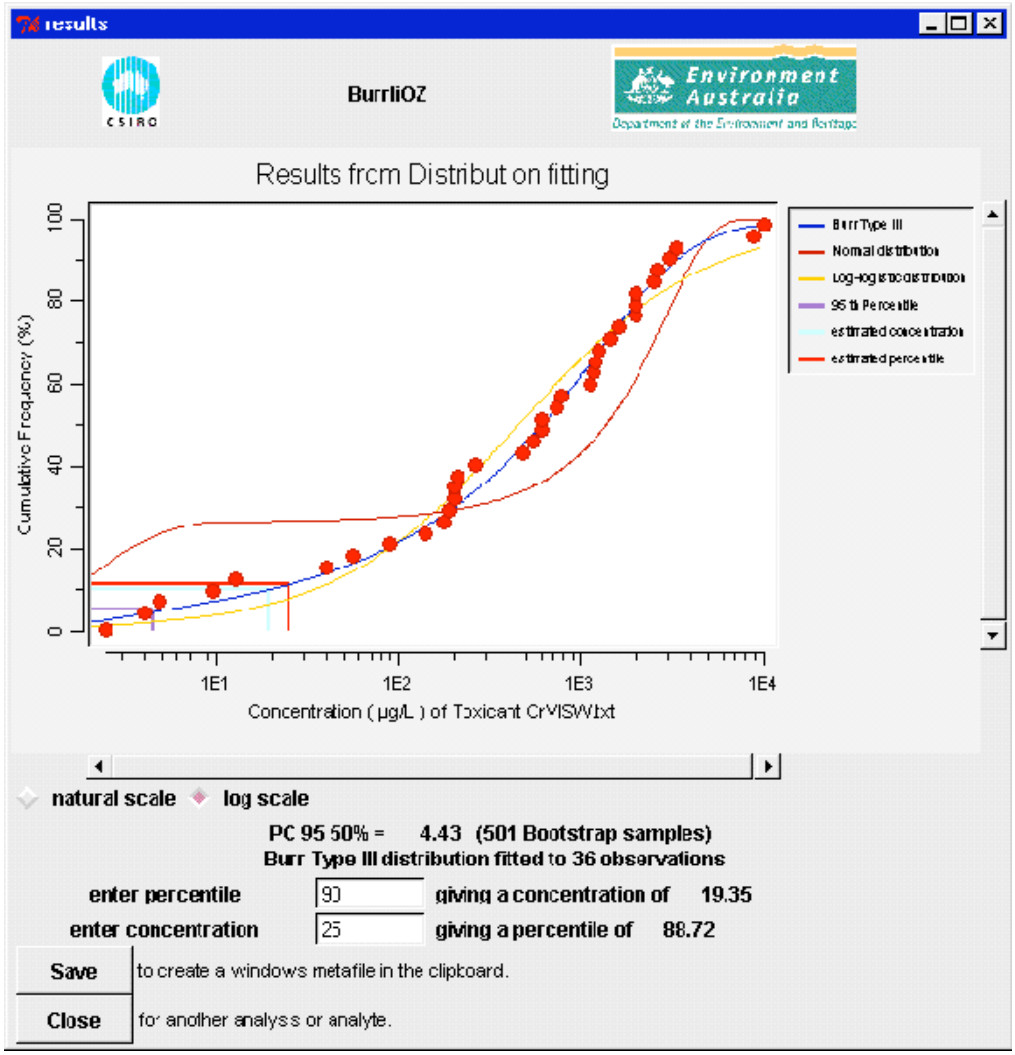
Environmental Managers responsible for implementing the Australian and New Zealand Water Quality Guidelines for Fresh and Marine Waters need to generate 'trigger values' (ie the maximum concentration of a chemical that should permit the integrity and function of aquatic environments to be maintained) for local conditions within Australia. To do this, they will utilise toxicant data and a statistical software package, BurrliOZ, developed by the CSIRO Environmetrics Group for Environment Australia. Another software package that calculates trigger values using the Aldenberg and Slob (1993) approach exists, however this has been shown to be a special case of the approach implemented in BurrliOZ (Shao, 2000). BurrliOZ uses a flexible family of distributions, the Burr Type III, to estimate the concentrations of chemicals such that a given percentage of species will survive.

Environment Australia
Department of the Environment and Heritage

This project makes available to the public, free of charge and subject to certain restrictions, a new software packages including both the 'Web' and a CD-ROM suitable for delivery with the Guidelines document. This software and delivery format addresses concerns raised during the 1999 public comment period. Download Burrlioz software.

The work is expected to facilitate approval of the final Water Quality Guidelines by the Australian and New Zealand Environment and Conservation Council (ANZECC) and the Agriculture and Resource Management Council of Australia and New Zealand (ARMCANZ) Ministers and also accelerate effective implementation of the Water Quality Guidelines. This work represents a significant advance in the methods used to derive water quality guidelines and it should have international implications and uses.

A screen shot of what BurrliOZ looks like



The Method

The protecting concentrations are estimated by fitting the Burr Type III distribution to the No Observed Effect Concentration (NOEC) data, collected for a range of species. This distribution is required by the Environment Protection Authority. Other distributions are fitted to the data, including the log-normal and log-logistic as these are familiar to environmental managers. However, they are provided only as a reference and are not used for the estimation of protecting concentrations.

The Burr III distribution is a very flexible three-parameter distribution, which can provide good approximations to many commonly used distributions such as the log-normal, log-triangular and Weibull. The cumulative distribution function for the Burr III distribution is

$$F(x) = \frac{1}{\left[1 + \left(\frac{b}{x}\right)^c\right]^k}$$

The three-parameters of the Burr III distribution, *b*, *c*, and *k* are estimated by maximum likelihood using the Nelder-Mead simplex algorithm, a derivative free optimisation technique.

A feature of the Burr Type III distribution is that as some of the parameters tend to limiting values the Burr Type III distribution tends to one of a set of limiting distribution (Shao, 2000). For example, as $k \to \infty$ the Burr III distribution tends to the reciprocal Weibull distribution. As $c \to \infty$ the Burr III distribution tends to the reciprocal Pareto distribution. In practice, if *k* is estimated to be greater than 100 in a fit of the Burr distribution, then the parameter estimation is repeated, a reciprocal Weibull is fitted. Similarly if *c* is estimated to be greater than 80 then the reciprocal Pareto distribution is fitted.

Estimating the protecting concentration

The protecting concentration, PC(q), is calculated from the Burr Type III distribution, or an associated limiting distribution. The user requires the concentration corresponding to the statement that ``q% of the species should be protected if the concentration of the chemical is less than the estimated protecting concentration". Thus, for a given value for q, the protecting concentration is estimated from the Burr III distribution fit as

$$PC(q) = \frac{b}{\left[\left(\frac{1}{1-q}\right)^{\frac{1}{k}} - 1\right]^{\frac{1}{c}}}$$

Typical values for q are 80, 85, 90 or 95.

Estimating a confidence interval for the protecting concentration

Unlike the estimation of the protecting concentration, there is no theoretically derived equation for estimating the lower bound of a confidence interval (CI) about the protecting concentration etimate, though Shao (1998) has shown that a delta method approximation works sometimes, particularly for large samples. Instead, a technique known as bootstrapping is used to estimate the lower bound of the CI. Bootstrapping is a standard statistical approach in situations where theoretical results are difficult to obtain, or require unrealistic assumptions (Efron and Tibshirani, 1993).

To perform the bootstrapping, a new dataset of the same size as the original dataset is created by selecting values from the original set at random, but with replacement. The PC(q) is estimated from this new dataset as above. This process is repeated many times. This gives a large set of estimates for the PC(q) which, in essence, is a representation of the distribution of the PC(q). The lower bound of a 90% confidence interval (for example) for the PC(q) can then be estimated by ordering all the PC(q) values and selecting the value that is ranked at 5%.

It should be noted that the estimated lower bound to the CI is based on a random sampling method and will not be exactly the same if the bootstrap procedure is repeated.

References:

Aldenberg, T. and Slob, W. (1993). Confidence limits for hazardous concentrations based on logistically distributed NOEC toxicity data. *Ecotoxicology and Environmental Safety*, **25**, 48-63

Efron, B. and Tibshirani, R.J. (1993). *An introduction to the Bootstrap*. New York: Chapman & Hall.

Shao, Q. (1998). *Statistical Review and Assessment of Water Quality Guidelines*, CSIRO Mathematical and Information Sciences Report No CMIS98/21

Shao, Q. (2000). Estimation for hazardous concentrations based on NOEC toxicity data: an alternative approach. (accepted by *Environmetrics*)

Contact Details: burrlioz@cmis.csiro.au

Download Burrlioz software.

To top

last updated November 07, 2002 11:52 AM
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Canadian Environmental Modelling Centre

Level I Model

Version 3.00 - September 2004

New in version 3.00!

A Level I simulation is of the equilibrium distribution of a fixed quantity of conserved (ie. non-reacting) chemical, in a closed environment at equilibrium, with no degrading reactions, no advective processes, and no intermedia transport processes (e.g. no wet deposition, or sedimentation). The medium receiving the emission is unimportant because the chemical is assumed to become instantaneously distributed to an equilibrium condition.

Physical-chemical properties are used to quantify a chemical's behaviour in an evaluative environment. Three types of chemicals are treated in this model: chemicals that partition into all media (Type 1), involatile chemicals (Type 2), and chemicals with zero, or near-zero, solubility (Type 3). The Level I Model assumes a simple, evaluative, closed environment with user-defined volumes and densities for the following homogeneous environmental media (or compartments): air, water, soil, sediment, suspended sediment, fish and aerosols.

This model is useful for establishing the general features of a new or existing chemical's behaviour. A Level I calculation gives the general impression of the likely media into which a chemical will tend to partition and an indication of relative concentrations in each medium. The results of changes in chemical and environmental properties may be explored.

Features of the Level I Program:
Provides a database of chemicals and chemical properties.
Permits temporary additions/changes of chemicals and their properties to a simulation.
Permits permanent additions, changes and deletions of chemicals and their properties to the chemical database.
Supplies default values for all input fields which may be easily changed. These values are regarded as typical, as discussed in the text referred to earlier.
Provides context-sensitive Help.
Displays and prints the Level I model calculations, as performed by the program.
Allows the printing of simulation tables and the summary diagram.
Allows the program results to be saved as a comma separated value (csv) file.

This program was based on the following publication:

Mackay, D. 2001. "Multimedia Environmental Models: The Fugacity Approach - Second Edition", Lewis Publishers, Boca Raton, pp. 1-261.

Other related publications:

Mackay, D., Paterson, S., Kicsi, G., Di Guardo, A., Cowan, C.E. 1996. Assessing the Fate of New and Existing Chemicals: A Five Stage Process. Environ. Toxicol. Chem. 15: 1618-1626.

Mackay, D., Paterson, S., Di Guardo, A., Cowan, E.C. 1996. Evaluating the Environmental Fate of a Variety of Types of Chemicals Using the EQC Model. Environ. Toxicol. Chem. 15: 1627-1637.

Mackay, D., Paterson, S., Kicsi, G., Cowan, E.C., Di Guardo, A., Kane, D.M. 1996. Assessment of Chemical Fate in the Environment Using Evaluative, Regional and Local-Scale Models: Illustrative Application to Chlorobenzene and Linear Alkylbenzene Sulfonates. Environ. Toxicol. Chem. 15: 1638-1648.

The required input data are:
Chemical Properties:

- chemical name
- molecular mass
- data temperature
- Type 1 chemicals

- water solubility
- vapour pressure
- log Kow
- melting point
- Type 2 and 3 chemicals

- partition coefficients

Environmental Properties:

- volumes for all 7 media
- densities for all 7 media
- organic carbon content (soil, sediment & suspended sediment only)
- fish lipid content (Type I chemicals only)

Emissions:

- chemical amount

Model Output:

- partition coefficients (Type 1)
- Z values
- fugacity of the system
- concentrations and amounts for each compartment
- a summary diagram

This program is only available in compiled form. A "readme.txt" file with more detailed technical information is included in the zipped file.

Minimum sytem requirements:
Pentium-75MHz with 8 Mb of RAM running Windows 95, 98, or XP. On some systems it may be necessary to adjust your screen resolution.

The Level I Model Version 2.11, released August 1999 continues to be available.

For non-Windows users the BASIC, evaluative, Level I, II and III fugacity models are available.

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Version 3.00 - September 2004

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Level I Software Update

Version 3.00 - September 2004

Since the Version 2.11 (August, 1999) release:

- A database of Environmental Properties was added.
- General layout and functionality were updated to be consistent with recent CEMC model releases.

Model Description

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Last updated September 23, 2004.

Canadian Environmental Modelling Centre

Level II Model

Version 3.00 - September 2005

New in version 3.00!

A Level II simulation describes a situation in which a chemical is continously discharged at a constant rate and achieves a steady-state and equilibrium condition at which the input and output rates are equal. Degrading reactions and advective processes are the loss or output processes treated. Intermedia transport processes (e.g. no wet deposition, or sedimentation) are not quantified. The medium receiving the emission is unimportant because the chemical is assumed to become instantaneously distributed to an equilibrium condition.

Physical-chemical properties are used to quantify a chemical's behaviour in an evaluative environment. Three types of chemicals are treated in this model: chemicals that partition into all media (Type 1), involatile chemicals (Type 2), and chemicals with zero, or near-zero, solubility (Type 3). The Level II model assumes a simple, evaluative environment with user-defined volumes and densities for the following homogeneous environmental media (or compartments): air, water, soil, sediment, suspended particles, fish and aerosols.

This model is useful for establishing the general features of a new or existing chemical's behaviour. A Level II calculation gives an indication of the likely media into which a chemical will tend to partition and an indication of relative concentrations in each medium. The distribution between media is the same as in Level I. The results of changes in chemical and environmental properties may be explored.

Three persistences are calculated, an overall value, T_O, and individual persistences attributable to reaction only, T_R, and advection only, T_A. Note that $1/T_O$ equals the sum of $1/T_R$ and $1/T_A$.

Consideration of advection and reaction rates allows for the calculation of chemical persistence. It provides a first estimate of overall environmental persistence, which is a critical property of the chemical. It also shows which loss processes are likely to be most important. A fast reaction or short half-life may not be significant if relatively little of the chemical is subject to this reaction by virtue of its partitioning. The potential for the chemical to be subject to long-range atmospheric transport is also indicated by the magnitude of the air advection loss. The global chemical persistence is best indicated by the reaction persistence, whereas the local persistence is indicated by the overall persistence.

Note that in this version, reaction half-lives are requested for all 7 media. In previous versions reactions in only 4 media were treated. The advective residence time selected for air also applies to aerosols and the residence time for water applies to suspended particles and fish. The advective residence time of aerosols, suspended particles and fish cannot be specified independently of the air and water residence times.

A Level II calculation is more realistic than a Level I calculation but requires additional information.

Features of the Level II Program:
Provides a database of chemicals and chemical properties.
Permits temporary additions/changes of chemicals and their properties to a simulation.

Permits permanent additions, changes and deletions of chemicals and their properties to the chemical database.
Supplies default values for all input fields which may be easily changed. These values match those in the EQC model.
Provides context-sensitive Help.
Displays and prints the Level II model calculations, as performed by the program.
Allows the printing of simulation tables and the summary diagram and charts.
Allows the program results to be saved as a comma separated value (csv) file readable by most spreadsheet software.

This program was based on the following publication:

Mackay, D. 2001. "Multimedia Environmental Models: The Fugacity Approach - Second Edition", Lewis Publishers, Boca Raton.

The required input data are:
Chemical Properties:

- chemical name
- molar mass
- data temperature
- reaction half-life estimates for

- air
- aerosols
- water
- suspended particles
- aquatic biota
- soil
- sediment
- Type 1 chemicals

- water solubility
- vapour pressure
- log Kow
- melting point
- Type 2 and 3 chemicals

- partition coefficients

Environmental Properties:

- volumes for all media
- densities for all media
- organic carbon content (soil, sediment, and suspended particles only)
- fish lipid content
- advective flow residence times for air (including aerosols), and water (including suspended particles and aquatic biota)
- advective flow residence time for sediment burial

Emissions:

- chemical input rate
- inflowing concentrations in air and water

Model Output:

- partition coefficients (Type 1)
- Z values
- fugacity of the system
- D values
- reaction and advection loss rates
- residence times or persistences (overall, reaction, and advection)
- concentrations and amounts for each compartment
- a summary diagram and charts

Minimum system requirements are an IBM-compatible PC running Windows 98 or XP.
This model will not run under Windows NT or 2000.

This program is only available in compiled form. A "readme.txt" file with more detailed technical information is included in the zipped file.

The Level II Model Version 2.17, released September 1999 continues to be available.

For non-Windows users the BASIC, evaluative, Level I, II and III fugacity models are available.

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Version 3.00 - September 2005

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Canadian Environmental Modelling Centre

Level II Software Update

Version 3.00 - September 2005

Since the Version 2.17 (September 1999) release:

Simulation ID

- There is now an input box for additional notes which is then inputted directly into the print simulation section and will appear on the final printout.

Chemical Properties

- There is a change to the half-life checkboxes. When the half-life checkbox is ticked so that the half-life is considered to be negligible and then the user enters a new half-life into the input box the check box is unchecked and the new value is stored.
- The Henry's Law Constant display has been removed from this form and is now only viewable in the results form. This has no affect the user's results.

Environmental Properties

- Addition of an environmental database. This database functions in the same manner that the chemical database functions.
- A water volume of 0 m^3 is now allowed. When this value is entered it will automatically change the volumes for sediment, fish, and suspended particles to zero m^3.

Emissions

- There are no changes to this section.

Chemical Parameters

- Same information is being displayed, it is organized differently.

Environmental Parameters

- Emissions and Inflows are now displayed on the Results form.

Results

- Unit conversions are displayed as options as opposed to buttons.
- Modified grids to match format of Level III.

- Concentration now displayed in alternate units.

Diagram

- The same information is being displayed, but appearance has been updated.

Charts

- Addition of charts to display Concentration (g/m^3), Amount (kg), and Relative Amount (%)

Error Checking

- Error checking for single corrected.

Calculations

- Fixed print out of calculations, it now correctly prints same information that is displayed

Print

- The option for printing the date and time when printing Tables has been corrected so that it works.
- Note: All corrections to units and calculations in above sections have carried over to the printout.

Save to File

- Now saves file as .csv format instead of a .txt format.

About

- The New Features Button.

Model Description

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Last updated October 26, 2005.

Canadian Environmental Modelling Centre

Level III Model

Version 2.80 - May 2004

New in version 2.80!

A Level III simulation describes a situation which is one step more complex and realistic than the Level II model. Like the Level II model, chemical is continuously discharged at a constant rate and achieves a steady state condition in which input and output rates are equal. The loss processes are degrading reactions and advection. Unlike the Level II model, equilibrium between media is not assumed and, in general, each medium is at a different fugacity. A mass balance applies not only to the system as a whole, but to each compartment. Rates of intermedia transport are calculated using D values which contain information on mass transfer coefficients, areas, deposition and resuspension rates, diffusion rates, and soil runoff rates. It is now essential to define inputs to each medium separately, whereas in Level II only the total input rate was requested.

Mass balances are calculated for the four bulk media of air (gas + aerosol), water (solution + suspended sediment + biota), soil, (solids + air + water), and sediment (solids + pore water). Equilibrium exists within, but not between media. For example, sediment solids and pore water are at equilbrium, but sediment is not necessarily at equilibrium with the overlying water.

Physical-chemical properties are used to quantify a chemical's behaviour in an evaluative environment. Three types of chemicals are treated in this model: chemicals that partition into all media (Type 1), involatile chemicals (Type 2), and chemicals with zero, or near-zero, solubility (Type 3). The model can not treat ionizing or speciating substances. The Level III model assumes a simple, evaluative environment with user-defined volumes and densities for the following homogeneous environmental media (or compartments): air, water, soil, sediment, suspended sediment, fish and aerosols.

This model gives a more realistic description of a chemical's fate including the important degradation and advection losses and the intermedia transport processes. The distribution of the chemical between media depends on how the chemical enters the system, e.g. to air, to water, or to both. This mode of entry also affects persistence or residence time.

Three persistences are calculated, an overall value, T_O, and individual persistences attributable to reaction only, T_R, and advection only, T_A. Note that $1/T_O$ equals the sum of $1/T_R$ and $1/T_A$.

The rates of intermedia transport are controlled by a series of 12 transport velocities. Reaction half-lives are requested for all 7 media. The advective residence time selected for air also applies to aerosols and the residence time for water applies to suspended sediment and fish. The advective residence time of aerosols, suspended sediment and fish cannot be specified independently of the air and water residence times.

Features of the Level III Program:
Provides a database of chemicals and chemical properties.
Permits temporary additions/changes of chemicals and their properties to a simulation.
Permits permanent additions, changes and deletions of chemicals and their properties to the database.
Provides a database of environments and environmental properties.
Permits temporary additions/changes of environments and their properties to a simulation.

Permits permanent additions, changes and deletions of environments and their properties to the database.
Provides context-sensitive Help.
Displays and prints the Level III model calculations, as performed by the program.
Allows the printing of simulation tables, the summary diagram, and a small selection of charts.
Allows the program results to be saved as a comma separated value file, readable by spreadsheet programs such as Excel.

This program was based on the following publication:

Mackay, D.2001. "Multimedia Environmental Models: The Fugacity Approach - Second Edition", Lewis Publishers, Boca Raton, pp.1-261.

The required input data are:
Chemical Properties:

- chemical name
- molecular mass
- data temperature
- reaction half-life estimates for

- air
- water
- soil
- sediment
- aerosols
- suspended sediment
- aquatic biota
- Type 1 chemicals

- water solubility
- vapour pressure
- log Kow
- melting point
- Type 2 and 3 chemicals

- partition coefficients

Environmental Properties:

- areas and depths for all bulk media
- volume fractions for all subcompartments
- densities for all subcompartments
- organic carbon content (soil, sediment & suspended sediment only)
- fish lipid content (Type I chemicals only)
- advective flow residence times for air (including aerosols), and water (including suspended sediment and aquatic biota)
- advective flow residence time for sediment burial
- transport velocities

- air side air-water mass transfer coefficient - water side air-water mass transfer coefficient - rain rate - aerosol deposition velocity (wet and dry combined) - soil air phase diffusion mass transfer coefficient - soil water phase diffusion mass transfer coefficient - soil air boundary layer mass transfer coefficient - sediment-water mass transfer coefficient - sediment deposition velocity - sediment resuspension velocity - soil water runoff rate - soil solids runoff rate

Emissions:

- chemical input rates for each bulk medium or compartment
- inflow concentrations in air and water

Model Output:

- partition coefficients (Type 1)
- Z values
- fugacity of each medium
- intermedia transport rates and D values
- reaction and advection D values and loss rates
- residence times or persistences (overall, reaction, and advection)
- concentrations and amounts for each medium
- a summary diagram
- charts of key results

This program is only available in compiled form. A "readme.txt" file with more detailed technical information is included in the zipped file.

Minimum sytem requirements:
Pentium-75MHz with 8 Mb of RAM running Windows 95. On some systems it may be necessary to adjust your screen resolution.

The Level III Model Version 2.70, released March 2002 continues to be available.

For non-Windows users the BASIC, evaluative, Level I, II and III fugacity models are available.

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Bug Report

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Canadian Environmental Modelling Centre

Level III Software License

Version 2.80 - May 2004

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Level III Software Update

Version 2.80 - May 2004

Since the Version 2.70 (March, 2002) release:

Simulation ID

- There is now an input box for additional notes which is then entered directly into the print simulation section and will appear on the final printout.

Chemical Properties

- There was an error in v. 2.70 which did not allow changes in the Chemical Properties and New Chemicals sections to be saved to the Database. This has been corrected and applies to all three types of Chemical.
- There is a change to the half-life checkboxes. When the half-life checkbox is ticked so that the half-life is considered to be negligible and then the user enters a new half-life into the input box the check box is unchecked and the new value is stored.
- In all input boxes on the Chemical Properties and New Chemical pages, when errors are caught the field in error is highlighted and cleared in order for the user to reenter an appropriate value.
- The Henry's Law Constant display has been removed from this form and is now only viewable in results. This was done to ensure a smoother run of the program. It will not affect the user's results in any way.

Environmental Properties

There is an increased flexibility for defining Environments.
- A water area of 0 m2 is now allowed. When this value is entered it will automatically change the water and sediment depths to 0 m.
- The areas of soil and sediment are no longer displayed on this input form.
- It is now impossible to enter a zero value for area or depth of air.
- There are more Standard Environments to choose from. The single Default Environment has been replaced by Default 1, 2 and 3. Three additional environments are included as described below. The user is not permitted to change the properties of these environments in the database. - Default 1 is similar to the Default Environment in v. 2.70 except that the air residence time has been changed to reflect a more realistic value. - Default 2 is based on the Southern Ontario region defined in ChemCAN v 6.00. - Default 3 is similar to the Shield Lake Region. - Shield Lake Region (Mackay, D., Webster, E., Woodfine, D., Cahill, T., Doyle, P., Couillard, Y., Gutzman, D. 2003. Towards Consistent Evaluation of the Persistence of Organic, Inorganic and Metallic Substances. Human and Ecological Risk Assessment (HERA). 9: 1445-1474.) - EQC - standard environment (Mackay, D., Di Guardo, A., Paterson, S., Cowan, C.E. 1996. Evaluating the Environmental Fate of a Variety of Types of Chemicals Using the EQC Model. Environ. Toxicol. Chem. 15: 1627-1637.) - Beyer Environment (Beyer, A., Mackay, D., Matthies, M., Wania, F., Webster, E. 2000. Assessing Long-range Transport Potential of Persistent Organic Pollutants. Environ. Sci. Tech. 34: 699-703.) Additional entries in the database can

be changed and are thus are the responsibility of the user.
- There was an error in v. 2.70 which did not allow changes in the Environmental Properties and New Environments sections to be saved to the Database. This has been corrected.
- Labeling on the Environmental Properties' tabs is now consistent, where titles and units are given only where necessary. There has been to reduce redundancy and to ensure that all appropriate units are displayed.
- It is now possible to enter a value of zero into any of the volume fraction boxes as long as the total value of the boxes is equal to one or another appropriate value.
- There is now a Help Button on the New Environment Form.

Emissions

- There are no changes to this section.

Chemical Parameters

- There are no changes to this section.

Environmental Parameters

- There are no changes to this section.

Results

- The Advection tab has been corrected and now includes the air residence time as defined in Chemical Properties by the user.
- The Results section has been corrected to correctly display the D-value units, and aquivalence units for Type 2 chemicals.
- A more balanced and easy to follow look has been given to the Results section.

Diagram

- When the diagram is closed the user's cursor now advances naturally onto the Charts button.

Charts

- Bar charts are used for the fugacities, masses and concentrations in each medium. Pie charts are used for relative amounts in each medium.

Error Checking

- The error message for a user entering a value that is Outside Reasonable Bounds has been updated so that it now states "The absolute value of the exponent is too large. Please enter a reasonable value".
- On the Densities Tab in Environmental Properties the appropriate error message is now displayed when a zero value is entered.
- Error checking has been corrected so that values larger than and smaller than the absolute value of 3e?38 are caught and the program does not crash.
- Error checking has been corrected so that when the area of water > area of air the appropriate messages are displayed and corrections can be input.

Calculations

- Z-value calculations for Type 3 chemicals has been corrected so that it displays the correct values for pore water in sediment.

Print

- The option for printing the date and time when printing Tables has been corrected so that it works.
- Note: All corrections to units and calculations in above sections have carried over to the printout.

Help Files

- The Environmental Properties Help File now contains a discussion of the database including source information.
- The Environmental and Chemical Database Operations' Help Files are now applicable to both types of operations.
- The Results Help File now contains an updated definition of fugacity, consistent with Level III, steady-state non-equilibrium, concepts.

About

- The About Button on the Main form has been altered so that it no longer includes the program's name.
- The New Features Button, which you have already used, is a New Feature to this program.

Since the Version 2.65 (February 2002) release:

- The chemical half-lives are now correctly saved to the database.
- It is now possible to add new Type 2 and 3 chemicals using the "New Chemical" button.
- The name of the environment is now displayed under the chemical name before printing the results.
- Added Chart display of selected results. These can also be printed with the rest of the results.
- Corrected the description of the save-to-file function in the general Help file.
- Updated the Help file for the Print function.

Since the Version 2.20 (December 1999) release:

- The aerosol deposition velocity parameter is now entered as the dry deposition velocity and a scavenging ratio rather than as a combined wet and dry velocity.
- Updated terminology to be consistent with recent work.

Suspended sediment is now more correctly referred to as suspended particles and "pure air" is now referred to as air vapour.
Molecular mass is now more correctly referred to as molar mass.

- An over-sight in the numerical formatting routine was corrected.
- Corrected model name in various Help files and in the readme.txt file.
- Calculations now print correctly.
- All model output, whether viewed on screen, printed, or saved to a file, are identical except that values in the file are not formatted. This allows the user to see the whole number calculated by the model without any rounding effects.
- Removed irrelevent D value totals.
- Improved error checking.
- Incorrect information in the Help files for the Environmental Properties and Emissions input forms

has been removed.

- In the display of results, the layout of the chemical parameters was improved.
- The aerosol-air partition coefficient is no longer displayed for Type 2 chemicals where it is not applicable.
- A label error in display of Intermedia Transport was corrected. "Water to soil" is now "Soil to air".
- Concentration (ug/g) in sediment solids was wrongly displayed as the value for soil pore air.
- Overall D values have been added to Results display.

- Results are now saved to a comma separated value file making it more generally accessible to a variety of spreadsheet programs.
- The units of Fugacity for Type 1 and 3 chemicals were corrected in the save-to-file output.
- The save-to-file output was recording the sediment D value for reaction as that of soil. This has been corrected.
- A listing of environment properties used were added to the save-to-file output.
- A date and time stamp was added to save-to-file.
- Layout of the save-to-file output was generally improved.

- All input values are italicized in the printed output to facilitate future simulation duplication.
- The layout of the printed output of chemical parameters was improved.
- The aerosol-air partition coefficient is no longer printed for Type 2 chemicals where it is not applicable.
- The aerosol-water partition coefficient is no longer printed for Type 1 where it is unnecessary and illogical.
- The "Save Diagram" option was removed. It did not work consistently. The diagram can be captured using the "Print Screen" button on the keyboard, and pasted into a file to be saved. A note was added to the Help file for the Diagram to indicate this.

- A date and time stamping option was added to the printed output.

Special thanks to Jenn Brimacombe, Angela McLeod, Chris Warren and the WE512 class of 2001 for checking the model results.

Since the Version 2.10 (September 1999) release:

- The values displayed in the Diagram for concentration in soil and sediment have been corrected. Previously there was an error in the unit conversion.
- The units listed for Fugacity in the Tables of Printed Results have been corrected.
- The typographical error in the "note" about the air and water densities was corrected.

Model Description

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Last updated May 25, 2004.

E_TX 1.3a

A Program to Calculate Confidence Limits for Hazardous Concentrations Based on Small Samples of Toxicity Data

Tom Aldenberg

rivm
National Institute of Public Health &
Environmental Protection
Bilthoven, The Netherlands

May 1993 719102015

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I. Introduction

Welcome to ***E_TX***, the Ecotoxicological Extrapolation Program from **rivm**!
E_TX is a computer program running on MS-DOS computers. *E_TX*, short for EcoToX, currently version *1.3a*, handles the extrapolation of laboratory toxicity data to values, that may be of interest to policy makers in setting standards for environmental protection. The program may also be of use in other areas, e.g. in human health-oriented problems.
As a short motivating example, suppose one is confronted with the next seven NOEC (No Effect) concentrations for Cadmium for various different soil fauna species:

```
0.97   3.33   3.63   13.5   13.8   18.7   154
```

in some unit. These are real data from Van Straalen & Denneman (1989), who adapted this extrapolation technique from Kooijman (1987). Then, *E_TX* calculates **`0.53`** as the estimate of the 5th percentile of the hypothetical statistical distribution from which the data are thought to derive. This 5th percentile is the so-called *hazardous* concentration, above which 95% of the species seems relatively safe. We also speak about 95% species protection. This hazardous concentration is also indicated as the HC_5.
The estimate of the hazardous concentration just employed is a so-called *median* estimate: if everyone would calculate this estimate for similar batches of seven data in the same manner, for instance by using *E_TX*, then the median of the distribution of answers, of which **`0.53`** is one particular instance, would equal the hazardous concentration.
E_TX also calculates a second value, **`0.03`**, for this example, that, if everyone

would do so for their data, would result in a distribution of answers of which the 95th percentile would equal the hazardous concentration. That is, we are *confident* that we *under*estimate the hazardous concentration by 95%. One can either think of this estimate as the *left confidence limit* of a 90% double-sided confidence interval, or as the one-sided 95% confidence underestimate.

The basic idea, henceforth, is that laboratory species display different sensitivities with regard to the adverse effects of a particular toxic substance, as expressed by NOEC concentrations or LC_{50} concentrations. If nothing is assumed mechanistically, these species NOECs, or whatever, are thought to derive from some statistical distribution. 'Extrapolation', as it is called, amounts to estimating percentiles of this distribution with a certain confidence from a perhaps small set of toxicity data.

The statistical theory behind extrapolation to percentiles is treated in Erickson & Stephan (1985), Kooijman (1987), Van Straalen & Denneman (1989), Wagner & Lokke (1991), and Aldenberg & Slob (1993). E_TX is conceived as a tool for the statistical analysis of toxicity data sets. Although E_TX is relatively user-friendly, and can be run by decision makers, it is not specifically designed as a decision support system for setting environmental standards. E_TX does not care about what the nature of the data is, one feeds to it. It may be used on NOEC concentrations, EC_5 concentrations, LC_{50} concentrations, etc. In fact, the data may not be toxicity data at all, but one should be aware of the fact that the data are always log transformed. The toxicity data may pertain to any taxon level: species, genera, or even higher taxa (e.g. Crustaceans, Mammals, etc.). This means that a toxicity data set may consist of a batch of species toxicity data, or a batch of toxicity data, one for each genus, a batch of phylum data, and so on.

Nor does E_TX know about any specific environmental protection terminology, such as permissible risk levels, maximum allowable concentrations, safe or reference or background concentrations. E_TX is a program to experiment with different toxicological data sets, different confidence levels, and different species protection levels. Right now, it handles three types of statistical distribution, i.e. the log-logistic, the log-normal, and the log-triangular, one species protection level (95%), and two levels of confidence of underestimation (95% and 50%). But these may be extended in future versions. Hence, E_TX may develop over time, as more analysis tools are incorporated. We would welcome any user remarks, that could lead to improvement.

The reader who wants more information about the practical and theoretical considerations in a decision makers framework is referred to Slooff (1992) and OECD (1992).

Next to the estimation of hazardous concentrations from laboratory toxicity data,

or *extrapolation*, initial steps have been taken in E_TX to incorporate the estimation of species hazard at given environmental or experimental concentrations, here called *hazard assessment*. Whereas extrapolation goes from a pre-set species protection level and a batch of toxicity data to concentrations to be declared as environmental standard, or objective, hazard assessment goes from current or predicted environmental concentrations to estimated species protection levels. Here also, a confidence approach would be implied, but more work has to be done on that. Extrapolation is treated in the literature cited, but hazard assessment, as defined here in a statistical extrapolation-oriented framework, is treated in Appendix A of this Manual.

Acknowledgments.

I would like to thank *Kees van Leeuwen* for being the motor behind this program, and for his incredible patience; *Hans Canton, Wilbert Slooff*, and *Wout Slob* for their stimulating interest. *Esther Guinée, Janneke Hoekstra, John Janus, Robert Luttik, Erik van de Plassche, Marieke Polder*, and *Theo Traas* commented on earlier versions of the program. The correspondence with *Nico van Straalen* is acknowledged. *Maarten 't Hart* helped with the final testing and documentation.

TA

II. User's Guide

A. Installation

E_TX can be run on MS-DOS Personal Computers, or so-called Compatibles, right out of the box from floppy disk. So, strictly speaking, there is no obligation to install *E_TX* on a hard disk. Obviously, it is more convenient to do so.
Installation under MS-DOS is very simple. Be sure, you see the DOS prompt **C:>** after starting the PC. If wanted, make a directory to place *E_TX* in, by typing:

```
MD ETX,
```

or some other directory name. Go to this directory:

```
CD ETX
```

Put the *E_TX* floppy disk in drive **A:** or **B:**. Copy all the files from the *E_TX* floppy disk to the hard disk (**C:**) by typing:

```
COPY A:*.*
```

or:

```
COPY B:*.*
```

After the files have been copied, remove the floppy disk from the floppy disk unit.
Now you are ready to run E_TX from the hard disk.

B. Running E_TX

Running E_TX is even simpler. If the file **ETX.EXE** is in the current directory, just type:

```
ETX
```

Otherwise, first go to the directory, where **ETX.EXE** is located. If the MS-DOS PATH is set by you, or someone else, to scan the **ETX-directory** for commands, then typing **ETX** will work from any directory. In the current version, data files that are saved by, or are to be used by E_TX are put into the same directory, as where the program runs. This might change in a future release.
E_TX is operated through a menu system. You may be familiar with menu systems by other programs. If not, learning to operate the E_TX menu system should not cause any problem. 'Menu' options constitute alternative choices for the user of a program to control a program.
Menu items are displayed vertically in E_TX. There may be ten items, but usually less. Each list of menu options makes a menu screen. Menu options ending with a slash (/) lead, when activated, to a submenu containing new options. Those ending with a period (.), when activated, cause some action to be taken by E_TX. Options within parentheses, if any, are currently not implemented.
The main menu screen of E_TX after starting the program reads:

```
ETX 1.3a:

     1. Data/
     2. Statistics/
     3. Extrapolation/
     4. Hazard/
     5. Results/
     6. Quit/

[Edit Keys] to Select; [Enter] to Activate:
```

All options have trailing slashes, so each choice, when activated, gives rise to a new menu. These six options form a logical sequence of doing an extrapolation analysis: getting data, study them, carry out extrapolating exercises

and hazard assessment, collect output, and quit the program. But they need not be chosen in this exact order. If you try to do illogical things, however, such as extrapolation without entering toxicity data, E_TX will complain.
One can activate a menu item in either of two ways. The first is by pressing the number that precedes the item. E_TX should immediately respond to that. Or, secondly, one can use the arrow keys, or edit keys: **[Down]**, **[Up]**, and so on, to highlight next and previous options. In this case, no action is taken, until you press the **[Enter]** key. The last line of the menu screen, the Active Key bar, indicates what keys are active. On the screen and in this manual, brackets denote a key to be pressed, not a sequence of characters. So, **[Enter]** is the Enter or Return key.
When you are in a submenu, or sub-submenu, pressing **[Esc]**, or **[PgUp]**, brings you up one level. Pressing **[F10]** brings you up to the main menu from anywhere in the tree. Pressing initial characters does *not* activate a menu item.
Above the menu options, you find the name of the program (**ETX**) and its current version number (**1.3a**). If it says also something like **Beta**, followed by a number, then you do not have an official release, but a version distributed for review.
This title bar of a menu screen is also used to indicate where the user is located in the menu hierarchy. When you are not at the main, or top menu level, then previous menu choices have been added to the program and version indicator, separated by slashes (**/**). This results in a representation of the path followed through the menu hierarchy (tree), similar to the way operating systems display directory hierarchies. In this way, going down the menu tree (if main menu is thought to be the highest level) makes the menu path string to grow, while going back up the hierarchy does make it shrink, until you are back at the top level, and only the program and version indicator remain.
Hence, if the path string at the top of a menu screen reads:

```
ETX 1.3 a/ Statistics/ Logarithms/ Toxicity:
```

one has apparently chosen option **2. Statistics** from the E_TX main menu, then **1. Logarithms** from the Statistics menu, then **1. Toxicity** from the Logarithms menu, and one is currently facing the two options and Active Key bar:

```
     1. As Is.
     2. Sorted.

[Edit Keys] to Select; [Enter] to Activate; [Esc] to Quit:
```

These options have trailing periods, so they will do something for you. Option

1 will show you a list of the $\log_{10}$s of the toxicity data, if there are any, in the order as they have been entered. Option 2 will do the same thing, only in sorted order from smallest to largest. Since the action follows immediately, and the menu screen will be cleared, these action options are not added to the menu path string anymore. Note the extended Active Key bar, with **[Esc] to Quit** added, indicating that **[Esc]** (the Escape key) brings you back up.
In the Reference Manual, we will represent subsequent menu choices by the path traveled through the menu tree, as given by the menu title bar, but with two slight modifications: the leading program version indicator, **ETX 1.3a**, is abbreviated to **ETX**, and last menu options with trailing periods that lead to an action are added to the path. So, referring to the previous example, the act of listing the toxicity data logarithmically in the original order is effectuated through this sequence of menu choices:

ETX/ Statistics/ Logarithms/ Toxicity/ As Is.

From now on, we refer to such strings as the menu path, or path, of a command. Uncomplete paths, ending with a slash, are also called paths.

C. Leaving E_TX

As soon as you are done, you can quit (leave) E_TX from main menu through the menu choices: **ETX/ Quit/ Leave ETX!** Note that we have used the path indication method explained in the previous paragraph. On the screen, menu option **Leave ETX** has a trailing exclamation mark, which indicates that there is no mercy in case you have not saved the data that you may have entered. There is *no extra warning* if you haven't done so!
You can find out about the status of the data under **ETX/ Data/ Show/**, that will display the current data set, as well as inform the user, where the data came from, and whether they were saved.
A very crude way to leave the program at any point in the menu hierarchy is pressing **[Ctrl]+[End]** and then **[Ctrl]+[Y]**. If you miss **[Ctrl]+[Y]**, you are back where you were. Use this only in a great hurry.
A real crash route is **[Ctrl]+[Break]**, which aborts the program at once.

III. Reference Manual

The Reference Manual consists of two parts:

A. an overview of the E_TX Menu hierarchy or tree, including a short description of what each option means or does, and

B. an alphabetical Reference list for lookup of terms relating to E_TX: menu options and general issues like Files, Version, and so on.

A. Menu tree

The E_TX menu system is a tree-like hierarchy. At the so-called root of the tree, usually considered the highest level of the menu, we have E_TX itself. This level is activated by typing **ETX** at the MS-DOS prompt. After clearing the opening screen, we arrive at the first level down the tree, with six branches. The menu screen reads:

```
ETX 1.3a:

1. Data/
2. Statistics/
3. Extrapolation/
4. Hazard/
5. Results/
6. Quit/
```

followed by the Active Key bar. The **Data** menu leads, when activated (see User's Guide), to another menu screen at depth two. This reads:

```
ETX 1.3a/Data:

1. Enter/
2. Read/
3. Show/
4. Edit/
5. Save/
```

Note the growing menu path at the first line. Now, activating menu option **Enter** leads to just another menu screen at depth three.
Below follows a complete representation of the tree with both the layout and decimal numbering indicating the hierarchical structure. Each option keyword is shortly explained between parentheses. If an option does not have a submenu, then it denotes some action to be taken by E_TX, often leading to further prompts for user action, like entering or modifying data, actions to save data in disk files, listing of results, statistical output, etc.

E_TX menu tree:

```
1 Data/              (data management)
     1.1 Enter/          (enter new data through the keyboard)
          1.1.1 Toxicity.     (enter laboratory toxicity data)
          1.1.2 Exposure.     (enter environmental exposure data)
     1.2 Read/           (read data from files)
          1.2.1 Toxicity.     (read toxicity data)
          1.2.2 Exposure.     (read exposure data)
     1.3 Show/           (look through the data)
          1.3.1 Toxicity/     (show toxicity data)
               1.3.1.1 As Is.      (in the original order)
               1.3.1.2 Sorted.     (in sorted order)
          1.3.2 Exposure/     (show exposure data)
               1.3.2.1 As Is.      (in the original order)
               1.3.2.2 Sorted.     (in sorted order)
     1.4 Edit/           (modify entered or read data)
          1.4.1 Toxicity.     (edit toxicity data)
     1.5 Save/           (save data to files on disk)
          1.5.1 Toxicity/     (save toxicity data)
               1.5.1.1 As Is.      (in the original order)
               1.5.1.2 Sorted.     (in sorted order)
          1.5.2 Exposure/     (save exposure data)
               1.5.2.1 As Is.      (in the original order)
               1.5.2.2 Sorted.     (in sorted order)
2 Statistics/        (look at statistical data evaluations)
     2.1 Logarithms/     (show log10 transformed data)
```

```
          2.1.1 Toxicity/     (logarithmic toxicity data)
               2.1.1.1 As Is.      (in the original order)
               2.1.1.2 Sorted.     (in sorted order)
          2.1.2 Exposure/     (logarithmic exposure data)
               2.1.2.1 As Is.      (in the original order)
               2.1.2.2 Sorted.     (in sorted order)
     2.2 Basic Statistics/(look at simple data summaries)
          2.2.1 Toxicity/     (of the toxicity data)
               2.2.1.1 Logistic.   (the logistic distribution)
               2.2.1.2 Normal.     (the normal distribution)
     2.3 Goodness-of-Fit/(Goodness-of-Fit of distributions)
          2.3.1 Toxicity/     (fitted on the toxicity data)
               2.3.1.1 Logistic.   (the logistic distribution)
               2.3.1.2 Normal.     (the normal distribution)
3 Extrapolation/    (look at extrapolation results)
     3.1 Logistic.       (for the logistic distribution)
     3.2 Normal.         (for the normal distribution)
     3.3 Triangular.     (for the triangular distribution)
4 Hazard/           (look at hazard assessment results)
     4.1 Logistic/       (for the logistic distribution)
          4.1.1 Fixed Hazard.(exposures at fixed hazard levels)
          4.1.2 At Exposure/  (at the exposure data)
               4.1.2.1 As Is.      (in the original order)
               4.1.2.2 Sorted.     (in sorted order)
5 Results/          (collect the results)
     5.1 Save/           (save results on disk)
          5.1.1 All.          (save all results)
6 Quit/             (quit ETX)
     6.1 Main Menu.      (no, back to main)
     6.2 Leave ETX!      (yes, definitely leave ETX)
```

B. Reference List

The Reference List serves as an explanatory alphabetic lookup table for E_TX related keywords. Among these are all menu options, and features of more general interest to the E_TX user. The Reference List is both indexed in the Table of Contents, as well as in the General Index at the back of the Manual. Some of the entries refer to related issues elsewhere in the list. If a keyword is a menu option, then the relevant menu paths are given first. The meaning and notation of menu paths, or paths for short, is explained in the User's Guide (Running E_TX).

1. All

Path: **ETX/ Results/ Save/ All.**

All is the only option under **ETX/ Results/ Save**, indicating that one can only save all the results to a file, not a selection of them. **All** prompts for a file name (default extension **.ETX**). One can edit the line that contains **.ETX** pre-written, including the extension. If no extension is given, extension **.ETX** is added by E_TX. Existing files can never be overwritten by E_TX.

2. As Is

Paths:
ETX/ Data/ Show/ Toxicity/ As Is.
ETX/ Data/ Show/ Exposure/ As Is.
ETX/ Data/ Save/ Toxicity/ As Is.
ETX/ Data/ Save/ Exposure/ As Is.
ETX/ Statistics/ Logarithms/ Toxicity/ As Is.
ETX/ Statistics/ Logarithms/ Exposure/ As Is.
ETX/ Hazard/ Logistic/ At Exposure/ As Is.

As Is always refers to the original order in which the data have been entered or read from a file. As can be seen from the above paths, **As Is** refers to the last menu screen to fire the complete command. On this last menu screen, it is always the first option of two, the second being **Sorted**. Hence, pressing **[Enter]** activates it as the default. What **As Is** actually does, depends on the previous menu options, to which the reader is referred..

3. At Exposure

Path: **ETX/ Hazard/ Logistic/ At Exposure/**

At Exposure is the second option of **ETX/ Hazard/ Logistic/**. It displays the estimated hazard at the entered or read exposure concentrations, given the logistic density estimate fitting the current toxicity data set. See: **Hazard**. The alternative option of **At Exposure** is **Fixed Hazard** (see there, and see **Hazard**, as well as Appendix A for the full story).
The two options of **At Exposure** are: **As Is** and **Sorted**. These refer to the on-screen representation order of the data, i.e. unsorted or sorted.

4. Basic Statistics

Path: **`ETX/ Statistics/ Basic Statistics/`**

`Basic Statistics` is the second option of **`Statistics`**. Most of the statistics shown on screen are used in the extrapolation and hazard calculations. There is no need to study or record these statistics, unless you want to check the extrapolation and hazard estimates by hand, study the influence of outliers on means and standard deviations, see where the data are located in log space, and so on.

`Basic Statistics` has only one option: **`Toxicity`**. No statistics are calculated in E_TX for the exposure data set. The exposure data are just used to estimate the hazard at each individual exposure value. The statistics are displayed with respect to two distributions: the logistic and the normal distribution. Both screens show the toxicity sample statistics: mean and standard deviation, and the respective extrapolation constants.

These extrapolation constants are given in Tables B1 (logistic) and B2 (normal). Table B1 is derived from Aldenberg & Slob (1993). Table B2 (95% confidence) is derived from Wagner & Lokke (1991). The median extrapolation constants for the normal distribution (Table B2: median) have been kindly provided by dr. R.J. van Wijk (AKZO Research CRL, Arnhem). These constants have been determined through simulation by drawing 5000 random samples for each sample size. We have not been able to check the performance of these constants, but they seem to match the median extrapolation constants for the logistic distribution quite well. No such table seems available in the statistical literature. Extrapolation constants for sample sizes not in Table B1 or B2, are estimated in E_TX by linear interpolation.

The logistic basic statistics screen presents some parameter estimates of the logistic distribution parameters, α and β. It is important to note that all are $\log_{10}$ values. Hence, they should be compared with the values as given under **`ETX/`**

`Statistics/ Logarithms/`. The moment estimates are those of Kooijman (1987):

$$\hat{\alpha} = \bar{x}$$

and

$$\hat{\beta} = s_n \cdot \frac{\sqrt{3}}{\pi}$$

In fact, for a toxicity data set of size n, s_n is the bias-corrected sample standard deviation on the basis of (n - 1). Hence, one could speak of bias-corrected moment estimates.
The maximum likelihood estimates of α and β are more difficult to estimate. We need them for the goodness-of-fit calculations for the Logistic distribution. Now, α and β have to be solved from the nonlinear equations:

$$\sum_i \frac{1}{1 + \exp((x_i - \alpha)/\beta)} - \frac{n}{2} = 0$$

and

$$\sum_i \frac{(1 - \exp((x_i - \alpha)/\beta)).(x_i - \alpha)/\beta}{1 + \exp((x_i - \alpha)/\beta)} + n = 0$$

The equations are given by D'Agostino & Stephens (1985). We did check out, that they indeed follow from a maximum likelihood argument. These equations must be solved numerically. We have used a discrete Newton-Raphson procedure to do so. A numerical subtlety turned out to be those cases where the x_i are symmetrically located around their average, for example: -1 and +1. Then the first equation with α equal to the x-average is uniformly satisfied for all β, which blows up the iterative procedure. We decided to put α equal to x-average, in these cases, and to iterate only the second equation to solve for β.
The logistic basic statistics screen further displays so-called HC_5 fitting estimates for the logistic parameters. These are described in Appendix A. See also **`Hazard`**. The idea is that, if an exposure value happens to be equal to the median (extrapolation) estimate of the HC_5, on the basis of the toxicity data,

then the estimated hazard at that exposure concentration should be 5%.Appendix A explains that this leads to the estimate:

$$\beta = k_L \cdot s_n / C_5$$

The **Basic Statistics** display screen for the Normal distribution contains analogous parameter estimates for location and scale parameter μ and σ. The moment estimates, corrected for bias, are identical to the sample mean and sample standard deviation. The maximum likelihood estimate of σ is the raw standard deviation of the sample, not corrected for bias, i.e. on the basis of *n*, the number of toxicity tests. These are not used by E_TX, but only given for completeness. For the normal case, goodness-of-fit calculations are based on the sample mean and sample standard deviations, not on the maximum likelihood estimates, as is the case with the logistic distribution.

5. Batch mode

The previous version of E_TX: ETX 1.2A did have a batch mode. You could type under MS-DOS a command line like: **ETX MYDATA.DAT 3**, in order to process the third line of the data in file **MYDATA.DAT**. Then, the menu system was by-passed, and an output file **MYDATA.3** was automatically generated. Hence, data files could consist of different sets of toxicity data, e.g. one line per toxic substance. A MS-DOS **.BAT** file, could consist of several such ETX command lines.
In the current version (*1.3a*), reading and saving of files has been much improved. Now, there is only one toxic substance per file, and different commented toxicity data are on separate lines. Again, a batch mode option would be feasible, but it has not been incorporated again. We would like to know whether there is a need for it.

6. Data

Path: **ETX/ Data/**

Data is the first option of the E_TX main menu screen. It is analogous to the first entry 'File' on the menu bar of many programs. **Data** gives rise to a submenu. One can enter data interactively through the keyboard (**Enter**), read data from disk files (**Read**), look through data, that were entered or read before (**Show**),

modify data (**Edit**), and save data to disk files (**Save**). The reader is referred to these options for further information.

7. Edit

Path: **ETX/ Data/ Edit/**

Edit is the fourth option of the **ETX/ Data/** menu screen. **Edit** allows the modification of a data set that has been entered through the keyboard, or read from a disk file. Currently **Edit/** has only one option: **Toxicity**. In this version, it is not possible to edit the exposure data from inside E_TX.
It is important to keep in mind, that **Edit** is not capable of editing data sets in the way an ASCII editor, or wordprocessor can do that. **Edit** is meant for correcting typing errors in data just entered, or to add comment strings to poorly annotated data; it can be used for sensitivity analysis, e.g. by changing data a little and calculating difference quotients, etc. For instance, <u>it is not possible, to delete data, or to add extra data to the set, or extra comment lines</u>, through **Edit**.
Data modifications, that do change the size of the data set, need an outside full-screen editor, such as the MS-DOS Editor, Turbo Pascal Editor, WordPerfect, or other word processors. In those cases, edit the disk file that contains the data. Hence, for data sets just entered: save them, leave E_TX, and start the editor of choice. Save the augmented data to a disk file, then open E_TX again and read in the modified file.
For modifications of existing data, **Edit** is fine. Initially, **Edit** works just like **Show** (see: **Show**). One can browse through the data page by page, entry by entry, until the entry to be modified is found, and highlighted, i.e. printed inversely. Then, pressing the **[Space]** bar, opens the possibility to edit the current entry. This Line edit mode is indicated by the extension of the highlight to the full length of the line (full highlight). In this state, the Edit keys (see: Edit keys) are active, and the entry can be modified, or extended. Invalid entries are not accepted. These are non-positive values, values not separated from the comment by white space (spaces and/or tabs), lines without a numeric 'head', and so on. In particular, one cannot enter a comment line starting with an exclamation mark. Pressing the **[Esc]** key, when still in Line edit mode (full highlight), <u>recovers the previous data line</u>.
After completing the modifications, pressing the **[Enter]** key makes the changes permanent. One stays in Browse mode, just as under **Show**, however. So, one can travel through the data again, entrywise, or pagewise, find a new

entry to be modified, press the **[Space]** bar to activate Line edit mode (full highlight), make modifications, press **[Enter]** to confirm, and so on, until you are done.
Now, there are two ways to leave **Edit**: through the **[Esc]** key, or through the **[Enter]** key. The **[Esc]** key restores the old data set, while **[Enter]** confirms all modifications. There are some extra questions asked for confirmation. Hence, there are several occasions in **Edit**, where you can change your mind and restore the previous situation.
One cannot edit exposure data right now. Apart from using an outside editor, there is a work-around in E_TX, if you know what you are doing (not recommended though). Read the **.EXP** file as toxicity data through **ETX/ Data/ Read/ Toxicity** (be sure to save the previous toxicity data!). Then, edit, save again, with extension **.EXP**, E_TX will not protest against that. The first line of the header of the file written by E_TX, however, is erroneous then, since it will read: **! ETX Data File: Toxicity Tests**. However, this information is not seen by E_TX, while reading the file as an Exposure data file. It is the responsibility of the user to correct this erroneous comment in the file afterwards with a real-world editor. Afer reading in the modified exposure set, be sure to erase the internal toxicity data set, that is still the exposure set just saved, by reading in a fresh genuine toxicity data set, or by entering new toxicity data.

8. Enter

Path: **ETX/ Data/ Enter/**

Enter is the first option of the **ETX/ Data/** menu screen. **Enter** allows the interactive entry of data through the keyboard, or of new data, overwriting existing data, previously entered, or previously read from a disk file.
Enter has two options: **Toxicity** and **Exposure**. **Toxicity** allows the entry of toxicity data, **Exposure** allows the entry of exposure data. Although the procedures of entering each category are identical, except that **Toxicity** asks for a Toxic substance name, while **Exposure** asks for an Exposure substance name, both sets are treated very differently inside E_TX. The toxicity data set is 'extrapolated' to HC_5 estimates, e.g. for setting standards, while exposure values are evaluated through their estimated hazard to species, on the basis of the toxicity data.
Enter is rather primitive, working on a line by line basis. It is impossible to go back to previous lines, in order to change them, or to delete previous entries. Typing errors, however, can be corrected through **Edit** (see **Edit**), after

completing data entry of the whole set. At present, one cannot add data to an already completed set, from within E_TX, nor can one delete one or more entries. This might change in future releases.
More flexible, full-screen editing, can be accomplished, however, with the aid of an editor or wordprocessor outside of E_TX. One has to save the data from E_TX, then, in order to apply these editors to the data.
`Enter` first asks for a toxic substance name, or exposure substance name. A highlighted entry line signifies that the Line edit mode is on (full highlight). Line edit mode is pretty sophisticated, though. One can enter a substance name, and edit the line with the Edit keys, until satisfied. Pressing **`[Esc]`** blanks the whole entry line. **`[Enter]`** terminates Line edit mode. If **`[Enter]`** is pressed immediately, without entering a name, **`Unnamed substance`** is assumed.
There is no check on the validity of a name entered, from the point of view of E_TX file reading conventions (see Files), so, if you do not follow these conventions, **`Enter`** may continue without complaint, the name may even be correctly saved to a file through **`Save`**, but E_TX may not be able to read in the file successfully lateron. The convention is: do not start the name with a numeric 'head', followed by white space (spaces and/or tabs). A numeric head, immediately followed by other non-white characters is fine (e.g. **`2,4-dimethyl ...`**). The reason is that E_TX will interpret the string with the white space as a concentration value followed by a comment, and assumes that the substance name was not given (**`Unnamed substance`**).
After successfully entering the substance name, one is prompted for the first numerical entry through **`1:`** followed by a full highlight, which means that Line edit mode is on again. This Line edit mode is exacty the same as the one for the toxic substance. Now, a numeric non-zero, non-negative, value, e.g. a concentration value, is expected. E_TX will respond with **`Entry xx is invalid`**, if it doesn't like it, and after pressing the **`[Enter]`** key, the entry line is blanked, and restored in full highlight. **`[Esc]`** blanks a non-empty entry line. If the entry is found OK, the next entry is prompted with **`2:`**. Up to a maximum of 300 data values can be entered for each data set.
One may enter bare numbers, and E_TX will not complain. But, one can make each entry self-documenting by adding additional information about the nature of the entry, such as the unit of measurement, a species name, a reference, anything informative. This information may be entered directly following the numeric value, i.e. in Edit line mode, but separated from it by at least one space or tab. The value and its comment string, as it is called, stay together as one data record. When the data is saved to a disk file, the complete data records are saved on a line by line basis.
To stop the entering process, press the **`[Enter]`** key while in Edit line mode,

with nothing entered on the highlight. E_TX will ask for confirmation, one may resume entering mode by pressing the **[Esc]** key. Pressing **[Esc]**, while in Edit line mode, with an *empty* highlight, will cause E_TX to ask you, whether you want to leave **Enter**ing mode, and restore the old data. If you confirm this, everything entered so far is deleted, and the previous situation (perhaps without data) is restored. To clear previous data, start **ETX/ Data/ Enter**, press **[Enter]** at the first numerical (empty) prompt, and press **[Enter]** to confirm. After completing **Enter**, E_TX immediately starts calculating all statistics and extrapolation estimates, as well as hazard estimates, if exposure data are available. Hence, there are no menu options or paths, that by themselves trigger calculations to be done. They have been done, as soon as data have been entered, edited, or read.
After having entered a complete data set, either toxicity data, or exposure data, or both, one can do several things. One can inspect the data, and browse through them, with **Show**. **Show** only lets you look through the data, while pointing (highlighting) individual entries. These are not full highlights, so you are not in Line edit mode. One can also **Edit** the data, that is make modifications, add comments and so on. It is impossible, right now, to add extra data to the sets, or to delete data. This has to be done outside of E_TX, with the aid of an ASCII editor, a wordprocessor, or a spreadsheet. A third possibility is to **Save** the data just entered to a disk file, leading to a permanent storage of the data, e.g. for distribution to colleagues, for coordinated data management within a work group, for outside editing, and so on. A fourth possibility is to go straight on to **Results/ Save**, and save the results of the calculations. A **Results** file does contain the data entered or read, so if you have a results file, the data can always be recovered. This is quite easy in fact, because the initial section of a results file is similar to a stand-alone E_TX toxicity or exposure data file. And of course, if you are just experimenting, you can walk the menu tree to study the results, and quit E_TX as soon as you are done. Then the data can not be recovered afterwards.

9. Exposure

Paths:
ETX/ Data/ Enter/ Exposure.
ETX/ Data/ Read/ Exposure.
ETX/ Data/ Show/ Exposure/
ETX/ Data/ Save/ Exposure/
ETX/ Statistics/ Logarithms/ Exposure/

Exposure always refers to an exposure data set, comprising similar concentration

values relating to one particular toxic substance under study. These values may be environmental or experimental concentrations of that substance, either measured, estimated, proposed, legally imposed, or whatever. The purpose of the exposure data is, that, given an extrapolation exercise, that is, given an impression of the distribution of species sensitivities for a specific toxic substance, one would like to assess the percentage of species that is harmed, or is safe, with respect to a set of given exposure concentrations relating to the toxic substance under study. These may be exposures in the past, at present, to be expected in the future. They may come from a survey, a set of scenario predictions, etc. What E_TX does is to try to estimate percentiles of the species sensitivity distribution at the given exposure concentrations. These need not be raw data, they may be calculated from other data, e.g to make them comparable to the nature of the toxicity data. One may also massage the toxicity data first to make them comparable to the environmental data. That is pretty much the responsibility of the user.
E_TX can have one exposure data set of maximally 300 values, including their comments. One may **`Enter`** them, **`Read`** them from a disk file, browse through them after entering or reading (**`Show`**), **`Save`** them to a disk file after entering or reading, study their log transformed values (**`Logarithms`**) on which all statistics are based. The reader is referred to these options.
Exposure data cannot be **`Edit`**ed at present from within E_TX. If the exposure data need to be edited, then save them, and use an outside editor to make modifications. There is a work-around to do it inside E_TX, by retreiving them as toxicity data (see **`Edit`**), but this is only feasible if you understand the structure of E_TX files.

10. Extrapolation

Path: **`ETX/ Extrapolation/`**

`Extrapolation` is the third option of the E_TX main menu screen. Extrapolation, in E_TX, is the estimation of the hazardous concentration at the 5th percentile of the distribution of species sensitivities for a toxic substance, and forms the main focus of the program.
Activating **`Extrapolation`** leads to a submenu with three options, since there are three statistical distributions involved: logistic (**`Logistic`**), normal (**`Normal`**), and triangular (**`Triangular`**). However, the statistical treatment of the triangular distribution differs in several respects from those of the logistic and normal distributions. See **`Triangular`** for some extra information about that.

The logistic and normal distribution version of extrapolation are very much akin. In both cases, the screen reports the species protection level (95%), that cannot be changed, the number of toxicity tests involved (minimum number is two), and the Median Estimate of the HC_5, printed bold on the screen, as well as the 95% Underestimate of the HC_5. These are based on extrapolation constants, reported under **`Basic Statistics`**. Tables of the extrapolation constants are reproduced in Appendix B.
In general, there is very little difference between the extrapolation answers of the respective distributions. Note that the HC_5 estimates are in the *original units* of the data. Hence, the $\log_{10}$ transformation of the data, that had been applied to do the statistics, has been removed in the HC_5 estimates. These estimates can be either directly used for setting environmental standards or objectives, or, depending on other considerations of a scientific, or policy nature, further calculations, e.g. involving extra safety factors, or partition coefficients, etc., may be applied to arrive at the final answers wanted. These considerations are outside the scope of E_TX.

11. Files

E_TX data files can come into existence in essentially two ways. One is by saving data from inside E_TX to a file. The menu path is: **`ETX/ Data/ Save/ Toxicity/ As Is`**, to save E_TX toxicity data, and: **`ETX/ Data/ Save/ Exposure/ As Is`**, in order to save E_TX exposure data.
The second way of coming into existence of an E_TX data file is by constructing it yourself with an editor, word processor or spreadsheet. Both possibilities are treated in the next two paragraphs.
In the current version of E_TX, files are saved into the same directory as where **`ETX.EXE`** is located. One can only read files from this same directory. Hence, do not try to change directory from within E_TX. This might change in future versions.

a. E_TX generated files

Files saved by E_TX can be read in again by E_TX. Saving a data file through E_TX, has the advantage that E_TX automatically includes all kinds of information in the header of the file, to be shown below. This identifies the file internally, e.g. date, time, a save serial number, etc.. Since they are readable ASCII files, this information can be inspected, printed, and edited.
The advantage of self-constructed files is that you can include a lot more

additional information into the data file than is currently possible through *E_TX*: how the data were selected, scope of the project, extra comments between data lines to identify taxa, or circumstances, and so on.

E_TX data files can be made almost self-documenting. There is no excuse anymore for unannotated toxicity data. Of course, both ways of constructing *E_TX* files can be combined. For example, one may enter data interactively in raw order, then save them in sorted form, and edit the file through adding additional annotation. If the very flexible rules of *E_TX* data formatting are maintained, the resulting file can be read again by *E_TX*. When more data become available, they may be added to the file, with ample space for documentation.

E_TX data files can have any extension. However, toxicity data saved by *E_TX* have default extension **.TOX**, while exposure data have default extension **.EXP**. Existing data files can never be overwritten by *E_TX*.

Both toxicity and exposure data files obey the same rules of formatting. *E_TX* cannot make a distinction between them, so reading an exposure file into the toxicity data structure is possible, but likely to result into non-sensical calculations.

Table B3 displays a toxicity data file as saved by *E_TX*. In fact, the lines starting with a **!** have been added by *E_TX* automatically. These are comment lines and serve as comments. They tell us that it is an *E_TX* toxicity data set, that it was saved with *E_TX 1.3a*, the name of the file (chosen by the user), date, time, a data save serial number as an extra lable in case of trouble, the name of the toxic substance and additional information about it, the number of toxicity data, and then the seven data values.

Note, that these are annotated data. The annotated data strings were entered from the keyboard in *E_TX*, including the lay-out to align decimal points and unit names. The comment strings following the data may have any form, and may contain any information. We have copied the information from Table 2 in Van Straalen and Denneman (1989). Unit, species, data reference, special circumstances: everything fitting in one line (80 characters) may be included in the comment string. If you enter the data through *E_TX*, save through *E_TX*, and read back into *E_TX*, it is impossible to separate the data values and their comment strings, although the latter are optional. Moreover, from inside *E_TX* it is impossible to overwrite a file. It simply refuses to save data to an existing file.

Table B4 displays an exposure data file as saved by *E_TX*. It has the same basic structure as an toxicity data file. The exposure substance is named differently here. The environmental or exposure concentrations may be of a different nature than the laboratory data.

b. Editor generated files

Editor files are data files meant to be read by E_TX, but not made through E_TX. The advantage, as already mentioned, is flexibility in documenting the data sets. Moreover, data files can be managed by a data manager independently of E_TX. Any ASCII editor can be used, e.g. MS-DOS 5.0 Editor, Turbo Pascal Editor, etc. Also, wordprocessors, spreadsheet, and data base programs. Do not use the internal format of wordprocessors. Use there ASCII export options.
Table B5 shows a fancy E_TX data file composed with WordPerfect. The lines are saved as 'ASCII Text (DOS)'. In this case, we have not tried to mimic the E_TX data file header, although one can take one from an E_TX data file and adapt it. The purpose of this example is to show how flexible E_TX data formatting is. Blank lines (lines with spaces, tabs, and a Carriage Return), and Comment lines with an exclamation mark in front, perhaps preceded by white space (spaces and/or tabs), can be put at any place in the file: at the beginning, at the end, and anywhere in between.
The first item to alert E_TX, while reading a data file, is the toxic substance name, or exposure substance name. If one lacks, E_TX assumes **`Unnamed Substance`**. These names are not preceded be an exclamation mark, and may contain spaces, and any additional information fitting on the line. Substance names may start with numeric information, but *not followed by spaces or tabs*. This is because a number followed by white space and additional characters is interpreted by E_TX as data: a value followed by a comment. So, as a substance name: **`2,4,5-T`** is fine, but **`2 4,5-T`** would be read as the value **`2`** and comment **`4,5-T`**. After a number has been seen, no names without exclamation marks may follow anymore. They are considered erroneous and E_TX will complain about an error in line number xx.
Hence, E_TX data, e.g. annotated concentrations of toxicity tests, consist of a number, optionally followed by a comment string, separated by white space (blanks and/or tabs). One blank suffices. Note that at least one blank, or tab, is obligatory now. So, **`15mg/l`** is *not* OK, in order to prevent typographic errors to pass by unnoticed, e.g. **`1o.7 ug/l`**. E_TX counts the data automatically. It can correctly distill a few numbers hidden within a heavily commented file.
Separate data must be on separate lines: the leading number on a line is taken as the value, while what follows, after white space, is interpreted as comment string. So, the line: **`2.0 1.0 5.0 ug/l (three reproduction values for Daphnia)`** contains *one* E_TX data value (**`2.0`**), and its comment string: **`1.0 5.0 ug/l (three reproduction values for Daphnia)`**.
There is only one substance per file. One cannot use a subset of the numbers in a file. If that is wanted, use an editor to select the numbers and save them in a

new file.
Since both the substance name, as well as the data comment strings are optional, a minimum E_TX data file consists of a bare list of anonymous numbers, separated by Carriage Returns. This is perhaps useful for numerical experimentation.

c. E_TX Results files

With the option **ETX/ Results/ Save/ All.**, one can save the results of an E_TX session to a disk file. The results saved always refer to the latest run. Hence, if one enters some toxicity data, and later reads new ones from a file, all internal results relate to the latest run. The single option **All** indicates that every result, whether it has been on the screen or not is saved. One cannot save part of them, e.g. just the extrapolation results.
In fact, there is no need to study any result on the screen. One can enter or read in the data, and go straight on to **ETX/ Results/ Save/ All.**, to save a printable ASCII file with everything in it, including the data themselves.
Table B6 shows the contents of the E_TX results file **CDVSTRAA.ETX** that corresponds to the E_TX data files **CDVSTRAA.TOX** (Table B3) and **CDVSTRAA.EXP** (Table B4). These files are also on the distribution disk.
The Results file is an ASCII printable file and gives an overview of all possible screen output appended to each other, with some additional comments. One can import this file into an editor or word processor, edit the text, and print it as a whole or in parts.
Results files have default extension **.ETX**. This can be changed, when prompted, but giving no extension is overruled by E_TX by adding **.ETX**. E_TX cannot overwrite existing files.

12. Fixed Hazard

Path: **ETX/ Hazard/ Logistic/ Fixed Hazard.**

Fixed Hazard is the first option of **ETX/ Hazard/ Logistic/**. The second option is **At Exposure** (see there, and see **Hazard**, as well as Appendix A for the full story).
Fixed Hazard refers to the display of estimated hypothetical exposure values at a range of fixed hazard percentages (1%, 2%, 5%, 10%, 25%, 50%, 75%, 90%, 95%, 98%, and 99%). This yields an impression of what the range of concentration values is that gives rise to these hazards. The median estimate of

the HC_5 is printed bold on the screen.
One may also print this list (from the **`Results .ETX`** file) for a given toxic substance of special interest, and use it as a lookup table for future exposure concentrations.

13. Goodness-of-Fit

Path: **`ETX/ Statistics/ Goodness-of-Fit/`**

When fitting distributions to data, in order to estimate percentiles, and the HC_5, it is important to assess, whether the data indeed seem to derive from the hypothesized distribution. This can be done with a goodness-of-fit test. One may be familiar with the well-known Kolmogorov-Smirnov test for goodness-of-fit (see almost any textbook on statistics). However, this test is designed for situations where the distribution generating the data is known, as well as its parameter values. In our case, the distribution parameters are estimated from the data. Hence, we arrive at a problem of circularity: the distribution is estimated from the data, can we test whether the data derive from the distribution?
D'Agostino & Stephens (1986) show that one can approach this matter with the same Kolmogorov-Smirnov test statistic:

$$D \cdot \sqrt{n}$$

only with modified critical values for this statistic, given a pre-set significance level. *D* signifies the maximum distance between the empirical distribution function (staircase) of the data, and the estimated distribution. Their tests, especially for the logistic distribution, distinguishes between different sample sizes: 5, 10, 20, 50, and infinity. (D'Agostino & Stephens, 1986, p.158), which seems quite relevant to the usual size of toxicity data sets. The table is reproduced as Table B7 in Appendix B. The parameters of the logistic distribution must be estimated from the data by maximum likelihood. Thus, we had to estimate the parameters this way (see **`Basic Statistics`**).
For the smallest sample size feasible for an extrapolation exercise, $n = 2$, we found that for any values of the two data points, the test statistic equals 0.458. It seems impossible to derive critical values in that case. We reasoned that the interpolating curve of critical values for intermediate sample sizes should all intersect at 0.458 at sample size two. Hence, we added this case to the table of critical values (Table B7, Appendix B).
Intermediate critical values are derived in E_TX through linear interpolation. E_TX

reports the goodness-of-fit for all four significance levels, and prints whether the hypothesis that the data derive from the logistic should be rejected, or not. The choice of significance level is up to the user.
For the normal distribution, D'Agostino & Stephens (1986, p. 123), present a modified Kolmogorov-Smirnov test statistic:

$$D \cdot (\sqrt{n} - 0.01 + 0.85 / \sqrt{n})$$

Critical values of this statistic for the same four significance levels are reproduced in Table B8 of Appendix B. Now, no further differentiation for low sample size is presented. We are unclear about the validity of the test for sample sizes much below 20. Hence, E_TX does present the goodness-of -fit for the normal distribution for small sample sizes, but the warning is printed: **Below *n* = 20, this test may not perform well**.'

14. Hazard

Path: **ETX/ Hazard/**

Hazard is the fourth option of the E_TX main menu. Hazard assessment, as defined in E_TX, is discussed in Appendix A. The purpose of hazard assessment is to estimate the hazard to species at given environmental exposure concentrations, that may be independent of the toxicity data. The exposure data set may refer to any predicted or measured data, perhaps adapted for comparison to the laboratory toxicity data. The only option of **Hazard**, currently, is **Logistic**, since the primary emphasis of the HC_5 has been on the logistic distribution.
The density estimate of the logistic distribution employed is calculated in such a way that, if an exposure value happens to be equal to the median estimate of the HC_5 on the basis of the current toxicity data set, then the estimated hazard is equal to 5%. Clearly, exposure values below the estimated HC_5 lead to hazards smaller than 5%, while those above lead to larger hazard percentages.
Under **Logistic**, two options are offered: **Fixed Hazard** and **At Exposure**. The first option displays hypothetical exposure values at a range of fixed hazard percentages (1%, 2%, 5%, 10%, 25%, 50%, 75%, 90%, 95%, 98%, and 99%). This yields an impression of what the range of concentration values is that gives rise to these hazards. One may also print this list (from the **Results .ETX** file) for a given toxic substance of special interest, and use it as a lookup table for future exposure concentrations.

The second option takes the exposure data as entered, or read from file, and evaluates the hazard at these values.

15. Leave E_TX

Path: **ETX/ Quit/ Leave ETX!**

After pressing **Quit**, you can either change your mind, through the first option (default): **Main Menu**. But, if you are definitely sure to leave E_TX, you can do so by activating the second option of **Quit**, i.e. **Leave ETX**. The trailing exclamation mark in a permanent warning that all internal data, or results, are lost by doing so! This warning is independent of whether you have saved the data, or the results, or not. If you haven't, no extra warning, or prompt follows, so, take care, when leaving E_TX.

16. Logarithms

Path: **ETX/ Statistics/ Logarithms/**

Logarithms is the first option of **Statistics**. E_TX data are entered or read as raw concentration values, densities, accumulated amounts, or other toxic substance measures. All statistical calculations and percentile estimates are carried out with the $\log_{10}$ transformed data. One can examine the data converted to logarithms through **Logarithms**. Further options allow one to choose between **Toxicity** and **Exposure**.
The data are always log-transformed, this cannot be circumvented once inside E_TX. If log transformation is not wanted, one may construct a raw data set consisting of ani-logs, i.e. powers to the base 10. The logs are always taken with respect to the base 10. Log transformation requires that the raw data are positive (non-zero, non-negative). Non-positive concentrations, while entered or read, lead to **Invalid Entry** errors. If the original data do contain zero values, correct them before feeding them to E_TX, by adding a small value, e.g. half the detection limit. One may add this 'starter' value to all the data if wished. Do not forget to substract these small amounts from the extrapolation estimates afterwards. These estimates are in the original units.
If **Logarithms** is activated, and the appropriate data set chosen, the screen displays log concentrations followed by an arrow (**<--**), followed by the original data, including their comments. One may browse through the log values in the

original order (**As Is**), or in sorted order (**Sorted**), by using the arrow keys **[Up]**, **[Down]**, **[Home]**, and **[End]**. If there are more than 20 values, one can page through the data set with **[PgUp]**, **[PgDn]**, and/or **[Up]** and **[Down]**. The entry highlight moves with the arrow and paging keys. It only indicates where one in located in the set, no editing is possible. Consecutive entries are numbered with a number followed by a colon (**:**). The end of the data set is indicated with: **(no more)**. End of page, with more values to follow, is indicated with: **(more)**.

17. Logistic

Paths: **ETX/ Statistics/ Basic Statistics/ Toxicity/ Logistic.**
ETX/ Statistics/ Goodness-of-Fit/ Toxicity/ Logistic.
ETX/ Extrapolation/ Logistic.
ETX/ Hazard/ Logistic/

Logistic refers to the so-called logistic distribution. This is a statistical distribution of a certain mathematical form. See Aldenberg & Slob (1993) for a review of some logistic mathematics. The logistic distribution looks very much like the normal distribution. It has two parameters α and β, closely related to the mean and standard deviation of the distribution.
Basic Statistics displays some sample statistics of the toxicity data and different estimates of α and β.
Goodness-of-Fit shows measures of departure of the toxicity data from the logistic distribution. If these measures are too high, doubt is thrown on the hypothesis that the logarithms of the toxicity data derive from the logistic distribution.
Extrapolation treats the estimation of the hazardous concentration (HC_5), being the 5th percentile of the logistic distribution, from the current toxicity data. Extrapolation can also be based on the normal and on the triangular distribution.
Hazard handles the assessment of the percentage of potentially harmed species at the current exposure data set. Hazard assessment is only done for the logistic distribution in the current version. See the options just mentioned for more details.

18. Main Menu

Path: **ETX/ Quit/ Main Menu.**

If you want to quit E_TX, but change your mind, e.g. to see if the data were saved, you can return to the E_TX main menu, by activating **Main Menu**. The alternative option is **Leave ETX**, see there.
[F10] brings you up to the main menu from anywhere in the menu tree.

19. Normal

Paths: **ETX/ Statistics/ Basic Statistics/ Toxicity/ Normal.**
ETX/ Statistics/ Goodness-of-Fit/ Toxicity/ Normal.
ETX/ Extrapolation/ Normal.

Normal refers to the well-known normal distribution from ordinary statistics. The normal distribution has two parameters μ and σ, called mean and standard deviation.
Basic Statistics displays some sample statistics of the toxicity data and different estimates of μ and σ.
Goodness-of-Fit shows measures of departure of the toxicity data from the normal distribution. If these measures are too high, doubt is thrown on the hypothesis that the logarithms of the toxicity data derive from the normal distribution.
Extrapolation treats the estimation of the hazardous concentration (HC_5), being the 5th percentile of the normal distribution, from the current toxicity data. Extrapolation can also be based on the logistic and on the triangular distribution. No hazard assessment is incorporated in E_TX as yet for the normal distribution. See the options just mentioned for more information.

20. Printer

There is currently no direct printer support in E_TX (version 1.3 a). However, all results can be saved into an ASCII printable file. This file can be imported into an ASCII Editor, or a wordprocessor for editing and printing. See **Results**, or **All**.

21. Quit

Path: **ETX/ Quit/**

Through **Quit** one can leave E_TX. E_TX won't let you do so immediately. A submenu follows with the first option: **Main Menu**, as default, meaning: return to the E_TX main menu screen. The second option **Leave ETX!** does end E_TX, without any further delay. The exclamation mark is a reminder that no warning is given, if you haven't saved your data or results. Any data entered, or results obtained, but not saved, is lost after activating **Leave ETX**.
A quick way to get out, from anywhere in the menu tree, is **[Ctrl]+[End]**, and **[Ctrl]+[Y]** to confirm. This certainly destroys all data entered, or results obtained. An emergency stop is given by **[Ctrl]+[Break]**.

22. Read

Path: **ETX/ Data/ Read/**

Read is the second option of **ETX/ Data/**. With **Read**, one can read data into E_TX from disk files. E_TX data files are ASCII printable files that are either saved through E_TX, or files made trough an ASCII Editor, a wordprocessor, or a spreadsheet. Use: save (export) as ASCII, or as a print file (often extension **.PRN**), in these programs.
The E_TX file conventions are explained under Files of the Reference List.
Read has two options: **Toxicity** and **Exposure**. A data file read under **Toxicity** fills the E_TX internal toxicity data set. A data file read through **Exposure** is put into the E_TX internal exposure data set. There is no essential difference between a toxicity and an exposure data file. Both have the same structure. While saving, default extensions **.TOX**, and **.EXP** are standard, but not obligatory, E_TX conventions. One may develop other conventions. Additional internal comment lines in data files, saved by E_TX, further indicate, whether we have a toxicity data file or an exposure data file, but this information is not interpreted by E_TX. Hence, there is good reason to stick to some extension convention, preferably that of E_TX, next to the informative and critical annotation of the toxic or exposure substance names and of the individual data entries.
Here we assume that there are valid E_TX files available in the directory where **ETX.EXE** is located. After activating **Read**, and choosing the type of data set, the menu screen clears and E_TX responds with:

Edit Search Profile for Data File to be Opened:
***.TOX**

This means that the MS-DOS search profile conventions, including wild cards, are supported. The highlighted edit line indicates that Line edit mode is on, with ***.TOX** already filled in as a default search profile. It means: list all the files with extension **.TOX**. Pressing **[Enter]**, accepts the default search profile, and indeed lists the files. With the Edit keys, one may change the search profile, or fill in a filename of specific interest. When no file conforms to the user-supplied search profile, E_TX says: **No file found on this Search Profile**.
It is currently *not* possible to specify a file including its directory path, such as **MYDATA*.TOX** (for files in the subdirectory of the one where E_TX is located), or **C:\RIVM\ALD*.TOX** (for complete paths). This feature is high on the list to be changed in a future version.
Once you have a list of files on the screen, you can browse through them with the arrow keys. The highlight indicates the position of the list you are pointing at. After having found the file to load, you can load it by pressing **[Enter]**. E_TX tries to read the file, as explained under Files, and if it runs into an offending line, if any, it will beep and say: **File Reading Terminated: Invalid Input at Line *xx*** and then, print the invalid line. The file is not processed any further. See Files for the expectations E_TX has about the structure of the information in E_TX data files.
Otherwise, if no errors are found, the file is read, and the data are stored internally. The screen says: **File Reading Successful: *n* Data Read**, pauses for a while, because E_TX will now calculate all statistics immediately. This may take some time for a large data set.

23. Results

Path: **ETX/ Results/**

Results is the fifth option of the main E_TX menu screen. In the present version of E_TX, **Results** is only used for saving the results of the calculations to a disk file. Hence, the only option is **Save**. Other options may be added in future versions, e.g. printer support, results selection, and so on. **Save** in turn has the only option **All**, to indicate that it is only possible now to save all results relating to the current data sets (toxicity data and exposure data).
Collecting results is only necessary, if one wants to save the data and the results in one file, for documentation, or later printing. There is no control over what is saved, and what not, nor about the order of the items saved. Everything that

E_TX calculates is saved, whether it *has been on-screen, or not*. Hence, a very quick way to do an extrapolation exercise, and hazard assessment, is to enter data, or load (read) a file, and save all results. The resulting **.ETX** file can be printed out, and studied. No menu tree walking, or on-screen displaying, is really necessary to obtain the results. As soon as the data are entered, or read, all calculations are done.

24. Save

Paths: **ETX/ Data/ Save/**
ETX/ Results/ Save/

ETX/ Data/ Save/ lets us save the data to disk, that previously have been entered, or read from disk files. In the current version, it is only possible to save files to the directory where the program runs.
E_TX may contain two data sets at once, differing in nature. The one set is formed by the (laboratory) toxicity data set; the other is the (environmental) exposure data set. Hence, **ETX/ Data/ Save/** has two further options: **Toxicity** and **Exposure**. The first option saves the toxicity data, the second the exposure data, but not before in each case the sorting order has been selected (**As Is**, or **Sorted**).
For saving either data set, a filename has to be chosen. A default extension, **.TOX**, or **.EXP** is given on an inverse edit line. One can use the Edit keys (see there), to enter/edit the filename, e.g. **CADMIUM.TOX**, **24DMP.TOX**, etc. The extension may be changed to something else, e.g. **.DAT**, or **.TX1**, etc., or it can be removed. But *E_TX* will add **.TOX**, or **.EXP**, as appropriate, if no extension is given.
E_TX is designed not to overwrite any existing file. If you try, *E_TX* will refuse, and say so. This is done with an eye to current trends in Good Laboratory Practice. Of course, one can fiddle in the files through MS-DOS. In fact, one must do so to add, or remove, data to an *existing* data set. Hopefully, the lack of the possibility to overwrite files from inside *E_TX*, as well as the in-file information that is written, should catch most common accidents.
ETX/ Results/ Save/ refers to the writing of all statistical, extrapolation, and hazard assessment results, *including* the data, to a disk file. See **Results** and **All**. Here also, an inverse edit line is offered with a pre-written extension **.ETX**. One can use the edit keys to edit the filename, e.g. **CADMIUM.ETX**, etc. The extension may be changed, or removed. If no extension is given, *E_TX* will nevertheless add **.ETX** to the filename. Filenames longer than eight characters are trimmed. An existing file of the same name cannot be overwritten.

25. Show

Path: **ETX/ Data/ Show/**

Show is the third option of **Data**. After having entered data (**Enter**), or having read data from file (**Read**), one may want to inspect the data, in order to see what they look like, whether there are any typing or reading errors, whether the comment strings annotating the data have to be extended or modified, and so on (**Show**).
Show allows one to browse through both the toxicity and the exposure data sets. Hence, **Show** has two options: **Toxicity** and **Exposure**. One may further choose to browse the data in the original order (**As Is**), or in sorted order (**Sorted**). **Sorted** only refers to the on-screen representation. The data are kept in the original order internally.
One may browse through the data by using the arrow keys **[Up]**, **[Down]**, **[Home]**, and **[End]**. If there are more than 20 values, one can page through the data set with **[PgUp]**, **[PgDn]**, and/or **[Up]** and **[Down]**. The entry highlight moves with the arrow and paging keys. It only indicates where one in located in the set, no editing is possible. Consecutive entries are numbered with a number followed by a colon (**:**). The end of the data set is indicated with: **(no more)**. End of page, with more values to follow, is indicated with: **(more)**.

26. Sorted

Paths:
ETX/ Data/ Show/ Toxicity/ Sorted.
ETX/ Data/ Show/ Exposure/ Sorted.
ETX/ Data/ Save/ Toxicity/ Sorted.
ETX/ Data/ Save/ Exposure/ Sorted.
ETX/ Statistics/ Logarithms/ Toxicity/ Sorted.
ETX/ Statistics/ Logarithms/ Exposure/ Sorted.
ETX/ Hazard/ Logistic/ At Exposure/ Sorted.

Sorted always refers to the order of the data after sorting from smallest to largest. As can be seen from the above paths, **Sorted** refers to the last menu screen to fire the complete command. On this last menu, it is always the second option of two, the first being **As Is**, meaning unsorted. Hence, **As Is** is the default, while **Sorted** needs an extra key press (**[Down]**) before it can be activated with the **[Enter]** key. What **Sorted** actually does, depends on the previous menu options, to which the reader is referred.
An additional subtlety of **Sorted** is that, for the on-screen actions (all except

Save), no physical sorting is done: it only refers to the on-screen representation. The data themselves are kept in the original order. In case of **ETX/ Data/ Save/**, however, the respective data are really saved in sorted order to disk. If this option is used, without an analogous action through **As Is**, the original order of the data can never be recovered from the sorted files.

27. Statistics

Path: **ETX/ Statistics/**

Statistics is the second option of the E_TX main menu screen. It allows the user to look at some statistical summaries of the data. **Statistics** gives rise to a submenu. One can look through the logarithms of the data, which essentially enter the statistical analysis (**Logarithms**), inspect some basic statistical summaries of the data, like means, standard deviations, and distribution parameter estimates (**Basic Statistics**), and one can examine the goodness-of-fit of some statistical distributions fitting the data (**Goodness-of-Fit**).

28. Toxicity

Paths:
ETX/ Data/ Enter/ Toxicity.
ETX/ Data/ Read/ Toxicity.
ETX/ Data/ Show/ Toxicity/
ETX/ Data/ Edit/ Toxicity.
ETX/ Data/ Save/ Toxicity/
ETX/ Statistics/ Logarithms/ Toxicity/
ETX/ Statistics/ Basic Statistics/ Toxicity/
ETX/ Statistics/ Goodness-of-Fit/ Toxicity/

Toxicity always refers to a toxicity data set, comprising similar concentration values relating to one particular toxic substance under study. These may be laboratory toxicity data for this toxic substance for different species or other taxa, either raw or averaged. A toxicity data set may also be a set of mesocosm, or field experiment, toxicity data for the particular toxic substance. The prime requirement is that it makes sense to assume that the toxicity data derive from a log-logistic, log-normal, or log-triangular distribution.
E_TX will try to estimate the 5th percentile for these distributions, based on the toxicity data set. This is called extrapolation. Furthermore, E_TX will try to estimate the distribution itself, in order to be able to estimate the hazard to

species, that is the percentage potentially harmed, at given environmental exposure concentrations. Hence, next to a toxicity data set, *E_TX* can have an exposure data set. Both sets refer to the same toxic substance, but their names (toxic substance name and exposure substance name) may differ, as well as their exact nature (total concentrations versus dissolved, or other fractions; conversion to standard conditions, e.g. sediment or soil characteristics).
Toxicity data may derive from a diversity of sources, as long as they refer to the same toxic substance. Some may be raw data, others calculated from other data, in order to obtain a consistent set, that is thought to derive from one statistical distribution. One may convert the toxicity data to values comparable to the exposure data, or adapt the exposure data to the laboratory conditions relating to the toxicity data. That is pretty much the responsibility of the user.
E_TX can have one toxicity data set of maximally 300 values, including their comments. One may enter them (**`Enter`**), read them from a disk file (**`Read`**), browse through them after entering or reading (**`Show`**), edit them to make modifications (**`Edit`**), or to extend the comment string (annotation); one may **`Save`** them to a disk file after entering or reading, study their log transformed values (**`Logarithms`**) on which all statistics are based.
One can study basic statistics of the toxicity data, as well as the distribution parameter estimates of distribution fitting them (**`Basic Statistics`**), and one can examine the goodness-of-fit of these distributions based on the toxicity data (**`Goodness-of-Fit`**) . The reader is referred to these options.

29. Triangular

Path: **`ETX/ Extrapolation/ Triangular.`**

`Triangular` is the third option of **`Extrapolation`**, and refers to the triangular distribution. The method implemented here is that of Erickson & Stephan (1988), called the FAV (Final Acute Value). See also OECD (1992). In the spirit of *E_TX*, the nature of the data is the responsibility of the user. Hence, the FAV may be applied to Chronic data, as well, and may be targeted on the taxon level preferred.
The statistics of the triangular distribution differs from the logistic and normal distributions. While the logistic and normal statistics are based on all the data points, the FAV is applied to the lower four points only. Since the four points are taken to derive from the lower tail of the distribution, they must be below the median of the data set. Hence, one needs a minimum of eight points to apply this method. The HC_5 is estimated from linear regression on these four points.

The advantage is that species insensitive to a toxic substance (the species at rank five or higher) have little influence on the estimate. On the other hand, the influence of the more sensitive species is increased.
One could device similar tail-oriented methods for the logistic and the normal distribution, and one could also develop all-points treatments for the triangular. We have not done so yet, since there is no need for a combinatorial proliferation of methods. In OECD (1992), it was found that the tail-oriented FAV on the basis of the triangular distribution yields results that correlate very well with the all-points median estimates of the HC_5 for the logistic and the normal distributions.
Perhaps, FAV falls into a caregory of its own. In a future release we might reorganize the **`Extrapolation`** section.

30. Version

The current program version is E_TX 1.3a. It is displayed on all E_TX menu screens as the first part of the menu title bar, e.g. **`ETX 1.3a/ Data/ Save/`**.

Appendix A Hazard Assessment

In this Appendix, our implementation of Hazard Assessment at given exposure concentrations is discussed, as well as some problems with a related formulation in the literature.

By Hazard Assessment in E_TX, we mean estimations of the hazard to species at one or more given concentrations, for example experimental or environmental concentrations. Such concentrations we call exposure concentrations.

For extrapolation, we work with the (laboratory) toxicity data at hand, and estimate the hazardous concentration for two levels of confidence. To estimate the hazard at concentrations that may or may not be equal to the hazardous concentration, or HC_5, we need an estimate of the statistical distribution that fits the toxicity data best.

Even if we confine ourselves to the logistic probability density function, there are several ways of fitting this distribution of species sensitivities to the toxicity data set. The first particular estimate, that comes to mind, is the density estimate based on the maximum likelihood estimate of the parameters of the logistic distribution. Another is based on the moment estimates of the parameters, and a third may be the one based also on the moment estimates, but now with the variance corrected for bias, i.e. $n/(n - 1)$ * variance.

All these estimates lead to different estimates of the logistic parameter β, and therefore different density estimates. These in turn result into different estimates of the hazard at given concentrations of exposure.

We decided that the density estimate should be the most accurate at concentrations around the HC_5, i.e. the hazardous concentration for 5% of the species.

In order to find the best β, we reasoned as follows. The ’best’ estimate of the

HC_5 is taken here as the median estimate, that in the long run will overestimate the HC_5 as often as it underestimates it. Now the median estimate of the logHC5 is calculated as:

$$\log HC_5 = \bar{x} - k_L \cdot s_n$$

with k_L depending on sample size as tabulated in Appendix B (Table 1).
If we take

$$\alpha = \bar{x}$$

then we can calibrate β of the unknown density in such a way that the HC_5 of this calibrated density corresponds exactly to the median estimate of the true HC_5 on the basis of the sample. Thus we must solve beta from the identity

$$\alpha - \beta \cdot C_5 = \bar{x} - k_L \cdot s_n$$

where:

$$C_5 = \ln(\frac{95}{5}) = \ln(19) = 2.9444$$

See Aldenberg & Slob (1993) for a review of some logistic formulae.
This leads to the estimate

$$\beta = k_L \cdot s_n / C_5$$

Hence, β of the estimated density is proportional to the sample standard deviation.
For example let's take the seven Cd data (Van Straalen & Denneman 1989) again: 0.97, 3.33, 3.63, 13.5, 13.8, 18.7, 154 [ug/g]. We have (after

transformation with $\log_{10}$):

$$\bar{x} = 0.9712$$

and

$$s_7 = 0.7028$$

Hence, with

$$k_7\ (50\%) = 1.78$$

it follows that

$$\alpha = 0.9712$$

and

$$\beta = 1.78 * 0.7028 / 2.9444 = 0.4249$$

Now that we have estimated α and β, we can estimate percentages of hazard for species, *p*, at given $\log_{10}$-transformed concentrations:

$$x = \log_{10}(\textit{Exposure concentration})$$

This can be easily done from the explicit cumulative logistic distribution function:

$$p = \frac{100}{1 + \exp(-(x-\alpha)/\beta)}$$

So, the percentage of species *un*protected at a proposed reference value (Van

Straalen and Denneman (1989), Table 3) of 0.8 [ug/g], i.e.:

$$x = \log_{10}(0.8) = -0.0969$$

yields:

$$p = \frac{100}{1 + \exp(-(-0.0969-0.9712)/0.4249)} = 7.5\%$$

Similarly, at 3.5 [ug/g] (between 2nd and 3rd NOEC), we would calculate a species hazard of:

$$p = 26.8\%$$

At 15 [ug/g] (between 5th and 6th NOEC), the hazard is

$$p = 61.8\%$$

These hazard estimates seem in line with the scatter of the seven toxicity data. Van Straalen and Denneman, however, calculate 15% hazard for the case where we have 7.5% (Table 3: 85% protection). The explanation is that the Van Straalen and Denneman formula (9) is based on the 95% confidence estimate of the HC_5 instead of the median estimate used here. Writing their formula (9) as:

$$p = \frac{100}{1 + \exp((\alpha - x)/\beta)}$$

with:

$$\alpha = \bar{x}, \quad x = \log_{10}(c), \quad \beta = 3 \,.\, d_n \,.\, s_n \,/\, \pi^2$$

we observe that the formulae are identical, except that their beta is proportional to the sample standard deviation with a different constant of proportionality. The essential difference, apart from the mathematical form, is that the constant dm refers to the 95% ’confidence’ column in Kooijman (1987, Table 1, delta2=0.05).

To illustrate, for the n = 7 case above, Van Straalen and Denneman have:

$$\beta = 3*2.82*0.7028/3.1416^2 = 0.6024$$

while we employ:

$$\beta = 1.78*0.7028/2.9444 = 0.4249$$

Indeed, by using the larger beta, we also arrive at p = 14.5%, i.e. 85.5% protection. Hence the difference between the two hazard estimates boils down to Van Straalen and Denneman having a broader density estimate on the basis of the same data. One would be inclined to think that hazard percentages sensu Van Straalen and Denneman at given concentrations tend to overestimate the true hazard percentages, and therefore, due to the 95% confidence factor d_n, could act as right confidence limits of these hazards. But, this has turned out not to be the case. If the log transformed exposure concentration happens to be equal to the sample average, both hazard percentages become 50%, while for exposure concentrations above the sample average, the Van Straalen and Denneman hazard percentages are *smaller* than those calculated on the basis of the median estimate. We think that an estimate of the species hazard at given exposure concentrations should not be based on an estimated standard deviation of the logistic distribution that results from matching the 5th percentile of that distribution with a deliberate underestimate of the true HC_5.

Appendix B Tables

Table B1. Extrapolation constants (Logistic distribution) for the 95% confidence underestimate and median estimate of the log HC_5.

n	95% confidence	median
2	27.70	2.49
3	8.14	2.05
4	5.49	1.92
5	4.47	1.85
6	3.93	1.81
7	3.59	1.78
8	3.37	1.76
9	3.19	1.75
10	3.06	1.73
11	2.96	1.72
12	2.87	1.72
13	2.80	1.71
14	2.74	1.70
15	2.68	1.70
20	2.49	1.68
30	2.28	1.66
50	2.10	1.65
100	1.95	1.64
200	1.85	1.63
500	1.76	1.63
inf	1.62	1.62

Table B2. Extrapolation constants (Normal distribution) for the 95% confidence underestimate and median estimate of the log HC_5.

n	95% confidence	median
2	26.206	2.35
3	7.656	1.94
4	5.144	1.82
5	4.210	1.78
6	3.711	1.77
7	3.401	1.76
8	3.188	1.74
9	3.032	1.72
10	2.911	1.70
11	2.815	1.69
12	2.736	1.68
13	2.670	1.68
14	2.614	1.68
15	2.566	1.68
20	2.396	1.67
30	2.220	1.67
50	2.065	1.67
100	1.927	1.65
200	1.840	1.65
500	1.763	1.645
inf	1.645	1.645

Table B3. Toxicity data set as saved by E_TX in file **CDVSTRAA.TOX**.

```
! ETX Data File: Toxicity Tests
! Saved with: ETX 1.3a
! Data File Name: cdvstraa.tox
! Date: Feb. 26, 1993
! Time: 15:46:42
! Data Save Serial Number: 1

! Toxic Substance:
Cadmium NOECs (Van Straalen & Denneman, 1989)

! Number of Data = 7

154    ug/g Dendrobaena rubida. Bengtsson et al. (1986)
 13.5  ug/g Lumbricus rubellus. Ma (1982)
 13.8  ug/g Eisenia foetida.    Malecki et al. (1982)
  3.63 ug/g Helix aspersa.      Russell et al. (1981)
  3.33 ug/g Porcellio scaber.   Van Capelleveen (1987)
  0.97 ug/g Platynothrus peltif.Van Straalen et al. (1989)
 18.7  ug/g Orchesella cincta.  Van Straalen et al. (1989)
```

Table B4. Exposure data set as saved by E_TX in file **CDVSTRAA.EXP**.

```
! ETX Data File: Exposure Values
! Saved with: ETX 1.3a
! Data File Name: cdvstraa.exp
! Date: Feb. 26, 1993
! Time: 15:47:27
! Data Save Serial Number: 2

! Exposure Substance:
Cadmium

! Number of Data = 1

  0.8 ug/g Reference Value proposed
```

Table B5. WordPerfect generated E_TX data file (**ASCII Text (DOS)**).

```
! This is an ETX data file

  ! describing the data set
  ! date, time, editor used, analyst, project
       !  any comments at any place

! The toxic substance:
  2,4-dimethylphenol

  0.1  ug/l Daphnia (geom. average of 3 reproduction tests)
  1.5  ug/l Pseudomonas (Canton, 1972b)
200    ug/l Lymnea (regression estimate)

! comments, empty lines  in between...
! (No Arthropods)

  0.67 ug/l Xenopus (Slooff, 1989)

! ...and at the end, plus some empty lines to follow
```

Table B6. Results as saved by E_TX in file **CDVSTRAA.ETX**.

```
! ETX Results File
! Saved with: ETX 1.3a
! Results File Name: CDVSTRAA.ETX
! Date: May  17, 1993
! Time: 18:45:14
! Results Save Serial Number: 1

! Toxic Substance:
Cadmium NOECs (Van Straalen & Denneman, 1989)

! Number of Data = 7
! Data Read from File CDVSTRAA.TOX

154    ug/g Dendrobaena rubida. Bengtsson et al. (1986)
 13.5  ug/g Lumbricus rubellus. Ma (1982)
 13.8  ug/g Eisenia foetida.    Malecki et al. (1982)
  3.63 ug/g Helix aspersa.      Russell et al. (1981)
  3.33 ug/g Porcellio scaber.   Van Capelleveen (1987)
  0.97 ug/g Platynothrus peltif.Van Straalen et al. (1989)
 18.7  ug/g Orchesella cincta.  Van Straalen et al. (1989)

---------Exposure Data---------------------

! Exposure Substance:
Cadmium

! Number of Data = 1
! Data Read from File CDVSTRAA.EXP

  0.8 ug/g Reference Value proposed

---------Log10 of Toxicity Data-----------------

As Entered/Read:

    Log10(Data)    Data
1:  2.1875 <-- 154    ug/g Dendrobaena rubida. Bengtsson et al. (1986)
2:  1.1303 <--  13.5  ug/g Lumbricus rubellus. Ma (1982)
3:  1.1399 <--  13.8  ug/g Eisenia foetida.    Malecki et al. (1982)
4:  0.5599 <--   3.63 ug/g Helix aspersa.      Russell et al. (1981)
5:  0.5224 <--   3.33 ug/g Porcellio scaber.   Van Capelleveen (1987)
6: -0.0132 <--   0.97 ug/g Platynothrus peltif.Van Straalen et al. (1989)
7:  1.2718 <--  18.7  ug/g Orchesella cincta.  Van Straalen et al. (1989)

Sorted:

    Log10(Data)    Data
1: -0.0132 <--   0.97 ug/g Platynothrus peltif.Van Straalen et al. (1989)
2:  0.5224 <--   3.33 ug/g Porcellio scaber.   Van Capelleveen (1987)
3:  0.5599 <--   3.63 ug/g Helix aspersa.      Russell et al. (1981)
4:  1.1303 <--  13.5  ug/g Lumbricus rubellus. Ma (1982)
5:  1.1399 <--  13.8  ug/g Eisenia foetida.    Malecki et al. (1982)
6:  1.2718 <--  18.7  ug/g Orchesella cincta.  Van Straalen et al. (1989)
```

```
7:  2.1875 <-- 154    ug/g Dendrobaena rubida. Bengtsson et al. (1986)

---------Log10 of Exposure Data-----------------

As Entered/Read:

    Log10(Data)    Data
  1:   -0.0969 <--   0.8 ug/g Reference Value proposed

Sorted:

    Log10(Data)    Data
  1:   -0.0969 <--   0.8 ug/g Reference Value proposed

---------LOGISTIC---------------------------------

Toxic Substance: Cadmium NOECs (Van Straalen & Denneman, 1989)

Sample statistics (log10s):
   XAverage =   0.9712
XStDev(n-1) =   0.7028
          n =   7
Extrapolation Constant (50%) =  1.7800
Extrapolation Constant (95%) =  3.5900

LOGISTIC Distribution Parameter Estimates (log10s):

(Moment Estimates, Bias Corrected)
   AlphaHat =   0.9712
    BetaHat =   0.3875

(Maximum Likelihood Estimates)
   Alphahat =   0.9445
    Betahat =   0.3727

(HC5 Fitting Estimates)
   AlphaHat =   0.9712
 MedBetaHat =   0.4248


Toxic Substance: Cadmium NOECs (Van Straalen & Denneman, 1989)

LOGISTIC Distribution, Goodness-of-Fit.

Number of Tests (n) = 7
Goodness-of-Fit, Kolm.-Smirn.: D*sqrt(n) =  0.512

Kolm.Smirn.   Crit.val.   Signif.   Logistic?
     0.512       0.657     10  %    Accepted
     0.512       0.699      5  %    Accepted
     0.512       0.743      2.5%    Accepted
     0.512       0.780      1  %    Accepted

---------Extrapolation, Logistic------------------

Toxic Substance: Cadmium NOECs (Van Straalen & Denneman, 1989)

LOGISTIC Distribution
Species Protection Level = 95%
```

```
Number of Tests = 7

Median Estimate Hazardous Concentration  =  5.2520E-0001
Underestimate (95% Confid.) Hazard.Conc. =  2.8076E-0002

---------Hazard Assessment, Logistic--------------

Toxic Substance: Cadmium NOECs (Van Straalen & Denneman, 1989)

Exposure Subst.: Cadmium

Exposure Values at Fixed Hazard Percentages:

Hazard      Exposure Value
   1%  <--  1.0448E-0001
   2%  <--  2.0789E-0001
   5%  <--  5.2520E-0001
  10%  <--  1.0909E+0000
  25%  <--  3.1953E+0000
  50%  <--  9.3593E+0000
  75%  <--  2.7414E+0001
  90%  <--  8.0299E+0001
  95%  <--  1.6679E+0002
  98%  <--  4.2135E+0002
  99%  <--  8.3836E+0002

---------Hazard at Exposure Data-----------------

As Entered/Read:

       Hazard       Exposure Data
  1:     7.49%  <--   0.8 ug/g Reference Value proposed

Sorted:

       Hazard       Exposure Data
  1:     7.49%  <--   0.8 ug/g Reference Value proposed


---------NORMAL-------------------------------------

Toxic Substance: Cadmium NOECs (Van Straalen & Denneman, 1989)

Sample statistics (log10s):
   XAverage =   0.9712
XStDev(n-1) =   0.7028
          n =   7
Extrapolation Constant (50%) =  1.7600
Extrapolation Constant (95%) =  3.4010

NORMAL Distribution Parameter Estimates (log10s):

(Moment Estimates, Bias Corrected)
      MuHat =   0.9712
   SigmaHat =   0.7028

(Maximum Likelihood Estimates)
    MuHatML =   0.9712
 SigmaHatML =   0.6506
```

```
Toxic Substance: Cadmium NOECs (Van Straalen & Denneman, 1989)

NORMAL Distribution, Goodness-of-Fit.

Number of tests (n) = 7
Goodness-of-Fit, Kolm.-Smirn.: D*(sqrt(n)-0.01+0.85/sqrt(n)) =  0.566

Beware: Below n=20, this Test may NOT Perform Well.

Kolm.Smirn.   Crit.val.   Signif.    Normal?
     0.566       0.819     10  %    Accepted
     0.566       0.895      5  %    Accepted
     0.566       0.995      2.5%    Accepted
     0.566       1.035      1  %    Accepted

---------Extrapolation, Normal----------------------

Toxic Substance: Cadmium NOECs (Van Straalen & Denneman, 1989)

NORMAL Distribution
Species Protection Level = 95%
Number of Tests = 7

Median Estimate Hazardous Concentration  =  5.4248E-0001
Underestimate (95% Confid.) Hazard.Conc. =  3.8120E-0002

---------No Hazard Assessment, Normal---------------

---------TRIANGULAR----------------------------------

---------Extrapolation, Triangular.

Toxic Substance: Cadmium NOECs (Van Straalen & Denneman, 1989)

To calculate the Final (Acute) Value, the minimum number of tests
needed is 8. For toxic substance 'Cadmium NOECs (Van Straalen & Denneman,
1989)'
you have entered only 7 tests

---------End of ETX Results (All) file---------------
```

Table B7. Goodness-of-Fit for the Logistic distribution. Critical values of

$$D \cdot \sqrt{n}$$

at four levels of significance (adapted from D'Agostino & Stephens, 1986, p.158).

n	10%	5%	2.5%	1%
2	0.458	0.458	0.458	0.458
5	0.643	0.679	0.723	0.751
10	0.679	0.730	0.774	0.823
20	0.698	0.755	0.800	0.854
50	0.708	0.770	0.817	0.873
inf	0.715	0.780	0.827	0.886

Table B8. Goodness-of-Fit of the Normal distribution. Critical values of

$$D \cdot (\sqrt{n} - 0.01 + 0.85 / \sqrt{n})$$

at four levels of significance (D'Agostino & Stephens, 1986, p.123).

	10%	5%	2.5%	1%
n	0.819	0.895	0.995	1.035

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RIVM report 601501028/2004

ETX 2.0

A Program to Calculate Hazardous Concentrations and Fraction Affected, Based on Normally Distributed Toxicity Data

P.L.A. van Vlaardingen*, T.P. Traas,
A.M. Wintersen and T. Aldenberg

This investigation has been performed for the account of the Directorate-General for Environmental Protection, Directorate for Chemicals, Waste and Radiation, in the context of the projects 'Setting (Inter)national Environmental Quality Standards'.

*Corresponding author. RIVM, Expert Centre for Substances, P.O. Box 1, 3720 BA Bilthoven, the Netherlands. E-mail: etx.info@rivm.nl

ETX 2.0 was programmed by Arjen Wintersen, working for Augustijn Onderzoek, WG-plein 406, 1054 SH Amsterdam.

National Institute for Public Health and the Environment, P.O. Box 1, 3720 BA Bilthoven, the Netherlands.
Telephone: 31-30-2749111; fax: 31-30-2742971

Rapport in het kort

E_TX 2.0. Een programma om 'hazardous concentrations' en 'fraction affected' te berekenen, gebaseerd op normaal verdeelde toxiciteitsgegevens.

Dit rapport is geschreven als handleiding bij het software programma E_TX 2.0. De rekentechnieken die met dit programma worden aangeboden worden onder andere gebruikt binnen het RIVM project '(Inter)nationale normstelling stoffen' (INS) maar ook bij de Europese risicobeoordeling van bestaande stoffen. In deze projecten worden milieurisicogrenzen afgeleid voor chemische stoffen. Zowel het INS- als het EU-raamwerk staat het gebruik van statistische extrapolatie toe wanneer voldoende toxiciteitsgegevens beschikbaar zijn. De resultaten van deze extrapolatie dienen als basis voor een milieurisicogrens (INS) of een geen-effect niveau (EU bestaande stoffen) van een chemische stof. In de wetenschappelijke literatuur is recent een methode beschreven om deze statistische berekening uit te voeren. Het programma E_TX 2.0 maakt deze methode toegankelijk voor hen die werkzaam zijn in de vakgebieden van de risicobeoordeling en/of normstelling. Het programma wordt samen met dit rapport verspreid op CD-ROM.

Trefwoorden: computerprogramma; soortsgevoeligheidsverdeling; statistische extrapolatie; risicobeoordeling.

Abstract

E$_T$*X* 2.0. A Program to Calculate Hazardous Concentrations and Fraction Affected, Based on Normally Distributed Toxicity Data.

This report was written as a manual for the software program, *E*$_T$*X* 2.0. The calculation techniques offered here are currently in use in the RIVM project, 'Setting (inter)national environmental quality criteria' (INS), and the EU risk assessment for existing substances. Environmental risk limits for chemical substances are derived here. Both the INS and EU frameworks allow for statistical extrapolation in the presence of sufficient toxicity data, which serves as a basis for an environmental risk limit (INS) or a predicted no-effect concentration (EU-existing substances) of a chemical substance. A statistical technique for achieving this result, recently described in the scientific literature, is made accessible to those working on risk assessment and/or standard-setting through the *E*$_T$*X* 2.0 program. A CD-ROM is delivered along with the report.

Keywords: software; species sensitivity distribution; statistical extrapolation; risk assessment; hazardous concentration.

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Samenvatting

Dit rapport is de handleiding van het softwareprogramma *ETX* 2.0. De rekentechnieken die dit programma biedt, zijn in gebruik binnen het RIVM project 'Internationale normstelling stoffen' (INS). Binnen dit project worden milieurisicogrenzen ('milieunormen') afgeleid in opdracht van het ministerie van VROM. Het richtsnoer voor de afleiding van deze risicogrenzen staat het gebruik van een statistische extrapolatietechniek toe, bij voldoende toxiciteitsgegevens. Het resultaat hiervan dient als basis voor een milieunorm. Een statistische techniek die voor dit doel geschikt is, is recentelijk beschreven in de wetenschappelijke literatuur. Het programma *ETX* 2.0 maakt de beschreven methode meer toegankelijk voor hen die werkzaam zijn op het gebied van normstelling. Het programma is ook bruikbaar bij risicoschattingen zoals die bijvoorbeeld worden uitgevoerd in Europese risicobeoordelingen van bestaande stoffen. Het programma wordt verspreid op CD-ROM, samen met dit rapport.

ETX 2.0 rekent op basis van de beschikbare toxiciteitsgegevens een zogenaamde soortsgevoeligheidsverdeling (SSD) uit. Vervolgens toetst het programma of deze verdeling voldoet aan de criteria van een normale verdeling. Van de SSD worden het 5^e percentiel en de mediaan berekend, beide met hun 90% betrouwbaarheidsinterval. Met de berekende SSD kan ook een fractie aangetaste soorten worden geschat bij een gegeven milieuconcentratie, of een verwacht ecologisch risico (EER) bij een serie van milieuconcentraties. Het programma biedt ook de mogelijkheid om van zeer kleine datasets het 5^e percentiel te schatten met behulp van de zogenaamde *small sample* methode.

Summary

This report is the manual of the software program *ETX* 2.0. The calculation techniques that are offered with this program are used within the RIVM project 'Setting international environmental quality criteria' (INS). Within this project, environmental risk limits ('environmental standards') are derived, by order of the Dutch Ministry of Housing, Spatial Planning and the Environment (VROM). The guidance followed for derivation of environmental risk limits allows for statistical extrapolation when sufficient toxicity data are available. The result of this extrapolation serves as a basis for an environmental standard. A statistical technique to achieve this result has recently been described in the scientific literature. The program *ETX* makes this method more accessible to those that work in the field of risk assessment of chemicals. *ETX* can also be used in effect assessments as carried out in e.g. the European risk assessments for existing substances. The program is distributed on CD-ROM together with this report.

ETX 2.0 calculates a normal distribution through the toxicity data entered by the user. This gives a so-called species sensitivity distribution (SSD). This distribution is subsequently tested on normality using statistical criteria. Of the calculated distribution, the estimated 5th percentile and median are presented, each with their respective two-sided 90% confidence interval. With the calculated SSD also the fraction of affected species at a given environmental concentration can be estimated, or an expected ecological risk (EER) at a series of environmental concentrations. The program also offers the opportunity to estimate the 5th percentile of very small data sets using the so-called 'small sample' method.

1. Introduction

This report is a user's manual to *ETX* 2.0. This program implements the theory of calculating hazardous concentrations and fraction affected from species sensitivity distributions as described in Aldenberg and Jaworska (2000). The program was developed in a stepwise manner, triggered by (i) the publication of the paper by Aldenberg and Jaworska (2000), (ii) the publication of the book 'Species sensitivity distributions in ecotoxicology' (Posthuma *et al.*, 2002) and (iii) the possibility to incorporate the 'small sample' method based on the papers of Luttik and Aldenberg (1997) and Aldenberg and Luttik (2002).

The first version of *ETX* was *ETX* 1.3a (Aldenberg, 1993) which runs under MS-DOS. *ETX* 1.3a enabled estimation of hazardous concentrations using logistic, normal and triangular distributions.

The sole purpose of *ETX* 2.0 is to offer the user the calculation methods as described in the supporting literature. The selection of data, applicability of the supporting theory to the data entered and interpretation of results is left entirely to the responsibility of the user.

ETX 2.0 is a software program written in Microsoft ® Visual Basic.NET (Edition 2003). Data can be entered simply as a column of values in the data input section. After performing the calculation, the output section shows statistics and graphical representations in different sheets.

Earlier versions of this program (in Microsoft ® Excel, called '*ETX* 2000') are now obsolete. All features and possibilities in earlier Excel versions are still present in *ETX* 2.0.

1.1 Referring to *ETX* 2.0

If you use the program in an official publication, book or report, it can be referred to it in the following way:

Van Vlaardingen PLA, Traas TP, Wintersen AM, Aldenberg T. 2004. *ETX* 2.0. A program to calculate hazardous concentrations and fraction affected, based on normally distributed toxicity data. Bilthoven, the Netherlands: National Institute for Public Health and the Environment (RIVM). Report no. 601501028/2004, 68 pp.

2. What can *ETX* 2.0 do for me?

As stated in the introduction, *ETX* 2.0 offers you the opportunity to apply statistical theory common to species sensitivity distributions (SSDs). This theory is most commonly applied in the field of ecotoxicology. In this scientific discipline, datasets will usually consist of end-points derived from toxicity studies with a given substance and a particular species or process representing a pre-defined environmental compartment or ecosystem. To speak in a more practical sense, your data may (e.g.) be chronic NOECs for freshwater organisms.

You can use *ETX* 2.0 to calculate the following items:

- The program calculates a normal distribution through your data set.
- The program will show the results of three goodness-of-fit tests that you can use to decide whether your data follow a normal distribution. The three tests are known as Kolmogorov-Smirnov, Anderson-Darling and Cramér-von Mises.
- Next, the program calculates the median HC_5 (hazardous concentration) plus its two-sided 90% confidence limit and the median HC_{50} plus its two-sided 90% confidence limit. At the HC_5 and HC_{50}, the corresponding median FA (fraction affected) is given (i.e. 5% and 50%, respectively) together with its two-sided 90% confidence limit.
- Results are graphically presented in a histogram and in a cumulative density function (the latter is commonly referred to as SSD).

If you have calculated a species sensitivity distribution, you have the possibility to calculate the FA at a given exposure concentration. The program gives you the median FA and its lower and upper estimates (5 and 95% confidence). If you have a series of exposure concentrations, you can also enter this series. This series is tested for normality of distribution with the Anderson-Darling goodness-of-fit test. Next, the expected ecological risk (EER) is calculated, making use of both the SSD and environmental concentrations. The result is graphically presented as a joint probability curve (JPC).

If you want to estimate the hazardous dose for 5% of mammals or birds (HD_5), but you only have a very small data set, you may want to use (what we call) the 'small sample' method. A standard deviation from a known, external data set of toxicity data is used to estimate the 5th percentile of your data set. The lower and upper limit of the two-sided 90% confidence interval are also calculated.

Note that the 'small sample' method is dependent on knowledge of both the toxicity of your compound to a few species, as well as an expectation of the variation in toxicity data of that compound, derived from a high number of data (in the form of an external standard deviation). The method of deriving HC_5 and HC_{50} values or FA values can be applied generically to any set of toxicity data (n>1).

3. User's guide

3.1 Program type and system requirements

E_TX 2.0 is a Microsoft© Windows application that runs using the Microsoft©.NET (dotnet) framework. The program should therefore be run on Personal Computers (PC) equipped with an operating system that supports Microsoft applications. The Visual Basic.NET compact framework (version 1.1) is included on the CD and will be installed if necessary. Proper functioning of *E_TX* was tested on several combinations of Windows operating systems and Microsoft Office versions. We cannot guarantee proper functioning of *E_TX* under Windows 98. In most occasions, we encountered no problems, while in some cases installation under Windows 98 was not successful for unknown reasons. For later versions of Windows, installation was successful in most cases. In those cases where installation was unsuccessful, installation of a recent version of Microsoft's Data Access Components (which can also be found on your *E_TX*-CD) solved the problem. In Appendix 1, a list of combinations tested and possible solutions when installation problems are encountered, is given.

An operating system (like Windows NT or XP) is necessary. For proper functioning, *E_TX* does not need MS Office. However, to use the export option, MS Excel is needed, because export reports are generated in an MS Excel spreadsheet. However, the program works equally well without making use of this export option.

3.2 Installing *E_TX* 2.0

- Insert the *E_TX*-CD in the CD drive of your PC.
- Start the Windows Explorer (Start button, Programs, Accessories, Windows Explorer).
- In the left side of your screen, click on the drive that is your CD drive.
- In the right half of your screen, double click on the file **Setup.Exe**.
- The installation procedure will now start. The following screen may appear:

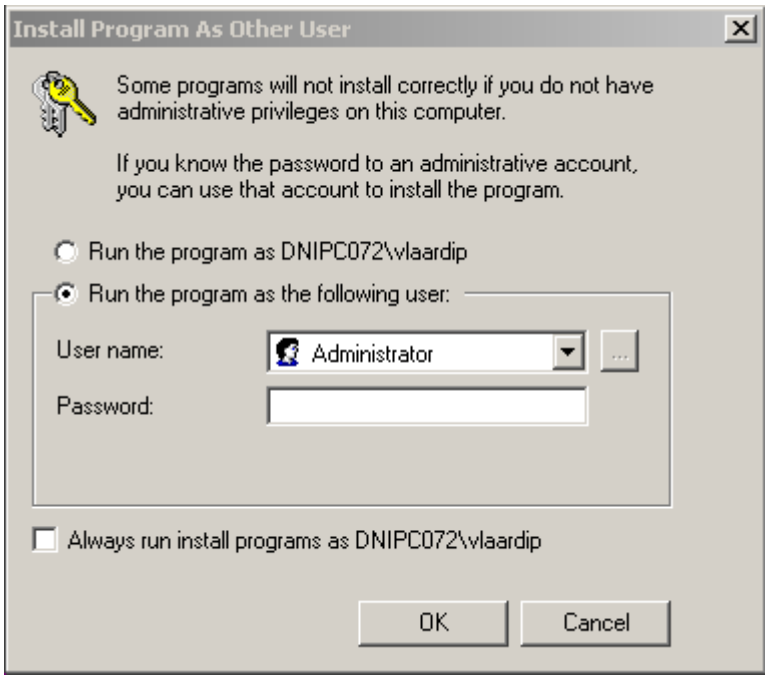

Figure 1. Intallation procedure – User screen.

You are asked to decide whether a person with administrator rights should install the program for you via the displayed dialog box. The choice for one of the options depends on your company's protocols. It is advised to install the program using a user account with administrator rights. Click **OK** after having selected the correct user.

– In the following screen, click **Next**.

Figure 2. Installation procedure - Welcome screen.

– Carefully read the license agreement that is displayed in the following dialog box:

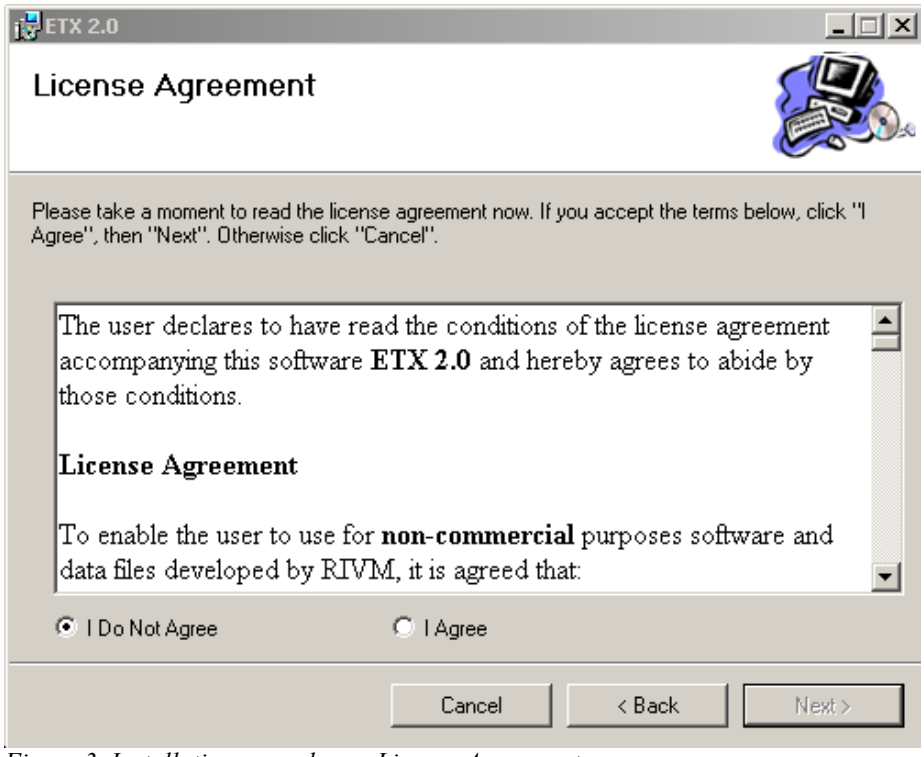

Figure 3. Installation procedure – License Agreement screen.

– If you agree with the content of this agreement, select the **I agree** option, and then click **Next**.

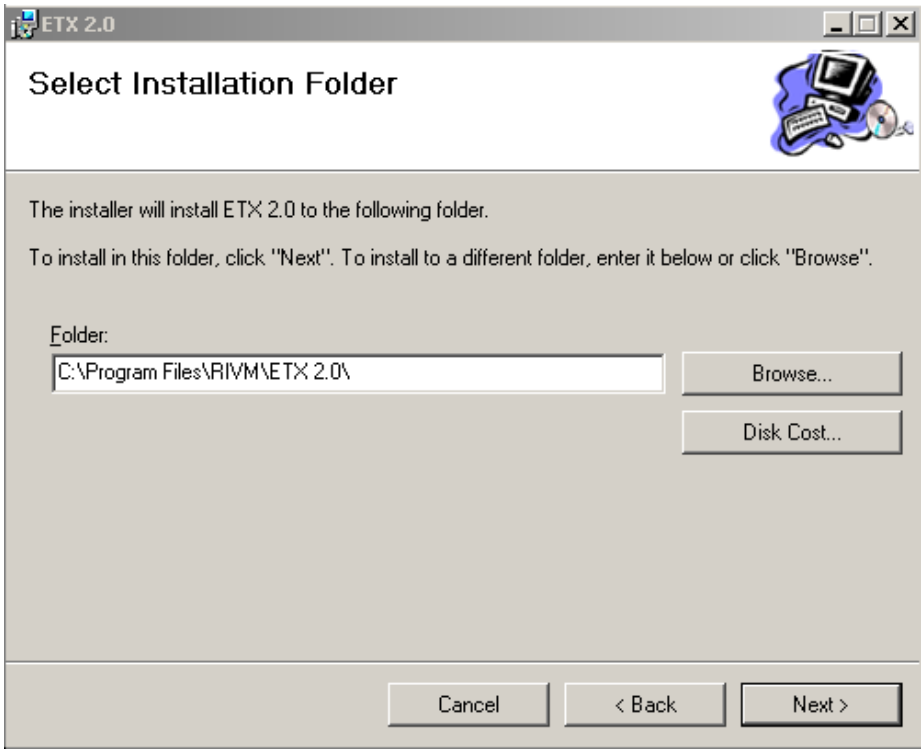

Figure 4. Installation procedure – Select Folder screen.

– In the dialog box displayed above, select the Folder in which you want E_TX to be installed.

The default directory is C:\Program Files\RIVM\ETX 2.0. If you want to install E_TX in an other directory, click Browse and select the directory of your choice.

– Click on **Next** to continue.

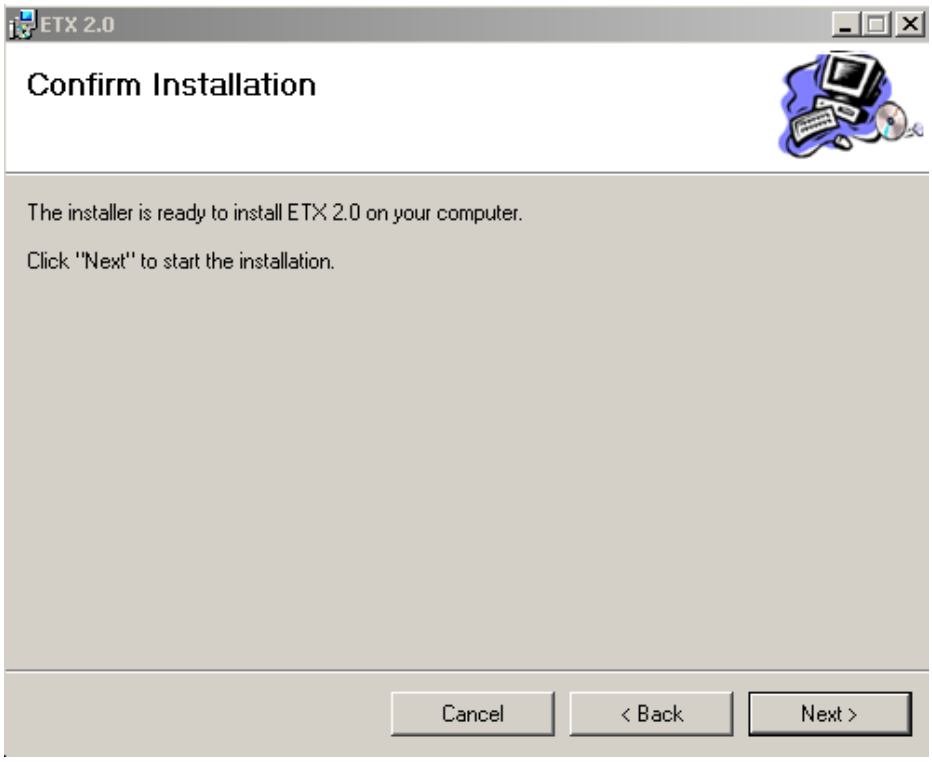

Figure 5. Installation procedure – Confirm Installation screen.

– In the dialog box displayed above, click **Next** if you want the installation to be carried out.
– Installation will now be performed. If the .NET framework is not yet installed on your computer, it will be installed. Installation of this framework takes several minutes.
– When the Installation is complete, the following screen appears. Click on **Close** to leave this screen and to finish the installation procedure.

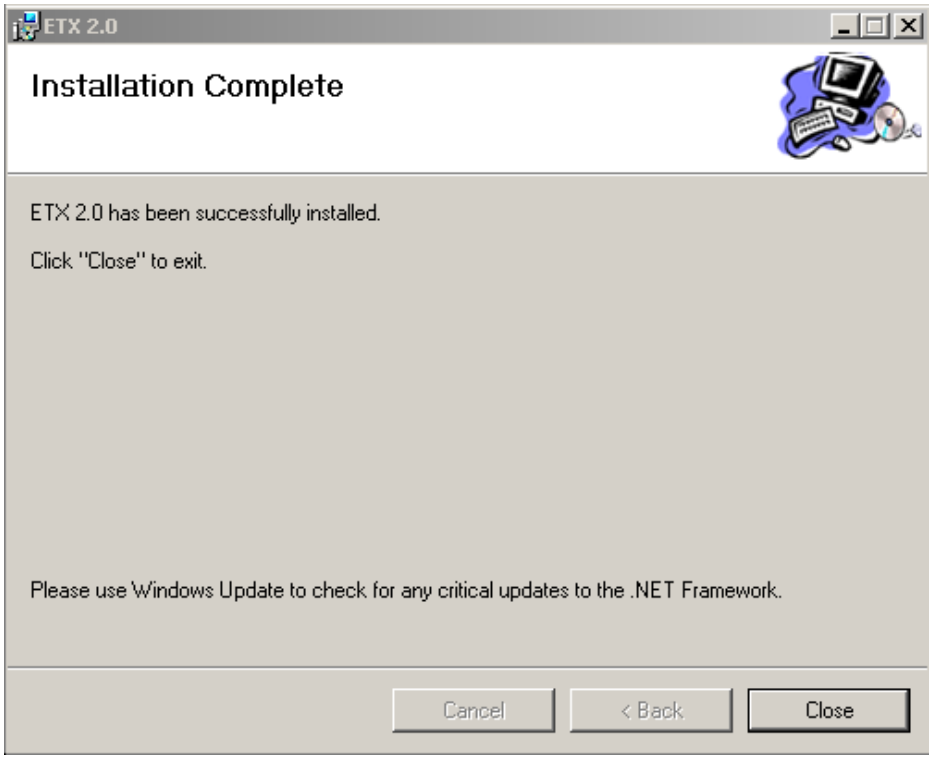

Figure 6. Installation procedure –Installation Complete screen.

3.3 Removing *ETX*

If you want to de-install (or remove) *ETX*, do the following.

- Under the Start button, click on Settings, Control Panel.
- In the Control Panel, double click the Add/Remove Programs icon.
- Select *ETX* from the list of currently installed programs. After clicking on *ETX* in this list, you can select Remove.
- *ETX* will now be removed from you computer.

3.4 Starting *ETX*

When *ETX* is installed successfully, the program can be found under the Start button in the lower left corner of your screen. It will be placed under: Programs, RIVM ETX, *ETX* 2.0. Click on the *ETX* 2.0 icon to start the program.

3.5 Saving data in *ETX*

If you save data in *ETX*, your data will be stored in a Project. This is a file with the extension: etx. To save a Project, Click on **File** on the Menu bar, then click **Save**.

In order to set or change the default directory where your *ETX* projects will be stored, see sections 5.1.5 and 5.9.4.

N.B. Your calculations and calculated results will *not* be stored together with your data. However, if you open an etx-Project that you had saved earlier, and press calculate again, all

results and output will be generated, together with the settings that were active at the time your Project was saved.

3.6 Starting a new project in *ETX*

The *ETX* opening screen is always an empty project. You can start directly with entering data here. Starting a new project can be performed by clicking on **File**, **New** in the Menu bar at the top of your *ETX* screen. Opening an existing project can be performed by clicking **File**, **Open input file**. The following dialog box appears:

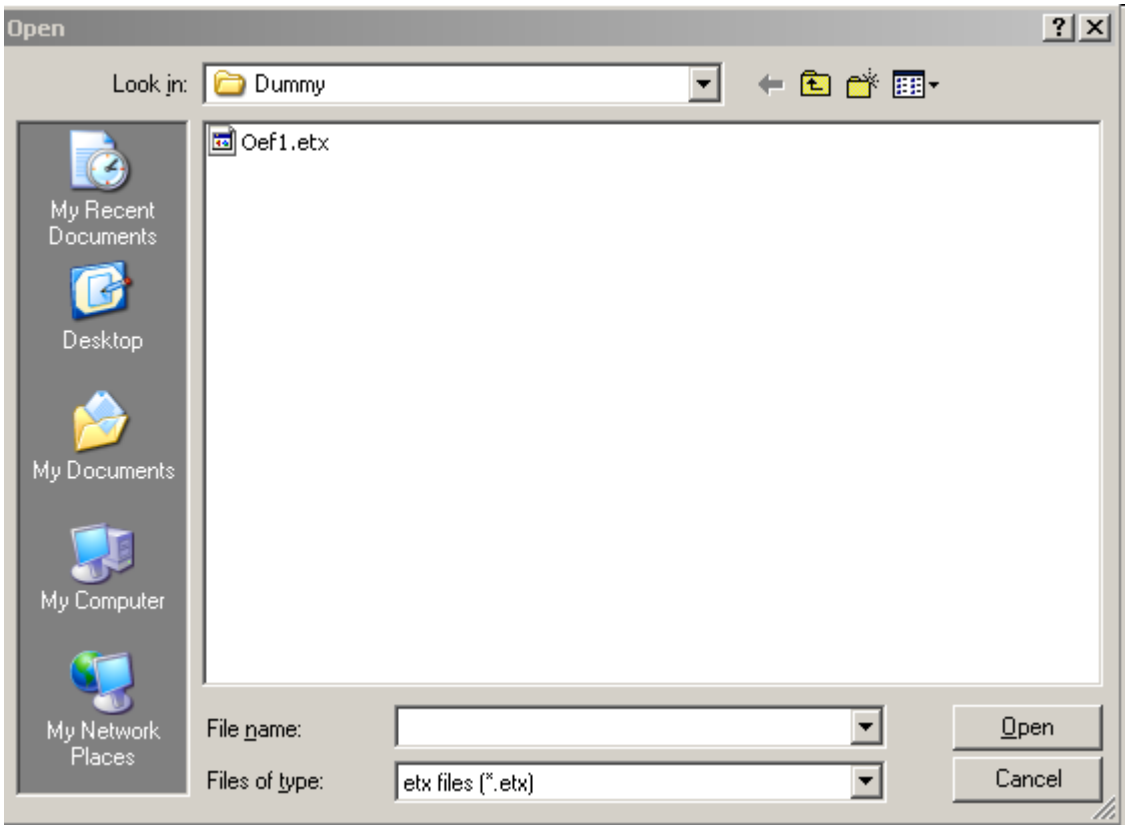

Figure 7. The dialog box shown after clicking **Open input file**.

Select the *ETX* project of you choice and click on **Open**. Your Project will now be retrieved and opened.

3.7 Leaving *ETX*

You can leave *ETX* 2.0 by choosing **File**, **Exit** from the Menu bar.

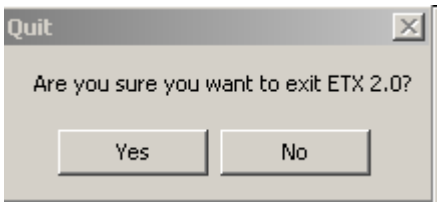

Figure 8. Dialog box shown upon leaving ETX.

Answer the question appearing in the dialog box (Figure 8) by clicking **Yes** or **No**.

3.8 Changing the settings for the decimal character

The choice of the character used as decimal symbol or digit grouping symbol in numerical values within *ETX* is determined by the regional settings of your PC. In English or American settings, the comma ',' is mostly used as digit grouping symbol, while the period '.' is used as decimal sign. In the Dutch language and settings, this is opposite, here the period '.' is used as digit grouping symbol and the comma ',' is the decimal sign. Please take notice that the regional settings will also apply to values printed along the axes of figures.

You may want to change these settings. Below, you find the route to the Control Box in which you can change your settings for several Microsoft operating systems.

3.8.1 Windows 98, NT, 2000 and ME

Click on the Start button in the lower left corner of your screen, then select Settings, Control Panel and Regional Settings (double click). In the Regional Settings properties box that has appeared, select the Number tab. In this screen you can either select a Region and obtain its accompanying settings or Customise your settings. After having made your selection, click on Apply and on OK. Changing of settings will have no effect unless you restart *ETX*.

3.8.2 Windows XP

Click on the Start button in the lower left corner of your screen, then select Settings, Control Panel, Regional and Language Options. Select the Regional Options tab. In this screen you can either select a Region and obtain its accompanying settings or Customise your settings. After having made your selection, click on Apply and on OK. Changing of settings will have no effect unless you restart *ETX*.

3.9 Comments on *ETX*

If you have comments on the program, its functioning or other ideas, you can send these by e-mail to etx.info@rivm.nl. Please note that this is *not* a helpdesk address. We will not respond to questions, but we will collect comments, possible errors and ideas for future development. Unfortunately, we are unable to help all users with problems or questions.

4. Reference manual

In section 4.1 we outline the different sections in which the program can be divided. We also name all sheets and briefly explain their contents. Section 4.2 explains the meaning of each of the items you may encounter in *ETX*. A list of abbreviations is included at page 63 of this report. How to use the information given in this chapter is explained to you in chapter 5 while chapter 7 tells you how to perform some calculations in practice.

4.1 Structure of the program

The program is divided in two major sections: an input and an output section. The input section has two subsections: **Input toxicity data** and **Input exposure data**. Each will be briefly discussed in the section 4.1.1. To get results, you have to invoke a calculation (section 5.7), which gives results in the **Output** section. The output section is divided in three sections, which will be introduced in section 4.1.3.

4.1.1 Data input

We discern two types of data: toxicity data and environmental concentrations.

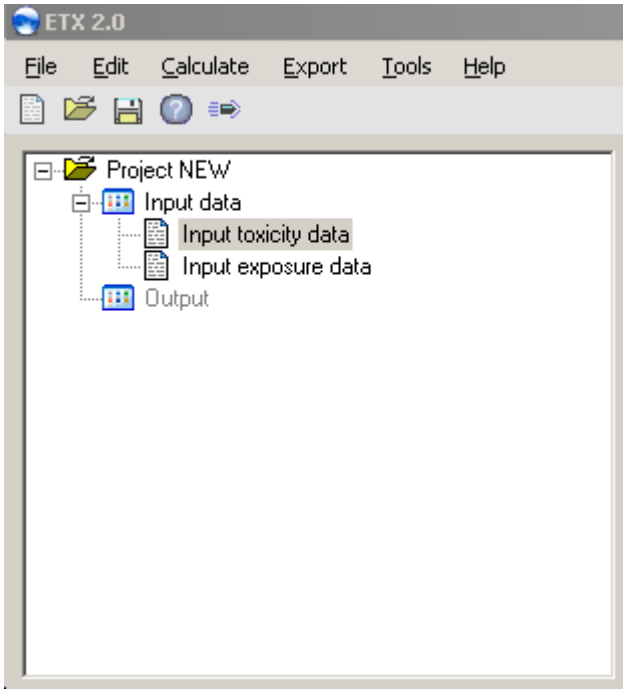

Figure 9. Subdivision of the input section.

4.1.1.1 Input toxicity data

Figure 9 shows the two sections of **Input data**.

- If you want to calculate an SSD and the accompanying HC_5 and HC_{50}, you should enter your data in the **Input toxicity data** sheet. If you want to calculate an FA, you need an SSD first. The output section will remain inaccessible until you have calculated an SSD.
- For calculation of the HD_5 for birds and mammals, there is room to enter a (small) data set of no more than 10 values. We call this the 'small sample' method. To use this method you have to select the check box labelled with **Use small sample method** in the lower right corner of the input screen (see Figure 10). You also have to enter a standard deviation

from an external data set. Entering data for the 'small sample' method is also done in the **Input toxicity data** sheet.

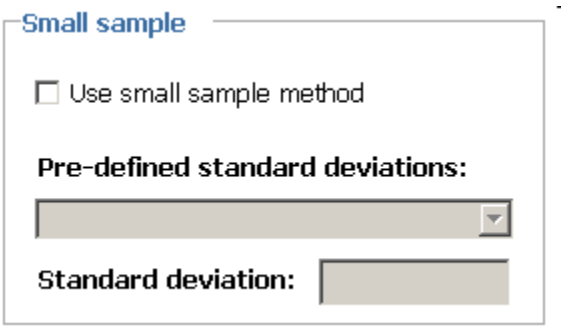

Figure 10. Small sample box.

4.1.1.2 Input exposure data

After having entered data in the **Input toxicity data** sheet and after you have calculated the accompanying SSD, you can use the **Input exposure data** sheet to calculate either an FA or an EER. There is the possibility for input of a single exposure concentration and a separate input section in case you have a series of exposure concentrations (like a measurement series).

4.1.2 Types of calculations

You can perform four types of calculations.

1. Calculate an SSD only.
2. Calculate an SSD and an FA. An FA can only be calculated when you have entered data in **Input toxicity data** and generated an SSD.
3. Calculate an SSD and an EER. An EER can only be calculated when you have entered data in **Input toxicity data** and generated an SSD.
4. Calculate a (small sample) HD_5. A maximum of 10 data can be entered. Calculation of an SSD is not needed in this case.

All calculations are performed by clicking **Calculate**, **Go** on the Menu bar in each of the two Input sections, or by clicking the **Calculate** button: . Please note that pressing the **enter** key on your keyboard does *not* invoke a calculation.
After selecting the **Calculate** button (or using the menu), the calculation is performed and the results will appear in one or more of the output worksheets or graphs (see section 4.1.3).

NB. The program will also generate results and graphics if the outcome of the goodness-of-fit tests imply that it is less probable that your data derive from a normal distribution. The program only calculates, it does not make decisions. It is up to you to decide whether you accept or reject the presented outcome of the calculations.

4.1.3 Output

4.1.3.1 SSD related output

The **Output** section contains three subsections and each of the subsections contains one or more sheets. Figure 11 shows the available output sheets in the program tree below **Output**. The contents of each sheet are outlined below.

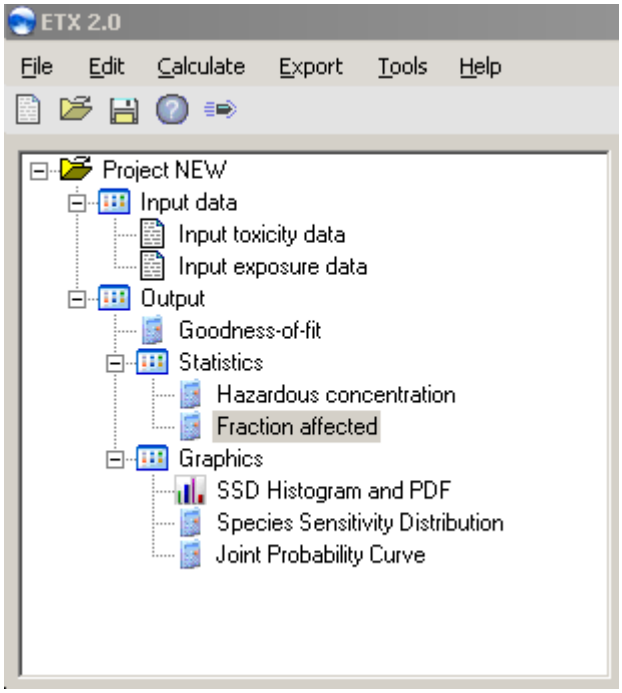

Figure 11. Subdivision of the output section for SSD calculations.

4.1.3.1.1 Goodness-of-fit

This sheet shows you the results of three goodness-of-fit (GOF) tests performed on your toxicity data. A brief explanation on the interpretation of these tests is also given. If you have entered a series of environmental concentrations in the **Input exposure data** sheet and have invoked a calculation, you will find the GOF test on these data here.

4.1.3.1.2 Statistics

In this section, two sheets can be found, the content of each is described below.

Hazardous concentration

In this sheet the mean and standard deviation (s.d.) of the normal distribution through your data are reported as well as the sample size. Furthermore, the HC_5, FA at the HC_5, the HC_{50} and the FA at the HC_{50} are reported. For each of these parameters, the lower and upper limit of the 90% confidence interval around the median estimate are reported.

Fraction affected

The estimated FA (plus lower and upper estimate of the two-sided 90% confidence interval) at the exposure concentration (EC) that you have entered in the **Input exposure data** sheet in the **single PEC** input cell is reported in this sheet. If you have entered a series of exposure concentrations in the **Input exposure data** sheet, the EER is reported.

4.1.3.1.3 Graphics

There are 3 sheets that show graphical output.

SSD Histogram and PDF

A histogram (or frequency distribution) of your toxicity distribution is presented when you have calculated an SSD. The bin width (classwidth) is calculated according to the method of Scott (1992) as:

$$binWidth = 3.5 \cdot \frac{standard\ deviation}{n^{1/3}}$$

The placement of bins on the *x*-axis is described in more detail in section 4.2.5. The height of the bars is expressed as the number of data they represent, which is plotted on the right hand *y*-axis. The normal distribution plotted in this graph is the probability density function (PDF) that is associated with your toxicity data sample. The left hand *y*-axis shows the density of the toxicity data. The left hand *y*-axis can also be used to read the densities of the bars in the histogram. For both the PDF and the histogram, the integral of all data, i.e. the sum of class-width × density, equals 1.

Species sensitivity distribution

If you have calculated an SSD, this is the cumulative density function (CDF) that is associated with your toxicity data sample. The dots in the graph are placed at the so-called Hazen plotting positions: $p_i = (i - 0.5)/n$ (see Aldenberg *et al.*, 2002).

Joint probability curve

This graph shows the joint probability curve (JPC). To obtain a JPC you have to enter toxicity data in the **Input toxicity data** sheet and a series (n>1) of exposure concentrations in the **Input exposure data** sheet. After having calculated an SSD, the JPC will be generated.

4.1.3.2 Small sample output

When the 'small sample' method is used, no SSD is required. The **Output** section only shows the **Small sample results** sheet (Figure 12). The content of the output sheet is outlined below.

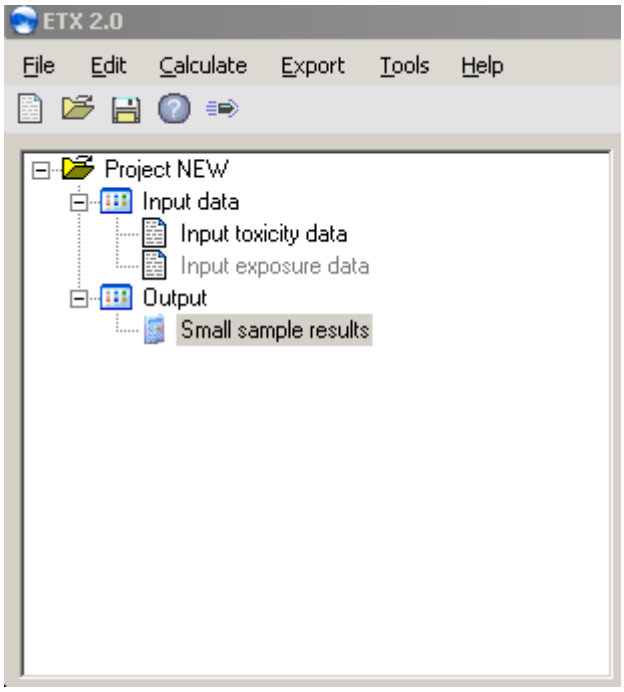

Figure 12. Subdivision of the output section for small sample calculations.

4.1.3.2.1 Small sample results

The median estimate of the HD_5 of your small data set is calculated and presented together with its 90% confidence interval limits. Also presented are the extrapolation factors that can be used to directly calculate the lower limit (LL), median or upper limit (UL) estimate of the HD_5 from the sample mean.

4.2 Glossary of keywords

In this section, a description of keywords is given, listed in alphabetical order. Keywords are those items you may encounter on the input or output screens of *ETX*. This section gives a brief explanation of each keyword, but we do not go deeply into the theoretical background of each item in this manual. For more background information, we refer to the underlying literature, which is listed in the Reference section of this manual.

4.2.1 Exposure concentration (EC)

In this manual and in *ETX* 2.0, the parameter 'exposure concentration' is synonym with 'environmental concentration'. Both can be abbreviated as EC and both are interchangeable in manual and program.

4.2.2 Expected Ecological Risk (EER)

An EER can be calculated if a set of predicted exposure concentrations (ECs) is entered in the input section of the program. Mean and s.d. are scaled relative to the mean and s.d. of the species sensitivity distribution. The EER literally is the probability that a randomly drawn species for a random draw of exposure is affected.

The following statistical parameters will appear in the **Fraction affected** output screen (in order of appearance):

SEC_{mean}, **SEC_{sd}** and **EER**

SEC stands for scaled environmental concentration.

- The SEC_{mean} is the scaled mean of the environmental concentration distribution. It is reported here as the $\log_{10}$ transformed value.
- SEC_{sd} is the scaled s.d. of the environmental concentration distribution. It is reported here as the $\log_{10}$ transformed value.
- EER is the expected (mean) ecological risk, given the SSD and the distribution of environmental concentrations. The EER is the area below the curve in the **joint probability curve** (**Output**, **Graphics**).

4.2.3 Extrapolation factor

In the **Small Sample Output** sheet, extrapolation factors are displayed. These can be found in the **HD_5 (median) results** box on your screen.

Extrapolation factors are factors to be applied multiplicatively to the geometric mean of the original (not log-transformed) toxicity data. Extrapolation factors depend on the FA, sample size, confidence level and on the standard deviation of the SSD (Aldenberg and Luttik, 2002). In *ETX* 2.0, extrapolation factors are given for an FA of 5% (HD_5) for the upper and lower limit of the 90% confidence interval of the HD_5.

4.2.4 Fraction affected (FA)

An FA can be calculated when one single predicted exposure concentration (EC, synonym with PEC) value is available. This EC value can be entered in the input section of the program. The following statistical parameters will appear in the **Output** screen. In order of appearance:

LL FA, Median FA and **UL FA**

Reported is the median estimate of the FA at the PEC you have entered. Also reported is the two-sided 90% confidence interval of the FA: LL FA represents the 5% confidence limit and

UL FA represents the 95% confidence limit. These calculations are based on repeated linear interpolation and are approximate values. The procedure is explained in section 8.2.3 of Aldenberg and Jaworska (2000). A precise answer can be obtained using the functions described in section 8.2.1 of that paper.

This routine does not yield results when your standardised mean logarithmic effect concentration is <-5 or >5. As a check, the value of the standardised logarithmic concentration calculated from your PEC value is shown in the **Fraction affected** output sheet. If this value is outside the range mentioned above, no results will be given. The message
'The method does not yield results because your standardised PEC exceeds the limits of <-5 or >5' will appear in red. The sheet will show 'Out of bounds!' as error values.

4.2.5 SSD Histogram and PDF

This graph is a histogram or frequency distribution in which the toxicity data are represented by bars. On the *x*-axis the $\log_{10}$ of toxicity values (NOEC, LC_{50}s etc.) is plotted. On the right hand *y*-axis, the frequency of the toxicity values is plotted. Toxicity values are distributed over frequency classes (often referred to as bins) that have a width calculated according to Scott (1992):

$$binWidth = 3.5 \cdot \frac{standard\ deviation}{n^{1/3}}$$

The placing of bins on the *x*-axis is worked out as follows:

1. The number of bins is calculated using the equation mentioned above;
2. Bins are divided over the range of toxicity data by centering around the mean (=sample mean, or mean of the toxicity data);
3. Sample values coinciding with a bin limit are dropped in the next lower bin.
4. In case the lowest sample value coincides with the lower limit of the lowest bin, this value is dropped in this lower bin.

In case of an even number of bins, we identify *two* middle bins. The mean of the toxicity data now coincides with the separation between the two middle bins. More precise, the mean value itself is chosen to coincide with the highest value of the left bin (due to point 3 above). In case of an uneven number of bins, there is *one* middle bin. In these cases, the middle of the middle bin is chosen to coincide with the mean of the toxicity data.

4.2.6 Goodness-of-fit

Whether the sample of toxicity data derives from a normal distribution can be assessed with goodness-of-fit tests. Two different types of tests are implemented, based on quadratic (vertical) distance and on the largest vertical distance. Well-known quadratic tests are the Anderson Darling test and the Cramér-von Mises test (cf. D'Agostino and Stephens, 1986). The Kolmogorov-Smirnov test is a well-known vertical distance test (D'Agostino and Stephens, 1986).

1. The Anderson-Darling goodness-of-fit test highlights differences between the tail of the distribution and the input data and is generally regarded as a very powerful general test (Aldenberg *et al.*, 2002).
2. The Kolmogorov-Smirnov test focuses on differences in the middle of the distribution and is not very sensitive to discrepancies of fit in the tail of the distribution.

<u>Interpreting Critical Values</u>
If a test statistic is above the 5% critical value, normality is rejected at the 5% critical value, indicating doubts about normality.

If a test statistic is below the 5% critical value, normality is accepted (not rejected) at the 5% critical value.
If a higher critical value is accepted (e.g. at 2.5% significance level), then the probability that these data derive from a normal distribution is smaller than at 5%, but it is not impossible that the sample derives from a normal distribution.
Some people find it confusing that a higher significance level, say 10%, has a lower critical value. 'Rejected' occurs more often with a higher significance level. In conclusion: a GOF test does NOT say that a sample cannot derive from a normal distribution, just that it becomes less probable with decreasing significance levels.

4.2.7 HC_5 and HC_{50}

Your toxicity dataset refers to a selection of species, which is treated as a sample drawn from a population (in a statistical sense). By definition, the calculated normal distribution encompasses all species inhabiting the environmental compartment of interest. It is up to you to determine whether your sample of species is representative for the population of species (in a biological sense) you want to derive HC values for. The distribution is the –estimated– function that relates the relative sensitivity of the species thought present in a given environmental compartment to (the logarithm of) the toxicant concentration. This distribution is a normal distribution (by definition) when you use *E_TX* 2.0 for your calculations. HC is short for 'hazardous concentration'. HC_5 and HC_{50} are the 5th and 50th percentile (median is synonymous for the latter) of the normal distribution that is fitted through the toxicity data you have entered. HC_5 and HC_{50} are expressed as a toxicant concentration (in the same units as the toxicity data you have entered in the input section). Hence, they represent the toxicant concentration that is hazardous to 5 or 50 percent of 'all' species. See section 4.2.11 for explanation of the HC parameters calculated by *E_TX* 2.0.

4.2.8 JPC

The abbreviation stands for joint probability curve. This is a graphical representation of the risk of a substance to the species, that may be used in risk characterisation. The type of graph *E_TX* shows is a cumulative profile plot. It is constructed by plotting FA values from the SSD (in CDF form) on the *y*- axis against exposure concentration distribution (ECD) values (also in CDF form) on the *x*-axis at corresponding log-exposure concentrations. The area under the curve (AUC) is equal to the expected ecological risk. For more detail, see Aldenberg *et al.* (2002). The numerical value of the AUC, or EER, is shown in the **Fraction affected** sheet (**Output**, **Statistics**).

4.2.9 PEC

If an environmental concentration of the substance of interest is the outcome of some model calculation rather than a measured value –or series of values– in the field, it is called a *predicted* environmental concentration. If you have a single PEC value and an SSD, you can calculate the fraction of species described by that SSD that is (potentially) affected by the substance.

4.2.10 Small Sample method

The idea to estimate a percentile of an SSD and its uncertainty for a very small sample of toxicity data has emerged from the field of pesticide registration. Due to the limited size of the sample, there is no reliable information on the standard deviation of the SSD. A standard deviation from a *different* sample, to which one attaches more confidence because it has higher reliability, is used to estimate the HD_5. Luttik and Aldenberg (1997) published this method for *logistically* distributed toxicity data.

The method that is currently implemented in *E_TX* 2.0 offers the possibility to calculate HD_5 values for birds or mammals based on *normally* distributed toxicity data (Aldenberg and Luttik, 2002). From a dataset of 55 pesticide LD_{50} values for birds a pooled variance estimate of the standard deviations of all LD_{50} values was calculated. The same was done for a dataset of 69 pesticide LD_{50} values for mammals. From both datasets the pooled variance estimates for carbamates and organophosphorous compounds were also calculated. All pooled variance estimates are listed in the **Input toxicity data** sheet in the **Small sample** box (under **Pre-defined standard deviations**). These estimates can be used as an ('external') standard deviation that is assumed to describe the spread of the population from which your (small) sample of bird/mammal data has been drawn.

Recommendations to the 'small sample' method:
(i) When there are indications that the (small) sample standard deviation does not reflect the population standard deviation, even when $n \geq 4$, consider using the pooled standard deviation (i.e. use the 'small sample' technique). A maximum of 10 entries is allowed for in the **Input toxicity data** sheet.
(ii) Use the LL HD_5 values or corresponding assessment factors when a 5% probability for overestimation of the HD_5 is desired. When the median HD_5 or its corresponding assessment factor is used, 50% probability for HD_5 overestimation is allowed.
(iii) When there are indications that the available data are derived from a test with a sensitive species, one could consider using the median estimate of the HD_5 or the corresponding extrapolation factor.

4.2.11 Statistics SSD

If an SSD has been calculated by *E_TX*, i.e. if a normal distribution has been fitted through your toxicity data, the following statistical parameters will appear in the **Hazardous concentration** output screen (in order of appearance).

Mean, s.d. and ***n***

Mean and s.d. are the sample mean and the sample standard deviation (n-1) of the normal distribution. These parameters are shown in $\log_{10}$ units and are the parameters that describe the normal distribution fitted through your toxicity data set. n is the sample size, i.e the number of toxicity data. It is shown because the size of n directly determines the size of the uncertainty in the HC_5 and HC_{50} (Aldenberg and Jaworska, 2000). These sample statistics are used to estimate the SSD parameters.

HC_5 results: **LL HC_5, HC_5, UL HC_5** and **sprHC$_5$**

These parameters are shown in the same concentration units as you entered your toxicity data in. Presented are the estimated 5th percentile of the normal distribution (HC_5) and its two-sided 90% confidence limits, called the lower limit (LL) and upper limit (UL), respectively. The HC_5 itself is a normally distributed statistic, and sprHC$_5$ is a measure of the width of the HC_5 distribution. It is calculated as the ratio of UL and LL.

FA at HC_5 results: **FA_{lower}, FA_{median}** and **FA_{upper}**

The median estimate of the FA at the toxicant concentration HC_5, is 5%, by definition, since the HC_5 is the 5th percentile of the SSD. The two-sided 90% confidence interval for the FA is also reported: FA_{lower} represents the 5% confidence limit of the FA and FA_{upper} represents the 95% confidence limit.

HC_{50} results: **LL HC_{50}, HC_{50}, UL HC_{50}** and **sprHC$_{50}$**

These parameters are shown in the same concentration units as you entered your toxicity data in. Presented are the estimated median or 50th percentile of the normal distribution (HC_{50}) and its two-sided 90% confidence limits, called the lower limit (LL) and upper limit (UL), respectively. The HC_{50} itself is a normally distributed statistic, and $sprHC_{50}$ is a measure of the width of the HC_{50} distribution. It is calculated as the ratio of UL and LL.

FA at HC_{50} results: **FA_{lower}, FA_{median}** and **FA_{upper}**
The median estimate of the FA at the toxicant concentration HC_{50}, is 50%, by definition, since the HC_{50} is the 50th percentile of the SSD. The two-sided 90% confidence interval for the FA is also reported: FA_{lower} represents the 5% confidence limit of the FA and FA_{upper} represents the 95% confidence limit.

4.2.12 SSD

E_TX calculates an SSD from your sample of toxicity data assuming that the (continuous) distribution describing the sensitivity of the population underlying your sample is normally distributed over log concentration. This Gaussian distribution is graphically presented in the **SSD Histogram and PDF** sheet (to be found under **Output**, **Graphics**). The data and the fitted distribution are also presented as a CDF plot in the **SSD** sheet (**Output**, **Graphics**). The statistical parameters derived from this distribution are presented in the **Hazardous concentration** sheet (**Output**, **Statistics)**.

5. Working with *ETX*

5.1 Menu bar and buttons

The menu bar and buttons that are available in *ETX* are shown in Figure 13. Throughout the program, the same menu bar and buttons will appear. All functions that may be accessed via the menu bar will not be described here individually, we will give a general description of each menu item. Most items you will encounter when you work through the manual or by just trying them!

Figure 13. Menu bar and buttons in ETX.

5.1.1 File

Options provided here allow you to:

- start a new *ETX* project (**New**).
- open an existing *ETX* project (**Open input file**). When you have saved your work in an *ETX* project, *ETX* does *not* save the calculated data and graphs. If you want to see the results again, simply press Calculate after opening an existing *ETX* project and your results will reappear. If you want to save all data, choose Export and all your results will be placed in an Excel spreadsheet.
- save your work (**Save**).
- save your project under a different name (**Save as**).
- leave *ETX* (**Exit**).

5.1.2 Edit

The options provided here allow you to handle individual cells or ranges of cells, that you can either delete, cut, copy and paste.

5.1.3 Calculate

The only option provided here is to invoke a calculation. The function of this menu is equal to that of the calculate button (section 5.1.7). For more information on the types of calculations you can perform, see section 5.7.

5.1.4 Export

The only option provided here is to export the data you have entered and calculated, to a separate file. The data will be exported in Microsoft Excel spreadsheet format. See also section 5.8. To change the default directory where projects and exported files are stored, see section 5.9.

5.1.5 Tools

There are four options here: **Labels**, **Sort toxicity data**, **Sort labels** and **Preferences**.

- Use **Labels** to attach label to the entries in the toxicity data sheet. For more information please see section 5.6.
- By clicking on **Sort toxicity data,** the toxicity data in the **Input toxicity sheet** will be sorted in increasing order. NB: this operation can not be undone.

- By clicking on **Sort labels,** the labels in the **Input toxicity sheet** will be sorted in alphabetical order. NB: this operation can not be undone.
- Use **Preferences** to define the default settings for the looks of your graphs and to set the default directory where projects and exported files are stored. For more information please see section 5.9.

5.1.6 Help

In the **Help** menu, there are two options to choose: ***ETX* Help topics** and **About *ETX* 2.0.** When you select the help topics, you can use the *ETX* 2.0 manual online. The content of this menu is equal to the content of this manual.

About *ETX* 2.0 gives you information on the version of this program. Information on earlier versions of *ETX* is also provided.

5.1.7 Buttons

The buttons have the following names and function:

New. This button opens a New *ETX* project.

Open existing project.

Save. Allows you to save the current project.

Help. Allows you to access the Help file.

Calculate. Invokes a calculation.

5.2 Navigating through *ETX*

After starting up *ETX*, the following screen will appear:

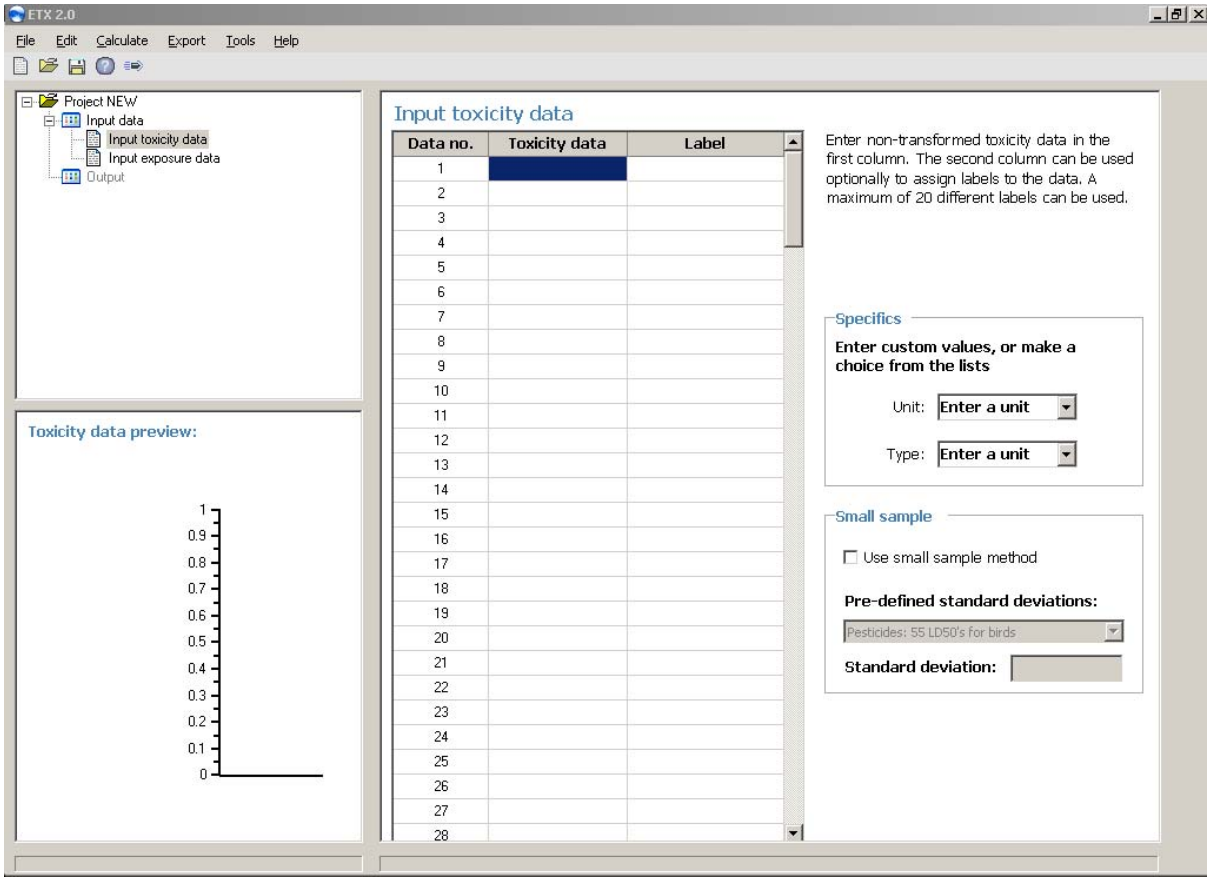

Figure 14. E_TX appearance after starting the program.

This screen is divided in three major parts: in the upper left corner: the navigating section, in the lower left corner: the **Toxicity data preview** section and the largest part is the right half of the screen: the **Input toxicity data** section. In the navigating screen, you find + or – signs. By clicking on these you can *unfold* or *fold* a specific part of the program and *view* or *hide* its contents. Use these buttons to find out that each E_TX project contains an **Input data** section and an **Output** section. If you select a specific section or sheet by clicking on it, it will be displayed in the right half of your screen. In the following, you will be guided through each of the different parts of the program.

5.3 Entering data

5.3.1 Toxicity data

- Go to the **Input toxicity data** sheet in the **Input data** section of E_TX.
- Go to the **Input toxicity data** box (this is the right part of your screen).
- Next, in the cells under **Toxicity data**, enter your toxicity values as a column, with one value per input cell. Enter the toxicity data in the original (non-transformed) values.
- For information on entering the unit of your data or the type of endpoint, see section 5.3.2.
- For information on labelling of your toxicity data, see section 5.6.
- Make sure *all* entries have the same unit: mg/l, µg/kg, ppm etc.
- You cannot enter the value 0 (zero). Your data will be $\log_{10}$-transformed for calculation and log(0) does not exist. If you enter a zero value, the error message **Please enter only**

positive values will be displayed at the bottom of your screen. Delete the zero value or enter a positive non-zero value to continue.
- You need not sort the data.
- You may leave blank cells, empty cells will not be included in the graph or in calculations.
- For HC_5 and HC_{50} calculation a maximum number of 200 data can be entered.
- For FA and FA-confidence limits the maximum number of data (n) =75 for FA at HC_{50} and n = 200 for FA at HC_5.

When you have finished entering data, see section 5.7.1 on how to calculate an SSD.

5.3.2 Assigning units to your data

You may enter the unit of toxicity data and/or exposure data. It is optional to do this, but there are two reasons to do so. First, if you are about to enter both toxicity and exposure data e.g. to calculate a fraction affected, the data should be entered in E_TX in the same units! Second, if you enter the unit of your data, this unit will be printed in the output of your data that is exported to Excel.

To assign a unit to your data go to the **Input toxicity data** section. In the lower right half of your screen, you find the **Specifics** box (Figure 15):

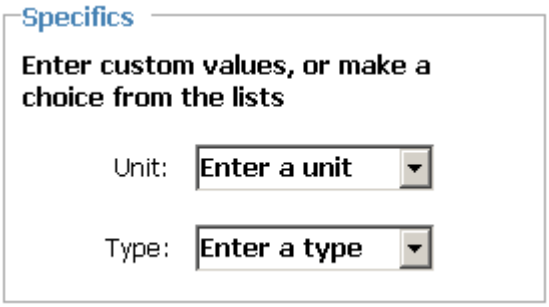

Figure 15. The specifics box.

- In the scrollbar to the right of **Unit**, you may type a unit of your choice or select the unit from the pulldown menu.
- In the scrollbar to the right of **Type**, you may type the endpoint of the toxicity data you are about to enter, or you can select an endpoint from the pulldown menu.
- The **Specifics** box functions as a piece of scrap paper. Both options in the box remind you that all toxicity data should be of the same unit and type. Unit and type are not linked to any calculation. They reappear in the **Input exposure data** section, to remind you that the units of data entered in that section should be identical to the units of the data entered in the **Input toxicity data** section.
- Use of the Specifics box is optional. E_TX works equally well when you clear the contents of the **Unit** and **Type** boxes.

5.3.3 Small sample data

- Go to the **Input toxicity data** sheet in the **Input data** section of E_TX.
- In the **Input toxicity data** box (this is the right part of your screen), click on the **Use small sample approach** check box in the **Small sample** box. The following dialog box will appear:

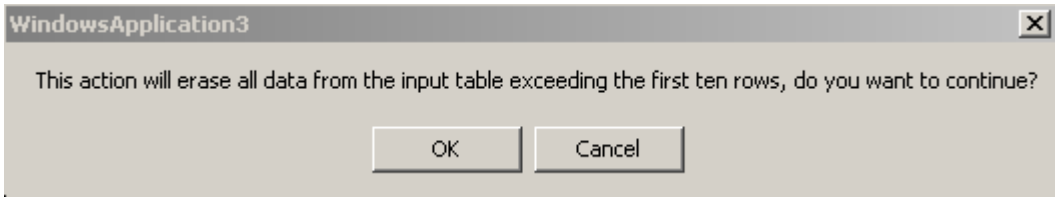

Figure 16. Small sample verification box.

If you had already typed data in the input section, these data will be lost when you switch to the Small sample input mode. Remember that this is a different method that does not require calculation of an SSD. So, if you want to keep the data you had entered before, click on **Cancel** and Save your work in an E_TX project. Then start a new project for your 'small sample' calculation. Otherwise, click on **OK**.

- The number of toxicity data that you can enter is now limited to 10.
- Enter your toxicity values as a column, with one value per input cell. Enter the toxicity data in the original (non-log transformed) format.
- Make sure *all* entries have the unit of mg/kg body weight.
- You cannot enter the value 0 (zero). Your data will be $\log_{10}$-transformed for calculation and log(0) does not exist.
- You need not sort the data.
- You may leave blank cells, empty cells will not be included in calculations.
- Enter a standard deviation. In the **Small sample** box at the lower right corner of your input screen, you can choose one of several pre-defined pooled standard deviations. The accompanying value that will be used for calculations appears in the **Standard deviation** box.

When you have finished entering data, see section 5.7.2 on how to calculate an HD_5.

5.3.4 Environmental concentrations

5.3.4.1 One environmental concentration

This calculation applies when you have only one environmental concentration, e.g. a PEC resulting from the exposure part of a risk assessment rather than a series of measurements.

- Go to the **Input exposure data** sheet in the **Input data** part of E_TX.
- You need to have an SSD before you can enter exposure data. Refer to section 5.3.1 for information on this subject. If you enter exposure data without having an SSD, the following message will pop up:

Figure 17. Message displayed upon FA calculation when no toxicity data have been entered.

- Enter your PEC value in the **Single PEC** box at the right part of your screen.
- Make sure that the unit of your PEC value is identical to the unit of the toxicity values that you have entered to generate your SSD! The unit of your toxicity data will be displayed in the **Specifics** box when you have made use of it while entering of your toxicity data.

- Enter a non-log transformed PEC value!
- This routine does not yield results when your standardised logarithmic PEC is <-5 or >5. The value of the standardised logarithmic concentration PEC will be shown in the **Fraction affected** sheet (**Output**, **Statistics**).
- You cannot enter the value 0 (zero). Your data will be $\log_{10}$-transformed for calculation and log(0) does not exist.

When you have finished entering data, see section 5.7.3 on how to calculate an FA.

5.3.4.2 A series of environmental concentrations

This calculation applies when you have a series of environmental concentrations, e.g. a measurement series of the compound of interest in an environmental compartment.

- Go to the **Input exposure data** sheet in the **Input data** part of E_TX.
- Go to the **Input environmental concentrations** box (this is the right part of your screen).
- In the cells under **Exposure data**, enter your toxicity values as a column, with one value per input cell.
- Enter the toxicity data in the original (non-transformed) values.
- Make sure that the unit of your environmental concentrations is identical to the unit of the toxicity values that you have entered to generate your SSD! The unit of your toxicity data will be displayed in the **Specifics** box when you have made use of it during entering of your toxicity data.
- Make sure *all* entries have the same unit: mg/l, µg/kg, ppm etc.
- You cannot enter the value 0 (zero). Your data will be $\log_{10}$-transformed for calculation and log(0) does not exist.
- You need not sort the data.
- You may leave blank cells, empty cells will not be included in the graph or in calculations.

When you have finished entering data, see section 5.7.4 on how to calculate an EER and JPC.

5.4 Clearing the contents of the input cells

5.4.1 Clearing a single cell

You can clear (or delete) data in a single input cell as follows.

- Select the cell you want to by clicking in the cell.
- Click on **Edit**, **Delete** in the Standard menu bar or press the Delete button on your keyboard to clear the content of the selected cell. The following message will appear:

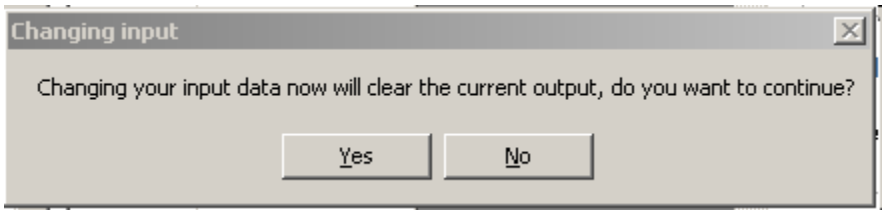

Figure 18. Message displayed when cell contents are about to be deleted.

- Click on **Yes** if to continue. The content of the cell will be deleted.

5.4.2 Clearing all cells

In order to clear a range of cells, do the following:

- Select the uppermost cell of the range of cells you want to clear, by clicking in the cell.
- Press the Shift button together with the Arrow Down (↓) button (both on your keyboard). While holding the shift button pressed down, you can select multiple cells by using the ↓ button repeatedly.
- When you have reached the bottom cell of the range you want to clear, stop holding down keys. Your selection of cells is now highlighted.
- Click on **Edit**, **Delete** in the Standard menu bar or press the Delete button on your keyboard to clear the content of the selected cells.

In order to clear all cells, do the following:

- Select the upper cell by clicking in it.
- Press the Shift button together with the Ctrl button. While holding these buttons pressed down, click on the Arrow Down (↓) button (all buttons are on your keyboard).
- All cells will now be selected (highlighted).
- Click on **Edit**, **Delete** in the Standard menu bar or press the Delete button on your keyboard to clear the content of the selected cells.

5.5 Importing data

You can also enter data (both toxicity data and environmental concentrations) from e.g. MS Excel. The procedure is as follows:

- The data you want to import should be placed in a column.
- Select the column containing your data and copy it
- Switch to E_TX and click once in the upper cell of the data column of the sheet in which you want to import your data.
- Paste the data.

Please refer to section 5.11 on how to use the decimal symbol in these type of operations.

5.6 Adding labels to toxicity data

NB. This function is optional. All other program functions can be executed equally well when the toxicity data are not labelled.

When entering toxicity data, you have the possibility to label your entries. This means that you can add a text label to toxicity data. You might, for example, want to discriminate between the different taxonomic levels in your SSD and add labels like *algae*, *crustacea*, *insecta* (or abbreviations). Apart from adding text labels, you can customise the appearance of the symbols that are linked to your labels. These symbols will be used to construct your SSD.

5.6.1 Creating a label collection and using labels

Before you can enter labels that will also appear in your SSD graph, you have to create a label collection. To create a label collection, do as follows:

- Click on **Tools, Labels** in the Menu bar and the **Input toxicity data labels** dialog box shown in Figure 19 will appear:

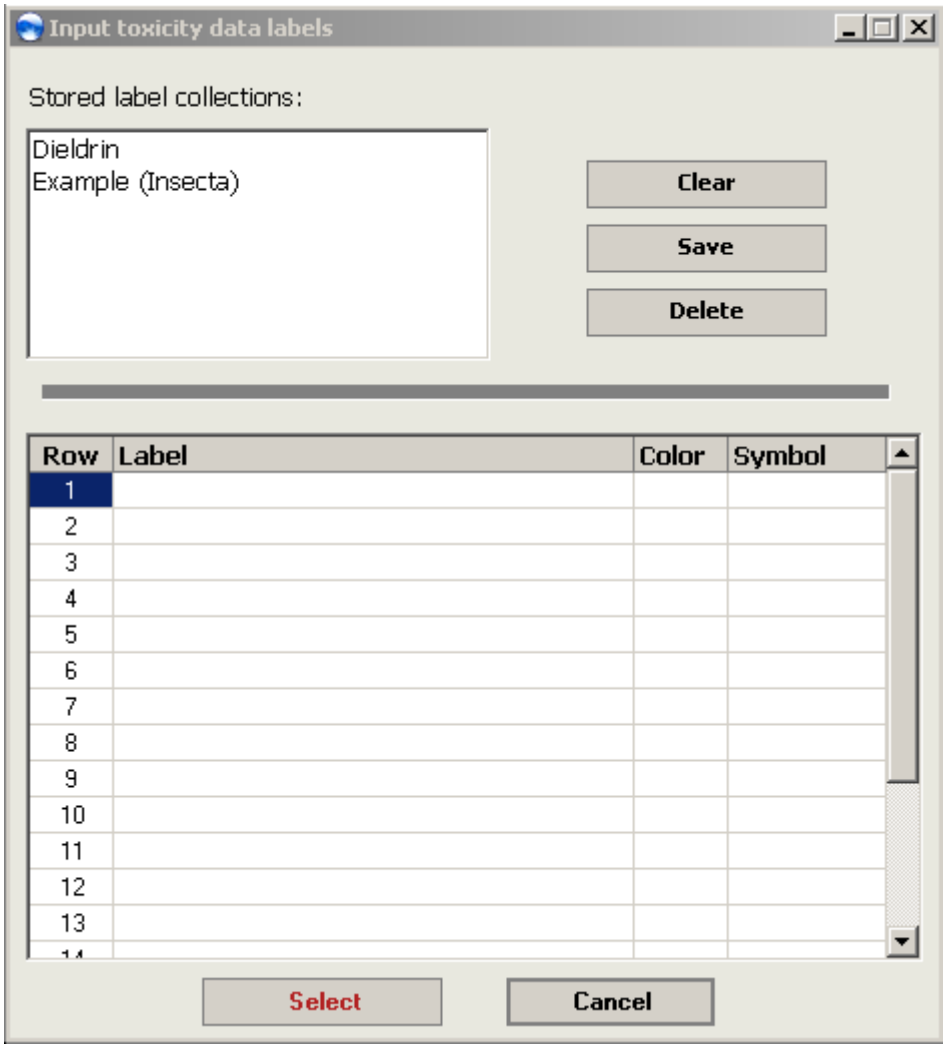

*Figure 19. The **Input toxicity data labels** box.*

- Next, type the name of the label in the column **Label** and assign a **Color** and a **Symbol** to the label in the following columns. Complete your label collection in this way.
- After having completed your label collection, click the **Save** button in the top part of the **Input toxicity data labels** box and type the name of your label collection. The name will now appear in the **Stored label collections** box visible at the top of the dialog box.
- You can select a label collection by clicking on its name in the **Stored label collections** box and subsequently press the **Select** button at the bottom of the label box. You then automatically return to the **Input toxicity data** sheet.
- Back in the **Input toxicity data** screen you see the selected label collection displayed in the lower right corner of your screen:

Figure 20. The active label collection display.

- Back in the **Input toxicity data** screen, behind each of the toxicity data that you enter, there is a **Label** cell. Using the pull down menu in each cell, you can now choose one of the

taxonomic groups (or 'labels') that are present in the label collection you have just selected.

5.6.2 Editing an existing label collection

Editing an existing label collection can also be performed via the **Input toxicity data labels** dialog box:

- Click on **Tools**, **Labels** in the menu bar and the **Input toxicity data labels** dialog box shown in Figure 19 will appear.
- Select the label collection in the **Stored label collections** box by clicking on it.
- Edit the label collection.
- Press the **Save** button to save any changes.
- Press the **Select** button if you wish to select the current label collection. You will automatically leave this dialog box after clicking **Select**.

5.6.3 Deselecting a label collection

In case you want to clear the connection between the toxicity data you have entered and the selected label collection, do the following:

- In the **Input toxicity data** screen you see the **Label collection display** in the lower right corner of your screen (Figure 20).
- Click on the **Deactivate** button to clear all labels entries behind your toxicity data.
- Note that this action will not erase your label collection or its settings, only its connection with the current dataset.

5.7 Performing calculations

5.7.1 Calculating an SSD

When you have finished entering toxicity data in the **Input toxicity data** sheet, you are ready to calculate an SSD.

- Select **Calculate**, **Go** from the Standard menu bar or press the **Calculate** button: to invoke the calculation of the SSD and its statistics.
- After performing the calculation, E_TX will automatically switch to the **Hazardous concentration sheet** in the **Output, Statistics** section.
- Switch manually to the **Goodness-of-fit** section in order to check the result of the normality tests performed on your toxicity data.
- Two graphs will be generated as well: the histogram and an SSD. Both can be found under **Output, Graphics**.
- If you have deleted or added data in the input section, choose **Calculate**, **Go** from the Standard menu bar (or press) again for an update of statistics and graphics.

5.7.2 Calculating a small sample HD_5

When you have finished entering toxicity data in the **Input toxicity data** sheet using the 'small sample' method, you are ready to calculate an HD_5.

- Select **Calculate**, **Go** from the Standard menu bar or press the **Calculate** button: to invoke the calculation of the HD_5 and its statistics.
- After performing the calculation, E_TX will automatically switch to the **Small sample results sheet** in the **Output, Statistics** section.

- If you have deleted or added data in the input section, choose **Calculate**, **Go** from the Standard menu bar (or press) again for an update of statistics.

5.7.3 Calculating an FA

When you have calculated an SSD and finished entering exposure data in the **Input exposure data** sheet, you are ready to calculate an FA.

- Select **Calculate**, **Go** from the Standard menu bar or press the **Calculate** button: to invoke the calculation of the FA and its statistics.
- After performing the calculation, *ETX* will automatically switch to the **Fraction affected sheet** in the **Output, Statistics** section.
- If you have deleted or changed your PEC in the input section, choose **Calculate**, **Go** from the Standard menu bar (or press) again for an update of statistics.

5.7.4 Calculating an EER and JPC

When you have finished entering a series of environmental concentrations in the **Input exposure data** sheet, you are ready to calculate an EER and JPC.

- Select **Calculate**, **Go** from the Standard menu bar or press the **Calculate** button: to invoke the calculation of the EER and its JPC.
- After performing the calculation, *ETX* will automatically switch to the **Fraction affected sheet** in the **Output, Statistics** section. This sheet shows the EER in the lower one of the two boxes.
- Switch manually to the **Goodness-of-fit** section in order to check the result of the normality test performed on your exposure data.
- A joint probability curve will be generated as well. It can be found under **Output, Graphics**.
- If you have deleted or added data in the input section, choose **Calculate**, **Go** from the Standard menu bar (or press) again for an update of statistics and the JPC.

5.8 Exporting results

Once you have generated results and statistics, you might want to save these results or store them in some other format. This can be done by using the **Export** function. You can find the **Export** function in the menu bar. Clicking on Export shows you one menu option: **Export current output**. After selecting this option, your data, statistical output en graphs will be exported to an MS Excel spreadsheet (extension .xls). The default filename is identical to the name of your *ETX* project. If you have not yet stored you data in an *ETX* project, the default filename will be NEW.xls. The following dialog box appears:

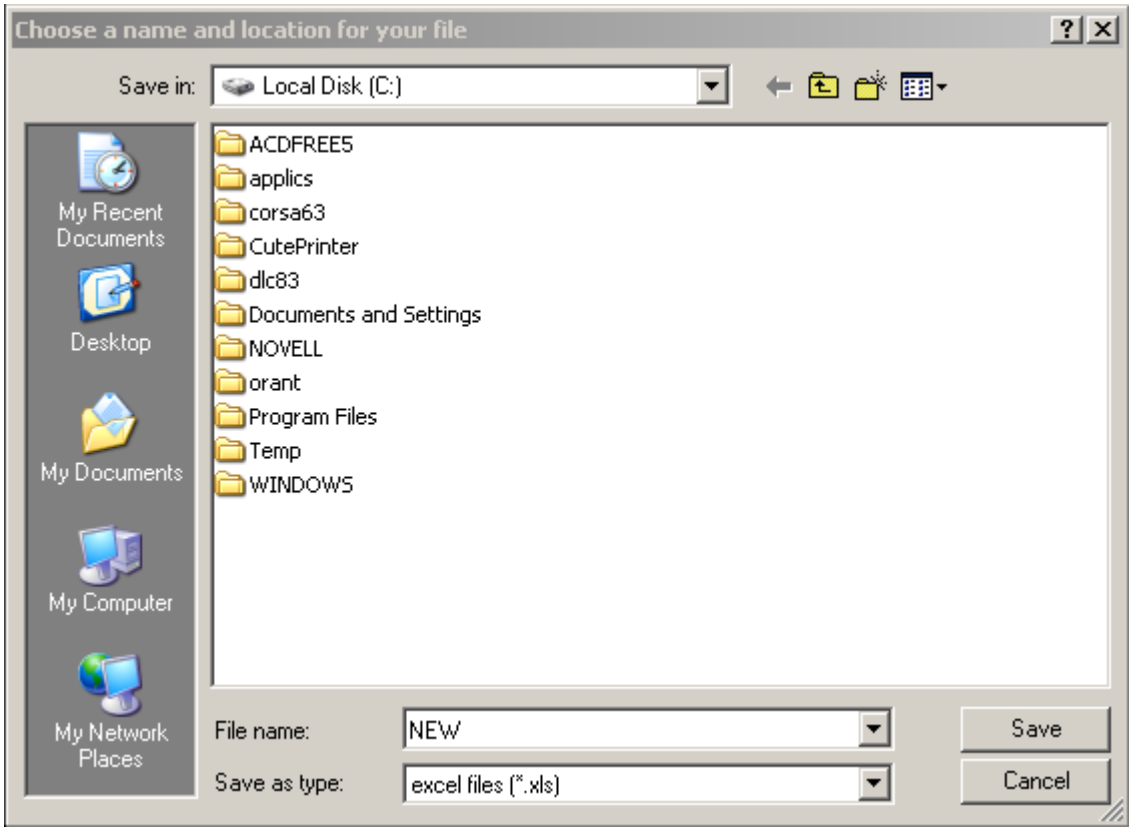

Figure 21. Save export file dialog box.

After having selected the location of your choice, click on **Save**. You will be asked if you want to open the export file directly or not:

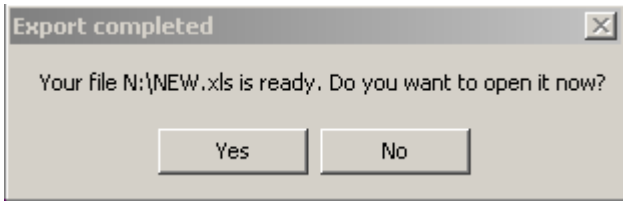

Figure 22. Export completed dialog box.

In order to have the exported (Excel)filenames corresponding with your *ETX*-project names, save your *ETX* data in an *ETX*-project before exporting data to an Excel sheet. The name of your *ETX*-project will then be chosen as default filename for your exported data file.

5.9 Preferences

5.9.1 Changing graph appearance in the *current* project

The three graphs that may be generated with *ETX* 2.0 can be edited to a limited extent. This section explains how.

- Go to one of the graphs that you have generated: **SSD Histogram and PDF**, **Species sensitivity distribution** or **Joint probability curve** under **Graphics**.
- In the graph of your choice, click with the right mouse button (left button for left handed mousers).
- A pop up-window appears in which you can select various parts of the graph that you might want to edit (e.g. Title, Title font, labels, line colour etc.).

– All changes that you have made using this option will be saved along with your project. When you re-open a project and press calculate, the settings you last made will appear in your graphs.

5.9.2 Changing the axis settings

There are three possible graphs in E_TX: an **SSD Histogram and PDF**, a **Species sensitivity distribution** and a **Joint probability curve**. The axis settings of the **SSD Histogram and PDF** can not be changed. Axis settings for the other two graphs can be changed as follows:

– Go to one of the graphs that you have generated: **SSD Histogram and PDF**, **Species sensitivity distribution** or **Joint probability curve** under **Graphics**.
– In the graph of your choice, click with the right mouse button (left button for left handed mousers).
– A pop up-window appears in which you can select various parts of the graph that you might want to edit (e.g. Title, Title font, labels, line colour etc.). Select **Axes settings** from the appearing menu. The following dialog box appears:

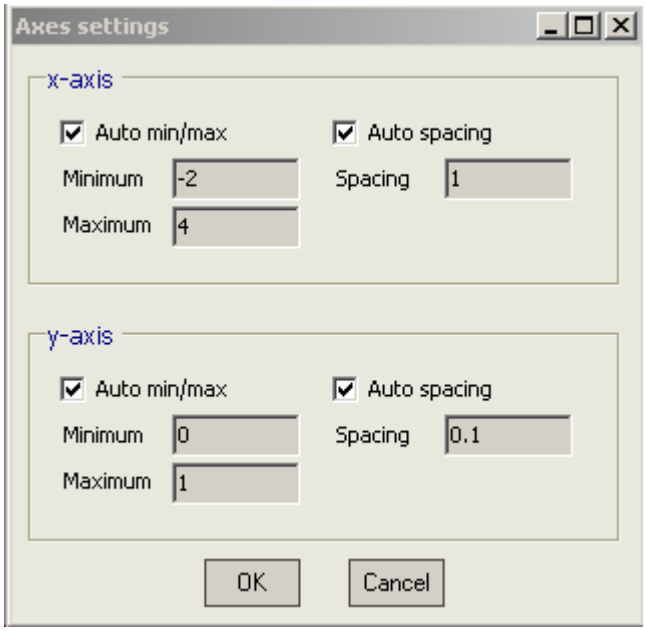

Figure 23. Axes settings dialog box.

Change the settings to your wishes and confirm by clicking **OK**.

5.9.3 Changing the default graph appearance

You may enter default values for the appearance of each of the three graphs via the **Tools**, **Preferences** menu that you can access via the menu bar. Figure 24 shows the dialog box that appears when you select this option.

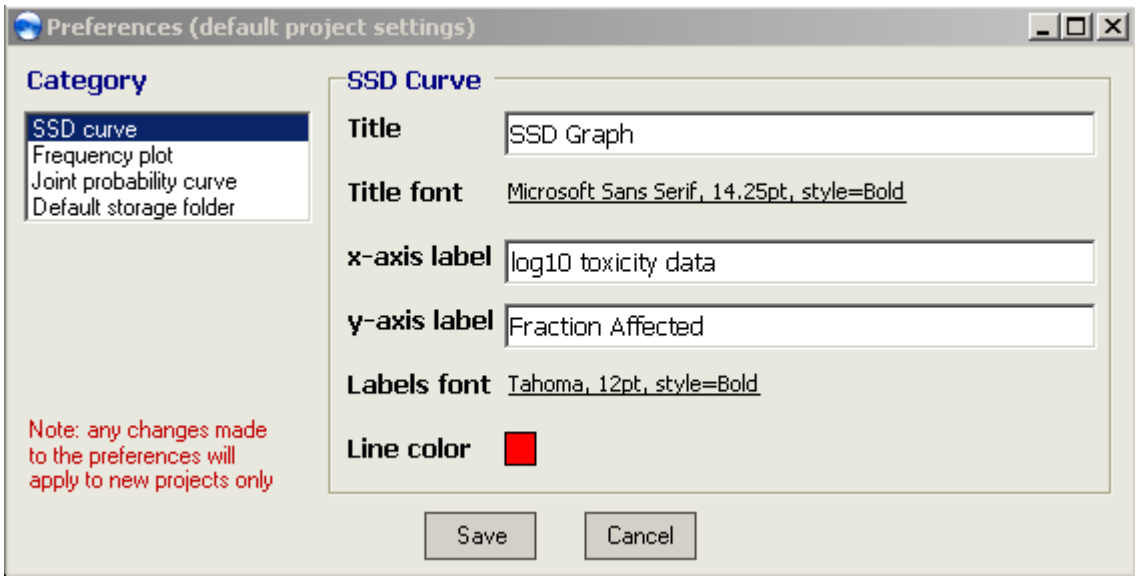

Figure 24. The default preferences dialog box.

- Select the graph of which you want to change the default settings in the box under **Category**.
- Edit the defaults in right half of the dialog box.
- After having made your changes, click on Save to save changes or on Cancel if you do not wish to keep your changes.
- Note that any changes you make will only apply to new projects that you will start after the current project. If you want to change the appearance of graphs in the current project, use the method described in the section above (5.9.1).

5.9.4 Changing the default file storage directory

You can select or change one directory where both your E_TX-project files as well as exported data files will be saved. To change this directory:

- Click on **Tools**, **Preferences**. The box shown in Figure 24 appears.
- Click on **Default storage folder** in the **Category** box. The box shown in Figure 25 appears.

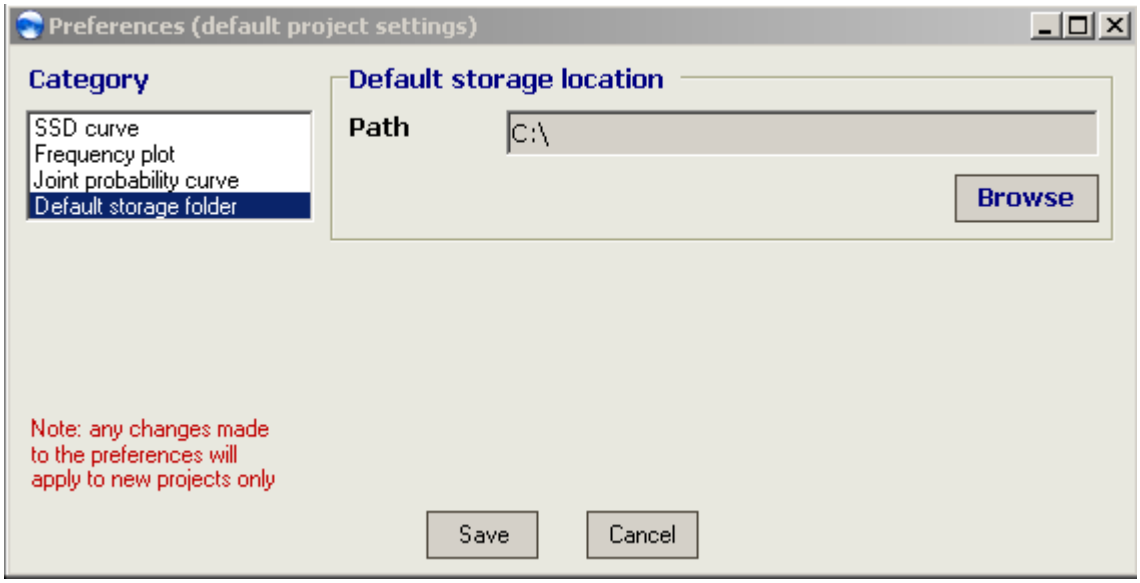

Figure 25. The default file storage location - dialog box.

- Type the directory of your choice behind **Path** or select a directory by browsing for it.
- Confirm your selection by clicking on **Save**. You will now leave the **Preferences** dialog.

5.10 Copying graphs

The three graphs that may be generated with E_TX can be copied to other programs. This section explains how.

- Go to one of the graphs that you have generated: **SSD Histogram and PDF**, **Species sensitivity distribution** or **Joint probability curve** under **Graphics**.
- In the graph of your choice, click with the right mouse button (left button for left handed mousers).
- A pop up-window appears; select **Copy**.
- You can now paste your graph in another program.

5.11 Use of the decimal symbol

The default setting of E_TX is that thousand separators will be ignored. In E_TX, the regional settings of your computer are applied to the figures you enter in input cells and to the graphs that are displayed under **Graphics**. For help on changing of these regional settings, please see section 3.8.

The default setting of E_TX has the following consequences. Example: if the period is your decimal symbol, the comma is usually the thousand separator. As long as you enter data with only a period as a decimal symbol, all is ok. You should enter figures higher than 999 *without* thousand separator: e.g. type 10000 rather than 10,000. As soon as E_TX recognises a thousand separator, a warning will be displayed in the status bar at the bottom of your E_TX screen: **Your data contains illegal decimal symbols**. This warning is displayed because otherwise, entering a figure like 13,1 would be entered as 131 and there is a fair chance that you might not notice this type of unexpected changes!

Therefore, two golden rules are:

1. **Do *not* use thousand separators when entering values.**
2. **The user determines the decimal symbol (settings) and is responsible for correct use.**

6. Limitations

6.1 SSD calculations

- For HC_5 and HC_{50} calculation a maximum number of 200 data can be entered.
- For calculation of the FA at the HC_{50} of your SSD (which is 50, by definition) and its accompanying lower and upper limit, the maximum number of toxicity data (*n*) is 75.

6.2 Calculation of the fraction affected

The calculation of the fraction affected that is calculated at a given environmental concentration (PEC) is limited by the height of the PEC value. The standardised logarithmic value of this PEC should be within the range -5 to 5. As a check, the value of the standardised logarithmic concentration calculated from your PEC value is shown in the **Fraction affected** output sheet. If this value is outside the range mentioned above, no results will be given. The message 'The method does not yield results because your standardised PEC exceeds the limits of <-5 or >5' will appear in red. The sheet will show 'Out of bounds!' as error values.

7. Examples

This section is a practical guide, which helps you through the calculation of an SSD or FA or other options in a stepwise manner.

7.1 Calculating an SSD

►Open *ETX* 2.0 or open a new project.
►In **Input data**, go to the **Input toxicity data** sheet, that is in the right part of your screen.
►Type the following data in the input cells in the column **Toxicity data**:

0.97
3.33
3.63
13.5
13.8
18.7
154

►In this example we will not add labels to the data. Leave the cells in the column **Label** empty.

These data are NOEC values for toxicity of cadmium to seven soil organisms, and are expressed in (µg Cd/g soil). The data are taken from Van Straalen and Denneman (1989) and are also used as an example in Aldenberg and Jaworska (2000).

►Go to the **Specifics** box in the **Input toxicity data** sheet. Click in the box to the right of **Unit**, and type: µg/g.
►In the **Specifics** box, click the pull down menu (downpointing arrow) and select NOEC.
►After having selected 'NOEC' in the **Specifics** box, press **Calculate, Go** in the Standard Menu bar. After performing the calculation, *ETX* automatically switches to the **Hazardous concentration sheet** in the **Statistics section** (Figure 26, shown at the next page).
►Go to the **Goodness-of-fit** sheet and check if your data are normally distributed (Figure 27, shown at the next page). In this example it is probable that the data derive from a normal distribution.

Parameters of the normal distribution

Name	Value	Description
mean	9.71E-1	mean of the log toxicity values
s.d.	7.03E-1	sample standard deviation
n	7.00E0	sample size

HC5 results

Name	Value	log10(Value)	Description
LL HC5	3.821E-2	-1.418E0	lower estimate of the HC5
HC5	5.678E-1	-2.458E-1	median estimate of the HC5
UL HC5	2.111E0	3.244E-1	upper estimate of the HC5
sprHC5	5.523E1	1.742E0	spread of the HC5 estimate

FA At HC5 results

Name	Value	Description
FA lower	0.34	5% confidence limit of the FA at standardised median logHC5
FA median	5.00	50% confidence limit of the FA at standardised median logHC5
FA upper	25.01	95% confidence limit of the FA at standardised median logHC5

HC50 results

Name	Value	log10(Value)	Description
LL HC50	2.852E0	4.551E-1	lower estimate of the HC50
HC50	9.359E0	9.712E-1	median estimate of the HC50
UL HC50	3.072E1	1.487E0	upper estimate of the HC50
sprHC50	1.077E1	1.032E0	spread of the HC50 estimate

FA At HC50 results

Figure 26. Output of statistical parameters forHC5, HC_{50} and FA calculation.

Toxicity data

Anderson-Darling test for normality

Sign. level	Critical	Normal?
0.1	0.631	Accepted
0.05	0.752	Accepted
0.025	0.873	Accepted
0.01	1.035	Accepted

AD Statistic: 3.15E-1
n: 7

Note: below n=8, this test may not perform well.

Kolmogorov-Smirnov test for normality

Sign. level	Critical	Normal?
0.1	0.819	Accepted
0.05	0.895	Accepted
0.025	0.995	Accepted
0.01	1.035	Accepted

KS Statistic: 5.66E-1
n: 7

Note: below n=20, this test may not perform well.

Cramer von Mises test for normality

Sign. level	Critical	Normal?
0.1	0.104	Accepted
0.05	0.126	Accepted
0.025	0.148	Accepted
0.01	0.179	Accepted

CM Statistic: 3.65E-2
n: 7

Note: below n=20, this test may not perform well.

Exposure data

Anderson-Darling test for normality

Sign. level	Critical	Normal?
0.1	0.631	Accepted

Figure 27. Output goodness-of-fit tests.

►Go to **Output**, **Graphics** to find the **SSD Histogram and PDF** sheet and the **SSD graph** sheet to view the graphical output (Figure 28).

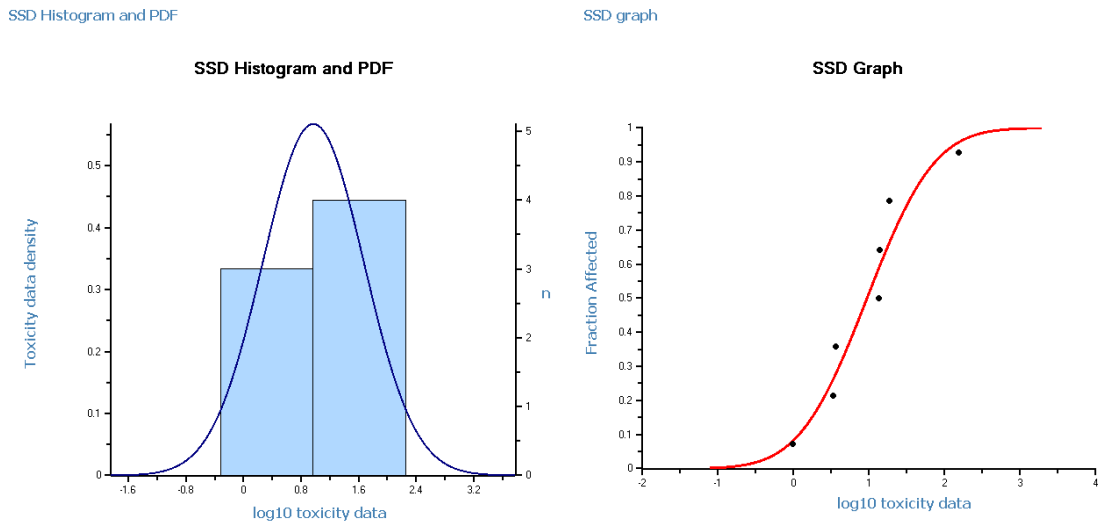

Figure 28. Histogram and PDF (left panel) and species sensitivity distribution (CDF, right panel).

7.2 Calculating a fraction of affected species

In order to calculate the fraction of species that is (potentially) affected at a given exposure concentration, we need the SSD of these species. So, you have to calculate an SSD first. In this example, we will use the SSD that was generated in section 7.1. Next, suppose we have one environmental concentration of 12 mg Cd/kg soil. The toxicity data were entered in the units of µg Cd/g soil. This is identical to mg Cd/kg soil. We have verified that units of toxicity data and PEC value are identical. Proceed as follows.

►Calculate an SSD (see section 7.1).
►Go to the **Input exposure data** sheet. In the right part of your screen, you see the box **Single PEC**.
►In the **Single PEC** box, click in the empty cell next to 'Enter a single PEC'; type 12 and press [enter].
►After having entered the PEC value, press **Calculate, Go** in the Standard Menu bar.
► E_TX will now switch automatically to the **Fraction affected** sheet in the **Output** section.
►Note that the value of the standardised logarithmic concentration calculated from this PEC is 0.5136. Since this value is >-5 and <5, an FA can be calculated by E_TX (see section 6 for limitations).
►The upper half of this sheet (the **FA results** box) shows your result (Figure 29): the median percentage of species in the soil that will be affected by this Cd concentration is 55.9%. The variation in the data tells you that there is 90% confidence that the percentage of affected species is between 31.6% and 78%.

FA results

FA results	Percent	Description
LL FA	31.60	Lower estimate (5% confidence) of the fraction affected
Median FA	55.85	Median estimate (50% confidence) of the fraction affected
UL FA	78.03	Upper estimate (95% confidence) of the fraction affected

The standardized logarithmic concentration calculated from your PEC value is: **1.536E-1**

These calculations are based on repeated linear interpolation and are approximate values.
The procedure is explained in Section 8.2.3 of Aldenberg & Jaworska 2000.
A precise answer can be obtained using the functions described in Section 8.2.1

Figure 29. The fraction of species affected by 12 mg/kg Cd.

7.3 Calculating an expected ecological risk

Suppose you have a series of Cd concentrations, measured in a field soil. The measured concentrations are 1.5, 7, 3, 12, 1, 11 and 6 (mg Cd per kg soil). You can now calculate an EER and generate its graphical representation as a joint probability curve. In order to calculate the EER for the organisms in the field soil, we need the SSD of these species for Cd. In this example, we will use the SSD that was generated in section 7.1.

►Calculate an SSD (see section 7.1).
►Go to the **Input exposure data** sheet in the **Input data** section.
►In the right part of your screen, called **Input environmental concentrations**, click in the first cell of the column under **Exposure data**. Enter the following values, each next value in a new input cell:

1.5
7
3
12
1
11
6

►After entering the last value, press **Calculate, Go** in the Standard Menu bar.
►In order to check if your data follow a normal distribution, go to the **Goodness-of-fit** sheet in the **Output** section. In the lower half of this sheet, in the **Exposure data** box, the results of the test for normality of your exposure data are shown (Figure 30). In this example it is probable that the data derive from a normal distribution.

Expected Ecological Risk

FA results	Value	Description
SEC Mean	-4.882E-1	Scaled mean of (log10) environmental concentration distribution
SEC sd	5.996E-1	Scaled S.D. of (log10) environmental concentration distribution
Exp. Ecol. Risk	3.377E1	Expected Mean Ecological Risk, given the SSD and the EC distribution

The mean and standard deviation are scaled relative to the mean and SD of the Species Sensitivity Distribution.
The expected (mean) ecological risk is the area below the Joint Probability Curve.

Figure 30. Results of GOF test for exposure data.

►Go to the **Fraction affected** sheet (**Output**, **Statistics** section). In the lower half of this sheet (the **Expected ecological risk** box) you see two statistical parameters that are used to calculate the EER. The EER itself amounts to 33.8%, which is the percentage of species likely to be affected, given the SSD and EC distribution based on the data you have entered.

Expected Ecological Risk

FA results	Value	Description
SEC Mean	-4.882E-1	Scaled mean of (log10) environmental concentration distribution
SEC sd	5.996E-1	Scaled S.D. of (log10) environmental concentration distribution
Exp. Ecol. Risk	33.77	Expected Mean Ecological Risk, given the SSD and the EC distribution

The mean and standard deviation are scaled relative to the mean and SD of the Species Sensitivity Distribution.
The expected (mean) ecological risk is the area below the Joint Probability Curve.

Figure 31. Results of the expected ecological risk calculation.

►Go to the **Joint probability curve** sheet (**Output**, **Graphics** section). The graph in Figure 32 should be displayed.

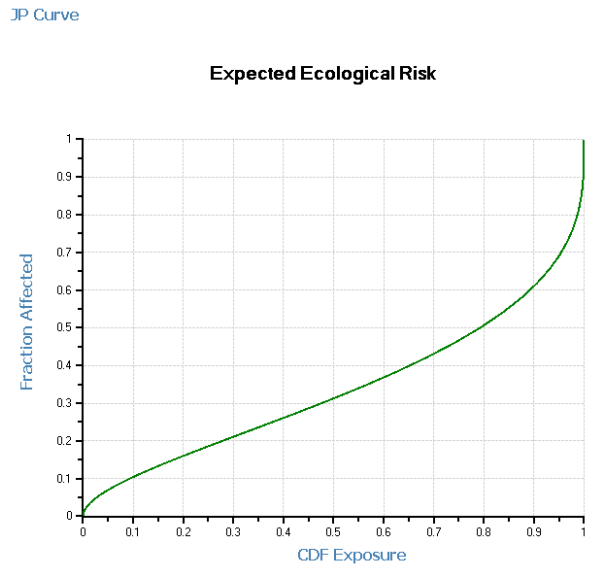

Figure 32. The joint probability curve belonging to the SSD from example 7.1 and the exposure data from example 7.3.

7.4 Calculating an HD_5 for birds or mammals from a small data set

In contrast to the previous examples, you do not have to generate an SSD before you can calculate an HD_5 for a small sample of toxicity data.

►Go to the **Input exposure data** sheet in the **Input data** section.
►In the **Input toxicity data** box (this is the right part of your screen), click on the **Use small sample approach** check box in the **Small sample** box. The following dialog box will appear:

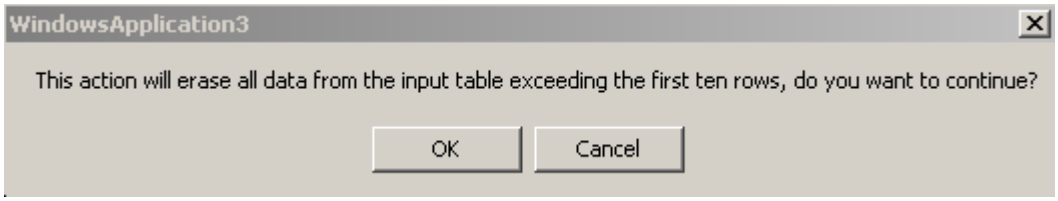

Figure 33. Small sample verification box.

If you had already typed data in the input section, these data will be lost when you switch to the Small sample input mode. Remember that this is a different method that does not require calculation of an SSD. You will have to start a separate project for each type of calculation that you perform. So, if you want to keep the data you had entered before, click on **Cancel** and save your work in an E_TX project. Then start a new project for your 'small sample' calculation. Since we want to use the 'small sample' method, click on **OK**.
►In the part of your screen called **Input toxicity data**, the number of input cells is now reduced to 10.
►In the **Input toxicity data** sheet, click in the first cell of the column under **Toxicity data**. If there are any values present, delete these data. Type the following –fictitious– data in the input cells, each next value in a new input cell:

120
550
630

Let us say that these values are three LD_{50} values for birds, for a pesticide that is not a carbamate nor an organophosphorous compound.

►From the list of **Pre-defined standard deviations** that is also shown in the **Small sample** box, in the lower right corner of your screen, select the value for 'LD_{50} data of 55 pesticides for birds'. The figure 0.465 will appear in the **Standard deviation** cell.
►Click on **Calculate**, **Go** in the **Standard** menu bar.
►After performing the calculation, E_TX automatically switches to the **Small sample output** sheet in the **Output**, **Statistics** section (Figure 34).

Parameters

Name	Value	Description
mean	2.540E0	mean of the log toxicity values
n	3	sample size
s.d.	0.465	preselected standard deviation

HD5 (median) results

Name	Value (mg/kg bwt)	Extrapolation factor (EF)
LL HD5	2.154E1	1.609E1
HD5 (median)	5.954E1	5.819E0
UL HD5	1.646E2	2.105E0

Figure 34. Output of the small sample *calculation with E_TX 2.0.*

►The estimated 5th percentile of HD_5 values is 60 mg/kg_{bwt}. There is 90% confidence that the HD_5 will lie between 22 and 165 mg/kg_{bwt}. The extrapolation factors shown in the second column can be used to calculate each of the three reported parameters directly from the sample mean. For further details we refer to Aldenberg and Luttik (2002).

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List of abbreviations

AUC	area under the curve
CDF	cumulative distribution function
DGM/SAS	Directorate General for Environmental Protection, Directorate for Chemicals, Waste and Radiation
EC	exposure concentration, in the context used here it is synonym to environmental concentration
ECD	exposure concentration distribution
EER	expected ecological risk
EU	European Union
E_TX	*E*co*T*o*X*
FA	fraction affected
GOF	goodness-of-fit
HC_5	hazardous concentration, 5th percentile of normally distributed toxicity data
HC_{50}	hazardous concentration, median or 50th percentile of normally distributed toxicity data
HD_5	hazardous dose, 5th percentile of normally distributed toxicity data
INS	Setting (Inter)national Environmental Quality Standards
JPC	joint probability curve
LC_{50}	toxicant concentration causing 50% mortality in test population
LL	lower limit (of a confidence interval)
MS	Microsoft ©
n	sample size
NOEC	no observed effect concentration
PAF	potentially affected fraction; identical to FA, but PAF is no longer used in E_TX 2.0
PDF	probability density function
PEC	predicted environmental concentration
RIVM	National Institute for Public Health and the Environment
RIKZ	National Institute for Coastal and Marine management
RIZA	Institute Inland Water Management and Waste Water Treatment
s.d.	standard deviation
SEC	scaled environmental concentration
SSD	species sensitivity distribution
UL	upper limit (of a confidence interval)
VROM	Dutch Ministry of Housing, Spatial Planning and the Environment

Appendix 1 Installation problems

This appendix gives you an overview of combinations of Microsoft operating systems and Microsoft Office combinations we have tested plus the results of these tests. For some problems you may have benefit of a solution that is offered here.

Table 1. List of results: installation of E_TX 2.0 on MS operating systems and MS Office versions plus reference to possible solutions where appropriate.

MS Windows version	MS Office version	Test result	Solution
Windows 98 SE	not installed	Installation successful	
Windows 98	Office 97	Installation unsuccessful	
Windows 2000	Office 97	Installation unsuccessful	try solution 1
Windows 2000	2000	Installation successful	
Windows NT	not installed	Installation successful	
Windows NT	Office 97	Installation successful	
Windows XP	not installed	Installation successful	solution 2
Windows XP	Office 97	Installation successful	solution 2
Windows XP	Office 2000	Installation successful	solution 2
Windows XP	Office XP	Installation successful	solution 2
Windows XP	Office 2003	Installation successful	solution 2

Solution 1
With older versions of Windows, you might need to install Microsoft's Data Access Components (MDAC) or a recent update of MDAC. One version of MDAC is placed as a compressed file on the E_TX-CD. It is called **MDAC_TYP.exe** (version 2.80). You may install the file provided to you on the E_TX-CD, however, since updates of MDAC frequently appear we advise you to visit the Microsoft website to check for possible more recent updates. Visit: http://www.microsoft.com and search for MDAC.

If there are no MDAC installed on your PC or there are no recent updates available, follow the installation procedure described below.

Installation of MDAC from the E_TX-CD.
- Insert the E_TX-CD in the CD drive of your computer.
- Start the Windows Explorer (Start button, Programs, Accessories, Windows Explorer).
- In the left side of your screen, click on the drive that is your CD drive.
- In the right half of your screen, double click on the file **MDAC_TYP.exe**.
- The installation procedure will now start. Complete the installation procedure.

Now try to install E_TX. We refer to section 3.2 for the installation procedure.

Solution 2
If you have a machine with a recent Windows version, but installation is still unsuccessful, try manual installation of E_TX on your hard disk. Do as follows:

Manually Installing *E_TX*

- Insert the *E_TX*-CD in the CD drive of your computer.
- Start the Windows Explorer (Start button, Programs, Accessories, Windows Explorer).
- Create a new directory on your hard disk (e.g. C:\My Documents\ETX TEMP) in which the installation files can be placed.
- Files\RIVM*E_TX* 2.0).
- Double click the file *E_TX* 2.0.msi that is on the hard disk of your computer to start MS Installer.
- Normally, *E_TX* should now be installed without problems.

Manually installing .NET framework

If the compact .NET framework is not installed on your computer, try to run the setup program manually:

- Insert the *E_TX*-CD in the CD drive of your computer.
- In the dialog box enter E:\dotnetfx.exe, where E is the letter of your CD drive.
- Normally, the .NET framework should now be installed without problems.
- Next carry out the procedure described above, under 'Manually installing *E_TX*'.

Appendix 2 Error messages

This appendix gives an overview of the error messages that can be displayed when using *ETX* 2.0. A short description or solution to the problem is given where appropriate.

Error messages displayed during starting

Message

Could not initialize application, make sure a recent version of Microsoft's Data Access Components (MDAC) are installed on your PC

Solution

See solution 1 in Appendix 1.

Error messages displayed during calculations or entering data

Message

You should enter a set of toxicity data as well, in order to perform any calculations

Solution

ETX can not perform calculation of an SSD and accompanying statistics (FA, HC etc.) unless you enter a toxicity data set in the **Input toxicity data** sheet. The minimum number of data is three.

The 'small sample' method can be used without calculating an SSD first.

Message

You haven't entered sufficient data!

Solution

ETX will not perform calculation of an SSD and accompanying statistics (FA, HC etc.) unless you enter a toxicity data set of at least three values in the **Input toxicity data** sheet.

ETX will not perform calculation of an HD_5 using the *small sample method* unless you enter at least one toxicity value in the **Input toxicity data** sheet.

Message

You haven't entered sufficient exposure data to calculate the Expected Ecological Risk and JPC curve

Solution

ETX will not perform calculation of an EER and JPC unless you enter at least three exposure concentrations in the **Input exposure data** sheet.

Message

A label collection is active, this means you have to assign labels to all entries in the toxicity input screen before you can calculate results

Solution

Go to the **Input toxicity data** sheet and check if all toxicity entries have a label attached to it. If you do not want your toxicity data to be labelled, go to the **Input toxicity data** sheet and click on the **De-activate** button in the lower right corner of your screen.

Message
You have to enter a prefixed standard deviation in order to perform small sample calculations
Solution
In the **Small Sample** box in the **Input toxicity data** sheet, select a predefined standard deviation or enter a custom value.

Error messages displayed when saving an *E_TX* file
Message
An error occurred while saving the file.
Solution
A single solution for this problem can not be given. Try copying the dataset or datasets you have entered to an other application. Then quit *E_TX*, and restart *E_TX* in order to retry your work.

Error messages displayed when opening an *E_TX* file
Message
An error occurred while opening the file.
Solution
Your file may be damaged or in the wrong format. Try to open your data in another application and copy them to *E_TX*.

Error messages displayed when exporting results
Message
Please (re)calculate your results before exporting
Solution
You have made changes to the data but you have not yet pressed the calculate button. Consequently, the results you are about to export do not belong to the dataset, which is currently entered in *E_TX*. In order to continue, you have to update your results first by performing a calculation.

Message
An error occurred while exporting, please make sure that a version of Microsoft Excel 97 or higher is installed on your PC.
Solution
A solution is given in the message; an Excel version as recent as Excel 97 should be used.

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Exposure Analysis Modeling System (EXAMS): User Manual and System Documentation

By

Lawrence A. Burns, Ph.D.
Ecologist, Ecosystems Research Division
U.S. Environmental Protection Agency
960 College Station Road
Athens, Georgia 30605-2700

National Exposure Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Notice

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Foreword

Environmental protection efforts are increasingly directed toward preventing adverse health and ecological effects associated with specific chemical compounds of natural or human origin. As part of the Ecosystems Research Division's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Ecosystems Assessment Branch studies complexes of environmental processes that control the transport, transformation, degradation, fate, and impact of pollutants or other materials in soil and water and develops models for assessing the risks associated with exposures to chemical contaminants.

Concern about environmental exposure to synthetic organic chemicals has increased the need for techniques to predict the behavior of chemicals entering the environment as a result of the manufacture, use, and disposal of commercial products. The Exposure Analysis Modeling System (EXAMS), which has been undergoing continual development, evaluation, and revision at this Division since 1978, provides a convenient tool to aid in judging the environmental consequences should a specific chemical contaminant enter a natural aquatic system. Because EXAMS requires no chemical monitoring data, it can be used for new chemicals not yet introduced into commerce as well as for those whose pattern and volume of use are known. EXAMS and other exposure assessment models should contribute significantly to efforts to anticipate potential problems associated with environmental pollutants.

Rosemarie C. Russo
Director
Ecosystems Research Division
Athens, Georgia

Abstract

The Exposure Analysis Modeling System, first published in 1982 (EPA-600/3-82-023), provides interactive computer software for formulating aquatic ecosystem models and rapidly evaluating the fate, transport, and exposure concentrations of synthetic organic chemicals – pesticides, industrial materials, and leachates from disposal sites. EXAMS contains an integrated Database Management System (DBMS) specifically designed for storage and management of project databases required by the software. User interaction is provided by a full-featured Command Line Interface (CLI), context-sensitive help menus, an on-line data dictionary and CLI users' guide, and plotting capabilities for review of output data. EXAMS provides 20 output tables that document the input datasets and provide integrated results summaries for aid in ecological risk assessments.

EXAMS' core is a set of process modules that link fundamental chemical properties to the limnological parameters that control the kinetics of fate and transport in aquatic systems. The chemical properties are measurable by conventional laboratory methods; most are required under various regulatory authorities. EXAMS limnological data are composed of elements historically of interest to aquatic scientists world-wide, so generation of suitable environmental datasets can generally be accomplished with minimal project-specific field investigations.

EXAMS provides facilities for long-term (steady-state) analysis of chronic chemical discharges, initial-value approaches for study of short-term chemical releases, and full kinetic simulations that allow for monthly variation in mean climatological parameters and alteration of chemical loadings on daily time scales. EXAMS has been written in generalized (N-dimensional) form in its implementation of algorithms for representing spatial detail and chemical degradation pathways; the complexity of the environmental description and the number of chemicals is fully user-controlled. This implementation allows for direct access file (UDB) storage of five interacting chemical compounds and 100 environmental segments; more complex configurations can be created and subsequently stored using EXAMS' WRITE command. EXAMS provides analyses of

Exposure: the expected (96-hour acute, 21-day and long-term chronic) environmental concentrations of synthetic chemicals and their transformation products,

Fate: the spatial distribution of chemicals in the aquatic ecosystem, and a sensitivity analysis of the relative importance of each transformation and transport process (important in establishing the acceptable uncertainty in chemical laboratory data), and

Persistence: the time required for natural purification of the ecosystem (via export and degradation processes) once chemical releases end.

EXAMS includes file-transfer interfaces to the PRZM terrestrial model and the FGETS and BASS bio-accumulation models; it is a complete implementation of EXAMS in Fortran 95.

This report covers a period from December 1, 1999 to September 15, 2000 and work was completed as of September 17, 2000. This version of the Manual reflects continuous maintenance and upgrade of EXAMS.

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1.0 Introduction to the Exposure Analysis Modeling System (EXAMS)

1.1 Background

Industrial production of agricultural chemicals, plastics, and pharmaceuticals has increased steadily over the past five decades. More recently, growth of the chemical industry has been accompanied by increasing concern over the effects of synthetic chemicals on the environment. The suspicion has arisen that, in some cases, the benefits gained by using a chemical may not offset the cost of incidental damage to man's natural life-support system – the biosphere. The toxicity of a chemical does not of itself indicate that the environmental risks associated with its use are unacceptable, however, as it is the dose that makes the poison. A rational evaluation of the risk posed by the use and disposal of synthetic chemicals must begin from a knowledge of the persistence and mobility of chemicals in the environment, which in turn establish the conditions of exposure leading to absorption of toxicological dose.

The Exposure Analysis Modeling System (EXAMS), developed at the U.S. Environmental Protection Agency's research laboratory in Athens, Georgia, is an interactive computer program intended to give decision-makers in industry and government access to a responsive, general, and controllable tool for readily deriving and evaluating the behavior of synthetic chemicals in the environment. The research and development effort has focused on the creation of the interactive command language and user aids that are the core of EXAMS, and on the genesis of reliable EXAMS mathematical models. EXAMS was designed primarily for the rapid screening and identification of synthetic organic chemicals likely to adversely impact aquatic systems. This report is intended to acquaint potential users with the underlying theory, capabilities, and use of the system.

1.2 Exposure Analysis in Aquatic Systems

EXAMS was conceived as an aid to those who must execute hazard evaluations solely from laboratory descriptions of the chemistry of a newly synthesized toxic compound. EXAMS estimates exposure, fate, and persistence following release of an organic chemical into an aquatic ecosystem. Each of these terms was given a formal operational definition during the initial design of the system.

1.2.1 Exposure

When a pollutant is released into an aquatic ecosystem, it is entrained in the transport field of the system and begins to spread to locations beyond the original point of release. During the course of these movements, chemical and biological processes transform the parent compound into daughter products. In the face of continuing emissions, the receiving system evolves toward a "steady-state" condition. At steady state, the pollutant concentrations are in a dynamic equilibrium in which the loadings are balanced by the transport and transformation processes. Residual concentrations can be compared to those posing a danger to living organisms. The comparison is one indication of the risk entailed by the presence of a chemical in natural systems or in drinking-water supplies. These "expected environmental concentrations" (EECs), or exposure levels, in receiving water bodies are one component of a hazard evaluation.

1.2.2 Persistence

Toxicological and ecological "effects" studies are of two kinds: investigations of short-term "acute" exposures, as opposed to longer-term "chronic" experiments. Acute studies are often used to determine the concentration of a chemical resulting in 50% mortality of a test population over a period of hours. Chronic studies examine sub-lethal effects on populations exposed to lower concentrations over extended periods. Thus, for example, an EEC that is 10 times less than the acute level does not affirm that aquatic ecosystems will not be affected, because the probability of a "chronic" impact increases with exposure duration. A computed EEC thus must be supplemented with an estimate of "persistence" in the environment. (A compound immune to all transformation processes is by definition "persistent" in a global sense, but even in this case transport processes will eventually reduce the pollutant to negligible levels should the input loadings cease.) The notion of "persistence" can be given an explicit definition in the context of a particular contaminated ecosystem: should the pollutant loadings cease, what time span would be required for dissipation of most of the residual contamination? (For example, given the half-life of a chemical in a "first-order" system, the time required to reduce the chemical concentration to any specified fraction of its initial value can be easily computed.) With this information in hand, the appropriate duration and pollutant levels for chronic studies can be more readily decided. More detailed dynamic simulation studies can elicit the probable magnitude and duration of acute events as well.

1.2.3 Fate

The toxicologist also needs to know which populations in the system are "at risk." Populations at risk can be deduced to some extent from the distribution or "fate" of the compound, that is, by an estimate of EECs in different habitats of single ecosystems. EXAMS reports a separate EEC for each compartment, and thus each local population, used to define the system.

The concept of the "fate" of a chemical in an aquatic system has an additional, equally significant meaning. Each transport or transformation process accounts for only part of the total behavior of the pollutant. The relative importance of each

process can be determined from the percentage of the total system loadings consumed by the process. The relative importance of the transformations indicate which process is dominant in the system, and thus in greatest need of accuracy and precision in its kinetic parameters. Overall dominance by transport processes may imply a contamination of downstream systems, loss of significant amounts of the pollutant to the atmosphere, or pollution of ground-water aquifers.

1.3 The EXAMS program

The need to predict chemical exposures from limited data has stimulated a variety of recent advances in environmental modeling. These advances fall into three general categories:

- Process models giving a quantitative, often theoretical, basis for predicting the rate of transport and transformation processes as a function of environmental variables.
- Procedures for estimating the chemical parameters required by process models. Examples include linear free energy relationships, and correlations summarizing large bodies of experimental chemical data.
- Systems models that combine unit process models with descriptions of the environmental forces determining the strength and speed of these processes in real ecosystems.

The vocabulary used to describe environmental models includes many terms, most of which reflect the underlying intentions of the modelers. Models may be predictive, stochastic, empirical, mechanistic, theoretical, deterministic, explanatory, conceptual, causal, descriptive, etc. The EXAMS program is a deterministic, predictive systems model, based on a core of mechanistic process equations derived from fundamental theoretical concepts. The EXAMS computer code also includes descriptive empirical correlations that ease the user's burden of parameter calculations, and an interactive command language that facilitates the application of the system to specific problems.

EXAMS "predicts" in a somewhat limited sense of the term. Many of the predictive water-quality models currently in use include site-specific parameters that can only be found via field calibrations. After "validation" of the model by comparison of its calibrated outputs with additional field measurements, these models are often used to explore the merits of alternative management plans. EXAMS, however, deals with an entirely different class of problem. Because newly synthesized chemicals must be evaluated, little or no field data may exist. Furthermore, EECs at any particular site are of little direct interest. In this case, the goal, at least in principle, is to predict EECs for a wide range of ecosystems under a variety of geographic, morphometric, and ecological conditions. EXAMS includes no direct calibration parameters, and its input environmental data can be developed from a variety of sources. For example, input data can be synthesized from an analysis of the outputs of hydrodynamic models, from prior field investigations conducted without reference to toxic chemicals, or from the appropriate limnological literature. The EECs generated by EXAMS are thus "evaluative" (Lassiter et al. 1979) predictions designed to reflect typical or average conditions. EXAMS' environmental database can be used to describe specific locales, or as a generalized description of the properties of aquatic systems in broad geographic regions.

EXAMS relies on mechanistic, rather than empirical, constructs for its core process equations wherever possible. Mechanistic (physically determinate) models are more robust predictors than are purely empirical models, which cannot safely be extended beyond the range of prior observations. EXAMS contains a few empirical correlations among chemical parameters, but these are not invoked unless the user approves. For example, the partition coefficient of the compound on the sediment phases of the system, as a function of the organic carbon content of its sediments, can be estimated from the compound's octanol-water partition coefficient. A direct load of the partition coefficient (KOC, see the EXAMS Data Dictionary beginning on page 176) overrides the empirical default estimate, however. (Because EXAMS is an interactive program in which the user has direct access to the input database, much of this documentation has been written using the computer variables (e.g., KOC above) as identifiers and as quantities in the process equations. Although this approach poses some difficulties for the casual reader, it allows the potential user of the program to see the connections between program variables and the underlying process theory. The EXAMS data dictionary in this document (beginning on page 176) includes an alphabetical listing and definitions of EXAMS' input variables.)

EXAMS is a deterministic, rather than a stochastic, model in the sense that a given set of inputs will always produce the same output. Uncontrolled variation is present both in ecosystems and in chemical laboratories, and experimental results from either milieu are often reported as mean values and their associated variances. Probabilistic modeling techniques (e.g., Monte Carlo simulations) can account, in principle, for this variation and attach an error bound or confidence interval to each important output variable, although the statistical distributions of chemical and environmental parameters are not often known in the requisite detail. Input time series that include ecophysiological and hydrologic variation directly transfer these variabilities to the outcomes of simulations. Standard EXAMS time-series and summary outputs reflect variation in response to meteorology, and find use in statistical analyses of the expected frequency and magnitude of toxicologically significant event durations. One objective of this kind of modeling, in the case of hazard evaluations, is to estimate the effect of parameter errors on the overall conclusions to be drawn from the model. This goal can

often be efficiently met by some form of sensitivity analysis.

1.4 Sensitivity Analysis and Error Evaluation

EXAMS does not provide a formal sensitivity analysis among its options: the number of sub-simulations needed to fully account for interactions among chemical and environmental variables is prohibitively large (Behrens 1979). When, for example, the second-order rate constant for alkaline hydrolysis of a compound is described to EXAMS via an Arrhenius function, the rate constant computed for each compartment in the ecosystem depends on at least six parameters. These include the frequency factor and activation energy of the reaction, the partition coefficient of the compound (KOC), the organic carbon content of the sediment phase, the temperature, and the concentration of hydroxide ion. The overall rate estimate is thus as dependent upon the accuracy of the system definition as it is upon the skill of the laboratory chemist; in this example, the rate could vary six orders of magnitude as a function of differences among ecosystems. In order to fully map the parameter interactions affecting a process, all combinations of parameter changes would have to be simulated. Even this (simplified) example would require 63 simulations (2^n-1, where n is the number (6) of parameters) merely to determine sensitivities of a single component process in a single ecosystem compartment.

Sensitivity analysis remains an attractive technique for answering a crucial question that arises during hazard evaluation. This question can be simply stated: "Are the chemical data accurate enough, and precise enough, to support an analysis of the risk entailed by releases of the chemical into the environment?" Like many simple questions, this question does not have a simple, definitive answer. It can be broken down, however, into a series of explicit, more tractable questions whose answers sum to a reasonably complete evaluation of the significance that should be attached to a reported error bound or confidence interval on any input datum. Using the output tables and command language utilities provided by EXAMS, these questions can be posed, and answered, in the following order.

- Which geographic areas, and which ecosystems, develop the largest chemical residuals? EXAMS allows a user to load the data for any environment contained in his files, specify a loading, and run a simulation, through a simple series of one-line English commands.

- Which process is dominant in the most sensitive ecosystem(s)? The dominant process, i.e., the process most responsible for the decomposition of the compound in the system, is the process requiring the greatest accuracy and precision in its chemical parameters. EXAMS produces two output tables that indicate the relative importance of each process. The first is a "kinetic profile" (or frequency scaling), which gives a compartment-by-compartment listing with all processes reduced to equivalent ($hour^{-1}$) terms. The second is a tabulation of the overall steady-state fate of the compound, giving a listing of the percentage of the load consumed by each of the transport and transformation processes at steady state.

Given the dominant process, the input data affecting this process can be varied over the reported error bounds, and a simulation can be executed for each value of the parameters. The effect of parameter errors on the EECs and persistence of the compound can then be documented by compiling the results of these simulations.

This sequence of operations is, in effect, a sensitivity analysis, but the extent of the analysis is controlled and directed by the user. In some cases, for example, one process will always account for most of the decomposition of the compound. When the database for this dominant process is inadequate, the obvious answer to the original question is that the data do not yet support a risk analysis. Conversely, if the dominant process is well defined, and the error limits do not substantially affect the estimates of exposure and persistence, the data may be judged to be adequate for the exposure analysis portion of a hazard evaluation.

1.5 EXAMS Process Models

In EXAMS, the loadings, transport, and transformations of a compound are combined into differential equations by using the mass conservation law as an accounting principle. This law accounts for all the compound entering and leaving a system as the algebraic sum of (1) external loadings, (2) transport processes exporting the compound out of the system, and (3) transformation processes within the system that degrade the compound to its daughter products. The fundamental equations of the model describe the rate of change in chemical concentrations as a balance between increases due to loadings, and decreases due to the transport and transformation processes removing the chemical from the system.

The set of unit process models used to compute the kinetics of a compound is the central core of EXAMS. These unit models are all "second-order" or "system-independent"models: each process equation includes a direct statement of the interactions between the chemistry of a compound and the environmental forces that shape its behavior in aquatic systems. Thus, each realization of the process equations implemented by the user in a specific EXAMS simulation is tailored to the unique characteristics of that ecosystem. Most of the process equations are based on standard theoretical constructs or accepted empirical relationships. For example, light intensity in the water column of the system is computed using the Beer-Lambert law, and temperature corrections for rate constants are computed using Arrhenius functions. Detailed explanations of the process

models incorporated in EXAMS, and of the mechanics of the computations, are presented in Chapter 2.

1.5.1 Ionization and Sorption

Ionization of organic acids and bases, complexation with dissolved organic carbon (DOC), and sorption of the compound with sediments and biota, are treated as thermodynamic properties or (local) equilibria that alter the operation of kinetic processes. For example, an organic base in the water column may occur in a number of molecular species (as dissolved ions, sorbed with sediments, etc.), but only the uncharged, dissolved species can be volatilized across the air-water interface. EXAMS allows for the simultaneous treatment of up to 28 molecular species of a chemical. These include the parent uncharged molecule, and singly, doubly, or triply charged cations and anions, each of which can occur in a dissolved, sediment-sorbed, DOC-complexed, or biosorbed form. The program computes the fraction of the total concentration of compound that is present in each of the 28 molecular structures (the "distribution coefficients," α).

These (α) values enter the kinetic equations as multipliers on the rate constants. In this way, the program accounts for differences in reactivity that depend on the molecular form of the chemical, as a function of the spatial distribution of environmental parameters controlling molecular speciation. For example, the lability of a particular molecule to hydrolytic decomposition may depend on whether it is dissolved or is sorbed with the sediment phase of the system. EXAMS makes no intrinsic assumptions about the relative transformation reactivities of the 28 molecular species, with the single exception that biosorbed species are unavailable to inorganic reactions. These assumptions are controlled through the structure of the input data describing the species-specific chemistry of the compound.

1.5.2 Transformation Processes

EXAMS computes the kinetics of transformations attributable to direct photolysis, hydrolysis, biolysis, and oxidation reactions. The input chemical data for hydrolytic, biolytic, and oxidative reactions can be entered either as single-valued second-order rate constants, or as a pair of values defining the rate constant as a function of environmental temperatures. For example, the input data for alkaline hydrolysis of the compound consists of two computer variables: KBH, and EBH. When EBH is zero, the program interprets KBH as the second-order rate constant. When EBH is non-zero, EBH is interpreted as the activation energy of the reaction, and KBH is re-interpreted as the pre-exponential (frequency) factor in an Arrhenius equation giving the second-order rate constant as a function of the environmental temperature (TCEL) in each system compartment. (KBH and EBH are both actually matrices with 21 elements; each element of the matrix corresponds to one of the 21 possible molecular species of the compound, i.e., the 7 ionic species occurring in dissolved, DOC-complexed, or sediment-sorbed form--as noted above, biosorbed forms do not participate in extra-cellular reactions.)

EXAMS includes two algorithms for computing the rate of photolytic transformation of a synthetic organic chemical. These algorithms accommodate the two more common kinds of laboratory data and chemical parameters used to describe photolysis reactions. The simpler algorithm requires only an average pseudo-first-order rate constant (KDP) applicable to near-surface waters under cloudless conditions at a specified reference latitude (RFLAT). To control reactivity assumptions, KDP is coupled to nominal (normally unit-valued) reaction quantum yields (QYIELD) for each molecular species of the compound. This approach makes possible a first approximation of photochemical reactivity, but neglects the very important effects of changes in the spectral quality of sunlight with increasing depth in a body of water. The more complex photochemical algorithm computes photolysis rates directly from the absorption spectra (molar extinction coefficients) of the compound and its ions, measured values of the reaction quantum yields, and the environmental concentrations of competing light absorbers (chlorophylls, suspended sediments, DOC, and water itself). When using a KDP, please be aware that data from laboratory photoreactors usually are obtained at intensities as much as one thousand times larger than that of normal sunlight.

The total rate of hydrolytic transformation of a chemical is computed by EXAMS as the sum of three contributing processes. Each of these processes can be entered via simple rate constants, or as Arrhenius functions of temperature. The rate of specific-acid-catalyzed reactions is computed from the pH of each sector of the ecosystem, and specific-base catalysis is computed from the environmental pOH data. The rate data for neutral hydrolysis of the compound are entered as a set of pseudo-first-order rate coefficients (or Arrhenius functions) for reaction of the 28 (potential) molecular species with the water molecule.

EXAMS computes biotransformation of the chemical in the water column and in the bottom sediments of the system as entirely separate functions. Both functions are second-order equations that relate the rate of biotransformation to the size of the bacterial population actively degrading the compound (Paris et al. 1982). This approach is of demonstrated validity for at least some biolysis processes, and provides the user with a minimal semi-empirical means of distinguishing between eutrophic and oligotrophic ecosystems. The second-order rate constants (KBACW for the water column, KBACS for benthic sediments) can be entered either as single-valued constants or as functions of temperature. When a non-zero value is entered for the Q_{10} of a biotransformation (parameters QTBAW and QTBAS, respectively), KBAC is interpreted as the rate constant at 25 degrees Celsius, and the biolysis rate in each sector of the

ecosystem is adjusted for the local temperature (TCEL).

Oxidation reactions are computed from the chemical input data and the total environmental concentrations of reactive oxidizing species (alkylperoxy and alkoxyl radicals, etc.), corrected for ultra-violet light extinction in the water column. The chemical data can again be entered either as simple second-order rate constants or as Arrhenius functions. Oxidations due to singlet oxygen are computed from chemical reactivity data and singlet oxygen concentrations; singlet oxygen is estimated as a function of the concentration of DOC, oxygen tension, and light intensity. Reduction is included in the program as a simple second-order reaction process driven by the user entries for concentrations of reductants in the system. As with biolysis, this provides the user with a minimal empirical means of assembling a simulation model that includes specific knowledge of the reductants important to a particular chemical safety evaluation.

1.5.3 Transport Processes

Internal transport and export of a chemical occur in EXAMS via advective and dispersive movement of dissolved, sediment-sorbed, and biosorbed materials and by volatilization losses at the air-water interface. EXAMS provides a set of vectors (JFRAD, etc.) that specify the location and strength of both advective and dispersive transport pathways. Advection of water through the system is then computed from the water balance, using hydrologic data (rainfall, evaporation rates, stream flows, groundwater seepages, etc.) supplied to EXAMS as part of the definition of each environment.

Dispersive interchanges within the system, and across system boundaries, are computed from the usual geochemical specification of the characteristic length (CHARL), cross-sectional area (XSTUR), and dispersion coefficient (DSP) for each active exchange pathway. EXAMS can compute transport of synthetic chemicals via whole-sediment bed loads, suspended sediment wash-loads, exchanges with fixed-volume sediment beds, ground-water infiltration, transport through the thermocline of a lake, losses in effluent streams, etc. Volatilization losses are computed using a two-resistance model. This computation treats the total resistance to transport across the air-water interface as the sum of resistances in the liquid and vapor phases immediately adjacent to the interface.

1.5.4 Chemical Loadings

External loadings of a toxicant can enter the ecosystem via point sources (STRLD), non-point sources (NPSLD), dry fallout or aerial drift (DRFLD), atmospheric wash-out (PCPLD), and ground-water seepage (SEELD) entering the system. Any type of load can be entered for any system compartment, but the program will not implement a loading that is inconsistent with the system definition. For example, the program will automatically cancel a rainfall loading (PCPLD) entered for the hypolimnion or benthic sediments of a lake ecosystem. When this type of corrective action is executed, the change is reported to the user via an error message.

1.6 Ecosystems Analysis and Mathematical Systems Models

The EXAMS program was constructed from a systems analysis perspective. Systems analysis begins by defining a system's goals, inputs, environment, resources, and the nature of the system's components and their interconnections. The system goals describe the outputs produced by the system as a result of operating on its input stream. The system environment comprises those factors affecting system outputs over which the system has little or no control. These factors are often called "forcing functions" or "external driving variables." Examples for an aquatic ecosystem include runoff and sediment erosion from its watershed, insolation, and rainfall. System resources are defined as those factors affecting performance over which the system exercises some control. Resources of an aquatic ecosystem include, for example, the pH throughout the system, light intensity in the water column, and dissolved oxygen concentrations. The levels of these internal driving variables are determined, at least in part, by the state of the system itself. In other words, these factors are not necessarily single-valued functions of the system environment. Each of the components or "state variables" of a system can be described in terms of its local input/output behaviors and its causal connections with other elements of the system. The systems approach lends itself to the formulation of mathematical systems models, which are simply tools for encoding knowledge of transport and transformation processes and deriving the implications of this knowledge in a logical and repeatable way.

A systems model, when built around relevant state variables (measurable properties of system components) and causal process models, provides a method for extrapolating future states of systems from knowledge gained in the past. In order for such a model to be generally useful, however, most of its parameters must possess an intrinsic interest transcending their role in any particular computer program. For this reason, EXAMS was designed to use chemical descriptors (Arrhenius functions, pKa, vapor pressure, etc.) and water quality variables (pH, chlorophyll, biomass, etc.) that are independently measured for many chemicals and ecosystems.

1.6.1 EXAMS Design Strategy

The conceptual view adopted for EXAMS begins by defining aquatic ecosystems as a series of distinct subsystems, interconnected by physical transport processes that move synthetic chemicals into, through, and out of the system. These subsystems include the epilimnion and hypolimnion of lakes, littoral zones, benthic sediments, etc. The basic architecture of a computer model also depends, however, on its intended uses. EXAMS was designed for use by toxicologists and deci-

sion-makers who must evaluate the risk posed by use of a new chemical, based on a forecast from the model. The EXAMS program is itself part of a "hazard evaluation system," and the structure of the program was necessarily strongly influenced by the niche perceived for it in this "system."

Many intermediate technical issues arise during the development of a systems model. Usually these issues can be resolved in several ways; the modeling "style" or design strategy used to build the model guides the choices taken among the available alternatives. The strategy used to formulate EXAMS begins from a primary focus on the needs of the intended user and, other things being equal, resolves most technical issues in favor of the more efficient computation. For example, all transport and transformation processes are driven by internal resource factors (pH, temperature, water movements, sediment deposition and scour, etc.) in the system, and each deserves separate treatment in the model as an individual state variable or function of several state variables. The strategy of model development used for EXAMS suggests, however, that the only state variable of any transcendent interest to the user is the concentration of the chemical itself in the system compartments. EXAMS thus treats all environmental state variables as coefficients describing the state of the ecosystem, and only computes the implications of that state, as residual concentrations of chemicals in the system.

Although this approach vastly simplifies the mathematical model, with corresponding gains in efficiency and speed, the system definition is now somewhat improper. System resources (factors affecting performance that are subject to feedback control) have been redefined as part of the system environment. In fact, the "system" represented by the model is no longer an aquatic ecosystem, but merely a chemical pollutant. Possible failure modes of the model are immediately apparent. For example, introduction of a chemical subject to alkaline hydrolysis and toxic to plant life into a productive lake would retard primary productivity. The decrease in primary productivity would lead to a decrease in the pH of the system and, consequently, a decrease in the rate of hydrolysis and an increase in the residual concentration of the toxicant. This sequence of events would repeat itself indefinitely, and constitutes a positive feedback loop that could in reality badly damage an ecosystem. Given the chemical buffering and functional redundancy present in most real ecosystems, this example is inherently improbable, or at least self-limiting. More importantly, given the initial EEC, the environmental toxicologist could anticipate the potential hazard.

There is a more telling advantage, moreover, to the use of environmental descriptors in preference to dynamic environmental state variables. Predictive ecosystem models that include all the factors of potential importance to the kinetics of toxic pollutants are only now being developed, and will require validation before any extensive use. Furthermore, although extremely fine-resolution (temporal and spatial) models are often considered an ultimate ideal, their utility as components of a fate model for synthetic chemicals remains suspect. Ecosystems are driven by meteorological events, and are themselves subject to internal stochastic processes. Detailed weather forecasts are limited to about nine days, because at the end of this period all possible states of the system are equally probable. Detailed ecosystem forecasts are subject to similar constraints (Platt et al. 1977). For these reasons, EXAMS was designed primarily to forecast the prevailing climate of chemical exposures, rather than to give detailed local forecasts of EECs in specific locations.

1.6.2 Temporal and Spatial Resolution

When a synthetic organic chemical is released into an aquatic ecosystem, the entire array of transport and transformation processes begins at once to act on the chemical. The most efficient way to accommodate this parallel action of the processes is to combine them into a mathematical description of their total effect on the rate of change of chemical concentration in the system. Systems that include transport processes lead to partial differential equations, which usually must be solved by numerical integration. The numerical techniques in one way or another break up the system, which is continuously varying in space and time, into a set of discrete elements. Spatial discrete elements are often referred to as "grid points" or "nodes", or, as in EXAMS, as "compartments." Continuous time is often represented by fixing the system driving functions for a short interval, integrating over the interval, and then "updating" the forcing functions before evaluating the next time-step. At any given moment, the behavior of the chemical is a complicated function of both present and past inputs of the compound and states of the system.

EXAMS is oriented toward efficient screening of a multitude of newly invented industrial chemicals and pesticides. Ideally, a full evaluation of the possible risks posed by manufacture and use of a new chemical would begin from a detailed time-series describing the expected releases of the compound into aquatic systems over the entire projected history of its manufacture. Given an equivalently detailed time-series for environmental variables, machine integration would yield a detailed picture of EECs in the receiving water body over the entire period of concern. The great cost of this approach, however, militates against its use as a screening tool. Fine resolution evaluation of synthetic chemicals can probably be used only for compounds that are singularly deleterious and of exceptional economic significance.

The simplest situation is that in which the chemical loadings to systems are known only as single estimates pertaining over indefinite periods. This situation is the more likely for the vast majority of new chemicals, and was chosen for development of

EXAMS. It has an additional advantage. The ultimate fate and exposure of chemicals often encompasses many decades, making detailed time traces of EECs feasible only for short-term evaluations. In EXAMS, the environment is represented via long-term average values of the forcing functions that control the behavior of chemicals. By combining the chemistry of the compound with average properties of the ecosystem, EXAMS reduces the screening problem to manageable proportions. These simplified "first-order" equations are solved algebraically in EXAMS's steady-state Mode 1 to give the ultimate (i.e., steady-state) EECs that will eventually result from the input loadings. In addition, EXAMS provides a capability to study initial value problems ("pulse loads" in Mode 2), and seasonal dynamics in which environmental driving forces are updated on a monthly basis (Mode 3). Mode 3 is particularly valuable for coupling to the output of the PRZM model, which can provide a lengthy time-series of contamination events due to runoff and erosion of sediments from agricultural lands.

Daily pesticide export values from PRZM are transferred to EXAMS as "pulse loading" events at the beginning of the day. The peak concentration on that day is then reported by EXAMS as the average of the start-of-day and end-of-day values. This approximation of PRZM runoff events does not introduce a gross distortion of the facts: For a 1-ha 2-m deep pond with an initial concentration of 1 mg/L of a pesticide with a 2-day half-life, EXAMS reports a first-day peak of 0.854 mg/L. If the same amount of pesticide is permitted to enter the pond as a steady load over 24 hours, the peak value is 0.849 mg/L, occurring at the end of the 24 hour period. If the load were to enter over a run-off duration of four hours, the pond would achieve a peak concentration of 0.989 mg/L.

Transport of a chemical from a loading point into the bulk of the system takes place by advected flows and by turbulent dispersion. The simultaneous transformations presently result in a continuously varying distribution of the compound over the physical space of the system. This continuous distribution of the compound can be described via partial differential equations. In solving the equations, the physical space of the system must be broken down into discrete elements. EXAMS is a compartmental or "box" model. The physical space of the system is broken down into a series of physically homogeneous elements (compartments) connected by advective and dispersive fluxes. Each compartment is a particular volume element of the system, containing water, sediments, biota, dissolved and sorbed chemicals, etc. Loadings and exports are represented as mass fluxes across the boundaries of the volume elements; reactive properties are treated as point processes within each compartment.

In characterizing aquatic systems for use with EXAMS, particular attention must be given the grid-size of the spatial net used to represent the system. In effect, the compartments must not be so large that internal gradients have a major effect on the estimated transformation rate of the compound. In other words, the compartments are assumed to be "well-mixed," that is, the reaction processes are not slowed by delays in transporting the compound from less reactive to more reactive zones in the volume element. Physical boundaries that can be used to delimit system compartments include the air-water interface, the thermocline, the benthic interface, and perhaps the depth of bioturbation of sediments. Some processes, however, are driven by environmental factors that occur as gradients in the system, or are most active at interfaces. For example, irradiance is distributed exponentially throughout the water column, and volatilization occurs only at the air-water interface. The rate of these transformations may be overestimated in, for example, quiescent lakes in which the rate of supply of chemical to a reactive zone via vertical turbulence controls the overall rate of transformation, unless a relatively fine-scale segmentation is used to describe the system. Because compartment models of strongly advected water masses (rivers) introduce some numerical dispersion into the calculations, a relatively fine-scale segmentation is often advisable for highly resolved evaluations of fluvial systems. In many cases the error induced by highly reactive compounds will be of little moment to the probable fate of the chemical in that system, however. For example, it makes little difference whether the photolytic half-life of a chemical is 4 or 40 minutes; in either case it will not long survive exposure to sunlight.

1.6.3 Assumptions

EXAMS has been designed to evaluate the consequences of longer-term, primarily time-averaged chemical loadings that ultimately result in trace-level contamination of aquatic systems. EXAMS generates a steady-state, average flow field (long-term or monthly) for the ecosystem. The program thus cannot fully evaluate the transient, concentrated EECs that arise, for example, from chemical spills, or from runoff events that induce significant hydrologic transients in the receiving water body. This limitation derives from two factors. First, a steady flow field is not always appropriate for evaluating the spread and decay of a major pulse (spill) input. Second, an assumption of trace-level EECs, which can be violated by spills, has been used to design the process equations used in EXAMS. The following assumptions were used to build the program.

- A useful evaluation can be executed independently of the chemical's actual effects on the system. In other words, the chemical is assumed not to itself radically change the environmental variables that drive its transformations. Thus, for example, an organic acid or base is assumed not to change the pH of the system; the compound is assumed not to itself absorb a significant fraction of the light entering the system; bacterial populations do not significantly increase (or decline) in response to the presence of the chemical.

- EXAMS uses linear sorption isotherms, and second-order (rather than Michaelis-Menten-Monod) expressions for biotransformation kinetics. This approach is known to be valid for the low concentrations of typical of environmental contaminants; its validity at high concentrations is less certain. EXAMS controls its computational range to ensure that the assumption of trace-level concentrations is not grossly violated. This control is keyed to aqueous-phase (dissolved) residual concentrations of the compound: EXAMS aborts any analysis generating EECs in which any dissolved species exceeds 50% of its aqueous solubility (see Chapter 2.2.2 for additional detail). This restraint incidentally allows the program to ignore precipitation of the compound from solution and precludes inputs of solid particles of the chemical. Although solid precipitates have occasionally been treated as a separate, non-reactive phase in continuous equilibrium with dissolved forms, the efficacy of this formulation has never been adequately evaluated, and the effect of saturated concentrations on the linearity of sorption isotherms would introduce several problematic complexities to the simulations.

- Sorption is treated as a thermodynamic or constitutive property of each segment of the system, that is, sorption/desorption kinetics are assumed to be rapid compared to other processes. The adequacy of this assumption is partially controlled by properties of the chemical and system being evaluated. Extensively sorbed chemicals tend to be sorbed and desorbed more slowly than weakly sorbed compounds; desorption half-lives may approach 40 days for the most extensively bound compounds. Experience with the program has indicated, however, that strongly sorbed chemicals tend to be captured by benthic sediments, where their release to the water column is controlled by their availability to benthic exchange processes. This phenomenon overwhelms any accentuation of the speed of processes in the water column that may be caused by the assumption of local equilibrium.

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2.0 Exposure Assessment: Mechanisms and Processes

Many excellent books, review articles, and journal reports have been written on the subject of the fate and transport of chemicals in the environment. This report is not intended as an exhaustive summary of the ideas and factual information available from the literature. EXAMS is a distillation of that literature, encoded in a computer program. This chapter (2) summarizes the fundamental ideas that were used to construct the EXAMS program. The references cited represent only the key findings or papers that directly influenced the EXAMS code. Additional detail and background information can be found in the works listed in the bibliography for this report.

2.1 Compartment Models and Conservation of Mass

EXAMS' environmental data are contained in a file (the "canonical environments file") that includes a series of concise descriptions of the aquatic systems of interest to a user. (The term "canonical" simply means that the data in the file includes only those quantities bearing directly on the fate and transport of synthetic organic chemicals.) Each water-body is represented via a set of N compartments or distinct zones in the system. The program is based on a series of mass balances, which give rise to a single differential equation for each compartment. Working from the transport and transformation process equations, EXAMS compiles an equation for the net rate of change of chemical concentration in each compartment. The resulting system of N differential equations describes a mass balance for the entire ecosystem. These equations have the general form of Equation (2-1):

$$V\frac{d[C]}{dt} = Le + Li - VK[C] \qquad (2\text{-}1)$$

where:

V is the volume of water in the compartment (liters),

[C] is the total chemical concentration as mg/liter of *V*,

Le is the total external loading on the compartment (mg/h),

Li is the total internal loading on the compartment (mg/h) resulting from contaminated flows among system compartments, and

K is an overall pseudo-first-order (/h) loss constant that expresses the combined effect of transport and transformation processes that decrease chemical concentration.

The "canonical environments file" currently supplied with the EXAMS computer program is intended primarily as a series of test values to establish that the program is operating correctly. Although the data supplied in this file are within the range of observed values, this file is not intended for production runs of the program. EXAMS has been designed to accept standard water-quality parameters and system characteristics that are commonly measured by limnologists throughout the world. EXAMS also includes a descriptor language (parameters JFRAD, JTURB, etc.) that simplifies the specification of system geometry and connectedness. The procedure for defining an EXAMS environment is illustrated in Chapter 3. The EXAMS code has been written in a general (N-compartment) form; the program allocates memory as required by the current description of the water body.

The chemical data base supplied with the program includes 11 compounds investigated by Smith and coworkers (1978). As with EXAMS' nominal environmental data base, these data should not be regarded as immutably fixed. In many instances the data of Smith et al. (1978) were augmented in order to illustrate EXAMS' data entry capabilities, and the assumptions used to fill gaps in the chemical data base are open to revision as additional experimental data become available.

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2.2 Equilibrium Processes

The kinetic properties of organic chemicals are often strongly influenced by the molecular state of the compound. Consider, for example, a compound that can both ionize and sorb to suspended sediments. In this case, the compound will be present in the water column in ionized, unionized, and sorbed states. In inland waters, where aerosol formation can be neglected, only the unionized, unsorbed molecule will volatilize across the air-water interface. An accurate evaluation of the tendency of the compound to volatilize thus cannot be obtained until ionization and sorption are incorporated in the estimation method. Ionization and sorption also affect the reactivity of chemicals to transformation processes, although the magnitude of the changes cannot be as readily predicted.

Laboratory determinations of kinetic rate constants are often limited to homogeneous phase (clean water) investigations. Modeling the behavior of a compound in real systems requires some knowledge, or some assumptions, about the effects of sorption and ionization on a chemical's behavior in the environment. EXAMS does not contain "hard-wired" assumptions that sorption either "protects" the compound, enhances its reactivity, or has no effect. Instead, the input chemical data include separate rate constants for each molecular form of the compound. This data array allows a user to include unique rate constants for ions and sorbed molecules when these are known. When heterogeneous phase (or pH dependent) chemical data are not available, the necessary assumptions are left to the user's discretion.

Ionization and sorption of synthetic chemicals are treated as thermodynamic or constitutive properties of each computational element in EXAMS. EXAMS treats these processes as local (within-compartment) reversible equilibria, rather than calculating a global (system-wide) equilibrium partitioning of the compound among its possible molecular species. The inclusion of partitioning to colloidal "dissolved" organic carbon precludes any need to explicitly account for "particle concentration" effects or desorption hysteresis (Gschwend and Wu 1985), (Morel and Gschwend 1987).

Ionization equilibria are usually achieved within a very short time, compared to the time-scale of transport and transformation processes, so a (local) equilibrium assumption is usually justified in natural systems. Desorption of neutral molecules bound to sediments, however, may be relatively slow for compounds that are extensively bound (large partition coefficients). EXAMS' evaluations do not explicitly include the effects of sorption/desorption kinetics on transport or transformation processes. The program does, however, compute the major transport effect of slow desorption, as an implicit function of interactions between benthic sediments and the overlying water column.

Extensively sorbed compounds are usually predominantly captured by the bottom sediments (benthic compartments) in an aquatic system. Release of the compound to the water column is then limited by the turnover rate of the bottom sediments themselves. The turnover times of benthic sediments, except during storm erosion, are longer than the desorption half-lives of organic chemicals. Consequently, the intrinsic kinetic limitations imposed by residence in bottom sediments generally exceed those attributable to desorption kinetics as such.

EXAMS allows for the existence of six ionized species, in addition to the parent unionized molecule. Each of these can complex with "dissolved" organic matter (EXAMS variable *DOC*), and sorb with the sediment phase and the biota in an ecosystem compartment (computational element). The program computes the fraction of the total chemical concentration present in each molecular structure. These distribution coefficients (α) are used as multipliers on the user-specified transformation rate coefficients for each decomposition process.

2.2.1 Ionization Reactions

According to the Brönsted-Lowry concept of ionization reactions, acids and bases react with solvent (water) to form a conjugate acid-base pair (Stumm and Morgan 1970). The EXAMS program regards any synthetic organic as potentially capable of acting as an ampholyte, forming both singly, doubly, and triply charged cations and anions in the aqueous medium. The unionized molecule is taken as the parent compound, and is denoted in the program documentation as "RH_3." The potential acid-base reactions are then:

(1) Basic reactions:

$$RH_3 + H_2O \leftrightarrow RH_4^+ + OH^- \qquad (2\text{-}2)$$

$$RH_4^+ + H_2O \leftrightarrow RH_5^{2+} + OH^- \qquad (2\text{-}3)$$

$$RH_5^{2+} + H_2O \leftrightarrow RH_6^{3+} + OH^- \qquad (2\text{-}4)$$

(2) Acidic reactions:

$$RH_3 + H_2O \leftrightarrow RH_2^- + H_3O^+ \qquad (2\text{-}5)$$

$$RH_2^- + H_2O \leftrightarrow RH^{2-} + H_3O^+ \qquad (2\text{-}6)$$

$$RH^{2-} + H_2O \leftrightarrow R^{3-} + H_3O^+ \qquad (2\text{-}7)$$

This set of chemical reactions describes the simultaneous existence of seven chemical species of the compound:

- the unionized parent molecule RH_3,
- a singly charged cation RH_4^+,
- a doubly charged cation RH_5^{2+},
- a triply charged cation RH_6^{3+},

- a singly charged anion RH_2^-,
- a doubly charged anion RH^{2-}, and
- a triply charged anion R^{3-}.

(Again, because EXAMS is an interactive program in which the user has direct access to the input data base, much of this documentation has been written using the input data variables as identifiers and as quantities in the process equations. Although this approach poses some difficulties for the casual reader, it allows the potential user of the program to see the connections between program variables and the underlying process theory. The Data Dictionary chapter of this document (beginning on page 176) contains an alphabetical listing and definitions of EXAMS' input variables. Input data are named with a terminal "G" ("Global"), and variables internal to the EXAMS program itself are named with a terminal "L" ("Local"). For example, "KPSG" can be specified by the user; "KPSL" is its internal equivalent.)

Most compounds do not exhibit the full range of behaviors given in Eq. (2-2)–(2-7). EXAMS' chemical input data stream carries, for each chemical, a vector (SPFLG) of 7 flags that tells the program which of the ionization reactions are appropriate for that compound. (A "flag" in this usage means a signal used to control execution of the program.) Setting an element of the SPFLG vector to "1" indicates that the corresponding chemical species in fact exists; setting an element of SPFLG to "0" (zero) indicates the chemical species does not exist. SPFLG(1) should usually be set to indicate the existence of the parent molecule. When, for example, the remaining flags (SPFLG(2...7)) are all zero, EXAMS treats the chemical as a neutral (unionizable) organic compound. When SPFLG(2) is set (=1), and SPFLG(3...7) are 0, the compound is taken to be an organic base forming only a singly charged cation (RH_4^+).

The equilibrium constants for the ionization reactions provide a measure of the strength of the organic acid/base relative to water. The basicity constants corresponding to Eq. (2-2), (2-3), and (2-4) are:

$$K_{b1} = [RH_4^+]\{OH^-\}/[RH_3]\{H_2O\} \quad (2\text{-}8)$$

$$K_{b2} = [RH_5^{2+}]\{OH^-\}/[RH_4^+]\{H_2O\} \quad (2\text{-}9)$$

$$K_{b3} = [RH_6^{3+}]\{OH^-\}/[RH_5^{2+}]\{H_2O\} \quad (2\text{-}10)$$

The acidity constants corresponding to Eq. (2-5), (2-6), and (2-7) are:

$$K_{a1} = [RH_2^-]\{H_3O^+\}/[RH_3]\{H_2O\} \quad (2\text{-}11)$$

$$K_{a2} = [RH^{2-}]\{H_3O^+\}/[RH_2^-]\{H_2O\} \quad (2\text{-}12)$$

$$K_{a3} = [R^{3-}]\{H_3O^+\}/[RH^{2-}]\{H_2O\} \quad (2\text{-}13)$$

These ionization constants are "mixed" constants (Stumm and Morgan 1970:82), which take pH = -log{H_3O^+} ({H_3O^+} or {H^+} is hydrogen ion activity, IUPAC convention), and the compound is expressed in concentration units. (Salt effects on pK values, and changes in pKw with temperature, are currently neglected in EXAMS.)

In dilute aqueous solutions (unit water activity, {H_2O}=1), the water terms in the equilibrium constants can be neglected. In benthic sediments, however, much of the compartment volume is occupied by solids, and the decreased activity of water must be considered. In EXAMS, this problem is overcome by referring all concentrations to the aqueous phase of the compartment (note dimensions of variables in Eq. (2-1)).

Basicity and acidity constants are entered to EXAMS as the negative of their Briggsian logarithms, that is, as pK values. The computer variables are PKB(1), PKB(2), and PKB(3) for the first, second and third basicity constants (generating RH_4^+, RH_5^{2+}, RH_6^{3+} and respectively) and PKA(1), PKA(2), and PKA(3) for the first, second and third acidity constants (generating RH_2^-, RH^{2-}, and R^{3-} respectively). The equilibrium constants can be entered either as single (temperature-independent) pK values or as functions of temperature. Temperature dependencies of the equilibrium constants are computed from an integrated form of the Gibbs-Helmholtz equation (Castellan 1964:215-217). Each computer input datum (PKB, PKA) has a corresponding enthalpy variable (EPK, EPK). When the enthalpy term (EPK) is zero, the PK datum is taken as a temperature-independent pK. When the EPK term is non-zero, the PK datum is interpreted as the constant in the equation describing the equilibrium constant as a function of temperature. For example: The *Handbook of Chemistry and Physics, Ed. 51* p. D122 (Weast 1971), gives the second acidity constant (K_{a2}) of phenol-sulfonic acid for 0° to 50°C (**Table 1**).

Table 1. K_{a2} of Phenol-Sulfonic Acid

T(°C)	$K_{a2}(\times 10^{10})$
0	4.45
5	5.20
10	6.03
15	6.92
20	7.85
25	8.85
30	9.89
35	10.9
40	12.0
45	13.1
50	14.2

EXAMS could be loaded with a typical value drawn from this data set, for example, at 25°C, K_{a2} = 8.85×10^{-10} and PKA(2) = 9.05 (also load EPK(2) = 0.0). The pKa will then be taken as 9.05 regardless of

the water temperature of the compartment.

Alternatively, the visible dependence of the acidity constant on temperature could be described to EXAMS via PKA(2) and a non-zero value of EPK(2). Statistical regression of these data on the model $K_a = A \exp(-B/RT)$, where R is the gas constant (1.9872 cal/deg mol) and T is absolute temperature, yields the parameters $A = 8.2724\times10^{-7}$ and $(B/R) = 2.0466\times10^{3}$ and accounts for 99.7% of the variation in K_a. EXAMS requires the logarithm of A, and B in kcal/mol, as input data. Therefore, the dependence of K_{a2} on temperature would be described to EXAMS via

PKA(2) = log A = −6.082

and

EPK(2) = (B/R)×R×0.001(kcal/cal) = 4.067 kcal/mol

EXAMS will then compute a local value of K_{a2} as a function of the water temperature (TCEL) in each system compartment, using the equation:

$$\log(K_a)=PKA(2)-[1000\times EPK(2)/\{2.303\times R\times(TCEL+273.15)\}]$$

2.2.2 Sediment Sorption

EXAMS computes a (local) equilibrium value for the partitioning of each chemical species (RH_3, RH_4^+, etc.) to sediment phases in the system. The chemical input data includes a vector of partition coefficients (KPSG) whose elements apply to each of the corresponding chemical species. That is, KPSG(1) is the partition coefficient for neutral organics or the unionized molecule (RH_3), KPSG(2) applies to the RH_4^+ molecule, etc.

EXAMS uses linear isotherms for all sorption computations, rather than the non-linear Freundlich or Langmuir formulations. (A linear isotherm is equivalent to a partition coefficient.) Linear isotherms are usually an adequate descriptor of the capture of neutral organics by sediments, at least up to 50% of their water solubility (Karickhoff 1999 (pers. comm.)) residual in the aqueous phase. For compounds whose melting point (EXAMS input parameter MP) is greater than the ambient temperature a crystal energy term is added (compare Eq. 12 in (Karickhoff 1984)):

$$\log X_{ss} = \log X_s + \frac{\Delta S_f (T_m - T)}{2.303RT}$$

in which X is mole fraction solubility, ΔS_f is the solute entropy of fusion, T_m is the melting point in K, T is absolute temperature, and R is the gas constant. ΔS_f is between 12 and 15 eu (entropy units, cal/mol K), so, for compounds that are solids at the ambient temperature EXAMS computes the limiting concentration C_l as

$$C_l = 0.5 \times SOL \exp\left(\frac{6.5(MP - TCEL)}{TCEL + 273.15}\right)$$

in which *SOL, MP,* and *TCEL* are EXAMS input parameters; the factor 6.5 results from ΔS_f/R. (For liquids, this correction is ignored.)

EXAMS restricts its operating range to ensure that the assumption of isotherm linearity is not violated. These restrictions are imposed by evaluating the external loadings to ensure that the inputs to the system are not excessive, and by a pre-output evaluation of the computed EECs in all compartments. Loadings via rainfall and groundwater seepage may not exceed solubility of the neutral species, evaluated using the pH and temperature of the receiving segment. Stream-borne and NPS loads, as with calculated EECs, may not exceed C_l in the dissolved neutral molecule. Upon detecting errors in loadings or in final EECs, EXAMS reports the problem and returns control to the user for corrections.

The uptake of neutral organic chemicals by soils and aquatic sediments apparently involves dissolution of the compound into the organic matrix of the soil/sediment, rather than a pure physical (surface) adsorption (see, for example, Chiou et al. 1979). Sorption of this class of chemical probably takes place by a hydrophobic mechanism, in which the compound (or more generally the RH_3 molecule of acids and bases) is driven from the water phase of the system by a large fugacity. This process is conceptually similar to the extraction and recovery of an organic pollutant from water using an organic solvent.

The partition coefficient (KPS) for a particular compound can be normalized to the organic content of soils (Chiou et al. 1979) or, equivalently, to the organic carbon content of aquatic sediments (Karickhoff et al. 1979). The resulting parameter (KOC) is a relatively stable, system-independent measure of an intrinsic property of organic compounds. KOC can be used to compute a local partition coefficient (KPSL) for sediment phases of an aquatic system, as a function of the organic carbon content (FROC, organic carbon as fraction of dry weight) of the sediment phase of each compartment.

KOC is strongly correlated with the octanol-water partition coefficient (KOW) (Karickhoff et al. 1979). For whole sediments, as used in EXAMS, KOC can be estimated (within a factor of 2.5) as 35% of KOW (Seth et al. 1999). The preferred approach is to include at least a measured Kow and Koc measured on aquatic sediment, as sediment Koc tends to be about twice that of soil Koc (Chiou et al. 1998).

EXAMS computes the RH_3 partition coefficient (KPSL(1)) for each system compartment via evaluation of these input data (KPSG(1), KOCG, KOWG). The KPSG datum is used as a system-wide partition coefficient whenever it is non-zero, giving

precedence to explicit user entries. KOCG is, however, the preferred datum, as it provides a system-independent measure of sorption affinity that can be tailored to the specific properties of each compartment. When KPSG is zero, and KOCG non-zero, a local (compartment-specific) KPSL(1) is computed from KOCG and the organic carbon content (FROC) of the sediment phase of each compartment. When KOCG is zero, but the KOWG entry is non-zero, KOC is computed as 0.35×KOWG, and conversely. KOW and KOC are also used to estimate KPB (see Chapter 2.2.3) and KPDOC (Chapter 2.2.4).

Organic ions can exchange with the normal soil ions, to an extent probably governed by the ion exchange capacity of a sediment. The particle size distribution of the sediment, however, apparently also governs the ability of the sediment to take up organic ions (Karickhoff and Brown 1978). The complexity of this process has hindered the development of robust, system- independent analogs of KOC for organic ions.

EXAMS includes a series of "system- independent" measures of ion sorption that can be invoked at the user's option. These parameters relate the (internal) KPSL for the organic ions to the ion exchange capacities of sediment phases in each system compartment. The computer variables are:

KIEC(1) for sorption of RH_4^+ – KPSL(2) computed from CEC

KIEC(2) for sorption of RH_5^{2+} – KPSL(3) computed from CEC

KIEC(3) for sorption of RH_6^{3+} – KPSL(4) computed from CEC

KIEC(4) for sorption of RH_2^- – KPSL(5) computed from AEC

KIEC(5) for sorption of RH^{2-} – KPSL(6) computed from AEC

KIEC(6) for sorption of R^{3-} – KPSL(7) computed from AEC

The units of KIEC are ((mg/kg)/(mg/L))/(meq/100 g dry weight); the cation (CEC) and anion (AEC) exchange capacities of system sediments are entered as milliequivalents (meq) per 100 grams dry weight of the sediment. When a single partition coefficient is preferred for all sediments in the system, it must be loaded via the appropriate element of the KPSG vector and the corresponding element in KIEC or KIEC must be set to zero.

EXAMS uses the internal value of the partition coefficient (KPSL) for each chemical species, however computed, to calculate the equilibrium sediment sorption of each species on each particulate sediment phase (P) throughout the system. The chemical equations and equilibrium expressions are similar for each chemical species:

$$(RH_3)+(P)\leftrightarrow(RH_3P);\quad KPSL(1)=\frac{[RH_3P]}{[RH_3][P]} \quad (2\text{-}14)$$

$$(RH_4^+)+(P)\leftrightarrow(RH_4P^+);\quad KPSL(2)=\frac{[RH_4P^+]}{[RH_4^+][P]} \quad (2\text{-}15)$$

$$(RH_5^{2+})+(P)\leftrightarrow(RH_5P^{2+});\quad KPSL(3)=\frac{[RH_5P^{2+}]}{[RH_5^{2+}][P]} \quad (2\text{-}16)$$

$$(RH_6^{3+})+(P)\leftrightarrow(RH_6P^{3+});\quad KPSL(4)=\frac{[RH_6P^{3+}]}{[RH_6^{3+}][P]} \quad (2\text{-}17)$$

$$(RH_2^-)+(P)\leftrightarrow(RH_2P^-);\quad KPSL(5)=\frac{[RH_2P^-]}{[RH_2^-][P]} \quad (2\text{-}18)$$

$$(RH^{2-})+(P)\leftrightarrow(RHP^{2-});\quad KPSL(6)=\frac{[RHP^{2-}]}{[RH^{2-}][P]} \quad (2\text{-}19)$$

$$(R^{3-})+(P)\leftrightarrow(RP^{3-});\quad KPSL(6)=\frac{[RP^{3-}]}{[R^{3-}][P]} \quad (2\text{-}20)$$

Sediment partition coefficients are usually reported as a ratio of the concentration of sorbed chemical (mg compound/g dry weight of sediment) to the residual aqueous phase concentration (mg/liter), in "dimensionless" units ((mg/kg)/(mg/L)). The sorption equilibrium constants are equivalent to conventional partition coefficients only so long as the concentration of particulate matter [P] is expressed as a "sediment:water ratio" ρ (kg dry weight/liter of water), and the chemical concentrations (e.g., $[RH_3P]$ and $[RH_3]$) are referred to the aqueous phase of the system and expressed as (mg compound/liter of water). EXAMS strictly adheres to this convention for its internal computations. EXAMS' output tables, however, are converted to conventional reporting units. For example, concentrations of sediment-sorbed chemicals are reported to the user as mg/kg dry weight of sediment, but are carried internally as (sorbed mg)/(liter of water).

The need for strict adherence to this convention arises from the very large sediment/water ratios of benthic sediments. Water column compartments can be assumed to have a water volume essentially the same as their environmental volume (VOL). For these compartments, EXAMS' internal variable (SEDCOL, the sediment/water ratio (ρ, kg/L)) is simply computed as 10^{-6} (kg/mg) times the input datum (SUSED, suspended sediments in mg/L).

Because the solid phase occupies a significant fraction of the total environmental volume of bed sediments, ρ (SEDCOL) is computed quite differently for benthic (TYPE "B") compartments. For benthic compartments, the input datum BULKD is the bulk density of the sediment (g/cc environmental volume). The sediment:water ratio is computed from the bulk density and water content (PCTWA, 100 × the fresh weight/dry weight ratio) of the sediment, and the total environmental volume (VOL, cubic meters) of the compartment. (The

computation takes ρ_w, the density of water, as 1 g/cm^3.) The equations (using the internal code variables) are:

$$SEDCOL = SEDMSL / WATVOL \qquad (2\text{-}21)$$

where

TOTMAS = BUKLD×VOL×1000.
SEDMSL = TOTMAS/(PCTWA/100.), and
WATVOL = (TOTMAS - SEDMSL)×ρ_w

Here TOTMAS is the total compartment mass (kg), SEDMSL is the mass of sediment in the compartment (kg), and WATVOL is the volume of water contained in the compartment (liters).

The sediment/water ratio can also be computed directly from the water content of the sediment (Eq. (2-22)):

$$SEDCOL = \frac{1}{\frac{PCTWA}{100} - 1} \qquad (2\text{-}22)$$

Eq. (2-21) is the more efficient computation for EXAMS, however, because the results of the intermediate computations (WATVOL, SEDMSL) are used elsewhere in the program.

2.2.3 Biosorption

The uptake of chemicals by living organisms is represented in EXAMS via seven simple bioconcentration factors or biomass partition coefficients (KPBG). KPBG is a vector of 7 elements, each of which applies to the corresponding chemical species (RH_3, RH_4^+, etc.). The chemical equations and equilibrium expressions are analogous to those for sediment sorption:

$$(RH_3) + (B) \leftrightarrow (RH_3B); \quad KPBL(1) = \frac{[RH_3B]}{[RH_3][B]} \qquad (2\text{-}23)$$

$$(RH_4^+) + (B) \leftrightarrow (RH_4B^+); \quad KPBL(2) = \frac{[RH_4B^+]}{[RH_4^+][B]} \qquad (2\text{-}24)$$

$$(RH_5^{2+}) + (B) \leftrightarrow (RH_5B^{2+}); \quad KPBL(3) = \frac{[RH_5B^{2+}]}{[RH_5^{2+}][B]} \qquad (2\text{-}25)$$

$$(RH_6^{3+}) + (B) \leftrightarrow (RH_6B^{3+}); \quad KPBL(4) = \frac{[RH_6B^{3+}]}{[RH_6^{3+}][B]} \qquad (2\text{-}26)$$

$$(RH_2^-) + (B) \leftrightarrow (RH_2B^-); \quad KPBL(5) = \frac{[RH_2B^-]}{[RH_2^-][B]} \qquad (2\text{-}27)$$

$$(RH^{2-}) + (B) \leftrightarrow (RHB^{2-}); \quad KPBL(6) = \frac{[RHB^{2-}]}{[RH^{2-}][B]} \qquad (2\text{-}28)$$

$$(R^{3-}) + (B) \leftrightarrow (RB^{3-}); \quad KPBL(7) = \frac{[RB^{3-}]}{[R^{3-}][B]} \qquad (2\text{-}29)$$

Bioconcentration factors (BCF, EXAMS input variable KPBG) should be entered to EXAMS on a dry weight basis. The expected units of KPBG are (µg/g(dry))/ (mg/L), or the numerically equivalent unit (mg/kg(dry))/(mg/L). EXAMS estimates KPB from KOW if the input data is not present. The estimation equation (Baughman and Paris 1981) is

$$KPB = 0.436 \times KOW^{0.907}$$

As with sediment sorption, EXAMS converts its input data for compartment biomasses to an internal variable (BIOTOL, "B" in Eq. (2-23)–(2-29)) with dimensions of kg dry weight per liter of water in the compartment. EXAMS' input datum for water column compartments (PLMASG in mg dry weight per liter) is simply multiplied by 10^{-6} (kg/mg) to yield BIOTOL in its proper units. For benthic compartments, the benthic biomass (BNMASG) is entered to EXAMS with dimensions of grams (dry weight) per square meter of bottom sediment surface. EXAMS converts this datum to its internal variable (*B* (BIOTOL), kg per liter of interstitial water) via Eq. (2-30):

$$B = \frac{AREAG \times BNMASG \times 0.001(kg/g)}{WATVOL} \qquad (2\text{-}30)$$

where *AREAG* is the (user-supplied) total surface area of the benthic compartment (square meters).

The actual quantities of synthetic organics captured by the biomass are often relatively small, compared to the amounts sorbed with sediments or dissolved in the aqueous phase of real systems. Thus, the biomass often plays a relatively minor role as a transport or capture medium affecting the fate of an organic pollutant. The role of the biomass as a food-chain vector can, however, have great ecotoxicological significance. (Biotransformation of chemicals is, of course, another matter altogether (see 2.3.6).) EXAMS does not include a mobile component of the biomass, that is, volitional movements of fishes (etc.) among compartments are not assessed. The plankton, however, is transported in accord with the hydrology of the aquatic system, carrying associated chemical with it. (The transport equations are discussed in Chapter 2.3.1.)

The KPB vector for organic compounds estimates organismal body-burdens from simple bioconcentration factors. Note, however, that EXAMS' computations are based on partitioning ratios to dissolved species of the chemical. EXAMS does not attempt to evaluate such things as the exposure of fishes to variable chemical concentrations as they migrate among different zones of the ecosystem, or food-chain

biomagnifications. If desired, measured fish bioconcentration factors or estimates based on Kow (Meylan et al. 1999) can be entered via KPBG and used as for preliminary evaluation of fish contamination, but transfer of EXAMS output exposure files to the BASS model is the preferred methodology.

2.2.4 Complexation with DOC

EXAMS treats complexation with the "dissolved" (i.e., colloidal and filtrable particulate) organic matter of natural waters via complexation constants for each of the ionic species (Eq. (2-31) – (2-37)) In these formulations, DOC is in kg/L, complexed species are in mg/kg (DOC), and dissolved chemical species are in mg/L; Kpdoc is conventionally regarded as being "dimensionless" or as having units of (mg/kg)/(mg/L) or L/kg, as in the discussion of sediment sorption in Chapter 2.2.2.

$$(RH_3) + (DOC) \leftrightarrow (RH_3 DOC);$$
$$KPDOCL(1) = \frac{[RH_3 DOC]}{[RH_3][DOC]} \quad (2\text{-}31)$$

$$(RH_4^+) + (DOC) \leftrightarrow (RH_4 DOC^+);$$
$$KPDOCL(2) = \frac{[RH_4 DOC^+]}{[RH_4^+][DOC]} \quad (2\text{-}32)$$

$$(RH_5^{2+}) + (DOC) \leftrightarrow (RH_5 DOC^{2+});$$
$$KPDOCL(3) = \frac{[RH_5 DOC^{2+}]}{[RH_5^{2+}][DOC]} \quad (2\text{-}33)$$

$$(RH_6^{3+}) + (DOC) \leftrightarrow (RH_6 DOC^{3+});$$
$$KPDOCL(4) = \frac{[RH_6 DOC^{3+}]}{[RH_6^{3+}][DOC]} \quad (2\text{-}34)$$

$$(RH_2^-) + (DOC) \leftrightarrow (RH_2 DOC^-);$$
$$KPDOCL(5) = \frac{[RH_2 DOC^-]}{[RH_2^-][DOC]} \quad (2\text{-}35)$$

$$(RH^{2-}) + (DOC) \leftrightarrow (RHDOC^{2-});$$
$$KPDOCL(6) = \frac{[RHDOC^{2-}]}{[RH^{2-}][DOC]} \quad (2\text{-}36)$$

$$(R^{3-}) + (DOC) \leftrightarrow (RDOC^{3-});$$
$$KPDOCL(7) = \frac{[RDOC^{3-}]}{[R^{3-}][DOC]} \quad (2\text{-}37)$$

Kpdoc should be measured on the material as it naturally occurs, rather than on humic acid or fulvic acid extracts. If, as is usually the case, a measured Kpdoc is not available, EXAMS estimates it from Kow as Kpdoc=0.074Kow. This value was derived from analysis of the data presented in Appendix A. This tabulation is a compendium of literature values for Koc measurements on natural water samples. Measurement methods include, *inter alia*, dialysis (Carter and Suffet 1982), reversed-phase separation (Landrum et al. 1984) and solubility enhancement (Chiou et al. 1986); values developed using fluorescence quenching methods (Gauthier et al. 1986) were excluded because this method is subject to interferences that often lead to over-estimates of Koc (Laor and Rebhun 1997), (Danielson et al. 1995), (Tiller and Jones 1997). Partitioning to DOC in benthic segments is calculated using the general Koc of the compound, as the available literature indicates a greater affinity of benthic DOC, as expressed via a mean Kp/Kow (0.46, Appendix A) that is well within the uncertainty (0.14Kow – 0.89Kow) of observations for particulate organic carbon (Seth et al. 1999).

2.2.5 Computation of Equilibrium Distribution Coefficients

EXAMS computes the distribution of the chemical among its 28 possible molecular structures (RH_3, RH_3P, etc.). This distribution is expressed as a vector of concentration ratios (α). Each element of α is the ratio of the concentration of a particular molecular species, to the total concentration of chemical in the system compartment (S_t, mg chemical per liter of water in the compartment). These α values enter the kinetic equations as multipliers on the user-supplied rate constants for transformation of each molecular species.

The logic of these computations can best be seen via a sample calculation. For example, consider the behavior of an organic acid in pure water, subject to the following ionization reactions:

$$RH_3 + H_2O \leftrightarrow RH_2^- + H_3O^+ \quad (2\text{-}38)$$

$$RH_2^- + H_2O \leftrightarrow RH^{2-} + H_3O^+ \quad (2\text{-}39)$$

In order to evaluate the effects of ionization on transformation and transport of the chemical, EXAMS requires three concentration ratios (***CR***):

(1) the fraction present as RH_3, or

$$CR_1 = [RH_3]/R_T \quad (2\text{-}40)$$

(2) the fraction present as RH_2^- ,or

$$CR_2 = [RH_2^-]/[R_T] \quad (2\text{-}41)$$

(3) the fraction present as RH^{2-}, or

$$CR_3 = [RH^{2-}]/[R_T] \quad (2\text{-}42)$$

The equilibrium constants for the chemical Eq. (2-38) and (2-39) are:

$$K_{a1} = \frac{[RH_2^-]\{H_3O^+\}}{[RH_3]} \quad (2\text{-}43)$$

$$K_{a2} = \frac{[RH^{2-}]\{H_3O^+\}}{[RH_2^-]} \quad (2\text{-}44)$$

As has already been mentioned, EXAMS computes $\{H_3O^+\}$ as 10^{-pH}. The equilibrium expressions, together with a concentration condition, provide enough information for computing the desired concentration ratios ***CR*** (Stumm and Morgan 1970:102). The concentration condition is simply a statement of the law of conservation of mass:

$$[R_T] = [RH_3] + [RH_2^-] + [RH^{2-}] \quad (2\text{-}45)$$

The concentration condition (Eq. (2-45)) and the definition of the first concentration ratio CR_1 (Eq. (2-40)) combine to give:

$$CR_1 = \frac{[RH_3]}{[RH_3] + [RH_2^-] + [RH^{2-}]} \quad (2\text{-}46)$$

The equilibrium expressions can now be solved for $[RH_2^-]$ and $[RH^{2-}]$ in terms of $[RH_3]$. To wit, Eq. (2-43) can be rearranged to give:

$$[RH_2^-] = \frac{K_{a1}[RH_3]}{\{H_3O^+\}} \quad (2\text{-}47)$$

and, from Eq. (2-44),

$$[RH^{2-}] = \frac{K_{a2}[RH_2^-]}{\{H_3O^+\}} \quad (2\text{-}48)$$

Substituting Eq. (2-47) into Eq. (2-48) yields:

$$[RH^{2-}] = \frac{K_{a1} \times K_{a2} \times [RH_3]}{\{H_3O^+\}\{H_3O^+\}} \quad (2\text{-}49)$$

Substituting Eq. (2-47) and Eq. (2-49) into Eq. (2-46), and canceling $[RH_3]$ from numerator and denominator, yields the desired result:

$$CR_1 = \frac{1}{1 + \frac{K_{a1}}{\{H_3O^+\}} + \frac{K_{a1} \times K_{a2}}{\{H_3O^+\}\{H_3O^+\}}} \quad (2\text{-}50)$$

The second distribution coefficient CR_2 can be computed in an analogous fashion. From the definition of CR_2 in Eq (2-41), and the concentration condition (Eq. (2-45)),

$$CR_2 = \frac{[RH_2^-]}{[R_T]} = \frac{[RH_2^-]}{[RH_3] + [RH_2^-] + [RH^{2-}]} \quad (2\text{-}51)$$

Solving Eq. (2-43) for $[RH_3]$, and Eq. (2-44) for $[RH^{2-}]$, yields the required expressions in $[RH_2^-]$:

$$[RH_3] = \frac{[RH_2^-]\{H_3O^+\}}{K_{a1}} \quad (2\text{-}52)$$

$$[RH^{2-}] = \frac{K_{a2}[RH_2^-]}{\{H_3O^+\}} \quad (2\text{-}53)$$

Substituting Eqs. (2-52) and (2-53) into Eq. (2-50)2.33, and canceling $[RH_2^-]$ from numerator and denominator, then gives an expression for CR_2:

$$CR_2 = \frac{1}{\frac{\{H_3O^+\}}{K_{a1}} + 1 + \frac{K_{a2}}{\{H_3O^+\}}} \quad (2\text{-}54)$$

This conventional solution for the distribution coefficient is somewhat unsatisfying for direct implementation in a computer program, however. Whenever the acidity constant (K_{a1}) is zero, the machine will, nonetheless, attempt the division and make an error. Of course, a separate segment of code could be written for each possible subset of the 28 potential molecular species, and the machine could be guided to the appropriate section of the code by a logic tree. Observe, however, that Eq. (2-54) can also be written as:

$$CR_2 = \frac{\frac{K_{a1}}{\{H_3O^+\}}}{1 + \frac{K_{a1}}{\{H_3O^+\}} + \frac{K_{a1}K_{a2}}{\{H_3O^+\}\{H_3O^+\}}} \quad (2\text{-}55)$$

This equivalent expression can be generated by simply substituting the second term in the denominator of Eq. (2-50) into its own numerator. Eq. (2-55) now has the advantage that a zero value for K_{a1} will not cause the computer to attempt a

"zero divide," and will nonetheless yield the proper value for CR_2, that is, zero.

In the same way, substitution of the third term in the denominator into the numerator of Eq. (2-50) gives:

$$CR_3 = \frac{\dfrac{K_{a1}K_{a2}}{\{H_3O^+\}\{H_3O^+\}}}{1+\dfrac{K_{a1}}{\{H_3O^+\}}+\dfrac{K_{a1}K_{a2}}{\{H_3O^+\}\{H_3O^+\}}} \qquad (2\text{-}56)$$

Eq. (2-56) is equivalent to the expression for CR_3 obtained via substitution of expressions for $[RH_3]$ and $[RH_2^-]$ (in terms of $[RH^{2-}]$) into the formula for CR_3 given by:

$$CR_3 = \frac{[RH^{2-}]}{[R_T]} = \frac{[RH^{2-}]}{[RH_3]+[RH_2^-]+[RH^{2-}]} \qquad (2\text{-}57)$$

Rearranging Eq. (2-54) gives $[RH_2^-]$ in terms of $[RH^{2-}]$:

$$[RH_2^-] = \frac{[RH^{2-}]\{H_3O^+\}}{K_{a2}} \qquad (2\text{-}58)$$

and Eq. (2-43) gives:

$$[RH_3] = \frac{[RH_2^-]\{H_3O^+\}}{K_{a1}} \qquad (2\text{-}59)$$

or, substituting Eq. (2-58) into Eq. (2-59),

$$[RH_3] = \frac{[RH^{2-}]\{H_3O^+\}\{H_3O^+\}}{K_{a1}K_{a2}} \qquad (2\text{-}60)$$

Substituting Eqs. (2-58) and (2-60) into Eq.(2-57), and canceling $[RH^{2-}]$ from numerator and denominator, then yields:

$$CR_3 = \frac{1}{\dfrac{\{H_3O^+\}\{H_3O^+\}}{K_{a1}K_{a2}}+\dfrac{\{H_3O^+\}}{K_{a2}}+1} \qquad (2\text{-}61)$$

which is equivalent to Eq. (2-56).

This example demonstrates that an algorithm for computing the distribution coefficients (α) of any multi-species mixture can be constructed in the following way.

(1) Write a concentration condition for $[S_t]$ that expresses the law of conservation of mass (Eq. (2-45)).

(2) Define the distribution coefficient for the parent molecule (RH_3) as $[RH_3]/[R_T]$ (Eq. (2-46)).

(3) Solve the equilibrium expressions for the full system (Eq. (2-43) and Eq. (2-44)) for each molecular species, expressing each species in terms of $[RH_3]$ (Eq. (2-47) and Eq. (2-49)).

(4) Cancel $[RH_3]$ from each of these expressions (Eq. (2-47) and (2-49)), thereby obtaining the contribution of each species (DISFCT(I)) to the denominator of Eq. (2-50).

(5) Compute a total denominator (SUMFCT) as (1 + these terms), as in Eq. (2-50) (that is,
DISFCT(1) = $[RH_3]/[RH_3]$ = 1).

(6) Compute each distribution coefficient (α_i) as DISFCT(I)/SUMFCT, where DISFCT(1) = 1 and, in this example,

DISFCT(2) = $K_{a1}/\{H^+\}$ and

DISFCT(3) = $(K_{a1})(K_{a2})/\{H^+\}\{H^+\}$

This computational procedure is general for all its subsets: when any K_a = 0, the computed distribution coefficient is zero. Furthermore, the α values always sum to 1.0, as they must in order to conform to the law of conservation of mass.

The EXAMS algorithm for computing distribution coefficients of the 28 (potential) molecular species of an organic chemical was constructed on this model.

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2.3 Kinetic Processes

"Kinetic" processes, unlike rapid (local) equilibrium processes such as ionization and sorption, occur on time scales that make their time-dependent behavior of direct concern in a hazard evaluation. (Very slow processes, at the further extreme of the temporal spectrum, are usually treated by modelers as absolute constants. For example, changes in the emission of light by the sun (the solar "constant") are usually modeled only by astrophysicists.) The kinetics of the transport regime in aquatic systems, and the kinetics of the transformation processes that degrade a chemical to innocuous forms, are the primary constituents of EXAMS' evaluative capabilities.

2.3.1 Transport

EXAMS calculates steady-state average transport of water, sediments, and planktonic organisms throughout the system. The flows of water, sediments, and plankton act as simple carriers for the dissolved, sediment-sorbed, DOC-complexed, and biosorbed forms of the synthetic organic chemical. These carrier flows are ultimately reduced to coefficients that express the effects of transport processes on the kinetics of the chemical; the vector of concentrations of the synthetic organic chemical itself thereby remains the only true time-dependent state variable in EXAMS.

A hydrologic sub-program was created for EXAMS in order to minimize the labor necessary to specify, or modify, the physical transport section of EXAMS' environmental data base. This data base is composed primarily of readily available and easily comprehended parameters, such as the volume, mean depth, and surface area of the system compartments. Any of these parameters can be modified by the user as desired. EXAMS then recomputes the exchanges of materials among compartments, and the net transport of materials through the system, in effect creating a new hydrologic model according to the user's modifications.

The hydrologic procedure operates on three sub-sets of EXAMS' environmental data base. The first is a description of the volumes of water entering each zone of the system from *external* sources. The second categorizes the geometry of the system, and the properties and distribution of biomass and sediments. The third sub-set contains structural properties of the ecosystem itself. This last (variables JFRAD, JTURB, etc.) specifies the direction and strength of the flow pathways interconnecting the system compartments. The flow of water through the system compartments is computed from a mass balance on water entering and leaving each segment.

EXAMS' flow pathways can be specified via advective or dispersive equations, or both. (Advection is like a freight train, dispersion is the macro-scale analogue of diffusion, operating like a drunken walk.) The program uses conventional equations for both processes. For compartments of constant volume, the

law of conservation of mass demands that the hydrologic inputs to a compartment be balanced by advected flows leaving the compartment. The expression used for dispersive or turbulent exchanges across compartment boundaries is, as usual, (DSP × XSTUR / CHARL) where XSTUR is the cross-sectional area of the exchange boundary (in square meters), CHARL is the "characteristic length" (meters) along the flow path (that is, the average length of the compartments or the distance between compartment centers, measured along the exchange axis), and DSP is the eddy dispersion coefficient (square meters/hour). For example, in a simple (two surface water compartments) model of a stratified lake, when XSTUR is the area of the thermocline and CHARL is one-half the mean depth of the lake, this expression describes the rate of exchange of water between the epilimnion and hypolimnion.

EXAMS also computes *sediment* transport via the general advective and dispersive equations, but an additional set of transport rules is superimposed on the sediment equations. For example, an advective pathway between water column compartments is permitted to carry along suspended sediments (and plankton) from one compartment to the next. An advective pathway from the water column into a benthic sediment is not allowed to carry particulate matter with it, however: This kind of pathway is reserved for water seepage into the sediment (along with dissolved and DOC-complexed chemicals), and ground-water recharge leaving the system. The sediment transport rules give EXAMS the ability to include riverine sediment wash-loads and bed-loads, groundwater seepage and recharge, and complex exchanges between the water column and benthic sediment deposits driven by physical and biological processes dominant in non-fluvial systems.

EXAMS does not explicitly represent sequential deposition and scour of benthic sediment zones, nor does it allow in most cases for a secular accumulation of bottom sediments with consequent burial of sorbed chemicals. In one sense, this limits EXAMS' utility in evaluative safety investigations. For example, run-of-the-river flood control reservoirs are very common in the USA, and many of them rapidly accumulate sediments and bury chemicals in their depths. The bottoms of many, if not most, free-flowing rivers and larger lakes accumulate sediments quite slowly, however. In addition, the synthetic chemicals captured by benthic sediments probably are frequently re-exposed to the overlying water column via water turbulence, physical disturbance by demersal fishes, and the internal stirring of sediments by benthic organisms (bioturbation). EXAMS therefore treats benthic sediments as bottom zone compartments with a fixed volume, subject to continual (albeit slow) exchanges with the overlying water column. At least for evaluation and screening purposes, it seemed unwise to suppose that buried synthetic chemicals will never reappear.

Where appropriate, however, net sedimentation and burial of synthetic chemicals can be readily evaluated, for the burial process can be represented via a first-order disappearance of the compound from benthic sediments. For example, given an active sediment depth of 10 cm, and a net burial of 1 mm/yr, the loss coefficient for a synthetic compound in the sediment would be 0.1/10 = 0.01 /yr with a half-life of 69 years. This approach should, however, only be used when the benthic zone is modeled as a single sediment layer.

EXAMS was designed for evaluative purposes, rather than for detailed site-specific applications. For this reason, EXAMS' transport algorithms were written in a very general form that uses an input description of the transport conditions in the system, rather than attempting to compute hydraulics and solids transport from first principles. Several cautions to the user defining an ecosystem for entry to the program are therefore in order.

First, because EXAMS is a compartment model, the representation of advected flows necessarily introduces some numerical dispersion into the computations. Although this poses little problem for general evaluations, it should be recognized that the concentrations computed by the program for a particular location are to a degree dependent on the spatial resolution used to represent the system. For example, EXAMS computes the average concentrations in a river reach, rather than the details of the (usually decreasing) profile of concentrations *within* the reach. As the number of compartments used to describe the reach increases, the compartmentalized representation begins to approach the more detailed profile predictable from an analytic solution to the governing partial differential equations. In general, for site-specific applications, simplified transport representations can be adjusted or "calibrated" to more faithfully depict transport detail, via initial matching of program outputs to a conservative tracer substance. Chloride concentration is often used as a calibration tracer in estuaries; temperature and dissolved substances can be used for calibration studies in lacustrine systems. Of course, if desired, EXAMS could be loaded via an analysis of the outputs of detailed hydraulic and sediment transport models.

Secondly, EXAMS does not impose a segment-by-segment mass balance on the solid phases (sediments and biota) that transport sorbed chemicals through the system. In most instances, sediment (detrital materials), "dissolved" organic matter, and biota are subject to significant creation and destruction in some areas of aquatic systems, so that, unlike water, these quantities cannot be treated as simple mass-conservative entities in a generalized algorithm. Thus, for example, mass balances for suspended sediments in EXAMS are left to the user's discretion. The EXAMS program, however, does not permit a failure to

conserve sediment mass to perturb the mass balance for synthetic organic chemicals.

Exchanges with sediment beds are described primarily via a dispersive exchange term (Chapter 2.3.1.4). This approach involves a statistical summary of the multitude of physical and biological transport mechanisms that have not been fully characterized in the literature. It has disadvantages in that the appropriate magnitudes for the input parameters (e.g., DSP) are only approximately known. The magnitudes of the descriptive parameters needed for a more mechanistic characterization of these multiple physical and biological transport pathways are, however, still less perfectly known. In general, the sensitivity of EXAMS' outputs to variation in sediment-water column exchange parameters should probably be routinely examined, at least for extensively sorbed compounds.

2.3.1.1 Hydrology and advection

Hydrologic inputs are specified in EXAMS' environmental data base via four variables: STFLO (stream flow), NPSFLO (non-point-source flow), SEEPS (ground-water inflows), and RAIN (rainfall). After subtracting evaporative water losses (EVAP), the sum of these terms is the total water flow entering a compartment from external sources. EXAMS adds to this sum the advected flows entering the compartment via other compartments in the system. This grand sum is the total amount of water advected into the compartment from all (internal and external) sources combined. The total advective flow through the compartment is then distributed among the flow paths specified for that compartment in the JFRAD and ITOAD structural vectors.

Three of the hydrologic input variables (STFLO, NPSFLO, and SEEPS) are vectors that include a separate entry for each compartment of the aquatic system described by the data base. The STFLO vector is used to enter point sources, tributary flows, stream flows entering a lake, and the discharge entering the uppermost reach of a river system. The NPSFLOs are used to enter non-point-flows and overland runoff flowing into the compartments. Ground- water seepage or subsurface flows are entered via SEEPS. STFLO, NPSFLO, and SEEPS all have units of cubic meters per hour; EXAMS allows each compartment to receive an entry from each category. These hydrologic inputs can in addition be specified for each month of the year.

Rainfall (RAIN) is a scalar variable in EXAMS, that is, the environmental descriptor is a single (monthly) value rather than a compartment-specific vector. RAIN has units of millimeter/month. EXAMS converts this climatological datum to a volume of water entering each compartment having an air-water interface. EXAMS detects the air-water interface, and decides whether to admit rainfall into the compartment, based upon the structure of the system. Rainfall is not permitted to enter compartment types (TYPE) "B" (benthic) or "H" (hypolimnion). The decision mechanism for L(ittoral) and E(pilimnion) compartments is more complex. For these compartment types, EXAMS checks the compartment numbered one less than the compartment under consideration (that is, if the current compartment is J, the decision is based on the properties of compartment (J-1)). If the preceding compartment is another element of the water column, rainfall is not allowed to enter the current (Jth) compartment.

At first glance, this decision seems trivial: after all, rain only falls on the water surface, therefore only these compartments can receive rainfall. The problem is complicated, however, by the fact that EXAMS was designed to allow a user to interactively modify any variable in the environmental data base. EXAMS therefore must be able to detect any change in the system structure and accurately recompute, in this case, a new hydrologic regime. Changes in system structure affect a number of other processes as well. For example, in computing vertical light extinction through the water column, EXAMS detects the top of the water column, compute the light levels in each successively deeper water-column compartment, and then restart the computation for each adjacent vertical section.

The problem, then, is somewhat more general than it first appears, and is not entirely trivial: the three-dimensional structure of the system must be decoded as an implicit function of the input environmental data. The decoded structure then serves as a guide for computing the kinetics of the transport and transformation processes. The decoding problem could, of course, be eliminated by requiring that the environmental data include a more complete set of structural descriptors. This approach, however, leaves the user in the uncomfortable position of having to memorize a large set of arbitrary, model-specific compartment descriptors of little intrinsic interest. EXAMS instead relies on a set of simple conventions for numbering and naming the compartments used to describe an aquatic system. These conventions can be stated as 4 definition rules:

(1) Compartments can be named (TYPE) either "L" (littoral), "E" (epilimnion), "H" (hypolimnion), or "B" (benthic). These names carry their usual implications: an "H" compartment lacks an air-water interface, a "B" compartment is a bottom sediment, etc. All system zones can be entered as vertical stacks of the same TYPE for added spatial detail.

(2) Compartment number 1 must be part of a water column and must be of TYPE "E" or "L".

(3) Each vertical segment must be numbered in increasing order with increasing depth. That is, when a vertical segment is divided into, say, 4 compartments, if the topmost compartment is numbered 5, the bottom compartment will be number 8.

(4) Every vertical segment must terminate in at least one bottom sediment ("B") compartment.

EXAMS' computations are somewhat more efficient if one more rule is observed:

(5) Vertical blocks of compartments are arranged, and numbered, along the main advective flow paths in the system.

EXAMS' internal decoding of the (implied) system structure thus avoids the problem of multiple model-specific parameters, but at some cost: EXAMS must assume that the user has scrupulously adhered to these rules. Suppose, for example, that a 10-mile stretch of river were described as 10 successive "L" compartments, and the benthic sediments were omitted: EXAMS would suppose the system to be a vertical, 10-mile-deep column of water. Again, should a surface-water compartment be designated "H", EXAMS will not allow rain to fall, nor chemicals to volatilize, from the compartment. Examples of improper and proper segmentations of a small river and lake system are given in **Figure 1** and **Figure 2**.

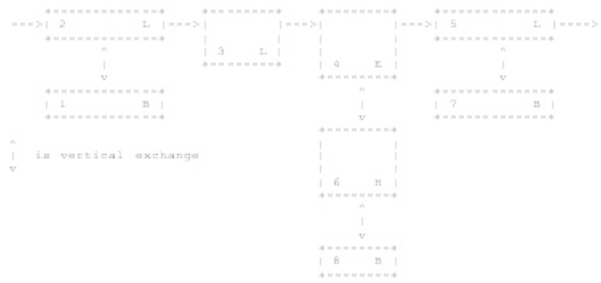

Figure 1. Improper segmentation and numbering: compartment number 1 is (B)enthic, benthic sediments are incomplete, and numbering is horizontally rather than vertically organized.

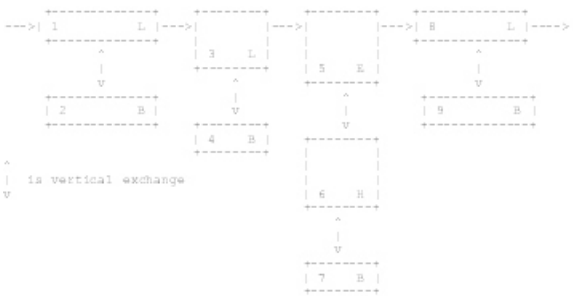

Figure 2. Proper segmentation: vertically organized numbering, all vertical segments include a bottom sediment, and compartment number 1 is of surface water type ("L" or "E").

EXAMS' final hydrological input quantity is a compartment-specific vector of monthly evaporative water loss rates, EVAP, with units (millimeter/month). A value of EVAP can be entered for any compartment, but EXAMS ignores inappropriate entries, that is, evaporation is allowed only for compartments with an air-water interface.

EXAMS can be operated with very generalized descriptions of aquatic systems typical of broad geographic regions, or with more detailed descriptions of particular sites and locales. The mechanics of EXAMS' transport computations can best be appreciated via a specific example. This example will be developed in some (site-specific) detail, so as to illustrate methods for preparing environmental data for EXAMS, computational mechanics, and the range of transport processes that can be accommodated by the program.

2.3.1.2 Advected water flows

EXAMS' advective flow computations are a direct application of the law of conservation of mass. Because changes in storage volumes are not permitted in Modes 1-3, the total inputs to each compartment must be balanced by advected outflows. The advective transport regime thus can be computed by imposing r (mass) balance on the hydrologic inputs to the system. gic of these computations can best be seen within the t of a specific example:

e **3** is a 9-compartment model of a portion of a slowly g slough or river system. Upstream discharge into rtment 1 is 10 cubic meters/h. The flow is split by an into compartments 3 and 5; 75% of the flow goes to compartment 3, the remainder to compartment 5. Compartment 3 also receives a tributary discharge of an additional 10 cubic meters/hour. Each segment is 100 m long and 2 m deep. The segment widths are 10 m for 1 and 7, but compartment 3 is 8 m, and compartment 5 is 2 m, wide. The rate of evaporative water loss (EVAP) is 146.1 mm/mo for all segments; no rain falls on the system. EXAMS' hydrologic input data, thus far, looks like this:

Table 2. Hydrologic input data for Noname Slough

CMPT	STFLO	AREA	EVAP	VOL	DEPTH
1	10	1000	146.1	2000	2
3	10	800	146.1	1600	2
5		200	146.1	400	2
7		1000	146.1	2000	2

EXAMS now converts STFLO and EVAP (using AREA) to the net liters/hour entering each compartment from external sources

(WATINL), and sums the total available flow (TOTIN), arriving at the hydrologic analysis shown in **Table 3**.

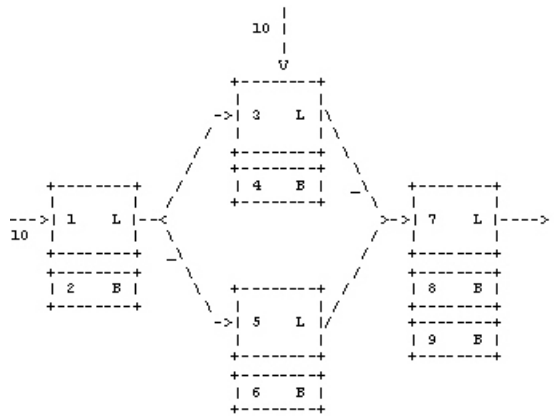

Figure 3. Nine-compartment model of Noname Slough.

Table 3. Advective inputs to Noname Slough

CMPT	STRMFL	EVAPL	WATINL
1	10,000	200	9,800
3	10,000	160	9,840
5	0	40	-40
7	0	200	-200
		TOTIN	19,400

The structure of the advective flow field is given by parameters JFRAD, ITOAD, and ADVPR. These names are acronyms for J FRom ADvection (JFRAD), I TO ADvection (ITOAD), and ADvection PRoportion (ADVPR), respectively. Vector JFRAD is the list of the source compartments for each flow. The corresponding member of ITOAD holds the number of the compartment receiving the flow, and ADVPR gives the fraction of the total flow through compartment JFRAD that follows the path to ITOAD. A zero (0) entered in ITOAD denotes an export from the system. EXAMS' report of the (partial) structure given for the slough system in **Figure 3** would appear as in Exams Output Table 1.

```
Name of environment: Noname Slough - Advection Test Data
Total number of segments (KOUNT) =   9
Segment Number:   1   2   3   4   5   6   7   8   9
Segment "TYPE":   L   B   L   B   L   B   L   B   B
-------------------------------------------------------------
Table 9.  Input specifications -- advective transport field.
-------------------------------------------------------------

J FR AD        1         1         3         5         7
I TO AD        3         5         7         7         0
ADV PR     0.750     0.250      1.00      1.00      1.00
 Path No.:     1         2         3         4         5
-------------------------------------------------------------
```

Exams Output Table 1. Partial advective structure of Noname Slough.

EXAMS now combines the information given in **Table 3** and Exams Output Table 1 into a set of input/output equations reflecting the conservation of water mass in the system. Taking X(I) to denote the total output flow from compartment (I), these equations can be written as:

```
OUTPUT   =   SUM OF INPUTS
 X(1)    =  9800
 X(3)    =  9840  + 0.75 X(1)
 X(5)    =   -40  + 0.25 X(1)
 X(7)    =   -200 + 1.00 X(3) + 1.0 X(5)
```

This is a set of 4 simultaneous equations in 4 unknowns; it can be solved by successive elimination of terms in the usual way. In this case, it is easy to see that:

```
X(1)                          =  9800
X(3) = 9840 + 0.75(9800)      = 17190
X(5) =  -40 + 0.25(9800)      =  2410
X(7) = -200 + 17190 + 2410    = 19400
```

EXAMS was written to accommodate N equations in N unknowns. In other words, the program solves the input/output advective equations for an arbitrary number (N) of compartments, any of which can receive, deliver, or exchange advected flows with any or all of the other compartments in the system. The N input/output equations are solved by a Gaussian elimination algorithm (Stuart 1970:304-311). This algorithm is a matrix solution of a normalized form of the input/output equations. The matrix (AMAT) is loaded in three stages: First, each value of WATINL is divided (normalized) by TOTIN, and loaded on the (N+1) column of AMAT. Next, the coefficients on the output (X) terms (which are always unity (1)) are loaded on the diagonal of AMAT. Finally, the ADVPR values are entered into AMAT with a row index given by ITOAD and a column index given by JFRAD. (The system export terms (ITOAD = 0) are not required for this part of the analysis.) Leaving aside Noname Slough's benthic compartments, the coefficient matrix would be (**Table 4**):

Table 4. Normalized coefficient matrix, advection equations

		JFRAD				WATFL / TOTIN
		1	3	5	7	
ITOAD	1	1.00	0.0	0.0	0.0	0.505155
	3	-0.75	1.0	0.0	0.0	0.507216
	5	-0.25	0.0	1.0	0.0	-0.002062
	7	0.00	-1.0	-1.0	1.0	-0.010309

The solution of this system of equations is:

X(1) = 0.505155
X(3) = 0.886082
X(5) = 0.124227
X(7) = 1.000000

where "X" is now the fraction of TOTIN passing through each compartment.

For each compartment, EXAMS computes the actual discharges along each flow path as the product of X, TOTIN, and the ADVPR for the pathway. This information is entered in a matrix (WATFL) of flows among segments. The row and column indices of WATFL are the same as those of AMAT, that is, the WATFL indices give the source and destination compartment number for each flow. Exports from the system (in liters per hour) are entered into a vector (WATOUL) of exports from each compartment. The exports from each (JFRAD) compartment are computed as the product of X, TOTIN, and ADVPR for those pathways having ITOAD = 0.

In the Noname Slough example, the discharges from segment number 1 are:

WATFL(3,1) = (0.505155)(19400)(0.75) = 7350,
and
WATFL(5,1) = (0.505155)(19400)(0.25) = 2450.

The only non-zero outlet flow is

WATOUL(7) = (1.0)(19400)(1.0) = 19400.

The WATFL matrix and the WATOUL vector for these sections of Noname Slough are shown in **Table 5**. EXAMS' outputs include a "transport profile" of the system, showing the advected flows through each segment. EXAMS also computes a (local) turnover or "water renewal" time (the volume/discharge ratio) for each compartment. EXAMS' transport profile for Noname Slough, as defined thus far, is given in Exams Output Table 2.

Table 5. Example WATFL matrix and WATOUL vector (L/h)

		JFRAD			
		1	3	5	7
ITOAD	1	0	0	0	0
	3	7350	0	0	0
	5	2450	0	0	0
	7	0	17190	2410	0
WATOUL		0	0	0	19400

```
CHEMICAL: Unspecified Chemical
ECOSYSTEM: Noname Slough - Advection test data
-----------------------------------------------------------------------
TABLE . TRANSPORT PROFILE OF ECOSYSTEM.
-----------------------------------------------------------------------
CP T*   VOLUME    SEDIMENT  WATER FLOW  SED. FLOW  RESIDENCE TIME (DAYS)
Y   (CUBIC M)  MASS (KG) (CU. M/DAY) (KG/DAY)     WATER    SEDIMENTS
-----------------------------------------------------------------------
1L   2.0000E+03             235.                   8.50
2B
3L   1.600E+03              413.                   3.88
4B
5L    400.                   57.8                  6.92
6B
7L   2.000E+03              466.                   4.30
8B
9B
-----------------------------------------------------------------------
* COMP. TYPE: "L"=LITTORAL; "E"=(EPI) AND "H"=(HYPO)LIMNION; "B"=BENTHIC
```

Exams Output Table 2. Partial transport profile for Noname Slough.

2.3.1.3 Advective sediment transport

Sedimentary materials (detritus) can be produced and destroyed biogenically within an aquatic ecosystem. Sediment transport thus is not computed in EXAMS via the simple mass balance constraints used to compute the transport of advected water masses. EXAMS instead treats advected sediment as a non-conservative substance whose transport is simply driven by the hydrodynamics of the system. The point- (STFLO) and non-point- (NPSFLO) external hydrologic inputs do contain coupled sediment loads (STSED and NPSED, kg/h). These variables are used to evaluate the chemical loadings (see Chapter 2.4); they do not enter the chemical transport equations.

EXAMS computes advective sediment transport as the product of the rates of water transport and the sediment/water ratio (SEDCOL, Eq. (2-21)) of the source compartments. WATFL and WATOUL are used to load an analogous sediment flow matrix (SEDFL) and export vector (SEDOUL), both having

units of kg sediment transported per hour. The equation for advective sediment transport among compartments is (2-62):

$$SEDFL(i,j) = WATFL(i,j) \times SEDCOL(j) \qquad (2\text{-}62)$$

and the equation for advected sediment export is

$$SEDOUL(j) = WATOUL(j) \times SEDCOL(j) \qquad (2\text{-}63)$$

These equations are not blindly executed for the entire system, however: The execution of the sediment transport equations (Eqs. (2-62) and (2-63)) is constrained by a series of special conditions, which can be expressed as a set of 5 sediment transport rules:

(1) An advected water mass leaving any water column compartment carries an entrained sediment washload, unless the flow enters a benthic compartment. A flow from the water column into a benthic sediment is an infiltration flow that does not transport sediments.

(2) Benthic sediment ("B") compartments can always export water across system boundaries, and can advect water to any other compartment in the system.

(3) A benthic compartment can export sediment (in addition to water) only when it occupies the sediment-water interface (that is, the (J-1) compartment is not of TYPE "B").

(4) Sediment cannot be advected from a benthic compartment to any element of the water column.

(5) When benthic compartments are not vertically adjacent (actually, when their compartment numbers differ by 2 or more), sediments can be advected from one to another (for example, along a bedload transport path).

These sediment transport rules allow EXAMS to include sediment washloads and bedloads, and seepage of groundwater both into and out of the system. One additional system definition rule must be observed, however, when a groundwater recharge is portrayed: The groundwater flow path must include at least 2 vertical benthic sediment compartments. If this definition rule is ignored, EXAMS will interpret the export flow leaving the benthic compartment as a bedload (rule 3) rather than as a groundwater recharge.

These concepts can be illustrated by expanding the definition of Noname Slough. In the expanded definition of **Figure 4**, one segment receives a groundwater input (SEEPS) of 0.2 cubic meters/hour. The groundwater seep passes through benthic compartment 6 and is advected into the overlying water (rule 2); by rule 4 the water flow does not entrain a sediment flow. The downstream segment (7) loses water to a groundwater recharge. The infiltration flow is 2% of the total advected flow through compartment 7 (ADVPR = 0.02). By rule 1, the infiltration does not entrain the suspended sediments. The groundwater recharge must be carried on from compartment 8 into compartment 9 before it can be exported from the system, however, or EXAMS would interpret the export as a bedload (rule 3) rather than as a flow of water only (rule 2). The bedload path (compartment 2 to 4 to 8), by rule 5, carries both water and sediments downstream. The bedload export at compartment 8 is enabled under rule 3. The washload (compartments 1 to 3, 5 to 7) moves through the system under rule 1; EXAMS computes the downstream transport of suspended sediment from Eq. (2-62).

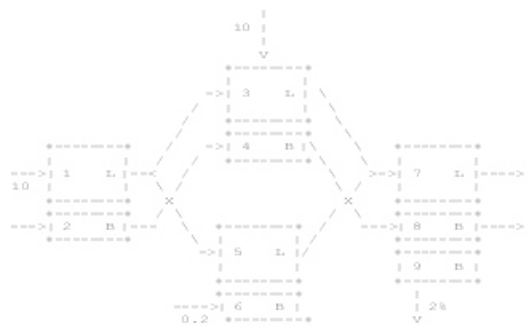

Figure 4. Noname Slough bedload, washload, and groundwater flows.

To complete this example, some additional properties of the sediments must be specified. Let, therefore, Noname Slough have a suspended sediment concentration (washload, SUSED) of 100 ppm, and stream-borne sediment loadings (STSED(1) and (3)) of 1.0 kg/h. (Note that this treatment imposes a mass balance on suspended sediments.) The depth of the surficial sediments (compartments 2, 4, 6, and 8) is 5 cm; each has a bulk density (BULKD) of 1.2 g/cc, and a water content (PCTWA) of 180%. Segment 9 is a 30 cm layer of sand with a bulk density of 1.95 g/cc, and a water content of 115%.

The bedload is, of course, another measurable property of the Slough. Suppose, for example, the measured bedload leaving the downstream segment of the Slough were 100 kg/h. The ADVPR for the crossed infiltration and bedload transport through compartment 8, and the upstream bedload inputs, can be developed from this datum and an assumed solids balance for the system.

The sediment/water ratio for the surficial sediments is 1.25 kg/liter (Eq. (2-22)); the water export associated with the bedload is, therefore, (100)/(1.25) = 80 liters per hour = 0.08

cubic meters/h. The groundwater infiltration was given as 2% of the available discharge passing through segment 7 (**Figure 4**). The total segment 7 discharge is 19.4 cubic m/h (**Table 5**), plus the groundwater seep entering via segment 6 (Figure), or 19.6 cubic meters/hour. The 2% infiltration is therefore (0.02)(19.6) = 0.392 cubic m/h, and the total flow through compartment 8 is 0.392 + 0.08 = 0.472 cubic m/h. The ADVPR for the throughput of infiltrated water is therefore (0.392)/(0.472) = 0.83; the ADVPR for the bedload is 0.17.

Finally, presuming the bedload originates in equal measure from the influent flows to compartments 2 and 4, the bedload inflows to both segments are 0.04 cubic meters of water per hour (STFLO(2) and (4)), with a parallel sediment load (STSED) of 50 kg/h. EXAMS' retrieval of the full advective specifications is shown in Exams Output Table 3, and EXAMS' computed advective "transport profile" is given in Exams Output Table 4.

```
Name of environment: Noname Slough - Advection Test Data
Total number of segments (KOUNT) =   9
Segment Number:   1   2   3   4   5   6   7   8   9
Segment "TYPE":   L   B   L   B   L   B   L   B   B
-----------------------------------------------------------------
Table 9.  Input specifications -- advective transport field.
-----------------------------------------------------------------

J FR AD        1         1         3         5         7
I TO AD        3         5         7         7         0
ADV PR     0.750     0.250      1.00      1.00     0.980
 Path No.:     1         2         3         4         5

J FR AD        7         2         4         6         9
I TO AD        8         4         8         5         0
ADV PR     2.000E-02  1.00      1.00      1.00      1.00
 Path No.:     6         7         8         9        10

J FR AD        8         8
I TO AD        9         0
ADV PR     0.830     0.170
 Path No.:    11        12
-----------------------------------------------------------------
```

Exams Output Table 3. Full advective structure of Noname Slough.

```
CHEMICAL: Unspecified Chemical
ECOSYSTEM: Noname Slough - Advective transport regime
-------------------------------------------------------------------------
TRANSPORT PROFILE OF ECOSYSTEM.
-------------------------------------------------------------------------
CP T*   VOLUME    SEDIMENT  WATER FLOW  SED. FLOW  RESIDENCE TIME (DAYS)
   Y   (CUBIC M)  MASS (KG) (CU. M/DAY) (KG/DAY)     WATER    SEDIMENTS
-------------------------------------------------------------------------
1L     2.000E+03   200.       235.       23.5       8.50       8.50
2B      50.0      3.333E+04  0.960      1.200E+03   27.8       27.8
3L     1.600E+03   160.       413.       41.3       3.88       3.88
4B      40.0      2.667E+04  1.92       2.400E+03   11.1       11.1
5L      400.       40.0      62.6        6.26       6.39       6.39
6B      10.0      6.667E+03  4.80       0.000       1.11
7L     2.000E+03   200.       470.       46.1       4.25       4.34
8B      50.0      3.333E+04  11.3       2.407E+03   2.35       13.8
9B      300.      5.087E+05  9.40       0.000       8.12
-------------------------------------------------------------------------
* COMP. TYPE: "L"=LITTORAL; "E"=(EPI) AND "H"=(HYPO)LIMNION; "B"=BENTHIC
```

Exams Output Table 4. Advective transport regime in Noname Slough.

2.3.1.4 Dispersive transport

The mean advected flow is not the only process governing the transport of synthetic chemicals in aquatic systems. Turbulence and shear flow in rivers, for example, combine to generate a wide spectrum of meso-scale advective processes. Similarly, in stratified lakes exchange across the thermocline is driven by molecular diffusion, wind-induced mixing, storm surges, and internal waves and seiches. These meso-scale processes can usually be described via a statistical summary (the dispersion equation) of their effects on the average transport of dissolved and entrained suspended substances (see, for example, Fischer et al. 1979). EXAMS' environmental data base includes 5 vectors that specify the direction (JTURB, ITURB), and strength (DSP, XSTUR, CHARL) of dispersive transport pathways in an aquatic system; dispersivity can be varied by month.

The corresponding members of the JTURB and ITURB vectors specify the pair of compartments that are exchanging materials via each dispersion pathway. For example, the 4th entry in the vectors could be used to specify an exchange between compartments 7 and 10, by setting JTURB(4) = 7, and ITURB(4) = 10. Because dispersion, unlike advection, is a symmetrical process, this pathway could also be specified as JTURB(4) = 10 and ITURB(4) = 7. Boundary conditions (dispersive exchanges with the external world) are specified by a 0 setting on either vector. In other words, the vectors can specify a turbulent exchange of, for example, compartment 10 (an embayment), with an external reservoir, via either (JTURB = 10; ITURB = 0) or (JTURB = 0; ITURB = 10). EXAMS computes the boundary exchanges as a simple displacement of contaminated, by chemical-free, water and sediments. Non-zero chemical boundary conditions are loadings, and thus would interfere with EXAMS' estimates of persistence (defined as the time to cleanse the system after all loadings terminate) in Mode 1. Non-zero (dispersive) chemical boundary conditions can if desired be introduced via an artificial point-source or non-point-source advective input, coupled with a symmetrical advective export from the compartment, or via a DRFLD (see Chapter 2.4).

The conventional dispersion equation used in EXAMS describes the rate of exchange of environmental volume across a boundary between two compartments. EXAMS' formula is:

$$F = \frac{DSP \times XSTUR}{CHARL} \qquad (2\text{-}64)$$

In this equation, XSTUR is the cross-sectional area of the pathway (in square meters), CHARL is the "characteristic length" of the path (m), and DSP is the dispersion coefficient or eddy diffusivity (square meters/hour). F is then a flow of environmental volume, with dimensions of cubic meters per hour. Equation (2-64) is homologous with the mathematics of simple Fickian molecular diffusion. The dispersion equation, however, is a statistical summary of the large-scale effects of

meso-scale advective processes; it is used when the meso-scale processes are so complex or sporadic that a detailed treatment is intractable. The net result of the meso-scale processes is similar to molecular diffusion in that dissolved constituents are transported along the gradients of concentration in the system. The apparent rate of transport of materials from areas of high, to areas of low, concentration is much faster than rates of molecular diffusion, however. For this reason, the kinetic parameter in Eq. (2-64) (DSP) is usually called a "dispersion coefficient," "turbulent diffusivity," or "eddy diffusivity," rather than a "diffusion" constant (Bird et al. 1960:629). The events described by dispersion are not fully homologous with Fickian diffusion, however, and the use of dispersion terms to depict chemical transport in sediments requires careful adjustment for effects of porosity, tortuosity, sorption, and ion exchange (Berner 1976).

From the dispersion equation (2-64), EXAMS computes a flux of water and sediments along the pathway specified by JTURB and ITURB. The fluxes between compartments are added to the advective flows in matrices WATFL and SEDFL, thereby completing EXAMS' description of the system's internal flow field. The boundary fluxes are added to the appropriate elements of WATOUL and SEDOUL; the exchange brings in a replacement volume of uncontaminated water and sediments.

The "characteristic length" (CHARL) of a pathway conventionally represents the distance between compartment centers, measured along the axis of the exchange. A single segment thus may have several characteristic lengths, depending on the geometric orientation of its linkages to adjoining segments. The cross-sectional area (XSTUR) for the exchange path also depends upon the orientation of the compartments. For a vertical exchange, as for example transport across the thermocline of a lake, XSTUR is usually the AREA of the hypolimnion compartment. Longitudinal dispersion in a river conventionally takes the flow cross section as XSTUR, however, and this does not correspond to any value of AREA. Adherence to these conventions is a responsibility of model construction. EXAMS does not attempt to evaluate the geometry of the system, but simply inserts the user's entries for CHARL and XSTUR into Eq. (2-64).

Although EXAMS does not evaluate the orientation of the dispersive exchange pathways, the program does adjust its computations according to the nature (that is, the TYPE) of the exchanging compartments. These adjustments are primarily important for the exchanges across the benthic boundary layer, because of the very different physical properties of the water column and a sediment bed. In this case, a simple symmetric exchange of environmental volumes would transport very different sediment masses and volumes of water. EXAMS allows for the possibility of biogenic production and decay of detrital sedimentary materials, and thus generally does not impose explicit internal mass-balance constraints on the transport of sediments in the system. In this case, however, the massive injection of bed sediments into the water column, with little or no resettlement, would amount to a gross distortion of sediment transport dynamics beyond the realm of biogenic possibility. The simple dispersion equation (2-64) thus requires situational adjustments. EXAMS therefore divides its dispersion computations into 3 distinct cases: (1) dispersion between water column compartments, (2) dispersion between benthic compartments, and (3) dispersion between a benthic sediment and the overlying water column.

2.3.1.4.1 Dispersion within the water column

The volumetric displacement of suspended sediments can almost always be neglected, so the water volumes and environmental volumes of water column compartments can be assumed not to differ. For example, a 15,000 mg/L washload with a density of 1.5 g/cc would perturb this assumption by only 1%. EXAMS therefore computes the exchange flow of water between water-column compartments (in liters/hour) as:

$$FLOW = \frac{1000(DSP)(XSTUR)}{CHARL} \qquad (2\text{-}65)$$

This value is added to the advective flows already in WATFL(I,J) and WATFL(J,I). (I is the compartment number held in ITURB; J is the compartment number held in JTURB.) The dispersive exchange is equivalent to a symmetric pair of advected (pseudo) flows between the compartments. If FLOW is a boundary condition, it is added to WATOUL(J), where J is the compartment number held by the non-zero member of the (JTURB, ITURB) couple.

The SEDFL matrix is updated via

SEDFL(I,J) ← SEDFL(I,J) + (FLOW)×(SEDCOL(J)) and

SEDFL(J,I) ← SEDFL(J,I) + (FLOW)×(SEDCOL(I));

the SEDOUL vector is updated via

SEDOUL(J) ← SEDOUL(J) + (FLOW)×(SEDCOL(J))

(SEDCOL is the sediment/water ratio, Eq. (2-22)). In this case, sediment mass need not be conserved. When the exchanging compartments have differing concentrations of suspended sediments, EXAMS permits a net flow of sediments along the concentration gradient. EXAMS assumes that biogenic production and decay of detrital materials within the compartments serves to maintain the gradient.

EXAMS computes lateral, vertical, and horizontal dispersion via this procedure. The equations thus account for several rather different processes. The effects of shear flow in rivers are

computed via a "longitudinal dispersion coefficient." Depending upon the geometry and slope of the channel, riverine longitudinal dispersion coefficients can vary from 2700 (Yuma Mesa A Canal (Schuster 1965)) to 5.4×10^6 (Missouri River near Blair, Nebraska; (Yotsukura et al. 1970)) square meters per hour (cited from Fischer et al. 1979:126). Some small lakes develop nearly uniform vertical density gradients that inhibit vertical exchange, while allowing rapid lateral dispersion, at all depths in the lake. Usually, however, the most important barrier to vertical transport in lakes is a localized region (the thermocline or metalimnion) with a steep temperature (density) gradient. The exchange of epilimnetic and hypolimnetic water masses is driven by wind-induced eddies, storm surges, and internal seiches (see, for example, Wetzel 1975:89-122). The net effect of these processes can usually be summarized via a dispersion equation. For example, Snodgrass (1977) used a "vertical diffusivity coefficient" to "integrate the effects of molecular diffusion, eddy diffusion, internal waves, seiches, standing waves, [and] hypolimnetic entrainment ... into a net transport process" across the thermocline of Lake Ontario. The average DSP during the stratified period (April to November) ranged from 1.0 to 4.1 square meters per day, over 6 years of measurements. A useful summary of the observed values of dispersion coefficients can be found in (Schnoor et al. 1987).

2.3.1.4.2 Dispersion within the bottom sediments

In some cases, exchanges among benthic compartments require adjustment for strongly differing properties of the exchanging segments. The surficial sediments of Noname Slough (**Figure 4**) are laterally homogeneous, for example, but the deeper sandy layer (compartment 9) differs substantially from the surficial layers in bulk density, water content, and organic carbon content. The sediment/water ratios of these layers can be compared by inserting their water contents (PCTWA) into Eq. (2-22). In the surficial sediments, the given water content is 180%, and SEDCOL = 1.25 kg sediment per liter of water. The sandy layer has a water content of 115%; its SEDCOL (6.67 kg/liter) is 5 times that of the surficial layers. Dispersion between benthic compartments therefore must allow for exchanges between segments of very different physical properties.

Furthermore, the water volume and the environmental volume of a benthic sediment are by no means the same. The surficial sediments of Noname Slough, to continue the example, have a given bulk density of 1.2 g/cc. The volumetric (liter/liter) water content ("porosity") can be computed via Eq. (2-21); the surficial sediments contain only 0.53 liters of water per liter of environmental volume. The porosity of the sandy layer (bulk density 1.95 g/cc) is only 0.25 L/L. Equation(2-65) thus cannot be used for a direct computation of dispersive transport of a synthetic chemical between benthic sediment compartments.

The distribution of chemicals within lacustrine and marine sediments has been successfully modeled via a vertical one-dimensional treatment of transport and chemical dynamics in this subsystem (Berner 1976, Imboden and Lerman 1978, Jones and Bowser 1978). These one-dimensional ("diagenetic") equations include the usual dispersive, advective, and reaction terms. The advective terms in these equations are often used to describe the net deposition of sedimentary materials, and the effective vertical flow of interstitial waters produced by compaction of the deposits. EXAMS precludes deposition and permanent burial of synthetic organic chemicals as inappropriate to an evaluative model, so its advective terms (Chapter 2.3.1.3) represent ground-water flows and, where appropriate, irrigation of benthic deposits by burrowing organisms.

The activities of burrowing organisms (bioturbation), physical disturbance by demersal fishes, and intermittent strong water turbulence tend to physically mix solids deposited on the sediment surface to appreciable depths. These actively mixed zones generally extend from about 2, to as deep as 50, centimeters in natural systems (Jones and Bowser 1978 and references therein). This physical reworking modifies observed concentration profiles in sediments, and has led Schink and Guinasso (1977) to propose the use of explicit solids mixing terms in the one-dimensional treatment of early diagenesis in sediments.

EXAMS makes use of a compartmentalized realization of these one-dimensional equations, but does not permit explicit mixing of sediment solids between benthic compartments. The depth of the sediment compartments used to describe a system is taken to be a depth through which the sediment can be regarded as "well-mixed." The mixing of solids is thus implicitly incorporated into the specifications of the structure of the system, rather than as direct terms in the simulation equations. In effect, therefore, EXAMS assumes that vertical concentration gradients within the benthic compartments do not greatly disturb the results of its evaluations.

There is some experimental evidence that the speed of internal mixing processes in surficial sediments is sufficiently rapid to justify EXAMS' discretized treatment. For example, McCall and Fisher ((1977), quoted from (Jones and Bowser 1978)) have shown that typical population densities of tubificid oligochaetes can completely rework the top 5 cm of sediments every 2 weeks in a laboratory setting. Vanderborght and Wollast (1977) found that the upper 3 cm of marine (North Sea) sediments exhibited an internal dispersion coefficient of 1×10^{-4} cm^2/s; this value implies a reworking time of only 25 hours.

When a dispersion term (lateral or vertical) is specified for exchange between benthic compartments, EXAMS computes a symmetrical exchange of water (only) between the compartments. This exchange flow is used to update the WATFL matrix. Generally the input dispersion coefficient in

such a case should be corrected only for tortuosity; the program itself corrects for the average porosity of the 2 compartments involved, and for sorption of the chemical to solid phases. EXAMS imposes no limitations on the magnitude of DSP. Irrigation of deep sediment zones by burrowing organisms can thus be represented via dispersion terms, if desired. A boundary condition for a bottom sediment compartment is computed in much the same way, except, of course, the porosity of the specified compartment is the only datum available for correction of the nominal DSP.

2.3.1.4.3 Exchanges between bed sediments and overlying waters

Capture of organic chemicals by sediment beds can occur via several processes. A dissolved phase can sorb directly to the surface of the bed, with the sorbed material being then subducted into the bed via bioturbation. Irrigation of the sediments by tube-dwelling animals can directly entrain a flow of contaminated water through the bed; the sediment solids will then tend to strip chemical from the water flow. Filter-feeding organisms can aggregate compounds sorbed with suspended fine particles and add material to the bed, as may the sequential deposition, internal mixing, and scour events characteristic of riverine systems. In lakes and oceans, sediment "bursting" (Heathershaw 1974) results in frequent saltation of bed solids, leading to sorption/desorption events and entrapment of free boundary waters in the redeposited sediment matrix.

Although direct sorption/desorption to the sediment surface is a continuous process, many of the interactions between the water column and benthic sediments are highly intermittent. For example, Heathershaw (1976) has estimated that, in well-mixed areas of the Irish Sea, as much as 70% of the Reynolds stress in the benthic boundary layer results from events occupying only 5% of the total time of record. Interactions mediated by the biota are presumably also intermittent and highly variable in their intensity. The most practical and efficient means of representing this array of interactions between the water column and benthic sediments is to use a statistical summary of their macro-scale effects, that is, a dispersion equation (Berner 1976). This strategy was adopted for EXAMS.

A dispersive exchange between a water column (L, E, or H) and a benthic (B) compartment is described to EXAMS via specification of a characteristic length (CHARL), cross-sectional area (XSTUR), and dispersion coefficient (DSP) for the water column–benthic element exchange pathway. The volumetric exchange given by FLOW (Eq.(2-65)) can be regarded (heuristically) as the saltation of a unit volume of the bed (containing water and solids), followed by equilibration with the water column and resettlement on the bed. EXAMS thus separates the rate of exchange of environmental volume given by (DSP)(XSTUR)/(CHARL) into distinct water and solids exchange components. The porosity of the benthic sediment is coupled to the dispersion equation to give a water-exchange term, via the expression:

$$\frac{WATVOL}{VOL} \times \frac{(DSP) \times (XSTUR)}{CHARL}$$

This water flow term (units of liters/hour) is then used to update symmetric locations in the WATFL matrix, giving an apparent rate of exchange of fluids between the water column and the interstitial pore waters of the benthic sediment compartment. Chemical transport can then be computed by treating these water flows as simple carriers for the dissolved fraction resident on either side of the benthic boundary layer.

In some cases, exchanges across the benthic boundary layer can be treated as being driven by gradients in dissolved chemical concentrations alone. Many synthetic organic chemicals, however, have very high partition coefficients, so that sorption onto the surface of the bed followed by bioturbational subduction is probably a significant mechanism of chemical transport for these compounds. The remaining exchange volume is therefore taken to represent a direct interaction of the bed solids with the water column compartment. First, an apparent "resuspension" or "bursting" term for the exposure of the bed solids to the water column is computed as the product of the sediment:water ratio (SEDCOL) of the benthic zone and the fluid exchange rate. The SEDFL matrix is thus updated by an apparent flow of bed sediments (TEMSED, units kilogram/hour) into the water column via the expression:

$$TEMSED = SEDCOL \times \frac{WATVOL}{VOL} \times \frac{(DSP)(XSTUR)}{CHARL} \qquad (2\text{-}66)$$

A naive "solids balance" now requires that an equal mass of sediment resettle on the bed, in order to maintain the notion of a stable (steady-state) bed thickness. The transport of a chemical across the benthic boundary layer could then be computed by regarding the solid phase as a simple carrier of sorbed chemicals, using sorbed concentrations (mg/kg solids) on either side of the boundary.

The foregoing is, for the most part, conventional compartment modeling. Still, because a multitude of processes have been summarized in a single kinetic expression, a careful independent trial of the approach seemed warranted. Although a number of experimental tests of the equations can be imagined, initial tests were conducted by comparing the output from the EXAMS program to a example situation constructed on theoretical grounds alone. This test was conducted on a reduced

subsystem of the Noname Slough ecosystem. Consider, for example, the vertical segment of Noname Slough that includes a 2 m water column underlain by a 5 cm mud deposit and a 30 cm layer of sand (**Figure 4**). If the transport characteristics of this subsystem are redefined to eliminate the bedload and groundwater infiltration, the dispersion equation can be used to describe vertical movement of a chemical in the subsystem.

Retaining the physical sediment characteristics (BULKD, PCTWA) developed in Chapter 2.3.1.3, the sorptive properties of the sediments must now also be specified. For the example, let the organic carbon content of the washload be 2% (FROC = 0.02), that of the mud layer 5%, and let the sand contain only 0.1% organic carbon. The characteristic length (CHARL) and exchange cross section (XSTUR) for the dispersive exchanges can in this instance be developed directly from the geometry of the system. These values, along with the kinetic exchange coefficients (DSP) are given in Exams Output Table 5. Vanderborght and Wollast (1977), working with rhodamine dye in North Sea sediments, found that physical turbulence induced benthic boundary layer exchange coefficients of 2.9×10^{-6} to $6.2\times^{-4}$ cm^2/s. The test DSP for Noname Slough were selected from this range of values.

```
Name of environment: Noname Slough - Dispersion Equation Test Data
Total number of segments (KOUNT) =   9
Segment Number:   1   2   3   4   5   6   7   8   9
Segment "TYPE":   L   B   L   B   L   B   L   B   B
-------------------------------------------------------------
Table 10.13.  Mean dispersive transport field.
-------------------------------------------------------------

J TURB            7         8
I TURB            8         9
XS TUR m2     1.000E+03 1.000E+03
CHARL m        1.02     0.175
DSP m2/hr*    1.500E-04 3.600E-05
 Path No.:        1         2
-------------------------------------------------------------
* Average of 12 monthly mean values.
```

Exams Output Table 5. Dispersive interconnections – test data.

In order to test the dispersive transport algorithm in isolation, the test chemical can be specified as a completely unreactive, non-volatile neutral compound, with a Koc of 3×10^5.

When the test chemical is introduced into the system, an equilibrium state could be rapidly generated by suspending the benthic layers in the water column, and thoroughly agitating the mixture. At equilibrium, this 4-phase system would exhibit a single aqueous concentration, and sorbed-phase concentrations differing as the ratio of their partition coefficients (i.e., in proportion with the organic carbon contents of the sediment phases). If the bed solids were then allowed to resettle, the simple separation of the materials would not result in any change in the dissolved (mg/L of water) or sorbed (mg/kg dry solids) concentrations. The environmental concentrations (mg/L of total environmental volume) could, of course, differ between the water column and the (restored) bed layers.

This situation also applies to an open system in a dynamic equilibrium or steady state. Suppose, for example, that water contaminated to a level of 1 µg/L (ppb) with the test chemical flows continuously through the Noname Slough subsystem. The dispersion equation controls only the rate of exchange of chemical between the water column and the benthic subsystem. At steady state, no concentration gradient remains to drive further net chemical exchange. In this instance of an unreactive compound, the final dynamic equilibrium is equivalent to the static case.

The resulting computer output is shown in Exams Output Table 6. The computations lead to a steady-state end point of equal *sorbed* concentrations for the washload and the mud layer, rather than equal *dissolved* concentrations. Although the concentration distribution between the bed sand and mud layers follows the theoretical expectations, this result for the washload and the mud layer is exactly opposite the expected outcome of the test.

```
CHEMICAL: Unreactive neutral compound -- Koc = 3.E5
ECOSYSTEM: Noname Slough -- Dispersion equation test data
-----------------------------------------------------------------------
DISTRIBUTION OF CHEMICAL AT STEADY STATE: IN THE WATER COLUMN:
-----------------------------------------------------------------------
COMP STEADY-STATE RESIDENT MASS     **** TOXICANT CONCENTRATIONS ****
        2                          TOTAL   DISSOLVED SEDIMENTS   BIOTA
     G/M       KILOS        %       MG/*     MG/L      MG/KG      UG/G
--- ------    ------     ------  --------- --------- --------- ---------
  1 2.000E-03 2.0001E-03 100.00  1.000E-03 6.250E-04  3.75
 SUBTOTAL:    2.0001E-03   1.21
 AND IN THE BOTTOM SEDIMENTS:
  2 0.125     0.1250      76.61   3.75     2.500E-04  3.75
  3 3.818E-02 3.8176E-02  23.39  7.505E-02 2.500E-04 7.501E-02
 SUBTOTAL:    0.1632      98.79
TOTAL MASS (KILOGRAMS) =    0.1652
-----------------------------------------------------------------------
* TOTAL CONCENTRATION AS MG/L IN WATER COLUMN, AS MG/KG IN SEDIMENTS.
```

Exams Output Table 6. Test of dispersive exchange equation.

Although the computed outcome could be rationalized in many ways, the fact remains that the program output did not reflect the assumptions and reasoning used to build the model; a naive "sediment balance" failed to provide an accurate simulation of chemical behavior and thus required revision.

Closer consideration of the heuristic logical structure used to adapt the dispersion equation to this application suggested an appropriate revision. At least nominally, in the case under consideration the suspended and bedded solids need never even come in contact, so there is no plausible way for sorbed chemical to experience a direct concentration gradient. The

capture of chemical by the bed is driven by fluid exchange, and by saltation of the bed solids, which allows them to interact directly with chemical dissolved in the water column. The root of the problem thus seems to lie with the difference in organic carbon content (i.e., partition coefficient) of the suspended and bedded sediments.

The sorbed concentrations computed for each compartment are based on properties of the sediments specified for the compartment, rather than on the properties of a saltatory transient. Therefore, it might serve the case to simply adjust chemical transport according to the ratio of the partition coefficients (Kp). In this way, for example, if the Kp of the bed sediment were 5 times that of the suspended sediment, the rate of capture of chemical by the bed would be proportionally larger than that suggested by Eq. (2-66) simply coupled to the concentration on the washload, and conversely.

Although organic carbon content governs the ability of a sediment to sorb neutral (uncharged) molecules, an organic acid or base will occur as both neutral and charged species, with a speciation governed by the pH of the system. The sorptive capacity of a sediment may thus depend on its carbon content, ion exchange capacity, and the pH of the compartment. Thus when necessary, the relative sorptive capacity of sediment phases can be computed via the distribution coefficients (α) and sediment:water ratios (SEDCOL) of the water-column and benthic compartments specified for an exchange pathway. Given $\alpha(d,w)$ and $\alpha(d,b)$ as the total dissolved fraction in the water column (w) and benthic (b) compartments, respectively, and $\alpha(s,w)$ and $\alpha(s,b)$ as the sediment-sorbed fractions, the return "flow" (SEDFL) of suspended sediment across the benthic boundary layer to the sediment compartment can be computed as:

$$TEMSED \times \frac{\alpha(d,w) \times SEDCOL(w)}{\alpha(s,w)} \times \frac{\alpha(s,b)}{\alpha(d,b) \times SEDCOL(b)}$$

This calculation yields the ratio of the sorptive capacity (overall partition coefficient, Kp) of the benthic sediment, to that of the washload. Thus for example, if the benthic sediments have a Kp twice that of the washload, the rate of capture of chemical by the bed (that is, the apparent pseudo-settlement rate of saltatory bed materials) must occur at twice the rate that would be inferred directly from the properties of the washload itself.

The effect of this revision can now be tested by execution of the test case described above; the results are given in Exams Output Table 7. The consequences of the calculation are now quite satisfactory: The calculated dissolved concentrations are uniformly 0.625 ppb, and the sorbed concentrations reflect the differences in organic carbon content of the system sediments. Note, however, that this computation is valid within the context of the EXAMS program only because sediment transport is not an explicit state variable in the program, i.e., the SEDFL matrix is not a description of sediment transport per se, but merely a computational device for computing the exchange of synthetic organic chemicals across the benthic boundary layer. "Solids balances" and stable bed thicknesses are the responsibility of the user when assembling an environmental description to drive the program; EXAMS simply processes these data (via the SEDFL matrix) to arrive at a proper characterization of chemical transport in the system.

```
CHEMICAL: Unreactive neutral compound -- Koc = 3.E5
ECOSYSTEM: Noname Slough -- Dispersion equation test data
-----------------------------------------------------------------------
DISTRIBUTION OF CHEMICAL AT STEADY STATE: IN THE WATER COLUMN:
-----------------------------------------------------------------------
COMP STEADY-STATE RESIDENT MASS    **** TOXICANT CONCENTRATIONS ****
        2                          TOTAL   DISSOLVED SEDIMENTS   BIOTA
     G/M       KILOS        %      MG/*     MG/L      MG/KG      UG/G
--- ------    ------     ------  --------- --------- --------- ---------
  7 2.000E-03 2.0000E-03 100.00  1.000E-03 6.250E-04  3.75
 SUBTOTAL:    2.0000E-03   0.49
 AND IN THE BOTTOM SEDIMENTS:
  8 0.313     0.3125      76.61   9.38     6.250E-04  9.38
  9 9.543E-02 9.5428E-02  23.39  0.188     6.250E-04 0.188
 SUBTOTAL:    0.4079      99.51
TOTAL MASS (KILOGRAMS) =    0.4099
-----------------------------------------------------------------------
* TOTAL CONCENTRATION AS MG/L IN WATER COLUMN, AS MG/KG IN SEDIMENTS.
```

Exams Output Table 7. Test of modified dispersive exchange procedure.

2.3.1.5 Transport of synthetic organic chemicals

EXAMS uses the transport field defined by WATFL, SEDFL, WATOUL, and SEDOUL to compute first-order coefficients that describe transport of chemical through the ecosystem. These coefficients describe the export of chemicals from the system, and the internal transport of the compound among the compartments used to define different physical sectors of the system.

The WATOUL and SEDOUL vectors are used to compute exports from each compartment. A value of EXAMS' internal vector EXPOKL, with dimensions of (liters/hour), is calculated for each compartment as

$$EXPOKL = (\alpha(29)+\alpha(31)+\alpha(32)) \times WATOUL + \alpha(30) \times SEDOUL/SEDCOL$$

where $\alpha(29)$, (30), (31), and (32) are the total fractions of the chemical in dissolved, sediment-sorbed, DOC-complexed, and planktonic biosorbed states, respectively.

Pollutants also leave each compartment via water and sediment flow pathways that connect the compartment to other sectors of the ecosystem. From the perspective of the donor compartment, these flows can be represented as a pure export of chemical across the boundaries of the compartment, despite the fact that the material may be returned from the receptor compartment at some later time. Each row of the WATFL and SEDFL matrices

gives the flows of water and sediments leaving a compartment, and the row sums are the total local (that is, within-system) outflows from the compartments. For each compartment, EXAMS computes a value of an internal variable (INTOUL, liters/hour) analogous to the export vector EXPOKL. This computation can be represented as

$$INTOUL = (\alpha(29)+\alpha(31)+\alpha(32)) \times SUMWAT + \alpha(30) \times SUMSED/SEDCOL$$

where SUMWAT and SUMSED are the appropriate row sums in the WATFL and SEDFL matrices, and SEDCOL is the sediment:water ratio for the donor compartment.

These transport terms (EXPOKL and INTOUL) must now be converted to pseudo-first-order coefficients that express their effect on the concentration of chemical in the source (donor) compartment. This coefficient (CONOUL, dimensions /hour) is computed as:

$$CONOUL = (EXPOKL + INTOUL)/WATVOL$$

where WATVOL is the volume of water (liters) present in the donor compartment. This coefficient (CONOUL) is the contribution of transport processes to the overall loss constant "K" of Eq. (2-1).

Intra-system transport also imposes chemical loadings on the compartments receiving the contaminated flows (factor "Li" in Eq. (2-1)). EXAMS combines the WATFL and SEDFL matrices into a new matrix (INTINL, dimensions liters/hour) needed for computing the internal loadings (Li) on each compartment. Each element of INTINL is first calculated from the sum of corresponding elements in WATFL and SEDFL via the expression:

$$(\alpha(29)+\alpha(31)+\alpha(32)) \times WATFL + \alpha(30) \times SEDFL/SEDCOL$$

using values of α, and SEDCOL for the donor compartment.

Multiplication of each element of INTINL in a given row, by the concentration of chemical in the donor compartment given by the successive column indices of the row, yields the magnitude of the loadings passed to the receptor compartment by each of the donors. The sum of these loadings is the internal load (Li, mg/h) on the receiving compartment. Li must also be divided by the aqueous volume of the receptor (*V* in Eq. (2-1)), in order to express the effect of the internal loadings on the concentration of chemicals in the receptor. EXAMS therefore divides each element of INTINL by the volume of the receiving compartment:

$$INTINL \leftarrow INTINL/WATVOL$$

and retains the resulting matrix of pseudo-first-order (dimensions /h) coefficients for subsequent use in its steady-state and kinetic simulation equations (Chapter 2.5).

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2.3.2 Volatilization

EXAMS uses a two-resistance model to compute transport across the air-water interface. EXAMS calculates the rate of interphase transport by computing the sequential resistance to movement through an aqueous and a gaseous "film" at the air-water interface. Although originally developed for industrial applications (Whitman 1923), these models have been adapted to environmental problems (Liss 1973, Liss and Slater 1974, Mackay and Leinonen 1975, Mackay 1978, Burns 1982, 1985). Whitman (1923) visualized the aquatic interface as "stagnant films" of air and water, bounded by well-mixed bulk phases on either side of the interface. **Figure 6** illustrates the conceptual model of chemical transport across the air-water interface.

Specifically, in **Figure 6**, C_l is the concentration of contaminant (mol·m^{-3}) in the bulk water phase; P_g is its partial pressure (atmospheres) in the bulk air above the interface; C_{sl} is its aqueous concentration at the interface; and P_{sg} is its partial

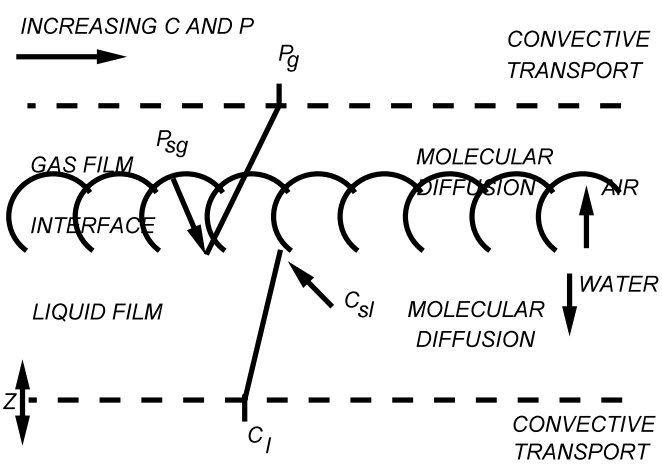

Figure 6. Whitman (1923) two-resistance or two-film model of a gas-liquid interface (after Liss and Slater 1974).

pressure on the atmospheric side of the interface. The flux of compound F (mol·m^{-2}·h^{-1}) through the aqueous film can be described using Fick's first law

$$F = D\frac{dC}{dZ} \qquad (2\text{-}67)$$

where D is the aqueous diffusion constant of the chemical in the film (m^2·h^{-1}), C is the concentration of unionized, unsorbed compound (mol·m^{-3}), and dC/dZ is the concentration gradient in the film.

Similarly, the flux of chemical through the stagnant atmospheric layer is

$$F = \frac{D}{RT}\frac{dP}{dZ} \qquad (2\text{-}68)$$

where D is now the diffusion constant of the compound in the air layer, dP/dZ is the partial pressure (atmospheres) gradient in the film, R is the gas constant (8.206×10^{-5} m^3-atm/mol-K), and T is Kelvin temperature.

Environmental gas exchange processes are often formulated in terms of an *exchange constant "k"*, that is, as a *conductivity* (the inverse of the film transport *resistance*). The exchange constant has dimensions of velocity (m·h^{-1}); it is also known as the "mass transfer coefficient," "permeability coefficient," "adsorption/exit coefficient," and "piston velocity." The flux of gas F through the stagnant layers is then

$$F_l = k_l\, dC \qquad (2\text{-}69)$$

in the ***l***iquid phase, and

$$F_g = k_g\frac{dP}{RT} \qquad (2\text{-}70)$$

in the ***g***as phase, where dC is the concentration difference across the film, dP is the partial pressure difference across the film, and $k_{(\cdot)} = D_{(\cdot)}/z_{(\cdot)}$, $z_{(\cdot)}$ the film thicknesses. The reciprocals ® = k^{-1}) of the exchange constants give the transport resistances r of the aquatic and atmospheric films.

Given negligible dynamic storage capacity in the films and consequent steady-state transport of gas through the interface[1], the mass fluxes through the stagnant layers of air and water (see **Figure 6**) must be the same. Therefore, $F_l \equiv F_g$, and we can set (2-69) equal to (2-70) and substitute the concentration differences (**Figure 6**), obtaining

$$k_l(C_{sl} - C_l) = \frac{k_g}{RT}(P_g - P_{sg}) \qquad (2\text{-}71)$$

where k_l is the liquid phase, and k_g the gas phase, exchange coefficient. The partitioning of the exchanging (unionized) substance across the air-water interface is given by Henry's Law: $P_{sg} = H\ C_{sl}$, where H is the Henry's Law constant (atm-m^3/mol). Using Henry's Law, C_{sl} and P_{sg} can be eliminated from (2-71), yielding an equation relating the transport flux F to the bulk phase concentrations only:

$$F = K_l\left(\frac{P_g}{H} - C_l\right) \qquad (2\text{-}72)$$

where K_l, the transport conductance, is defined by

$$\frac{1}{K_l} = \frac{1}{k_l} + \frac{RT}{Hk_g} \qquad (2\text{-}73)$$

The total resistance to transfer of a gas across the air-water interface ($R_l = K_l^{-1}$) is thus the sum of the series of resistances in the liquid (k_l^{-1}) and gas ($RT/(H\,k_g)$) phases of the interface. The two-resistance model assumes that transport resistance *at* the interface can be neglected; although generally this is the case, under very turbulent conditions or in the presence of surface-active contaminants (surfactants) this assumption is less tenable (Bird et al. 1960:652)).

The "two-film" picture of the air-water interface (**Figure 6**) is physically inexact, although events at molecular scales undoubtedly affect interphase transport. Both atmospheric and hydrodynamic eddy turbulence often extend to the air-water interface, however, so the idea of a discontinuous transition from turbulent flow to a stagnant film near the air-water interface cannot be seriously entertained. The supposition that the interface is composed of stable, uniform films is still less plausible. The two-resistance models do, however, explicitly recognize that transport resistance occurs both in the aqueous and in the atmospheric regions of the air-water interface. There is ample precedent (see, for example, Fischer et al. 1979) for amalgamating the effects of intermittent turbulent and advective transport events occurring in the interfacial zone, into an empirical dispersion coefficient D or exchange constant k. Furthermore, predictions derived from two-resistance models usually differ very little from the predictions of more complex (e.g., surface-renewal theory) models (Danckwerts 1970). Laboratory studies of the volatilization of chlorohydrocarbons from dilute aqueous solution (Dilling et al. 1975, Dilling 1977) have provided further evidence that two-resistance models are good predictors of fluxes of organic chemicals across the air-water interface.

A two-resistance model has been used to compute the transport of atmospheric contaminants (sulfur dioxide, carbon tetrachloride, *etc.*) into the world ocean (Liss and Slater 1974). Such an application requires a knowledge of P_g, the bulk atmospheric partial pressure. Lacking a measured value of P_g, it can in some circumstances (general circulation models of the atmosphere, plume (stack gases) dispersion models) be calculated and coupled to a two-resistance interphase transport model. Usually, however, bulk atmospheric transport of synthetic organics volatilized from aquatic systems rapidly removes them from the vicinity of the interface, so that P_g can be neglected (Mackay and Leinonen 1975, Mackay 1978). This approach was adopted for EXAMS, resulting in a simplification of (2-71), yielding

$$F = -K_l C_l \qquad (2\text{-}74)$$

Because EXAMS was designed, among other things, for pre-manufacture evaluation of new chemicals and pesticides, there was, in any case, little likelihood that measured values of P_g would be readily available for use in the model. EXAMS does not entirely preclude atmospheric inputs, however. EXAMS' loading functions allow for entry of spray drift (DRFLD), and for rain-out (PCPLD) loadings, where these can be computed.

For use in EXAMS, (2-74) must be rephrased to give the effect of volatilization on the concentration of pollutant in each sector of the ecosystem (compartment, segment) having an air-water interface. EXAMS' concentration variable *[C]* is the total concentration of pollutant in units of mg/Liter of aqueous volume. Multiplication of both sides of (2-74) by *MWT A/V*, where *MWT* is the gram molecular weight of the compound, *A* is the area of the air-water interface (square meters), and *V* is the volume (m^3) of the compartment, gives

$$\frac{d[C]}{dt} = -K_l\,\frac{A}{V}\,\alpha_1[C] \qquad (2\text{-}75)$$

The factor α_1 is the fraction of the total pollutant concentration [*C*] present as a volatilizable (unionized, unsorbed) chemical species. The group $K_l A \alpha_1 / V$ is a pseudo-first-order rate constant with units h^{-1}. This rate constant is computed by EXAMS in a specific module, and the volatilization contribution is then added to the total pseudo-first-order rate constants used internally by EXAMS to simulate pollutant dynamics within environmentally stable time segments.

[1] Note that this is a *microscopic*, rather than a *macroscopic*, assumption--that is, these extremely thin interfacial films are merely assumed to maintain a rapid equilibrium with the adjacent, themselves fully dynamic, bulk layers.

EXAMS' two-resistance model reduces at this point to a computation of the transport resistances (or exchange constants) of chemical pollutants in the liquid (k_l^{-1}) and atmospheric ($RT/(H\ k_g)$) zones of the air-water interface. These transport resistances are governed by the intensity and duration of physical turbulence and convective motions in the interface zones. Expanding upon a suggestion of Liss and Slater (1974), EXAMS indexes the transport resistance of chemical pollutants against the exchange properties of well-studied environmental substances: oxygen and water vapor.

The transport of oxygen across the air-water interface of aquatic systems (reaeration) has been studied for many years. Oxygen transport is controlled by resistance in the liquid phase (Liss 1973). The exchange constant for dissolved oxygen thus provides a measure of turbulence on the *liquid* side of the air-water interface. Water itself, as the solvent for chemical pollutants in aquatic systems, has no transport resistance in the liquid phase of the interface: its transport is controlled by events in the *atmospheric* zone of the interface.

Given exchange constants for oxygen and for water vapor (note that the latter is not the same as the evaporation rate), it remains to index the transport resistances of the pollutant to those of the environmental referents. Several indexing methods have been proposed. Kinetic theory suggests that the ensemble molecular kinetic energies *KE* of all chemicals present in a given zone of the interface are the same, and thus, as $KE = \frac{1}{2}mv^2$, that average molecular velocities in a multi-component mixture must be distributed in proportion to the square root of the molecular weights of the components.

EXAMS uses this method for relating the exchange constant for water vapor to the vapor-phase volatilization resistance of pollutants. The temperature of the vapor film is assumed to be the same as the water temperature specified for the appropriate aquatic compartment. EXAMS thus computes the vapor-phase transport resistance R_g from the equation

$$R_g = \frac{RT}{V_w H \sqrt{18 / MWT}} \qquad (2\text{-}76)$$

where T is Kelvin temperature, V_w is the water vapor exchange constant (piston velocity, m $\cdot h^{-1}$), H the Henry's Law constant, the molecular weight of water is taken as 18 g/mol, and *MWT* is the molecular weight of the volatilizing chemical.

To arrive at the total transport resistance, we must also compute the liquid-phase resistance in the interface zone. Reasoning from the Stokes-Einstein equation, Tsivoglou (1967) suggested that the (liquid-phase dominated) exchange constants for molecular oxygen *vs.* the normal atmospheric gases (Kr, Ra, He, *etc.*) are linearly related to their relative molecular diameters or, equivalently, their molecular diffusion constants in water. A literal interpretation of the Whitman "two-film" derivation gives much the same result. In contrast, models based on surface-renewal theories suggest that relative exchange constants should vary as the square root of diffusivities (Danckwerts 1970:100). Dobbins (1964) constructed an elegant hybrid of film and surface-renewal theory that collapses to a Whitman model under quiescent conditions, and to a surface-renewal model under more turbulent conditions. He also found, via laboratory studies, that the appropriate root of the diffusivity ratio for the nitrogen/helium gas pair tended from 0.985 to 0.648 with increasing water turbulence, as expected from his theoretical equations. Given the uncertainties in estimating or averaging oxygen exchange constants, however, a full development of the Dobbins model for inclusion in EXAMS has thus far seemed unwarranted.

The molecular diffusivity of a new organic chemical is not often known, although it can be estimated from other chemical properties (Reid et al. 1977). The molecular weight of an organic compound is almost always available, however, so EXAMS uses Liss and Slater's (1974) molecular weight corrector as its default technique for relating the liquid-phase transport resistance of a pollutant to exchange constants of dissolved oxygen (EXAMS input parameter *KO2*, a piston velocity for molecular oxygen). The liquid-phase transport resistance R_l is then simply

$$R_l = \frac{1}{K_{O_2} \sqrt{32 / MWT}} \qquad (2\text{-}77)$$

where K_{O2} is the oxygen (molecular weight 32) exchange constant.

The total transport resistance of the pollutant is the simple sum of the individual phase transport resistances, $R_l + R_g$. The exchange constant of the contaminant (K_l, the conductivity) is the reciprocal of that sum:

$$K_l = \frac{1}{R_l + R_g} \qquad (2\text{-}78)$$

Thus, EXAMS completes computation of the pseudo-first-order volatilization rate constant as $K_l \alpha_l A/V$.

2.3.2.1 Chemical Data Entry

The chemical parameters governing volatilization of a pollutant from aquatic systems can be entered into EXAMS' chemical data base in several ways. The gram molecular weight of the pollutant *MWT* (EXAMS parameter MWT) is required, for computation of the vapor-phase transport index (2-76). The Henry's Law constant (H, input parameter HENRY) can be loaded, however, either as a single value of HENRY (atm-m^3/mol), or as a function of temperature. When input parameter E_H (input datum EHEN) is loaded as a non-zero

value, EXAMS computes the Henry's Law constant at local temperatures T (TCEL) from the relationship

$$\log H = H - \frac{1000 E_H}{4.58(T + 273.15)} \quad (2\text{-}79)$$

When no data for the Henry's Law constant is available at run time, but EXAMS detects the presence of a non-zero value of the vapor pressure of the contaminant, EXAMS internally computes the Henry's Law constant from the vapor pressure/solubility ratio (Mackay and Wolkoff 1973, Mackay and Leinonen 1975). If either the vapor pressure or the solubility of the compound have been entered as functions of temperature, these data are adjusted to local (TCEL) temperatures (via Eq. (2-80) and/or Eq. (2-81)), prior to computation of HENRY.

$$\log(VAPOR) = VAPR - [1000 \times EVPR] / [4.58(TCEL + 273.15)] \quad (2\text{-}80)$$

$$SOL = 1000 MWT \times 10^{[SOL - \{(1000 ESOL)/[4.58(TCEL + 273.15)]\}]} \quad (2\text{-}81)$$

Note that, although a simple (temperature invariant) pollutant solubility is entered in units of mg/L (ppm), EXAMS expects solubility as a function of temperature to be entered via the ideal solubility law, that is, as the dependence of molar solubility on temperature.

2.3.2.2 Exchange Constants for Water Vapor

The water vapor exchange constant (V_W, Eq. (2-76)) used to compute the vapor-phase transport resistance of pollutants is not itself a direct user input to EXAMS. Liss (1973), in a series of wind-tunnel experiments, found the piston velocity of water vapor to be a linear function of wind speed. EXAMS takes, as its user input variable, the average wind speed at a height of 10 cm above the water surface (input variable WIND, m $\cdot s^{-1}$). The exchange constant for water vapor (V_W) is computed separately for each compartment from these data. Liss' results can be represented via a linear regression equation that includes the shift in units from m $\cdot s^{-1}$ for wind speed to m $\cdot h^{-1}$ for the water vapor exchange constant

$$V_W = 0.1857 + 11.36 \times WIND \quad (2\text{-}82)$$

in which changes in wind velocity at 10 cm above the water surface (WIND) account for 98.3% of the variance in the exchange constant for water vapor (V_W, m $\cdot h^{-1}$) over a range of wind speeds (at 10 cm height) from 1.6 to 8.2 m $\cdot s^{-1}$.

Wind speeds observed at other heights can be converted to wind speed at 10 cm via the usual assumption of a logarithmic wind profile (Israelsen and Hansen 1962). Wind speeds U_1 and U_2 at heights Z_1 and Z_2 are related by

$$U_1 / U_2 = \log(Z_1/Zo) / \log(Z_2/Zo)$$

where Zo is the "effective roughness height." The roughness height is generally on the order of millimeters; wind measurement heights can conveniently be expressed in mm in order to achieve a vertical translation of an observed wind speed datum. For example, many terrestrial USA weather stations measure wind speeds at 18-20 feet (6 m) above ground level. Wind speed at 10 cm can be estimated by multiplication of this datum by (log 100)/(log 6000), that is, by reducing the observation by a factor of 1.89. The standard observational height for wind speed data in oceanographic investigations is 10 m, in this case requiring reduction of the data by a factor of 2, to generate values of WIND for EXAMS. Wind speeds read by EXAMS from a PRZM meteorological file are automatically translated to 10 cm height.

2.3.2.3 Exchange Constants for Molecular Oxygen

Hydrodynamic turbulence near the air-water interface is generated by a variety of mechanisms. In swiftly flowing streams and rivers, bed shear stress on the moving waters generates eddy turbulence that can keep the entire water column in a state of constant agitation. Where rivers widen into coastal estuaries, advection velocities decrease, but the motion of the tides tends to maintain strong turbulence in the surface waters. In lakes and in the open ocean, wind stress is a primary force producing turbulent motions in the upper part of the water column. Wind waves travel far beyond the storm systems producing them in the largest lakes and in the oceans, and the great ocean currents and upwelling zones generate upper water turbulence beyond that attributable to the winds alone. In smaller lakes, wind stress may be directly responsible for most of the hydrodynamic motion in the system.

EXAMS requires an oxygen exchange constant as an input datum for each compartment from which a pollutant can volatilize. The input datum (KO2, cm$\cdot h^{-1}$) is assumed to be the exchange constant measured at 20 °C, or corrected to that temperature. EXAMS uses the conventional engineering correction (equivalent to an Arrhenius expression) for converting KO2 to the temperature (TCEL) of each compartment (Kramer 1974)

$$KO2L = (KO2/100) \cdot 1.024^{(TCEL-20)} \quad (2\text{-}83)$$

(KO2 is also divided by 100 to convert cm$\cdot h^{-1}$ to m $\cdot h^{-1}$).

Reaeration rates can be measured in the field in a number of ways, including tracer techniques (Tsivoglou et al. 1972) and oxygen release into a nitrogen-sparged dome (Copeland and Duffer 1964, Hall 1970). Lacking measured values, oxygen exchange constants can in many instances be estimated from other properties of the system. Kramer (1974) has briefly reviewed the available predictive equations for estimating oxygen exchange coefficients in streams and rivers. Most of these contain terms for flow velocities and depth. Many also include longitudinal dispersion coefficients, energy grade lines,

and channel widths. Although predictive equations have been successfully used for riverine systems, generally these equations significantly under-predict reaeration in estuarine systems. Oxygen exchange constants in rivers are generally on the order of 5 to 20 cm·h^{-1}. In estuaries, exchange constants of 4 to 25 cm·h^{-1}, and as large as 100 cm·h^{-1}, have been observed. Liss and Slater (1974) estimated an average exchange constant for the open sea of 20 cm·h^{-1}.

In the more quiescent waters of lakes and ponds, reaeration may be primarily determined by the local winds. Banks (1975, Banks and Herrera 1977) showed that the effect of wind on reaeration rates can be separated into two distinct zones. At wind speeds (at 10 m height) less than about 5.5 m ·s^{-1}, exchange constants correlate with the square root of wind speed. At higher wind speeds, the exchange constant increases as the square of the wind velocity. Banks (1975) gives, for $U < 5.5$ m ·s^{-1},

$$KL = 4.19 \times 10^{-6} \sqrt{U} \qquad \text{(2-84)}$$

and, for 5.5 m ·s^{-1} ≤ $U < 30$ m ·s^{-1},

$$KL = 3.2 \times 10^{-7} U^2 \qquad \text{(2-85)}$$

where KL is the oxygen exchange constant (in m ·s^{-1}) and U is wind speed (m ·s^{-1}) at 10 m above the water surface. Over a range of wind speeds from 1 to 30 m ·s^{-1}, the oxygen exchange constant thus would change from 1.5 to 104 cm·h^{-1}. When the oxygen piston velocity is not entered, EXAMS uses Eq. (2-84) or Eq. (2-85) to calculate its value. Banks' equations are not temperature-specific; they were derived as an amalgam of studies at many temperatures. Exams takes the result of Banks' equations and adjusts for the ambient water temperature using (2-83)

2.3.2.4 Validation and Uncertainty Studies

A number of reports on volatilization from natural water bodies have been published. These studies provide good illustrations of the general utility and level of reliability of the two-resistance model developed for EXAMS.

2.3.2.4.1 Radon in small lakes in the Canadian Shield

Emerson (1975) conducted an experimental investigation of the loss of radon gas (Rn_{222}) from small lakes in Canada's Experimental Lakes Area (ELA). He reported his results in terms of exchange constants for Rn gas; the "best estimate" was 0.16 to 0.40 m/d. Average wind velocities, measured 1 m above the water surface, were about 1.5 m ·s^{-1}. Summer epilimnion temperatures in these lakes are about 20 °C (Schindler 1971). Wind speed and temperature suffice, given the Henry's Law constant for Rn, to derive an independent estimate of the Rn exchange constant from EXAMS' two-resistance model.

EXAMS computes both a gas- and liquid-phase transport resistance. Rn transport is usually controlled by the liquid-phase resistance. Under a sufficiently stagnant air mass, however, gas-phase resistance can be greatly magnified. In this instance, computation of the gas-phase resistance serves to illustrate EXAMS' procedure, and to demonstrate that Rn transport is controlled by events in the liquid phase of the air-water interface of these lakes.

Table 6. Rn Solubility

T°C	10^4X	10^2H
0	4.24	4.25
5	3.40	5.31
10	2.77	6.50
15	2.31	7.81
20	1.95	9.24
25	1.68	10.8
30	1.46	12.3
35	1.29	14.0
40	1.16	15.6
45	1.05	17.2
50	0.96	18.8

Wilhelm, Battino, and Wilcock (Wilhelm et al. 1977) give the aqueous solubility of radon gas as the mole fraction X under 1 atm partial pressure (**Table 6**). The Henry's Law constant (H, atm-m^3 mol^{-1}) of Rn gas between 0 and 50 °C can be computed from these data.

Regression of these data on the model H = A exp(-B/RT) where R is the gas constant (1.9872 cal/deg mole) and T is Kelvin temperature, yields A = 660.5 and B/R = 2615, accounting for 99% of the variation in the Henry's Law constant with temperature. EXAMS' input data thus could include HENRY = logA = 2.82, and EHEN = (B/R)×R×0.001 (kcal/cal) = 5.197 kcal/mol. EXAMS would then compute local (compartment-specific) values of the Henry's Law constant for radon, as a function of environmental temperatures (TCEL), via Eq. (2-79). In what follows, the Henry's Law constant at 20 °C will be taken as 0.09239 atm-m^3/mol.

A piston velocity for water vapor (V_W, Eq. (2-82)) can be computed from the observed wind speed (1.5 m ·s^{-1} at 1000 mm height). EXAMS' input (WIND) is referenced to a 10 cm height above the water surface. The observed wind speed can be corrected to a 10 cm height by assuming a logarithmic wind velocity profile, giving WIND=1.5 (log 100/log 1000)=1.0 m ·s^{-1}. The water vapor exchange constant (from Eq. (2-82)) is then V_W = 0.1857+(11.36)(1.0)=11.5 m ·h^{-1}, and the gas-phase transport resistance (R_g in Eq. (2-76)) is

$$R_g = \frac{293.15 \times 8.206 \times 10^{-5}}{11.5 \times 0.09239 \times \sqrt{18/222}} \qquad \text{(2-86)}$$

$$= 0.079 \text{ h·m}^{-1}$$

Emerson's (1975) investigations were conducted in small (3.6-5.6 ha), shallow (mean depth 3.6-5.6 m) dimictic lakes with relatively long hydraulic residence times (3.2-4.2 yr)

(Brunskill and Schindler 1971). The hydrodynamics of these lakes is clearly dominated by wind stress, and Banks' (1975) equations (Eqs.(2-84) and (2-85)) can be used to estimate an exchange constant for molecular oxygen. The input datum for these equations should be referenced to a height of 10 m above the water surface. The observed datum thus must be translated to 10-m height via $U = 1.5$ (log 10000 / log 1000) = 2.0 m $\cdot s^{-1}$. U is less than 5.5 m $\cdot s^{-1}$; Eq.(2-84) therefore applies and $KL = 4.19 \times 10^{-6} \sqrt{20}$ = 5.93×10^{-6} m $\cdot s^{-1}$. EXAMS' input datum (KO2) has dimensions of cm$\cdot h^{-1}$; the units conversion yields KO2 = 2.13 cm$\cdot h^{-1}$ for direct entry. (Recall, however, that EXAMS will use Banks' equations to generate KO2 when only the wind speed is entered (1.0 m $\cdot s^{-1}$ at 10 cm).)

EXAMS' estimates the liquid-phase transport resistance using the molecular weight of the pollutant as an indexing factor. The temperature of the epilimnion (20°C) in this case obviates the need for conversion of KO2 to a differing value at the temperature of the environment (Eq. (2-83)). The liquid-phase Rn transport resistance (R_l in Eq. (2-77)) can be computed as

$$R_l = \frac{1}{0.0213\sqrt{32/222}} \qquad (2\text{-}87)$$

= 123.66 h$\cdot m^{-1}$.

Resistance in the liquid phase thus amounts to 99.9% of the total Rn transport resistance (Rt = Rg + Rl = 123.74 h$\cdot m^{-1}$). The estimated exchange constant for Rn gas is therefore Rt^{-1} = 8.08×10^{-3} m $\cdot h^{-1}$ = 0.19 m/d, which value can be compared to Emerson's (1975) experimental estimate of 0.16 - 0.40 m/d.

Other models considered for indexing oxygen piston velocity to a study compound use the relative diffusivities of oxygen and the material of interest (see page 35). Under these models, Eq. (2-77) for the liquid phase transport resistance becomes

$$R_l = \frac{1}{KO_2 \times K_{VO}} \qquad (2\text{-}88)$$

Where K_{VO} is a liquid-phase transport index measured by the techniques of Hill et al. (1976), or estimated from the aqueous diffusivity of the pollutant, expressed as a ratio of diffusivities or as some fractional power of that ratio. A comparison of results from these models applied to Rn evasion provides a measure of "model uncertainty;" here we will contrast the sensitivity of estimated volatilization to the model chosen, as against the values chosen for the parameters used to calculate model results (i.e., parameter uncertainty).

Emerson (1975), citing Rona (1918) via Peng (1973) gives a diffusion constant for Rn of 1.37×10^{-5} $cm^2 \cdot s^{-1}$ at 25 °C. The diffusion constant of molecular oxygen in water at 25°C is 2.41×10^{-5} $cm^2 \cdot s^{-1}$ (Vivian and King (1964), cited from Reid, Prausnitz, and Sherwood (1977:576)). The diffusivity ratio ($D(Rn)/D(O_2)$) is thus 1.37/2.41 = 0.568. Application of Eq. (2-88) then yields a liquid-phase transport resistance in these small lakes of $R_l = 1/(0.0213\times0.568) = 82.6$ h$\cdot m^{-1}$ and a Rn exchange constant ($1/(R_l+R_g)$) of 0.29 m/d. Application of surface renewal theory would give $R_l = 1/(0.0213\times\sqrt{0.568}) = 62.3$ h$\cdot m^{-1}$ and a Rn exchange constant of 0.38 m$\cdot d^{-1}$.

Tsivoglou (1967) measured simultaneous exchange constants for oxygen and Rn in laboratory experiments, arriving at a ratio between them of 0.70. (This value corresponds to the 0.63 root of the diffusivity ratio.) Application of Eq. (2-88) in this case yields $R_l = 1/(.0213\times0.70) = 67.1$ h$\cdot m^{-1}$, and a Rn exchange constant of 0.36 m/d. The model estimates of the Rn exchange constant (0.19, 0.29, 0.36, and 0.38 m/d) thus all fall within the range of Emerson's (1975) experimental "best estimates" of 0.16 to 0.40 m/d; there is no basis to prefer one model to another in this application.

Liss and Slater (1974) have estimated average exchange constants for oxygen (20 cm$\cdot h^{-1}$) and water vapor (3000 cm$\cdot h^{-1}$) applicable to the surface of the open sea. These values have on occasion been recommended as appropriate to estimation of the volatilization of pollutants from inland waters. For Rn transport in these small ELA lakes, use of Liss and Slater's (1974) oceanic exchange constants would give

$R_g = (293.15\times8.206\times10^{-5})/(30.0\times0.09239\times\sqrt{[18/222]})$
$= 0.0305$ h$\cdot m^{-1}$

$R_l = 1/(0.2\times\sqrt{[32/222]}) = 13.17$ h$\cdot m^{-1}$

$R_t = R_g + R_l = 13.2$ h$\cdot m^{-1}$

and a Rn exchange constant (1/Rt) of 1.8 m/d. The dangers of uncritical extrapolation of environmental driving forces (in this case the reaeration rate or oxygen piston velocity) between systems is apparent: The ELA Rn exchange constant, estimated from oxygen and water vapor transport in the open sea, is an order of magnitude too large, as compared with either the measured values, or to estimates from volatilization models parameterized via wind speed and Banks'(1975) compilation of oxygen exchange rates as a function of wind velocity. The critical element in an accurate application of EXAMS to this situation is therefore, the selection of appropriate values for the environmental driving variables (WIND and KO2), rather than the choice of a model for indexing Rn liquid-phase transport resistance against EXAMS' environmental descriptors.

2.3.2.4.2 1,4-Dichlorobenzene in Lake Zurich

Schwarzenbach et al. (1979) conducted a one-year study of the fate and transport of 1,4-dichlorobenzene (DCB) in Lake Zurich, Switzerland. Contaminated effluents from waste-water treatment plants are the primary source of DCB loadings entering the lake (the material is used as a residential toilet cleanser). The concentration of DCB in these effluents is

relatively constant among treatment plants and over time, providing an opportunity for a case-history trial of EXAMS' use (in Mode 1) as a steady-state evaluative model.

DCB is not subject to appreciable degradation by chemical or biochemical processes in aquatic systems (Callahan et al. 1979); its behavior is therefore governed by volatilization, transport, and sorption phenomena. EXAMS in this instance requires 4 chemical descriptors: the molecular weight (MWT), solubility (SOL), octanol-water partition coefficient (KOW), and Henry's Law constant (HENRY). The molecular weight of DCB ($C_6H_4Cl_2$) is 147.0. The aqueous solubility and octanol-water partition coefficient of DCB have been measured by Banerjee et al. (1980). DCB is soluble to 0.502 mM in water at 25 °C (SOL = 73.8 ppm). Its octanol-water partition coefficient (KOW) is 2340.

The Henry's Law constant of DCB has not been measured, but it can be estimated (for 25 °C, the temperature of the solubility observation) from the vapor pressure/solubility ratio (Mackay and Wolkoff 1973, Mackay and Leinonen 1975). Para-DCB is a solid at normal environmental temperatures (mp 53.1 °C (Weast 1971). The vapor pressure (Pv) of solid 1,4-DCB at 10, 30, and 50 °C is 0.232, 1.63, and 8.435 torr, respectively (Darkis et al. 1940). Regression of these data on the model Pv = A exp(-B/T) yields A = 9.63×10^{11}, B = 8223, and accounts for 99.99% of the variation in Pv with temperature. EXAMS could be loaded with the results of this regression analysis, i.e., VAPR=logA=11.98, and EVPR=(B)(R)(0.001)=16.34 kcal/mol. Alternatively, the Henry's Law constant can be estimated via interpolation of the observed vapor pressure to 25°C. The latter procedure was used for this analysis of DCB in Lake Zurich. The interpolated value of Pv is 1.011 torr at 25 °C. The Henry's Law constant is therefore (1.011/760)/0.502 = 2.66×10^{-3} atm-m^3/mol.

EXAMS also requires environmental input data describing Lake Zurich. In this case, a "canonical" data set need only include information relevant to transport, sorption, and volatilization of neutral organics. Schwarzenbach et al. (Schwarzenbach et al. 1979) restricted their investigation to the central basin of Lake Zurich. Both the upper and the central basins receive DCB-contaminated waste- water effluents. The central basin can be modeled in isolation, however, by treating inputs from the upper basin as advected loadings to the (downstream) central basin. Except as noted otherwise, the environmental description given below was drawn from Schwarzenbach et al. (1979).

The central basin has an average hydraulic residence time of 1.2 years. Banks' (1975) method for estimating KO2 from wind speed thus seems most appropriate, lacking extensive direct field measurements of the oxygen exchange constant. The annual mean wind speed for the period 1955-63, 1965-69 was 2.6 m $\cdot s^{-1}$ (5.1 knots) (unpublished data for Zurich, Switzerland/Kloten, summarized by the U.S. Air Force Environmental Technical Applications Center, supplied courtesy of NOAA). Although a station history was not available, these data were in all probability collected at the conventional meteorological screen height (6 m). Wind speed at 10 m height would be 2.6(log 10000/log 6000) = 2.75 m $\cdot s^{-1}$. Computation of KO2 via Eq.(2-84) then gives 2.5 cm$\cdot h^{-1}$ via

$$KO2 = 4.19\times10^{-6}\sqrt{2.75}\times3600(s/h)\times100(cm/m)$$

Average wind speed at 10 cm height (EXAMS' input parameter WIND) would be 2.6(log 100/log 6000) = 1.38 m $\cdot s^{-1}$.

The mean depth of the central basin is 50 m, and the surface area is 68 km^2, giving a total volume of 3.4×10^9 m^3. The lake stratifies during the summer (May through September); the thermocline sets up at a depth of 10 m by early May and remains at about that depth until fall turnover (Li 1973). A simple "box" model of the lake can be constructed for EXAMS by dividing the lake into 3 vertical zones, each with an area (AREA) of 68 km^2 or 6.8×10^7 m^2. For the epilimnion segment (compartment 1, TYPE(1) = "E"), DEPTH(1) = 10 (m), and VOL(1) = 6.8×10^8 (m^3). The hypolimnion (compartment 2, TYPE(2) = "H") then has DEPTH(2) = 40, and VOL(2) = $6.8\times10^7\times40 = 2.72\times10^9$ m^3. Assuming a 2 cm depth of active benthic sediments (compartment 3, TYPE(3) = "B") gives DEPTH(3) = 0.02, and VOL(3) = 1.36×10^6 m^3.

Li (1973) computed the vertical eddy diffusion coefficient in Lake Zurich, as a function of depth and season, from observed monthly temperature profiles averaged over 10 years of record. The annual mean temperature of the epilimnion (0-10 m depth, TCEL(1)) was 11°C; the mean hypolimnion temperature was 5.6°C (TCEL(2)). The eddy dispersion coefficient at 10 m depth averaged 0.058 $cm^2 \cdot s^{-1}$ during the stratified period and was about 1 $cm^2 \cdot s^{-1}$ during the balance of the year. The annual mean value (DSP for parameterizing average transport between the epilimnion and hypolimnion) was 0.6 $cm^2 \cdot s^{-1}$; EXAMS' input value of DSP = 0.2 $m^2 \cdot h^{-1}$. The dispersion coefficient for exchange between the hypolimnion and benthic sediments was taken as 10^{-4} $m^2 \cdot h^{-1}$.

In order to compute sorption of DCB to sediment phases, EXAMS requires a description of the benthic and suspended sediments in the system (FROC, BULKD, PCTWA). Given the size of Lake Zurich (i.e., the relatively small overall sediment:water ratio), and the small octanol:water partition coefficient of DCB (2340), DCB will occur primarily in the dissolved state in the water column of this lake. The values chosen for FROC, BULKD, and PCTWA are therefore not critical to the outcome of the simulation, so long as they are representative. **Table 7** summarizes the observed and assumed values that were used to describe the central basin of Lake Zurich to EXAMS.

Table 7. Environmental Data for Central Basin of Lake Zurich

Parameter	Compartment		
Number	1	2	3
Type	E	H	B
Area, m^2	6.8×10^7	6.8×10^7	6.8×10^7
Depth, m	10	40	0.02
Vol, m^3	6.8×10^8	2.72×10^9	1.36×10^6
Sused (mg/L)	5	5	
Bulkd (g/cm^{-3})			1.5
Pctwa, %			150
Froc	0.02	0.02	0.02
Wind, $m\cdot s^{-1}$@10cm	1.38		

The combined flow from the upper basin (2,500), small creeks draining into the central basin (100), and treatment plant effluents (28) was $2{,}628\times10^6$ m^3/yr, giving STFLO(1) = 3×10^5 $m^3\cdot h^{-1}$. The total load of DCB on the central basin was 88 kg/yr, of which 25 kg derived from the upper basin, 62 kg from treatment plant effluents discharged into the central basin, and 1 kg/yr from other minor sources. For the EXAMS simulation, these loadings were summed to give a STRLD(1) to the epilimnion of the central basin of 0.010 kg $\cdot h^{-1}$. (Chapter 3.4 demonstrates the entry of these data into EXAMS, and the command sequences used to conduct the analysis.)

EXAMS (Exams Output Table 8 and Exams Output Table 9) predicted a total mass of 37 kg DCB resident in the water column (DCB concentration 10.7 ng/L), a flux of DCB to the atmosphere of 59.4 kg/yr, and water-borne export of 28.2 kg/yr. By comparison, Schwarzenbach et al. (1979) estimated a resident mass of 38 kg (11.2 ng/L) in the lake, and, from a mass balance for DCB, estimated the flux to the atmosphere to be 60 kg/yr, with a water-borne export of 28 kg/yr.

During the stratified period, contaminated treatment plant effluents spread laterally through the metalimnion of the lake and mix with both the hypolimnion and the epilimnion (Schwarzenbach et al. 1979). Assuming that the summertime loadings mix upward and downward in equal measure, EXAMS' loadings can be modified to account for this phenomenon. The summer (5 month) DCB load to the hypolimnion would amount to (5/12)(62)/2 kg/yr, which can be entered to EXAMS as a "drift" load (DRFLD(2)) of 1.5×10^{-3} kg $\cdot h^{-1}$. Proportionate reduction of the DCB load on the epilimnion gives STRLD(1) = 8.5×10^{-3} kg $\cdot h^{-1}$. Given this modification, EXAMS predicted a larger concentration of DCB in the hypolimnion (13.5 ng/L), and a resident mass of 44 kg DCB; the predicted fluxes and DCB concentration in the epilimnion (10.7 ng/L) were unchanged.

A test of other transport indices requires knowledge of DCB diffusivity. The aqueous diffusivity of DCB can be estimated from molar volume at the normal boiling point (V_b), and V_b can itself be estimated from V_c, molar volume at the critical temperature (Reid et al. 1977). V_c for p-DCB is 372 cc/g-mole; $V_b = 0.285(V_c^{1.048})$ (Tyn and Calus method) = 140.9 cc/g-mole. The aqueous diffusivity of p-DCB at 25 °C, computed via the Hayduk-Laudie revision of the Othmer-Thakar relationship, is $(13.26\times10^{-5})\ (0.8904^{-1.4})(140.9^{-0.0589}) = 8.46\times10^{-6}\ cm^2\cdot s^{-1}$, taking the viscosity of water at 25 °C as 0.8904 cp (Weast 1971:F-36). The diffusivity ratio $D(DCB)/D(O_2)$, given the diffusivity of molecular oxygen $D(O_2)$ as $2.41\times10^{-5}\ cm^2\cdot s^{-1}$, is 0.35; its square root is 0.59.

Substituting these values for EXAMS' molecular weight transport index ($\sqrt{32/147}$ = 0.47) gave estimated resident DCB masses of 43.8 kg (12.9 ng/L), and 31.0 kg (9.1 ng/L), respectively. Simulation using Liss and Slater's (1974) open-sea transport parameters (with the molecular weight transport index) predicted a resident mass of only 6.6 kg (2.0 ng/L). These comparisons are summarized in **Table 8**.

Table 8. Results of EXAMS simulations of the behavior of DCB (1,4-dichlorobenzene) in Lake Zurich, Switzerland

Method	Conc ng/L	Mass kg	Volatile kg/yr	Export kg/yr
Measured	11.2	38.	60.	27+1
$\sqrt{32/147}$	10.7	37.	59.4	28.2
Partial load hypolimnion	10.7(E) 13.5(H)	44.	59.4	28.2
D_{DCB}/D_{O2}	12.9	44.2	53.7	33.9
$\sqrt{D_{DCB}/D_{O2}}$	9.1	31.3	63.7	24.0
$\sqrt{32/147}$ K_{O2}=20cm/h V_W=30m/h	1.95	6.69	82.5	5.13

Predicted concentration, resident mass in water column, and fluxes vary as a function of load routing, method used to index interphase transport against its environmental referents, and environmental transport parameters. The default molecular weight transport index provided the most accurate prediction of

the volatilized flux of DCB from Lake Zurich. As was the case for Rn transport in ELA lakes, however, the selection of proper values for environmental driving forces seems to be more critical, than is the choice taken among methods of indexing pollutant transport across the air-water interface against its environmental referents.

```
Ecosystem: Lake Zurich - central basin (Untersee)
Chemical:  1,4-Dichlorobenzene
-----------------------------------------------------------------
Table 15.01.  Distribution of chemical at steady state.
-----------------------------------------------------------------
Seg  Resident Mass   ******** Chemical Concentrations *********
 #                     Total    Dissolved  Sediments    Biota
     Kilos      %       mg/*     mg/L **     mg/kg       ug/g
--- -------- ------  ---------  ---------  ---------  ---------
In the Water Column:
  1  7.3      20.00  1.074E-05  1.074E-05  1.759E-04   0.00
  2  29.      80.00  1.074E-05  1.074E-05  1.759E-04   0.00
    ======== ======
     37.      99.33

 and in the Benthic Sediments:
  3 0.24     100.00  1.798E-04  1.065E-05  1.744E-04   0.00
    ======== ======
    0.29       0.78
Total Mass (kilograms) =     36.75
-----------------------------------------------------------------
 * Units: mg/L in Water Column; mg/kg in Benthic Zone.
** Excludes complexes with "dissolved" organics.
```

Exams Output Table 8. Predicted concentration and resident mass of DCB.

```
Ecosystem: Lake Zurich - central basin (Untersee)
Chemical:  1,4-Dichlorobenzene
-----------------------------------------------------------------
Table 20.01.  Exposure analysis summary.
-----------------------------------------------------------------
Exposure (maximum steady-state concentrations):
 Water column: 1.074E-05 mg/L dissolved; total = 1.074E-05 mg/L
 Benthic sediments: 1.065E-05 mg/L dissolved in pore water;
   maximum total concentration = 1.798E-04 mg/kg (dry weight).
 Biota (ug/g dry weight): Plankton:          Benthos:

Fate:
 Total steady-state accumulation:  36.8     kg, with  99.33%
   in the water column and   0.67% in the benthic sediments.
 Total chemical load: 0.24     kg/  day.  Disposition:   0.00%
   chemically transformed,   0.00% biotransformed,  67.79%
   volatilized, and  32.21% exported via other pathways.

 Persistence:
  After  216.       days of recovery time, the water column had
  lost  50.52% of its initial chemical burden; the benthic zone
  had lost  19.55%; system-wide total loss of chemical =  50.3%.
  Five half-lives (>95% cleanup) thus require ca.    35. months.
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Exams Output Table 9. EXAMS summary of DCB in Lake Zurich.

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2.3.3 Direct Photolysis

EXAMS includes two entirely separate methods to compute rates of direct photolysis. These methods are mutually exclusive, and accept different kinds of input data. The first, mechanized in procedure "PHOTO1," begins from a pseudo-first-order rate constant (KDP) representing the photolytic decomposition rate in near-surface waters under cloudless conditions at a specified reference latitude (RFLAT). This input rate constant datum is taken as the annual mean value averaged over the entire diel (24-hour) cycle.

The second method, in procedure "PHOTO2," works from measured light absorption spectra and reaction quantum yields of the compound. Because this method is intrinsically more accurate, it is to be preferred whenever possible.

EXAMS selects the appropriate procedure via an audit of the structure of the chemical input data. For the existing ionic species (RH_3 et al. – see SPFLG and Chapter 2.2.1), when at least one value of ABSORG, the light absorption spectrum of the molecule, is non-zero, EXAMS calls on procedure PHOTO2 to compute the photolysis rate of the chemical. (Technically this test is executed on a summation of the ABSORG vector of the ionic species; a positive value of this sum (internal variable ABSTOL) invokes the call to PHOTO2.) Note that the structure of this decision in effect gives ABSOR a higher computational priority than KDP, that is, if any ABSOR are positive, EXAMS will use PHOTO2 and the absorption spectrum for its computations, and will ignore all entries in the KPD vector.

The techniques used within EXAMS for computing rates of direct photolysis have been derived in large part from the work of Zepp and coworkers (Zepp et al. 1975, Zepp et al. 1976, Zepp and Cline 1977, Zepp et al. 1977, Zepp 1978, Zepp and Baughman 1978, Miller and Zepp 1979a, b, Zepp 1980). Zepp (1980) and Zepp and Baughman (1978) summarized techniques

for predicting direct photolysis in natural waters; a computer code for evaluating this transformation pathway was described by Zepp and Cline (1977).

2.3.3.1 Direct photolysis in aquatic systems

Direct photochemical reactions are a consequence of the absorption of electromagnetic energy by a pollutant molecule. In this "primary" photochemical process, absorption of a photon promotes the molecule from its ground state to an electronically excited state. The excited molecule then either reacts to yield a photoproduct, or decays via some other mechanism (fluorescence, phosphorescence, etc.) back to the ground state. The efficiency of each of these energy conversion processes is called its "quantum yield" Φ; the law of conservation of energy requires that the primary quantum efficiencies sum to 1.0. These ideas are expressed by two fundamental laws of photochemistry. The first, the "Grotthus-Draper" law, states: "Only the light which is absorbed by a molecule can be effective in producing photochemical change in the molecule." Simple irradiation of a system does not necessarily result in photochemical reactions; the light must be of wavelengths that can be absorbed by the chemical. Conversely, laboratory irradiation of a chemical with wavelengths that are not found in natural waters (<280 nm) is of little value for predicting the behavior of the compound in the environment. The second law of photochemistry, the "Stark-Einstein" law, was formulated after the discovery that interactions of light and matter are restricted to discrete (quantized) events. This second law in its modern form (Calvert and Pitts 1966:20) states: "The absorption of light by a molecule is a one-quantum process, so that the sum of the primary process quantum yields must be unity."

The rate of photolytic transformations in aquatic systems depends upon both the light intensity in the medium (in other words, the dose rate), and on the response of the irradiated pollutant. The chemical response is composed of two factors: the pollutant's absorption spectrum ϵ_λ (EXAMS' input ABSORG), and its quantum efficiency for photochemical transformations Φ (reaction quantum yield, EXAMS' input QYIELD). The logic of the situation can be developed in terms of monochromatic light, with spectral effects subsequently incorporated via integration or summation across the solar spectrum. In EXAMS, the solar spectrum is subdivided into 46 wavelength intervals (**Table 9**), and the total rate constant is computed as the sum of contributions from each spectral interval. In what follows, however, the spectral subscripts have in most cases been omitted, in the interest of notational simplicity.

Light intensity decreases exponentially with depth in any absorbing medium. This phenomenon is known as the Beer-Lambert law, and can be stated mathematically as:

$$\frac{dEo}{dz} = -KEo \qquad (2\text{-}89)$$

where Eo = photon scalar irradiance, photons $cm^{-2}s^{-1}$
z = depth, m (EXAMS variable DEPTHG)
K = diffuse attenuation coefficient for irradiance, /m, and

$$K = D \times a + (Bb) \qquad (2\text{-}90)$$

(Smith and Tyler 1976), where
D is the mean optical path per unit z (dimensionless),
a is the absorption coefficient for the medium (/m), and
(Bb) is the back-scattering coefficient.

Photon scalar irradiance (Eo) is the sum of two contributing light fields in natural waters, the downwelling (Ed) and upwelling (Eu) irradiances. Field measurements, although for the most part restricted to marine systems, have in almost all cases resulted in measured values of Eu of only 2% or less of Ed. Upwelling irradiance can, however, contribute significantly to Eo at visible wavelengths in the clearest ocean waters, where molecular back-scattering can be significant, and over white sandy bottoms of high albedo (Jerlov 1976). Although seldom measured in freshwater systems, these studies in marine waters indicate that back-scattering is generally very small and can safely be neglected (Jerlov 1976). In the following discussion, photon irradiance is therefore designated E and is treated as being identical with Ed or Eo; Eu is neglected.

Integration of Eq. (2-89) yields an expression for the residual irradiance after transmission through a homogeneous layer of depth z:

$$E(z) = E(0)\exp(-Kz) = E(0)\exp(-Daz) \qquad (2\text{-}91)$$

where $E(0)$ is the irradiance at the top of the layer. The rate of light absorption Ew (photons cm^{-2} s^{-1}) in the layer is ($E(0)-E(z)$), or

$$Ew = E(0)(1 - \exp(-Kz)) \qquad (2\text{-}92)$$

For photochemical purposes, it is most convenient to express light absorption on a volumetric molar basis (Bailey et al. 1978:223) (one mole of photons is an Einstein, E). The rate of light absorption Iw, in $EL^{-1}s^{-1}$, is:

$$Iw = \frac{Ew}{(A)(z)} \times 1000\,\frac{cm^3}{L} \times 0.01\,\frac{m}{cm} \qquad (2\text{-}93)$$

where A = 6.023×10^{23} photons/mole (Avogadro's number). Denoting E(0)/A as Io (Einsteins $cm^{-2}s^{-1}$), the volumetric absorption rate Iw (in E L^{-1} s^{-1}) is thus

$$Iw = 10\frac{Io}{z}(1 - \exp(-Kz)) \qquad (2\text{-}94)$$

The electronic absorption spectra of synthetic organic chemicals are usually reported as (decadic) molar absorptivities or

extinction coefficients ϵ, with units (cm^{-1} $(mole/liter)^{-1}$) or ($cm^{-1}M^{-1}$) (EXAMS' input variable ABSORG). The defining equation is:

$$\varepsilon = \frac{Ab}{l \times [P]} \qquad (2\text{-}95)$$

where *Ab* is the absorbance measured in a spectrophotometer, *l* is the path length in cm, and [*P*] is the concentration of the chemical in moles per liter. The presence of the chemical in a natural water body increases the absorption coefficient (units m^{-1}) of the water from (*a*) to ($a + 100(\frac{cm}{m})(\ln 10)\varepsilon[P]$). The total rate of light absorption in the water body then becomes, by substitution into Eq. (2-94),

$$Iw = 10\frac{Io}{z}\{1 - \exp(-D\{a + 100 \times 2.303 \times \varepsilon[P]\}z)\} \qquad (2\text{-}96)$$

where *D* is the relative optical path in the water body (Eq. (2-90)). The fraction of this light absorbed by the pollutant itself is:

$$\frac{2.303 \times 100\varepsilon[P]}{a + 2.303 \times 100\varepsilon[P]}$$

and the rate of light absorption by the pollutant Ia, in E L^{-1} s^{-1}, is:

$$Ia = \frac{2303Io\{1 - \exp(-D\{a + 230.3\varepsilon[P]\}z)\}\varepsilon[P]}{\{a + 230.3\varepsilon[P]\}z} \qquad (2\text{-}97)$$

At trace levels of the pollutant (EXAMS' operating range), by definition the quantity (230.3ϵ[*P*]) << *a*, and (a + 230.3ϵ[P]) can be approximated by the natural absorption coefficient of the water body, *a*. Equation (2-97) in these circumstances reduces to:

$$Ia = \frac{1000 \times 2.303(\varepsilon)Io(1 - \exp(-Daz))}{(a)(z)}[P] \qquad (2\text{-}98)$$

The quantity *Ia/[P]* is called the "specific sunlight absorption rate" of the pollutant, *Ka* (Zepp 1980).

Table 9. Spectral intervals used in EXAMS, and spectral absorption coefficients of water η_w (m^{-1}), chlorophylls + pheophytins η_p ($m^{-1}(mg/L)^{-1}$), (humic) dissolved organic carbon η_{doc} ($m^{-1}(mg/L)^{-1}$). Suspended sediments η_s taken as uniformly 0.34 $m^{-1}(mg/L)^{-1}$. See section 2.3.3.2

λ center (nm)	Δ λ (nm)	η_w	η_p	η_{doc}	λ center (nm)	Δ λ (nm)	η_w	η_p	η_{doc}
280.0	2.5	0.288	145	8.35	380.0	10.0	0.0220	46	1.96
282.5	2.5	0.268	138	8.05	390.0	10.0	0.0191	42	1.69
285.0	2.5	0.249	132	7.77	400.0	10.0	0.0171	41	1.47
287.5	2.5	0.231	126	7.49	410.0	10.0	0.0162	39	1.27
290.0	2.5	0.215	120	7.22	420.0	10.0	0.0153	38	1.10
292.5	2.5	0.194	115	6.97	430.0	10.0	0.0144	35	0.95
295.0	2.5	0.174	109	6.72	440.0	10.0	0.0145	32	0.82
297.5	2.5	0.157	106	6.48	450.0	10.0	0.0145	31	0.71
300.0	2.5	0.141	101	6.25	460.0	10.0	0.01566	28	0.61
302.5	2.5	0.133	95	6.03	470.0	10.0	0.0156	26	0.53
305.0	2.5	0.126	90	5.81	480.0	10.0	0.0176	24	0.46
307.5	2.5	0.119	85	5.61	490.0	10.0	0.0196	22	0.40
310.0	2.5	0.105	80	5.41	503.75	17.5	0.0295	19	0.33
312.5	2.5	0.0994	78	5.21	525.0	25.0	0.0492	14	0.24
315.0	2.5	0.0952	75	5.03	550.0	25.0	0.0638	10	0.17
317.5	2.5	0.0903	72	4.85	575.0	25.0	0.0940	8	0.12
320.0	2.5	0.0844	70	4.68	600.0	25.0	0.244	6	0.08
323.1	3.8	0.0793	68	4.47	625.0	25.0	0.314	5	
330.0	10.0	0.0678	64	4.05	650.0	25.0	0.349	8	
340.0	10.0	0.0561	59	3.50	675.0	25.0	0.440	13	
350.0	10.0	0.0463	55	3.03	706.25	37.5	0.768	3	
360.0	10.0	0.0379	55	2.62	750.0	50.0	2.47	2	
370.0	10.0	0.0300	51	2.26	800.0	50.0	2.07	0	

Ka can also be computed from the average light intensity in any layer of the water body (Miller and Zepp 1979a). In this approach, the average light intensity Em (photons $cm^{-2}s^{-1}$) is found by integration of Eq. (2-91) over the depth of the layer z, followed by division of the resulting integral by z:

$$Em = \frac{E(0)(1-\exp(-Daz))}{Daz} \qquad (2\text{-}99)$$

where *E(0)* is the intensity at the top of the layer. Em (photons $cm^{-2}s^{-1}$) can be converted to molar units (Im, E $cm^{-2}s^{-1}$) via division by Avogadro's number *A*:

$$\mathrm{Im} = \frac{Em}{A} = \frac{E(0)}{A} \times \frac{1-\exp(-Daz)}{Daz} \qquad (2\text{-}100)$$

which, as $Io = E(0)/A$,

$$= \frac{1}{D} \times \frac{Io(1 - \exp(-Daz))}{(a)(z)}$$

The term $Io(1\text{-}\exp(Daz))/az$ in this equation is embedded in Eq. (2-98); Ia and Ka can thus be computed from the average light intensity Im via the equivalent expressions (2-101) and (2-102):

$$Ia = 2.303 \times 1000 \frac{cm^3}{L} (\varepsilon)(\mathrm{Im})(D)[P] \qquad (2\text{-}101)$$

$$Ka = 2303(\varepsilon)(\mathrm{Im})(D) \qquad (2\text{-}102)$$

Light absorption is a one-quantum process, so Ia ($E\ L^{-1}s^{-1}$) also gives the rate of electronic activation of the pollutant (M/s). Ka, the specific sunlight absorption rate, thus has units s^{-1}. If each photon absorbed by the chemical pollutant resulted in photochemical transformation of one molecule, Ka would amount to a pseudo-first-order rate constant for photolysis of the pollutant. This, however, is rarely the case in solution-phase systems.

The efficiency of the (secondary) photochemical transformation process is called the "reaction quantum yield" Φ (EXAMS input parameter QYIELD), with ("dimensionless") units of moles/Einstein. Zepp (1978) has described procedures for measuring Φ of organic chemicals in dilute air-saturated aqueous solutions; the measurement of Φ is described in EPA Guideline OPPTS 835.2210 (*Direct Photolysis Rate in Water by Sunlight,* report EPA 712-C-98-060, January 1998). The rate of photochemical transformation of a pollutant is given by:

$$\frac{d[P]}{dt} = (\Phi)Ia = (\Phi)(Ka)[P] \qquad (2\text{-}103)$$

The quantity $(\Phi)(Ka)$ is the pseudo-first-order photolysis rate constant. Multiplication of this quantity by 3600 s/h gives the photolytic contribution to the overall transformation rate constant K in Eq. (2-1).

Although the foregoing discussion has been phrased in terms of monochromatic light, the effect of spectral differences can be readily incorporated via integration or summation (in discrete wavebands) across the solar spectrum. The rate of photolysis of a synthetic organic compound thus can be computed from the absorption spectra and reaction quantum yields of the several ionic species of the chemical, via a coupling of these parameters to the (spectrally-dependent) behavior of light in natural waters (EXAMS' procedure PHOTO2).

When the absorption spectrum of a compound has not been quantified (although the spectral position of absorption maxima may be known). EXAMS provides an additional procedure, PHOTO1, designed to accept pseudo-first-order photolysis rate constants as its primary input data. For example, Smith et al. (1978) attempted to measure the absorption spectrum of Mirex, but the absorptivity was below the detection limit of their instrument (0.1 $cm^{-1}M^{-1}$). Experimental studies, conducted via continuous exposure of an aqueous solution of Mirex to ambient sunlight at Menlo Park, CA for a period of 6 months, demonstrated that Mirex is photochemically reactive in aqueous solution with a pseudo-first-order rate constant of $3.7\times10^{-3}d^{-1}$. (A pseudo-first-order rate constant determined via a brief experiment, for example at midsummer local noon, must be adjusted for annual mean sunlight intensity and day length prior to entry in EXAMS.)

So long as the reaction mixtures absorb a negligible fraction of the ambient light ($\mathrm{Im} \approx Io$), this observed rate constant ($K_{DP}(0)$, i.e., K at z=0) is equivalent to:

$$K_{DP}(0) = \Phi Ka = 2303\ \Phi\ \epsilon\ Io\ D$$

integrated across the solar spectrum. The average photolysis rate constant $K_{DP}(z)$ in a layer of appreciable depth z is then

$$K_{DP}(z) = K_{DP}(0)\frac{1 - \exp(-Daz)}{Daz} \qquad (2\text{-}104)$$

where the absorption coefficient (a) for the water body is some appropriate single value. EXAMS also computes a correction term for effects of cloudiness and geographic latitude. EXAMS' input variable (KDP, units h^{-1}) is taken as the near-surface, 24-hour annual average pseudo-first-order photolysis rate constant under cloudless conditions at a specified latitude RFLAT. RFLAT is expressed in degrees + tenths. For example, Menlo Park, California, is at 37°27' N; EXAMS' input would be RFLAT = 37.4.

2.3.3.2 Light attenuation in natural waters

The attenuation of irradiance in natural waters is described by the diffuse attenuation coefficient or "K-function," K (Eq. (2-90)), with units m^{-1}. The numerical value of K depends upon both the absorbance of the medium (a), and upon the relative optical path in the water body (D). The absorbance of a natural water body results from absorption of light by the water itself, plus absorption by green plants, dissolved organic matter (primarily humic materials), and suspended sediments. The optical path parameter D depends on the angle of incidence of the light source(s), and on forward scattering of the light within the water body itself.

2.3.3.2.1 Distribution functions (D) in natural waters

The optical parameter D is the mean optical path per unit vertical depth in the system; D may be called a "distribution

function" as proposed by Priesendorfer ((1958b, 1958a), quoted from Smith and Tyler (1976)), or an "inverted value of an average cosine" where the average cosine is defined as *a/K* (Jerlov 1976). (The term "inverted value of an average cosine" originated from a generalization of the fact that the path length of the solar beam is given by the secant (1/cos) of the angle of refraction of the beam.) In the case of a collimated light beam incident normal to the water surface, $D = 1.0$. In the case of a completely diffused light field, D reaches its maximum value of 2.0 (Leighton 1961:24ff).

In the clearest natural waters, the distribution function is dominated to appreciable depths by the geometry of incident sky radiation and the solar beam. When the sun is in the zenith, the solar $D = 1.0$; D increases with increasing zenith angle. When the sun is near the horizon, D reaches a limiting value of about 1.5, because of refraction of the solar beam as it crosses the air-water interface. At low solar elevations, however, the underwater light field in the photochemically significant portion of the solar spectrum is dominated by contributions from diffuse skylight.

The collimating effect of transmission across the air-water interface reduces the distribution function for diffuse skylight from a D of 2.0 in the atmosphere, to a submarine value of about 1.19 ((Poole and Atkins 1926), quoted from (Hutchinson 1957:391)). This value corresponds to an equivalent solar elevation of about 44°. The total incident photochemically active irradiance (wavelengths ≤370 nm) is dominated by skylight at solar altitudes less than 45°, and irradiance at wavelengths ≤330 nm is dominated by sky radiation at all solar elevations (Leighton 1961:23ff). A distribution function of 1.19 is thus an adequate approximation for the near-surface zone, and to some considerable depth for the clearest natural waters.

In most natural waters, and in the deeper parts of clear waters, the radiance distribution approaches an asymptotic value in which forward scattering by suspended particles is balanced by light absorption, and the distribution coefficient attains a stable value. At shallow depths in natural waters containing scattering particles, D is usually larger than the value suggested by the solar elevation. For example, in the Baltic Sea and in the Mediterranean, D has been measured at 1.40 and 1.25, respectively ((Jerlov (Johnson) and Liljequist 1938, Hojerslev 1973, 1974); quoted from (Jerlov 1976:88)). The corresponding solar beam D values were only 1.14 and 1.04 respectively, indicating a strong effect of particle scattering in these waters. Miller and Zepp (1979a) measured light scattering by 6 natural sediment suspensions. The distribution function ranged from 1.3 to 2.0, but showed little correlation with the suspension concentrations of the sediments (17–105 mg/L).

The distribution function for each element of the water body is an (environmental) input parameter to EXAMS. These parameters (DFACG) can be set at any value between 1.0 and 2.0. If an input value is <1 or >2, however, EXAMS resets the distribution function of the segment to DFACG = 1.19 for surficial (type L, E) waters, and to 1.50 for profundal (H) segments.

2.3.3.2.2 Absorption coefficients (a) in natural waters

EXAMS computes separate values of the spectral absorption coefficients (a) for each sector of the water body. Absorption is computed from the sum of the contributions of water itself, plant pigments, dissolved organic carbon (primarily attributable to humic materials of molecular weight >1000 (Mickle and Wetzel 1978)), and suspended sediments. Absorption coefficients for water itself, and the specific absorption coefficients for the other absorbing species, are given in **Table 9**.

EXAMS computes the total absorption coefficient (a, units /m) for each spectral interval in each water column compartment via Eq. (2-105):

$$a = \eta_w + \eta_p[CHL] + \eta_{doc}[DOC] + \eta_s[SUSED] \quad \text{(2-105)}$$

The spectral specific absorption coefficients supplied with the program (η_w, η_p, η_{doc}, η_s) are given in **Table 9**. The environmental concentrations of the absorbing species (CHL, DOC, and SUSED (mg/L)) are entered as part of the environmental data base for each water-column compartment of each ecosystem.

Absorption by plant pigments is keyed to the concentration of total chlorophyll-like pigments (chlorophylls + pheopigments) in each sector of the water column (input variable CHL, units mg/L). Under very eutrophic conditions, Chl *a* can attain 2 mg/L ((Talling et al. 1973), quoted from (Wetzel 1975:337)). In oligotrophic alpine and arctic lakes, pigment concentrations can be as low as 0.001 mg/L (Wetzel 1975:334). Smith and Baker (1978, Baker and Smith 1982) determined the contribution of total chlorophyll-like pigments (CHL) to the K- function of marine systems via regression analysis; the resulting spectral K values differed little from spectrophotometrically determined absorbance of phytoplankters. EXAMS' specific absorption coefficients (η_p in Eq. (2-105) and **Table 9**) were developed by division of Smith and Baker's ((1978)) "k2" by an assumed average distribution function of 1.20.

EXAMS' specific absorption coefficients for DOC (η_{doc}) (**Table 9**), representative of freshwater aquatic humus, were calculated from the expression

$$\eta_{doc} = 0.71 \exp(0.0145(450-\lambda))$$

where λ is the wavelength in nm (Zepp and Schlotzhauer 1981).

Light absorption by suspended sediments may vary across the solar spectrum, but interference by particle scattering has

hampered investigation of this phenomenon. Miller and Zepp (1979a) determined both D- and K- functions for 331 nm light, via actinometer experiments conducted on a series of 6 natural sediment suspensions. The specific absorbance coefficient ((K/D)/[S], where [S] (i.e., SUSED) is the concentration of suspended sediments in mg/L) varied from 0.19 to 0.59, with a mean value of 0.34, $m^{-1}(mg/L)^{-1}$. EXAMS includes a 46-element vector of specific sediment absorption coefficients η_s; this vector is currently uniformly filled with a value of 0.34.

When the absorption spectrum of the compound is not available for coupling to the absorption spectrum of the water body, procedure PHOTO1 requires appropriate single absorption coefficients "a" for each aquatic segment. These values are calculated from (2-105). The wavelength interval selected for this computation can be specified via the input chemical data describing the compound: The chemical data base includes a variable (LAMAX, nm) that can be used to specify the desired wavelength interval for computing *a*. The region of greatest overlap of the absorption spectrum of the chemical with the solar spectrum is perhaps the most appropriate value for LAMAX. Usually, however, it is the spectral location of peak absorbance that is readily available, in which case this value can be used for LAMAX. If LAMAX is outside the relevant portion of the solar spectrum (that is, <280 or >825 nm), EXAMS computes LAMAX via (2-105) at 300 nm (interval 9 in **Table 9**). Input values of LAMAX need not be restricted to the centers of the wavebands in **Table 9**; EXAMS selects the specific absorption coefficients for computing LAMAX via a matching of LAMAX to the appropriate spectral intervals in the Table. For example, if LAMAX = 306, EXAMS selects absorption coefficients from waveband 11 in **Table 9**; a LAMAX of 442.2 selects waveband 30; etc.

2.3.3.3 Reaction quantum yields (Φ; Qyield)

A photoactivated organic molecule can undergo a variety of secondary (thermal) transformations, including photoaddition and substitution reactions, cycloadditions, isomerizations and rearrangements, and photofragmentations and eliminations (Turro 1978). The efficiency of photochemical processes is expressed in terms of the "quantum yield" Φ, that is, the number of moles of photochemical activity per mole of photons (Einsteins) absorbed. Photoactivated molecules are subject to numerous physical and chemical processes, and the efficiency of each of these processes can be expressed as a quantum yield (examples include the fluorescence quantum yield, phosphorescence quantum yield, quantum yield for formation of a specific product molecule, etc.) The quantum yield of significance for EXAMS is the "disappearance" quantum yield (input parameter QYIELD), that is, the number of moles of parent compound transformed to daughter products per mole of photons absorbed.

The (secondary) transformation processes often involve thermal reactions, and the disappearance quantum yield therefore can be slightly temperature dependent. These thermal reactions are very fast, as they must be in order to compete with thermal reversion of the unstable intermediates to the original pollutant molecule. The activation energies of the thermal transformation reactions are on the order of only 1-2 kcal/mol; EXAMS therefore does not include an option for description of temperature effects on disappearance quantum yields.

Unlike vapor-phase photochemical reactions, the disappearance quantum yields of organic molecules in aqueous solution are generally independent of the wavelength of incident radiation, at least within the environmentally significant portion of the solar spectrum. This difference arises from the enhanced opportunity for energy transfer to the solvent in condensed-phase systems. In solution-phase irradiation, the rapid (radiationless) decay of excited molecules from second or higher electronic states, to their first excited state, normally precludes reaction from the higher states (Zepp 1978). Some organic dyes, stable under visible light but photochemically labile under UV, are notable exceptions to this rule. This phenomenon should be suspected when a >100 nm gap is present in the compound's absorption spectrum. In such a case the assumed lack of wavelength dependence of Φ should be tested by experiments conducted in both absorbing regions of the spectrum. If necessary, the photochemically inactive section of the compound's absorption spectrum can be omitted from the input data (ABSORG). Very small organic molecules, and some coordination compounds, can exhibit a wavelength dependence of Φ. The photochemistry of iron (II) cyanide complexes is one example of this phenomenon ((Balzani and Carassiti 1970), quoted from (Zepp 1978)). Most small organic molecules in aqueous solution are photochemically unreactive in sunlight, however. The disappearance quantum yields used as input to EXAMS should in all cases be derived from experiments using wavelengths that are part of the environmentally relevant portion of the solar spectrum, rather than far UV (< 280 nm).

Φ can also be affected by the chemistry of the water solution itself. The quantum yields of the ionic species of an organic acid or base generally differ. This phenomenon leads to an apparent dependence of Φ on the pH of the medium. EXAMS allows for the entry of a separate value of Φ (QYIELD) for each ionic species of the compound. This information can be deduced from a knowledge of the pK(s) of the compound, absorption spectra of its ionic species, and quantum yield experiments conducted at several pH values. For example, Zepp (1978) has described methods for determining disappearance quantum yields via comparison of the rate of transformation of a test pollutant P to that of a reference compound R, of known absorptivity ϵ(R) and quantum yield Φ(R). The method depends on a comparison of the slopes *S* of the (pseudo- first-order) ln[P] and ln[R] disappearance curves over time, under irradiation at a selected wavelength (e.g., 313 nm). The reference compound serves to

normalize the experiment for light intensity and the geometry of the photochemical apparatus. For a neutral molecule,

$$\Phi(P) = \frac{S(P)}{S(R)} \times \frac{\varepsilon(R) \times \Phi(R)}{\varepsilon(P)} \qquad (2\text{-}106)$$

The apparent Φ of an organic acid or base will depend on the pH of the system. For a fixed pH, Eq. (2-106) can be rewritten to include the ionization equilibria and separate absorptivities and quantum yields of the various ionic species of the pollutant P. For example, a monoprotic organic acid will distribute between its uncharged RH_3 molecule and its anion RH_2^- (see Chapter 2.2.4) as:

$$\alpha(RH_3) = \frac{1}{1 + \frac{Ka}{\{H^+\}}} \qquad (2\text{-}107)$$

and

$$\alpha(RH_2^-) = \frac{Ka / \{H^+\}}{1 + \frac{Ka}{\{H^+\}}} \qquad (2\text{-}108)$$

where α is the fraction of the total pollutant present as each of the molecular species (*Ka* here is the acidity constant). Equation (2-106) then becomes

$$\begin{aligned} &\alpha(RH_3) \times \varepsilon(RH_3) \times \Phi(RH_3) + \\ &\alpha(RH_2^-) \times \varepsilon(RH_2^-) \times \Phi(RH_2^-) = \\ &\frac{S(P)}{S(R)} \times \varepsilon(R) \times \Phi(R) \end{aligned} \qquad (2\text{-}109)$$

Suppose, for example, that P is a monoprotic organic acid whose pKa = 5.0. At pH 5, the compound would distribute equally between RH_3 and the RH_2^- anion. At pH 4.5, the compound would distribute as 76% RH_3 and 24% RH_2^-. Given, for example, ϵ of RH_3 as 5000, and ϵ of RH_2^- as 10000 at 313 nm, and experimentally determined values for the right side of Eq. (2-109) as 10 and 20 at pH 4.5 and 5.0 respectively; the quantum yields of the molecular species can be calculated via simultaneous solution of the equations:

1: $(0.76)(5000)(\Phi(RH_3)) + (0.24)(10000)(\Phi(RH_2^-)) = 10$

2: $(0.50)(5000)(\Phi(RH_3)) + (0.50)(10000)(\Phi(RH_2^-)) = 20$

giving a reaction quantum yield Φ for the uncharged molecule RH_3 of 1.5×10^{-4}, and $\Phi(RH_2^-) = 3.9\times10^{-3}$.

Zepp and Baughman (1978) have discussed the effect of other dissolved species on the direct photolysis of synthetic organic molecules. Dissolved oxygen in some instances "quenches" photochemical reactions via energy transfer from a pollutant molecule to the oxygen molecule at the expense of transformation pathways. Disappearance quantum yields should be determined in air-saturated pure water to allow for this effect; EXAMS does not include an explicit algorithm to make allowances for varying dissolved oxygen concentrations (as sunlit waters are very rarely anaerobic). Photochemical reactions with dissolved nucleophilic species such as hydroxide, chloride, bromide, and sulfide can change the reaction quantum yield of a pollutant from the value determined in pure water system. The concentrations of these species in natural fresh waters are, however, typically much too small for them to compete with nucleophilic displacements by water itself. In marine systems, chloride and bromide occur at concentrations (0.6 and 0.001 molar, respectively) high enough to compete, in principle, with water.

Some organic compounds that are not photoreactive in pure water are photoactive when complexed with metal ions. For example, NTA and EDTA are photochemically activated by complexation with iron (III). Photoactive co-dissolved substances (e.g., dissolved humic materials) can also mediate photoreactions of pollutant chemicals via direct energy transfer to the pollutant molecule, or by generation of reactive intermediates (e.g., singlet oxygen). These phenomena are properly termed "indirect" or "sensitized" photolysis, however, as opposed to the "direct" phototransformations that are the subject of this Chapter.

2.3.3.4 Absorption spectra (ABSORG)

The absorbance of organic acids and bases in aqueous solution varies with pH, as a result of differential light absorption by the neutral molecule and its ions. The rate of photolytic transformation of an organic acid or base in natural waters thus depends on the pH of the system. EXAMS' computations are keyed to the species-specific absorption spectra of the pollutant chemical (uncharged parent molecule and its ionic species), measured in pure water. EXAMS links the average spectral solar intensities in each layer of the water body to the absorption spectra of the compound, and thereby computes a value of Ka (Eq. (2-102)) for each dissolved molecular species.

EXAMS' dynamic state variable is the total concentration of pollutant in each ecosystem segment, referred to the aqueous phase of the compartment. The fraction of this total concentration present as each molecular species is computed via the equilibrium ionization and sorption distribution coefficients α (Chapter 2.2.4). Once in possession of Ka (Eq. (2-102)) values for the several ionic species, EXAMS computes the contribution of each to the total pseudo-first-order direct photolysis rate constant via the expression (compare Eq. (2-103)) $\alpha_i \times \Phi_i \times Ka_i$ where the subscript (i) refers in turn to each of the ionic species.

This computational loop is actually iterated 3 times for each ionic species, because EXAMS incorporates the effects of sorption to sediments and complexation with DOC via a set of 3 values of QYIELD for each ionic species. In other words, for each ionic species *i*, EXAMS computes the total contribution of that species to the overall direct photolysis rate constant by fixing the value

of *i*, and summing the expression

$$\{\alpha(i,k) \times QYIELD(i,k) \times Ka(i)\}$$

over the k=1 (dissolved), k=2 (sediment sorbed), plus k=3 (DOC-complexed) forms of the compound in each sector of the ecosystem. The mechanics of this computation allow the user to control the photoreactivity of sorbed molecules via the entries in the QYIELD chemical input vectors.

Sorption of the pollutant to suspended sediments and complexation with "dissolved" organic carbon (DOC) can induce complex changes in both the light absorption spectra and the reaction quantum yields of the compound, and can "protect" the molecule from exposure to sunlight via migration or dissolution into the (darkened) interior of sediment particles. EXAMS' first-order evaluations use the quantum yield parameter (QYIELD) as a mechanism for approximating the effects of sorption on the photoreactivity of pollutant chemicals; the phenomena involved are discussed in greater detail in Chapter 2.3.3.5.

In order to compute the effects of pH on light absorption and on photolytic rate constants, EXAMS requires a specific absorption spectrum (ϵ, EXAMS ABSORG vector) for each (dissolved) molecular species of the pollutant chemical. These absorption spectra can be deduced from the pK(s) of the compound and the absorption spectra of aqueous solutions of the chemical, measured at several pHs. The procedure is analogous to that described for reaction quantum yields in Chapter 2.3.3.3. For example, Smith and coworkers ((1978)) measured the absorption spectrum of p-Cresol at pH 5.1, 7.0, and 8.9 (**Table 10**). Para-cresol is a weak organic acid (pKa = 10.2); at pH 5.1, 7.0, and 8.9 the anion is present as only 0.00079, 0.063, and 4.77 percent of the total concentration. The observed spectra (**Table 10**) clearly indicate that the anion is the more strongly absorbing species.

Table 10. Light absorption spectra of p-Cresol in pure water. Measured values at pH 5.1, 7.0, and 8.9 from Smith et al. 1978. Calculation of molecular species absorbance and estimated pH 7 solution absorbance described in text. pKa=10.2

Center	Spectral Absorption Coefficients ϵ, $cm^{-1}M^{-1}$					
λ, nm	pH 5.1	pH 7.0	pH 8.9	RH_3	RH_2^-	pH 7.0
297.5	14	18	193	14	3767	16
300.0	3.8	7.2	173	3.8	3551	6.0
302.5	2.4	3.8	150	2.4	3097	4.4
307.5	0	2	92.6	0	1941	1.2
310.0		2	63.5		1331	0.8
312.5		1	40.3		845	0.5
315.0		0	24.1		505	0.3
317.5			13.0		272	0.2
320.0			6.2		130	0.08
323.1			3.8		80	0.05
330.0			0			

The observed absorption coefficient at any fixed wavelength is the sum of absorbance attributable to the uncharged (RH_3) molecule, plus that attributable to the anionic (RH_2^-) species. Denoting the observed absorption coefficient as ε_0, this sum can be expressed algebraically:

$$\varepsilon_o = \alpha(RH_3) \times \varepsilon(RH_3) + \alpha(RH_2^-) \times \varepsilon(RH_2^-) \quad (2\text{-}110)$$

This equation can be used to estimate the separate absorbances of the RH_3 and RH_2^- molecules. For example, at 297.5 nm, for pH 7.0:

$$\epsilon o = 18 = (0.999369)\ \epsilon(RH_3) + (6.31\times10^{-4})\ \epsilon(RH_2^-)$$

and at pH 8.9,

$$\epsilon o = 193 = (0.952)\ \epsilon(RH_3) + (0.0477)\ \epsilon(RH_2^-)$$

Simultaneous solution of these equations yields

$\epsilon(RH_3) = 15.6$ and
$\epsilon(RH_2^-) = 3734$.

The uncharged molecule is present as 99.9992% of the total concentration at pH 5.1, so the pH 5.1 spectrum can be taken as a direct experimental measurement of $\epsilon(RH_3)$. Given this, the absorption spectrum of the (RH_2^-) anion can be calculated using the pH 8.9 spectrum and Eq. (2-110). For example, at 297.5 nm,

$$193 = (0.952)(14) + (0.0477)\ \epsilon\ (RH_2^-)$$

gives ϵ (RH_2^-) = 3767. The accuracy of this procedure can now be evaluated by using Eq. (2-110) to predict absorbance of the solution at pH 7.0:

$$(0.999369)(14) + (6.31\times10^{-4})(3767) = 16\ (cm^{-1}M^{-1})$$

as compared to the experimental value of 18 $cm^{-1}M^{-1}$. The computed absorption spectra of the uncharged RH_3 molecule and the RH_2^- anion of p-Cresol are also shown in **Table 10**, along with the projected absorption coefficients at pH 7.0. The absorption spectra of the individual molecules are the appropriate data for entry into EXAMS' chemical data base (input vectors ABSORG).

2.3.3.5 Effects of sorption on photolysis rates

The effects on direct photolysis of sorption to suspended material are incorporated into EXAMS via separate disappearance quantum yields (QYIELD) for the sorbed forms of each dissolved species (RH_3, RH_2^-, etc.) of the compound. Although sorption can produce subtle and complex changes in the photochemistry of pollutants, light extinction by suspended particulate matter, and capture of sorption-prone chemicals by bottom sediments, relegate the effects of sorption to a secondary role. It should not be assumed, however, that sorption inevitably "protects" a chemical from direct interaction with solar radiation, so EXAMS allows for alternatives to this assumption via the QYIELD chemical input vector. (This capability is only available for compounds for which the absorption spectrum is known.)

The "sorption" process includes adsorption of a chemical onto particle surfaces, dissolution of uncharged species into suspended organic materials, and migration into the interior of particles via diffusion along pore channels. The particle microenvironment is often very different from that of the surrounding aqueous milieu. For example, the surface acidity of clay minerals can result in protonation of organic bases beyond that predicted by solution-phase pH and pK (Karickhoff and Bailey 1976). This effect can, at least in principle, be represented via EXAMS' separated partition coefficients for the ionic species of a pollutant (Chapter 2.2.2). The extent of the sorption/protonation process is influenced, however, by particle size, interactions with the solution-phase carbonate system, and inorganic cations adsorbed on the clay surface. These complexities, and the fact that mineral clays constitute a varying proportion of natural sediments, restrict EXAMS to the phenomenological approach described in Chapter 2.2.2. The photoreactivity of an organic acid or base can be affected by ionic speciation at the surface of adsorbent particles. Bailey and Karickhoff (1973) demonstrated this effect via its converse: these authors showed that UV spectroscopy can be used to monitor surface acidity of clay minerals via the shift in the absorption spectrum of adsorbed organic bases from that of the uncharged, to the protonated, molecular species.

The dissolution of neutral organic pollutants into suspended organic matter or surface organic films also removes the chemical from aqueous solution to a very different microenvironment. This organic microenvironment may alter the absorption spectrum, quantum yields, and photochemical reactions of a sorbed molecule, for organic sorbents usually differ from water in both refractive index and polarity. A change in the refractive index of the absorbing medium implies changes in spectral radiation density (erg cm^{-3} per unit frequency range) in the medium, and therefore in the apparent absorption spectrum of a pollutant chemical. Although the effects of such phenomena can be computed in some cases (Strickler and Berg 1962), the heterogeneity of natural suspended organic matter defies description. Particle size distribution (i.e., light extinction in the interior of the particle) would also affect the average radiation density experienced by a sorbed-phase pollutant.

In addition, reaction conditions within a suspended particle microenvironment must differ from those of aqueous solution; these differences can alter the reaction quantum yields and the kinds of photochemical products that result from irradiation of the system (Miller and Zepp 1979b). Suspended sediments may also retard sorbed-phase photoreactions by quenching excited states of the molecule, and may enhance photoreaction via indirect processes or "sensitized" reactions. Possible indirect reactions include the production of excited states or free radicals via irradiation of the organic matrix of the suspended particles, and photoelectric excitation of semiconductors, such as TiO2, which are a common constituent of many natural sediments (Oliver et al. 1979).

A few phenomenological investigations of the effects of natural suspended sediments on photochemical kinetics have appeared in the literature; the complexity of the phenomena has led their authors to describe their findings via apparent effects on reaction quantum yields. Oliver, Cosgrove, and Carey (Oliver et al. 1979) compared the effect of purified TiO2 semiconductor to the photochemical efficacy of Ti ores (ilmenite and rutile) and natural river suspensoids. Although purified TiO2 was an efficient photochemical catalyst, the Ti ores and the natural sediments alike simply suppressed the photochemistry of the test materials via competitive light absorption. Miller and Zepp (1979b), from studies of the photolysis of DDE and m-trifluoromethylpentadecanophenone (TPP) in natural suspended sediments, concluded that the sediment microenvironment is similar to a saturated hydrocarbon solvent. These authors reported an apparent increase in the disappearance quantum yield of sorbed DDE to 1.5 times its value in aqueous solution, and a factor of 2 to 6 decrease in the apparent quantum yield of TPP. Both results were consistent with the behavior of these compounds in organic solvents. Miller and Zepp (1979a) concluded that the competitive absorption of light by suspensoids is nonetheless the dominant effect of suspended particles on photolysis in natural waters.

2.3.3.5.1 Sensitivity analysis of sorption effects on direct photolysis

Photolytic transformation of pollutant chemicals is an important process in many aquatic systems, most especially when photochemical transformation is the only degradation process capable of limiting organism exposures under environmental conditions. This process is critically dependent on competitive light absorption by suspended materials, and on the effects of sorption on the availability of a pollutant to photochemical processes.

In a natural water body, capture of a pollutant by benthic sediments removes the compound to a photochemically inactive (dark) sector of the ecosystem. The net photochemistry of a pollutant chemical thus depends on solution- and sorbed-phase photoreactivity, competitive light absorption by suspensoids, and capture of the pollutant by the benthic subsystem. The interactions among these processes can be explored via EXAMS. For the example simulations, the ecosystem was a small (1 ha) static pond, 2 m deep, with a 1 cm active benthic subsystem of bulk density 1.75 g/cc and water content 150%. The example compound had a near-surface half-life of 1 hour in solution, but was a full order of magnitude more photoreactive when sorbed with suspended sediments (QYIELD(1,1) = 1.0, QYIELD(2,1) = 10.0). The distribution function (DFACG) was taken as 1.20; EXAMS used the sum of light absorption by water itself (at 300 nm), plus the absorbance attributable to suspended sediments, to compute the average light intensity in the water column (Eq. (2-104)). Systematic changes in the partition coefficient of the chemical (KPS) and the concentration of suspended sediments (SUSED) were then used to elucidate their net effect on the photochemistry of the compound, under conditions most favorable for enhancement of phototransformation kinetics by sorption.

The results of simulations using a suspended sediment concentration of 10 mg/L and varying partition coefficients ($0–1\times10^6$ L/kg) are given in **Table 11**. These results are given in terms of pseudo-first-order half-lives for the water column subsystem alone, and for the entire pond ecosystem. (The whole-system half-lives assume that the rate of transport from the benthic subsystem into the water column does not limit the rate of photochemical transformation of the compound.) Under these environmental conditions, less than 1% of the compound in the water column is in the sorbed state for a partition coefficient less than 1000 L/kg. When the partition coefficient is greater than 1000, however, more than 85% of the resident material is captured by the (dark) benthic subsystem. The system-level half-life of the compound increases steadily with increasing Kp, despite the greater photoreactivity of the sorbed material.

The effect of competitive light absorption by suspended materials was examined by fixing the partition coefficient at 100 L/kg, and systematically increasing the concentration of suspended sediments from 0 to 10000 mg/L (**Table 12**). In this case, light absorption by the suspended sediments rapidly increased the photochemical half-life of the compound. This effect overwhelmed the enhanced photoreactivity of the sorbed material, despite the fact that more than half of the total compound in the system resided in the water column (at steady state).

Table 12. Effect of suspended sediment concentration [S] on net photoreactivity when partition coefficient Kp = 100 L/kg, and suspended sediment concentration = 10 mg/L (Average light intensity in water column 11.8% of surface value)

[S] mg/L Kp L/kg	% of Water Column in Dissolved State	% of Total Resident in Benthic Zone	Mean Iz/Io	Pseudo-First-Order Halflives, h Water Column	Whole System
0	100	36.96	84.8	1.18	1.87
1	100	36.96	59.3	1.68	2.67
10	99.0	36.93	11.8	8.42	13.47
100	99.0	36.73	1.22	75.2	119.01
1000	90.9	34.7	0.12	449	688
10000	50.0	22.6	0.012	1484	1918
10000	90.9	98.2		4.68	253
100000	50.0	99.7		1.55	452
1000000	9.09	99.8		0.93	492

The system-level pseudo-first-order half life indicates the outcome of the interaction between competitive light absorption by suspended materials, capture of the compound by bottom sediments, and enhanced photoreactivity in the sorbed state. **Table 13** gives the system-level photochemical half life of a compound that is 100 times more reactive in the sorbed, than in the dissolved, state, for a range of Kp and sediment concentrations unlikely to be exceeded in nature. As compared with the 1.18 hour half-life of the unsorbed, clean-water baseline, an increase in sorption leads to a net suppression of the rate of photochemical transformation of the compound in all cases, despite the uniquely (and unrealistically) favorable conditions assumed for the analysis. In sum, the effects of residence in the sorbed state on photoreactivity are of secondary importance, and can be adequately summarized via a simple descriptive parameter (QYIELD).

Table 13. Effect of suspended sediment concentration (mg/L) and partition coefficient (Kp, L/kg) on system-level pseudo-first-order photochemical half-life (hours) when sorbed chemical is 100 times more reactive than dissolved species

Kp L/kg	Suspended Sediment Concentration, mg/L					
	0	1	10	100	1000	10000
0	1.18	1.69	8.52	82.2	819	8182
1	1.19	1.70	8.57	81.8	749	4157
10	1.25	1.79	8.93	79.1	437	861
100	1.87	2.65	12.3	65.4	125	209
1000	8.06	10.5	29.1	51.7	63.3	137
10000	69.9	50.0	45.9	49.0	56.6	130
100000	689	89.6	49.2	48.6	55.9	129
1000000	6876	97.4	49.6	48.6	55.8	129

The effects of sorption to organic slicks at the air-water interface are not included in EXAMS for similar reasons: Although the concentration in the slick can be large, the total fraction of the pollutant resident in the film is probably too small to have much effect on the system-wide kinetics of pollutant chemicals (Zepp and Baughman 1978).

EXAMS represents the photochemical effects of sorption to suspended sediments, and complexation with DOC, via separate entries in the QYIELD vectors. Note that these vectors represent the effect of residence in the biosorbed state on the direct photolysis of the pollutant; they are not intended to represent photosensitization or photobiological transformation of pollutants by phytoplankton. Although qualitative studies have indicated that this pathway exists, as yet a quantitative basis for predicting its magnitude and importance in natural systems has not been developed (Zepp 1980).

2.3.3.6 Near-surface solar beam and sky irradiance

The spectral light field is calculated by EXAMS as a vector ("WLAM" for W_λ) of 46 photon irradiances. W_λ is the total (solar beam plus skylight) irradiance under clear (cloudless) conditions, just below the air-water interface (that is, after subtracting reflected light from the light incident on the surface). EXAMS corrects the input irradiance for effects of cloud cover using the empirical relationship:

$$W_\lambda = W_\lambda (1 - 0.056(Cloud)) \qquad (2\text{-}111)$$

(Büttner 1938), cited from (Zepp 1980); see also (Schultz and Gräfe 1969).

The cloudiness (EXAMS' input *CLOUD*) term is the average opaque sky cover in tenths, with a range from 0 (clear sky) to 10 (full cover). Opaque sky cover may also be reported in oktas; an okta is one eighth of the celestial dome. Conversion from oktas to tenths may be made as follows:

WMO Code	Oktas	Tenths
0 (clear)	0	0
1	1 okta or less, but not zero	1/10 or less, but not zero
2	2 oktas	2/10 - 3/10
3	3 oktas	4/10
4	4 oktas	5/10
5	5 oktas	6/10
6	6 oktas	7/10 - 8/10
7	7 oktas or more, but not 8 oktas	9/10 or more, but not 10/10
8	8 oktas	10/10
9	sky obscured by fog or other meteorological phenomenon	
15	cloud cover indiscernible for reasons other than fog or other meteorological phenomenon, or observation not made	

Clear-sky irradiance at the earth's surface depends on latitude, site elevation, atmospheric turbidity and water vapor content, and the ozone content of the stratosphere (Leighton 1961). Computational methods for estimating spectral irradiance have been explored by a number of authors (e.g., Leighton 1961, Green et al. 1974, Dozier 1980, Green et al. 1980, Green and Schippnick 1980, Green and Schippnick 1982). Zepp and Cline ((1977)), using a computer program ("SOLAR") available on request from those authors, calculated photon scalar irradiance W_λ at 39 of the wavelength intervals adopted for EXAMS. (They reported "midseason," "midday" spectral irradiance at 40° N latitude. For EXAMS, such values must be reduced by a day length factor (daylight hours/24), and sinusoid averaging over the photoperiod (i.e., multiplied by $2/\pi$).

Procedure PHOTO1 begins from near-surface pre-computed photolysis rate constants (KDP), and thus does not use the spectral irradiance vector W_λ in its computations. PHOTO1 adjusts KDP via a cloudiness correction (2-111), and also corrects KDP for the geographic translation from the latitude at which each KDP was measured (RFLAT) to the latitude of the ecosystem (LAT). The correction term is computed from the

total annual solar + sky radiation received at latitudes RFLAT and LAT. Ground-level radiation was computed as a function of latitude at 10 degree intervals via procedures described by List (1966) using an atmospheric transmission coefficient of 0.90. Estimated total radiation increased from 1.038×10^5 cal cm^{-2} yr^{-1} at the pole, to 2.744×10^5 langley yr^{-1} at the equator. Regression of the (8) estimates on:

$$Y = a + b\cos(2L)$$

where L is the latitude in radians, yielded $a = 1.917\times10^5$, $b = 8.705\times10^4$, and accounted for 99.7% of the variation in total irradiance (Y) with latitude. In procedure PHOTO1, the correction term for KDP is computed as:

$$KDP \leftarrow KDP \times \frac{a + b\cos(0.0349\,LAT)}{a + b\cos(0.0349\,RFLAT)}$$

For example, for a rate constant measured at the equator and a polar ecosystem,

$$KDP \leftarrow KDP \times \frac{a + b\cos(0.0349 \times 90)}{a + b\cos(0.0349 \times 0)}$$

This procedure is based on total solar energy input, and thus may underestimate the latitude dependence of photochemical transformation of pollutants that absorb sunlight most strongly at wavelengths < 320 nm.

2.3.3.7 Input data and computational mechanics – Summary

Procedure PHOTO1 was designed to evaluate chemicals whose absorption spectrum has not been quantified. Its primary input datum, KDP, is a vector of pseudo-first-order photolysis rate constants. A separate value of KDP can be entered for each existing ionic species (RH_3, RH_4^+, etc.). KDP must be calculated as an annual average value applicable to near-surface waters, under cloudless conditions and full-day average solar irradiance. EXAMS then adjusts the rate constant for light extinction in the water column, effects of cloud cover, and departure of the latitude of the environment (LAT) from the latitude at which the rate constant was measured (RFLAT). Effects of sorption and DOC-complexation cannot be represented; only the dissolved form of the chemical photolyzes.

The computations executed by procedure PHOTO1 are inherently less accurate than wavelength-specific computations based on the chemical's absorption spectrum (PHOTO2), because PHOTO1 cannot evaluate the effects of spectrally differentiated light extinction in the water column.

Procedure PHOTO2 couples the absorption spectra of the compound (ABSORG(1-46,k)) to the irradiance spectrum incident on the water body (Wλ). The QYIELD matrix contains measured disappearance quantum yields; it is also used in EXAMS to account for effects of sorption and complexation with DOC.

Both photolysis procedures operate on the incident light field to compute the average light intensity in each compartment of the ecosystem. (In PHOTO1, the incident light field has a nominal value of 1.0, because KDP has built into it the clear-sky irradiance at latitude RFLAT.) PHOTO1 uses a spectral composite light absorption coefficient for each sector of the water body computed via Eq. (2-105) at the user-specified wavelength (LAMAX); PHOTO2 computes the absorption coefficient for every spectral waveband (**Table 9**) from the pigment (CHL), dissolved organic carbon (DOC), and suspended sediment (SUSED) concentrations in each compartment (Equation (2-105)).

The water column ("E" and "H" compartment types) can be subdivided into as many horizontal slices as seems appropriate for a particular water body. EXAMS traces light extinction vertically through the slices by computing irradiance at the bottom of each compartment, as well as the average irradiance used for computing photolysis rate constants. When the (J-1) compartment is another E or H segment, irradiance at the bottom of the (J-1) compartment is taken as the starting point for irradiance computations in the current (J) sector. This scheme will fail, however, if the system definition rules given in Chapter 2.3.1.1 are disregarded.

An example of a logical, but improper, segmentation scheme is shown in **Figure 7**.

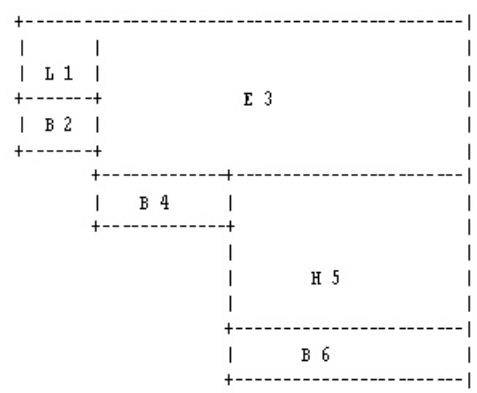

Figure 7. Improper segmentation: incomplete vertical definition

Calls to EXAMS' photolysis procedures are executed in compartment order. For this ecosystem, the first call computes photolysis in compartment 1, a (L)ittoral water column compartment. The incident light field at the air-water interface is identified as the light intensity at the top of the compartment, and EXAMS computes both average light intensity and irradiance at the bottom of compartment 1. Compartment 2 is a (B)enthic compartment; EXAMS simply sets the photolysis rate to 0 and does not call a photolysis procedure. Upon reaching compartment 3, EXAMS checks the compartment type of the

(J-1) compartment. As compartment 2 is “B” (benthic), the incident light field is used to start the computations. A photolysis procedure is not invoked for (B)enthic compartment 4. When EXAMS now calls for irradiance computations for the (H)ypolimnion compartment (5), an error occurs. EXAMS inspects (J-1) compartment 4, finds it to be (B)enthic, and starts its computations for the hypolimnion using the surface incident light field, rather than intensity at the bottom of the epilimnion.

The proper system definition is shown in **Figure 8**.

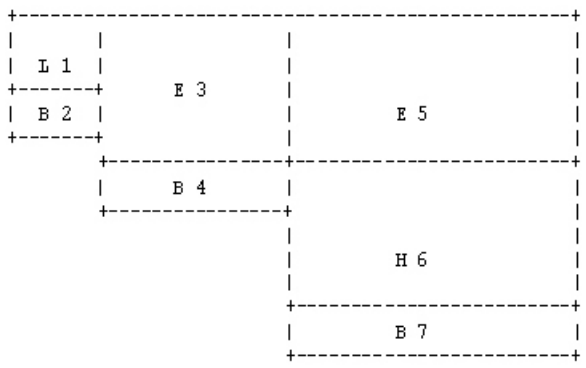

Figure 8. Proper segmentation: complete vertical definition.

In this case, upon initiation of computations for the hypolimnion (now numbered 6), EXAMS finds that the (J-1) compartment (5) is not (B)enthic, as it is an (E)pilimnion segment. The light intensity at the bottom of compartment 5 (internal variable BOTLIT in PHOTO1, vector BOTLAM in PHOTO2) is therefore retrieved and used to start the irradiance computations for the hypolimnion.

EXAMS reports the average light intensity in each sector of the ecosystem as part of its “canonical profile” of the system. These reports are given as a percentage of the light field incident on the water body, integrated over the ultraviolet portion of the spectrum (278.75–395 nm).

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2.3.4 Specific Acid, Specific Base, and Neutral Hydrolysis

Many organic compounds react directly with water in the aqueous solvent system. In addition, water dissociates into hydronium and hydroxide ions, and the concentrations of these subsidiary species often affect the rates of chemical transformations. EXAMS includes kinetic constants for three kinds of hydrolytic pathways: specific-acid (H_3O^+) catalyzed, neutral hydrolysis, and specific-base (OH^-) catalyzed transformations.

The breakdown of esters to yield a carboxylic acid and an alcohol is a convenient example of hydrolytic transformations. The overall reaction is:

$$RCOOR' + H_2O \rightarrow RCOOH + R'OH \qquad (2\text{-}112)$$

where *R* and *R'* can be any alkyl or acyl moiety. Although this equation accurately depicts the stoichiometry of ester hydrolysis, it does not serve as a defining equation for computing the velocity of the reaction. The rate of transformation of any specific ester is fundamentally dependent on its chemical structure. The speed of the reaction often depends on the pH of the medium as well, however, because ester hydrolysis can proceed via three distinct pathways (acid/base catalysis, neutral) with identical net stoichiometry.

Because chemical reactions involve shifts in electronic bonding orbitals, organic compounds are most readily attacked by groups that can donate or accept electrons from the target molecule.

Electron-deficient chemical species (e.g., hydronium ions, H_3O^+) are called "electrophiles." Electrophiles are particularly attracted to atoms with negative charge, to a lone pair of electrons, and to the electron-dense region of a double bond. Chemical groups with extra non-bonding electrons are called "nucleophiles." The electronegative hydroxide ion is a relatively strong nucleophile. The water molecule is itself nucleophilic, because the oxygen atom of this "polar" molecule has a lone pair of electrons.

The mechanisms of the formation and hydrolysis of organic esters have been reviewed by Kirby). Tinsley (Tinsley 1979:105 ff) has summarized the routes and mechanisms of ester hydrolysis under environmental conditions, where in all probability only the "A(AC)2"and "B(AC)2"mechanisms are significant. Although all three routes of ester hydrolysis involve nucleophilic phenomena, the mechanism of the pathway is somewhat different in each case.

Acid-catalyzed ester hydrolysis is a true "catalysis" reaction in that the hydronium ion participates in the reaction but is not consumed by the reaction sequence. In the first step of this pathway, the electrophilic hydronium ion protonates the carbonyl (C=O) oxygen. The protonated ester then undergoes a nucleophilic addition of water to give a tetrahedral intermediate; this step is catalyzed by a second water molecule acting as a general base. Finally, the tetrahedral intermediate breaks down via two additional (fast) steps to yield the product carboxylic acid and alcohol, and to regenerate the catalytic hydronium ion.

Because two water molecules are involved in the formation of the tetrahedral intermediate, the specific-acid catalyzed hydrolysis of the ester bond is "second-order" in water. With water as the solvent medium for the dissolved phase of the compound, however, the water concentration does not change during the course of the reaction and need not be incorporated in the kinetic expression. The observed rate constants are nonetheless subject to solvent effects and should be measured using pure water as the solvent whenever possible. The direct involvement of the water molecule in the reaction also imposes a need for care in the extrapolation of hydrolysis rate constants (measured in pure water) to compounds sorbed with sediments.

In EXAMS, all concentrations are referenced to the water phase of each compartment (Eq. (2-1)). The total pollutant concentration [*C*] (units mg/liter of water), when multiplied by the appropriate distribution coefficient α, gives the dissolved concentration of pollutant in the aqueous phase of each compartment, including that in the interstitial pore water of a benthic sediment. This fraction of the pollutant hydrolyzes at the rate measured via a homogeneous phase (pure water) experiment. EXAMS computes the effects of residence in a sorbed state (where water concentration can be quite small) on the reactivity of the compound via an additional set of input parameters (Chapter 2.3.4.3).

Neutral hydrolysis of organic esters proceeds via a mechanism similar to that of the second stage of the acid-catalyzed pathway. Two molecules of water are again involved in the formation of a tetrahedral intermediate, with one molecule of water acting as the nucleophile and a second water molecule acting as a general base catalyst. Although the neutral reaction is usually treated as a simple first-order process (Wolfe 1980), it is in fact technically second-order in water concentration. This reaction is thus also subject to solvent effects, and requires the same caution in extrapolation to sorbed states as was mentioned above for acid-catalyzed hydrolysis.

Alkaline hydrolysis, the third hydrolytic mechanism considered in EXAMS, is not strictly speaking a hydroxide-"catalyzed" reaction, for hydroxide ion is consumed in the reaction sequence, yielding the ester's constituent alcohol and the anion of its carboxylic acid. At trace concentrations of the ester in buffered natural waters, however, this distinction is of no practical significance. As in the neutral and acid-catalyzed pathways, a tetrahedral intermediate species is probably involved in alkaline hydrolysis. In this case, however, the intermediate is usually envisioned as resulting from a direct nucleophilic attack of hydroxide ion on the carbonyl carbon, with formation of the tetrahedral intermediate as the rate-limiting step in the reaction pathway. The tetrahedral intermediate then breaks down via release of an $R'O^-$ anion, and rapid proton transfer (to $R'O^-$), to yield the products of the reaction (R'OH and $RCOO^-$).

The overall rate of hydrolytic transformation is thus the sum of three competing reactions, and the observed rate constant (K_{obs}, units /h) can be computed as the sum of contributions from acid-catalyzed (KAH), neutral (KNH), and base-catalyzed (KBH) reactions (Wolfe 1980):

$$K_{obs} = KAH[H^+] + KNH + KBH[OH^-] \quad (2\text{-}113)$$

K_{obs} is a pseudo-first-order (h^{-1}) rate constant under the specified environmental conditions (pH, pOH) in pure water. After incorporation of the effects of ionization and sorption on reactivity, K_{obs} becomes the hydrolytic contribution to the overall pseudo-first-order rate constant *K* of Eq. (2-1). The second-order transformation rate constants are part of EXAMS' input chemical data base. KAH and KBH have units of reciprocal molarity and reciprocal hours ($M^{-1}h^{-1}$). KNH, the neutral hydrolysis rate constant, has units h^{-1}. The environmental data for this computation are entered as a separate pH and pOH for each sector (compartment) of the ecosystem; the EXAMS variables are "PH" and "POH," respectively.

The utility of this approach is not, of course, limited to chemical transformations of carboxylic acid esters. For example, amides, carbamates, and organophosphates break down via hydrolytic

mechanisms (Tinsley 1979). Also, many halogenated compounds are subject to unimolecular and bimolecular nucleophilic substitution (SN_1 and SN_2) or elimination (E_1 and E_2) reactions whose kinetics can be represented via Eq. (2-113).

Experimental studies of the rate of hydrolysis in buffered aqueous solution can be used to determine K_{obs} at fixed pH levels. In many cases KAH and KBH can be determined at low and high pH, respectively, where only one reaction pathway is significant. The pH-rate profile, a plot of log K_{obs} vs. pH, then includes a descending (acid catalyzed) and ascending (alkaline) limb, with slopes of -1.0 and +1.0, respectively (**Figure 9**). These lines intersect at the theoretical rate minimum, giving the best pH for an experimental determination of any neutral contribution (KNH). One or more of the reaction pathways may be undetectably slow for a particular compound, resulting in a simplified pH-rate profile. The use of pH-rate profiles for calculating hydrolysis rate constants has been described in more detail by Kirby (Kirby 1972:153) and by Mabey and Mill (1978).

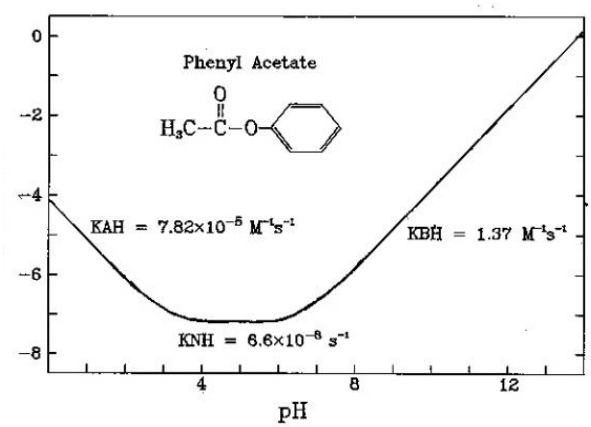

Figure 9. Hydrolysis pH-rate profile of phenyl acetate at 25°C. Profile constructed via rate constant data summarized by Mabey and Mill 1978 .

Reported chemical rate constants are often based on the second or minute as the unit of time. For use in EXAMS, such data must be converted to units based on the hour. For example, the neutral hydrolysis rate constant of phenyl acetate is 6.6×10^{-8} s^{-1} (**Figure 9**). EXAMS' chemical input parameter (KNH, units /h) would be 6.6×10^{-8} (s^{-1})×3600 (s/h)=2.38×10^{-4} h^{-1}.

2.3.4.1 Temperature effects

Each hydrolytic rate constant in EXAMS' chemical data base (KAH, KNH, KBH) has a paired input parameter that allows for alternative entry of the chemical information as an (Arrhenius) function of temperature. The pairings are KAH–EAH, KNH–ENH, and KBH–EBH, respectively. The rate constant variables (KAH etc.) are interpreted as the (Briggsian logarithm of the) "pre-exponential" or "frequency" factor in an Arrhenius function, only when the parallel activation energies (EAH *etc.*) are non-zero. When the input energy parameter is set to zero, EXAMS accepts the kinetic parameter (KAH, etc.) as the rate constant itself (compare Chapter 2.3.2.1). For example, an activation energy (*Ea*) for the neutral hydrolysis of phenyl acetate (ENH) of, say, 20,000. cal/mole would imply a frequency factor A =KNH / exp(-Ea/RT), (*T* in Kelvin) or, given KNH = 2.38×10^{-4} h^{-1} at 25° C (**Figure 9**), A=2.38×10^{-4}/exp(-20000./(1.99×298.15)) = 1.04×10^{11} h^{-1}, and log A, the EXAMS input (KNH) = 11.02 h^{-1}.

In this instance, if EXAMS were loaded with KNH=2.38×10^{-4} and ENH = 0.0, KNH would be used as the rate constant for neutral hydrolysis irrespective of the temperature (environmental input parameter TCEL) obtaining in the system compartments. Alternatively, EXAMS could be loaded with KNH = 11.02 and ENH = 20.0. In the latter case EXAMS would compute local (compartment specific) values of the neutral hydrolysis rate constant KNH via:

log KNH = KNH−((1000×ENH)/4.58(TCEL+273.15))

or, at TCEL = 25°C,

log KNH = 11.02−(1000×20)/(4.58×298.15) = −3.626

and

KNH = 2.36×10^{-4} h^{-1}.

In many cases the temperature dependence of a chemical rate constant is reported in terms of transition state theory, that is, as an enthalpy (H) and entropy (S) of activation. Given H in calories/mole and S in cal/deg/mole (also called "entropy units," e.u.), data reported under this convention can be converted to Arrhenius functions via (Bunnett 1961):

$$Ea = H + RT \tag{2-114}$$

and

$$\log A = \frac{S}{4.58} + \log T + 14.319 \tag{2-115}$$

in which *Ea* has units of calories/mole, and A is in h^{-1}. (Because the RT term is only about 600 cal/mol at room temperature, however, in many cases reported values of H are in fact uncorrected Arrhenius activation energies (*Ea*).)

For example, Wolfe and coworkers (Wolfe et al. 1977) found that malathion (O,O-dimethyl-S- (1,2-dicarbethoxy) ethylphosphorodithioate) breaks down via an acid catalyzed degradation with an enthalpy of activation (*H*) of 22.3 kcal/mol and an entropy of activation (*S*) of -4.1 eu. Using 15°C as the temperature for conversion, Eq.(2-114) gives Ea = 22300 + (1.987)(288.15) = 22872 cal/mol and an EXAMS input of EAH = 22.87 kcal/mol. The frequency factor *A* (Eq.(2-115)) would be: log A = −4.1/4.58 + log(288.15) + 14.319, yielding log A = 15.88 h^{-1} = KAH.

When a compound is subject to more than one degradation pathway, the rate constants must be combined prior to entry in EXAMS' chemical data base. For example, malathion undergoes an alkaline carboxyl ester hydrolysis plus an E_2 elimination reaction kinetically dependent on hydroxide ion concentration [OH^-] (Wolfe et al. 1977). These authors computed entropies and (uncorrected) enthalpies of activation for both reactions; this information could be used to generate an Arrhenius approximation for the total alkaline disappearance rate constant KBH via the transition state theory equation

$$KBH\ (h^{-1}) = (7.5018\times10^{13})(T)\times\exp(-H/RT)\times\exp(S/R),$$

where H = Ea - RT, as in Eq.(2-114). Whenever possible, however, it is probably better to rely on experimental determinations of the total disappearance rate constant, measured at environmentally relevant temperatures. In this case, the total (second-order) disappearance rate constant was measured at 0° and at 27° C; it was 0.067 and 5.5 $M^{-1}s^{-1}$, respectively. The activation energy and frequency factor can be easily computed from these data, giving KBH = 23.67 h^{-1} and EBH = 26.6 kcal/mol.

2.3.4.2 Ionization effects

Anions and cations of organic acids and bases can hydrolyze at rates differing greatly from those of the parent unionized species. This phenomenon can give rise to pH-rate profiles very unlike the archetypal example of phenyl acetate (**Figure 9**), including an apparent kinetic dependence on fractional powers of {H_3O^+} or {OH^-}. In order to encompass these phenomena, each of EXAMS' input kinetic parameters (and parallel activation energies) is set up as a 3×7 matrix of variables. The second index of these parameter matrices specifies the ionic species for which a particular rate constant applies. The first index allows for specification of the effects of sediment sorption and DOC complexation on reactivity; this aspect of EXAMS' input data is discussed in Chapter 2.3.4.3.

Consider, for example, the hydrolysis of the series of substituted 2- phenyl-1,3-dioxanes studied by Bender and Silver (1963). All the acetals in the series showed the usual acid-catalyzed hydrolysis, but those members containing an *o*- or *p*-phenolic substituent were reactive at alkaline pH as well. The pH-rate profile for one member of this series, 2-(4-hydroxy-5-nitrophenyl)-1,3-dioxane ("HND"), is shown in **Figure 10**. This profile includes a descending limb of slope -1.0 at low pH, a zone of little change in K_{obs} suggestive of a neutral mechanism, followed by a second descending limb in the alkaline pH range, which begins in the vicinity of pH = pKa.

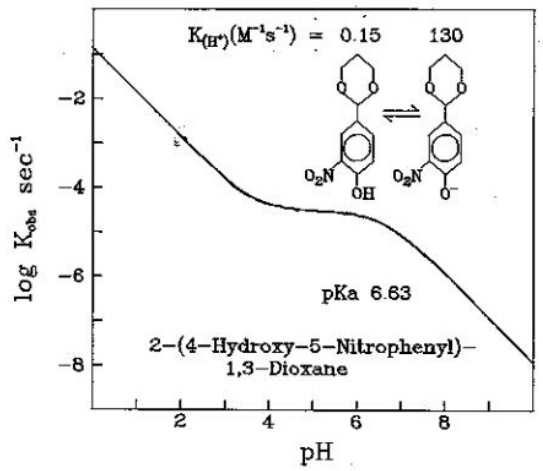

Figure 10. Hydrolysis pH-rate profile for a substituted 2-Phenyl-1,3-Dioxane. Data from Bender and Silver 1963.

From a comparison of the kinetics of *o*- and *p*-phenolic substituted acetals, and from the effect of deuterium oxide on these kinetics, Bender and Silver (1963) concluded that the hydrolysis of these compounds does not in fact proceed via a neutral mechanism. Instead, the initial descending limb is the result of the usual acid-catalyzed hydrolysis of the unionized species, and the descending limb in the alkaline pH region results from a similar acid- catalyzed hydrolysis of the phenolate anion (**Figure 10**). The anion is 860 times more reactive than the unionized species. The uniformity of K_{obs} at intermediate pH results from the increasing importance of the phenolate anion, as a fraction of the total concentration, in this pH range.

The hydrolytic kinetics of HND can be completely specified in EXAMS' chemical data base via the pKa of the compound and the rate constants for acid hydrolysis (KAH) of the uncharged and the anionic species. The existence of the unionized species and the phenolate anion is signaled by setting SPFLG(1) and SPFLG(5) to 1 (Chapter 2.2.1), and the pKa of HND is specified via PK(1) = 6.63. The second-order rate constants are 540 and 4.68×10^5 $M^{-1}h^{-1}$ for the parent compound and the anion respectively (**Figure 10**). This information is loaded to EXAMS by setting KAH(1,1) to 540, and KAH(1,5)=4.68E5. The first index (Chapter 2.3.4.3) simply denotes the form of the compound (1=dissolved). The second index specifies the ionic species to be transformed. Subscript (1,1) thus specifies the unionized dissolved HND as reacting at rate (540)[H_3O^+] h^{-1}, and subscript (1,5) specifies the phenolate anion as reacting at rate (4.68×10^5)[H_3O^+] h^{-1}.

2.3.4.3 Sorption effects

Sorption of a compound with sediment phases or complexation with DOC removes the compound to a microenvironment that can be very different from the free water phase of the system. For example, Miller and Zepp (1979) found that the daughter

product yields resulting from photolysis of DDE shifted from p,p'-dichlorobenzophenone toward DDMU (1,1-bis(p-chlorophenyl)- 2- chloroethylene) when the parent DDE was sorbed with suspended sediments. Photolysis of DDE dissolved in hexane also gave enhanced yields of DDMU. The authors concluded that the sorbed compound experienced a microenvironment similar to that of an organic solvent, very different from that of the aqueous phase.

Similar effects can be postulated for the majority of modes of chemical reaction of organic compounds in the environment. Presumably reactions like the neutral hydrolysis of carboxylic acid esters, in which the water molecule participates in the reaction, would be substantially inhibited by residence of the target molecule in a sorbed state. An E_1 or SN_1 reaction might be little affected, however. Furthermore, the possibility of accelerated (sediment "catalyzed") reactions cannot be disregarded. Although no definitive studies on the effects of residence in a sorbed state on chemical reactivity have appeared in the literature, such exploratory experiments as have been undertaken indicate that sorption "protects" many compounds from hydrolytic transformation. This is not a universal phenomenon, however, for in some cases the reactivity of compounds was not affected by residence in a sorbed state (Macalady and Wolfe 1985).

Obviously, then, the differences between the sorbed form of an organic compound and its dissolved phase can be as profound as the differences between, for example, an organic acid and its anions (Chapter 2.3.4.2). EXAMS therefore provides for the entry of rate constants (or Arrhenius functions) that specify the kinetics of sorbed forms completely independently of the reactivity of the aqueous dissolved phase of the compound. Each named kinetic parameter is a matrix with 21 elements, allowing for up to 7 ionic species with 3 forms (dissolved, sediment-sorbed, and DOC-complexed) of the parent (uncharged) compound and of its ions.

EXAMS computes the rate of reaction of the sorbed species under the assumption that the reaction is first-order in sorbed substrate. The model used to calculate these reaction rates can be described via a simplified example. In general, the rate of transformation of dissolved compound is given by:

$$\frac{d[C_W]}{dt} = -K_W[C_W] \qquad (2\text{-}116)$$

where $[C_W]$ is aqueous concentration (mg/L) and K_W is a first-order (or pseudo-first-order) rate constant (units h^{-1}). Similarly, the rate of transformation of the sorbed phase of the compound can be taken as:

$$\frac{d[C_S]}{dt} = -K_S[C_S] \qquad (2\text{-}117)$$

where $[C_S]$ is the concentration of the sorbed phase of the compound (mg/kg dry sediment) and K_S is a first-order rate constant.

Under EXAMS' assumption that a rapid (i.e., faster than the reaction rates) sorption equilibrium is maintained, $[C_W]$ and $[C_S]$ are in constant proportion to $[C_T]$, where $[C_T]$ is the total concentration of pollutant in the system. (In this context, "system" is equivalent to a single ecosystem sector (compartment), a well-mixed chemical apparatus, etc.) Within EXAMS, chemical concentrations are carried internally in units of mass/unit aqueous volume. Consequently the total rate of transformation of a compound is represented as:

$$\frac{d[C_T]}{dt} = K_W[C_W] + \rho K_S[C_S] \qquad (2\text{-}118)$$

where ρ is the sediment/water ratio (kg/L), that is, SEDCOL in the language of Chapter 2.2.2.

Given that the assumption of a rapid local sorption equilibrium holds good, however,

$$[C_W] = \alpha_1[C_T] \qquad (2\text{-}119)$$

and

$$\rho[C_S] = \alpha_2[C_T] \qquad (2\text{-}120)$$

where $\alpha_1=1/(1+\rho K_p)$, and $\alpha_2=\rho K_p/(1+\rho K_p)$, K_p the partition coefficient as described in Chapter 2.2.4. Substitution of Eq. (2-119) and Eq. (2-120) into Eq. (2-118) gives:

$$\frac{d[C_T]}{dt} = (\alpha_1 K_W + \alpha_2 K_S)[C_T] \qquad (2\text{-}121)$$

Equation (2-121) is (a simplified form of) the defining equation used to build EXAMS' algorithm for combining the reactivity of dissolved and sorbed forms into a single pseudo-first-order rate constant.

This formulation makes the conversion of experimental observations into a form suitable for EXAMS relatively straightforward. Suppose, for example, that a neutral organic compound ("NOC"), subject to a pH-independent transformation, is observed to have a half-life in pure water of 33 hours. The rate constant describing this process is $K_w=-(\ln 0.5)/33=0.021\ h^{-1}$.

This rate constant enters EXAMS' chemical data base via KNH(1,1) = 0.021. The first subscript of KNH denotes the dissolved form (1) of the compound; the second denotes an uncharged molecule. (As NOC is a neutral compound, only SPFLG(1) is set (i.e., = 1), and SPFLG(2...7) are 0, denoting the non-existence of any ionic species.)

Suppose, now, that NOC has a partition coefficient on a particular sediment of 90000 (mg/kg)/(mg/L), and an experimental determination is made of the half-life of the compound after sorption equilibration on a 100 mg/L

suspension of the sediment. (So long as local sorption equilibrium is maintained, the half-life can be ascertained by following either C_W or C_S over time.) The fraction of C_T present as dissolved and as sorbed NOC can be computed using ρ and K_p. The sediment/water ratio ρ is (100 mg/L)×(10^{-6} kg/ml) = 10^{-4} kg/L; the dissolved fraction is thus $\alpha_1=1/(1+\rho K_p)$ = $1/(1+(90000\times10^{-4}))$ = 0.10. Similarly, the fraction sorbed is $\alpha_2=\rho K_p/(1+\rho K_p)$ = $(90000\times10^{-4})/(1+(90000\times10^{-4}))$ = 0.90.

This experiment has three obvious possible outcomes. First, sorption may have no effect on the reactivity of the compound. Second, the observed half- life may be increased in strict proportion with α_1, that is, sorption may "protect" the compound. Finally, an altered half-life may be indicative of an altered, but non-zero, reactivity of the sorbed phase of the compound.

In the first case, when the presence of the sediment suspension has no effect on the rate of transformation of the compound, K_S is identically the same as K_W. EXAMS could then be loaded with KNH(2,1) = 0.021; the subscript "2" denotes the sediment-sorbed form of NOC.

When residence in a sorbed state inhibits the transformation reaction, the observed rate constant Kobs will decrease in proportion with the residual water concentration of the compound. From Eq. (2-121), Kobs = α_1Kw + α_2Ks. In this example, α_1 = 0.10, and, if Ks = 0, then Kobs = (0.10)(0.021) = 0.0021 h^{-1}.

The possibility that sorption "protects" the compound can thus be evaluated via the compound's half-life in a sediment suspension. Here, given Kobs = 0.0021, the half-life τ is given by:

$$\tau = -(\ln 0.5)/(0.0021) = 330 \text{ hours.}$$

In other words, an observed half-life that was not significantly different from 330 hours would be a clear indication that Ks = 0, and EXAMS could be loaded with KNH(2,1) = 0.

Finally, the observed half-life may be neither 33 nor 330 hours, indicating that the sorbed state, while reactive, does not transform at the same rate as the aqueous-phase dissolved compound. (In the event that the observed half-life were longer than 330 hours, Ks would be negative. The most probable explanation of such an event, however, is that either the sediment was contaminated with the study compound prior to the experiment, or that the assumption of rapid local equilibrium has been violated.) Any half-life >0 and ≤ 330 hours can be converted to a value of Ks via Eq. (2-121). If the half-life were less than 33 hours, the transformation must have been accelerated in the sediment phase and Ks > Kw. Suppose, however, that the half-life of NOC in the 100 mg/L sediment suspension was 150 hours. The first-order rate constant Kobs is then:

$$\text{Kobs} = -(\ln 0.5)/(150) = 4.621\times10^{-3}.$$

Given $K_{obs} = \alpha_1 K_W + \alpha_2 K_S$, then

$$4.621\times10^{-3} = (0.1)(0.021) + (0.9)\ \text{Ks}$$

and Ks = 2.80×10^{-3}. The rate of reaction of NOC in the sorbed state was thus 13.3% of that of the dissolved phase of the compound. This information could now be entered into EXAMS via the command SET KNH(2,1)=2.8E-3.

Second-order pH-mediated reactions occurring on sediments are accommodated in EXAMS in a wholly analogous way. EXAMS uses the solution-phase pH and pOH to compute rates of reaction, so of course the input data must also be developed from this perspective. The full 21-element matrices of KAH, KNH, and KBH allow for the specification of effects of both sediment sorption and DOC complexation on first-order, $[H_3O^+]$ mediated, and $[OH^-]$ mediated reactions. In addition, any of these rate parameters can alternatively be specified via an Arrhenius function, as described in Chapter 2.3.4.1.

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2.3.5 Indirect Photochemistry, Oxidation and Reduction

Direct photolysis is not the sole pollutant transformation process driven by the solar flux in aquatic systems. The simultaneous occurrence of plant decomposition products ("humic materials"), dissolved oxygen, and sunlight often results in an acceleration of the rate of transformation of organic pollutants (Zepp 1988a). Zepp et al. (1977a), for example, found that methoxychlor, with a direct photolysis halflife of more than 300 hours, had a halflife of as little as 2.2 hours under irradiation in natural waters containing dissolved humic materials. Further, Ross and Crosby (1975) found that a solution of aldrin in water from a taro paddy can be photochemically converted to dieldrin, despite the fact that aldrin does not absorb sunlight.

These kinds of reactions are usually termed "indirect" or "sensitized" photolysis. Indirect photolysis can be subdivided into two general classes of reactions. First, "sensitized photolysis" *per se* involves sunlight absorption and electronic excitation of a sensitizer (humic) molecule, followed by direct chemical interaction between the excited state of the sensitizer and a pollutant molecule. Possible chemical reactions include a direct energy transfer to the pollutant molecule, hydrogen atom transfer from pollutant to sensitizer to give free radicals, and union of sensitizer and pollutant yielding an excited-state complex or "exciplex" (Zepp and Baughman 1978). The resulting free radicals or exciplexes can then react with dissolved molecular oxygen, a process termed "type I sensitized photooxidation" by these authors.

The second class of indirect photolysis involves the formation of chemical oxidants in natural waters, primarily via the interaction of sunlight, humic materials, and dissolved oxygen (type II sensitized photooxidation (Zepp and Baughman 1978)). The primary oxidants known to occur in natural waters are hydroxyl (OH•) and peroxy (ROO•) radicals (Mill et al. 1978), singlet oxygen ($^1O_2$) (Zepp et al. 1977b). Alkoxy radicals and diradicals may also contribute to environmental oxidation of some compounds, but their presence in natural waters has not been conclusively demonstrated (Mill 1980, Mill et al. 1980).

2.3.5.1 Oxidation

EXAMS represents the oxidative transformation of pollutants via a phenomenological coupling of a second-order rate constant (KOX, units $M^{-1}h^{-1}$) to the molar concentration (OXRADL, moles/liter) of oxidants in each ecosystem compartment. The pseudo-first-order contribution of oxidation processes to the overall transformation rate constant K of Eq. (2-1) is computed for each (J) compartment via:

$$K\ (h^{-1}) = \text{KOX} \times \text{OXRADL}(J)$$

The input parameter KOX is a 3×7 matrix, allowing for separate entry of rate constants of ionic species and for control of the effects of sorption on reactivity. The subscripts have the same significance and use as described for KAH etc. in Chapter 2.3.4. Effects of temperature are entered via a parallel matrix of Arrhenius activation energies EOX (kcal/mol), again as described in Chapter 2.3.4 for hydrolytic reactions.

The occurrence and concentration of oxidants in natural waters has been investigated via the irradiation of chemical "probes" in a laboratory setting. Zepp et al. (1977b) studied the generation of singlet oxygen using solutions of 2,5-dimethylfuran (DMFN) in natural waters. DMFN gives 1,2-diacetylethylenes via 1,4-addition of singlet oxygen. The speed of this reaction upon irradiation of the solution gives a quantitative measure of the steady-state concentration of singlet oxygen in the solution. Similarly, Mill et al. (1978, 1980) have used cumene (isopropylbenzene) and pyridine as chemical probes for the steady-state concentrations of peroxy and hydroxyl radicals in irradiated natural waters.

Some results of these studies are given in **Table 14** (Data from Zepp et al. 1977b, Mill et al. 1980). These concentrations were determined via photolysis of thin layers of solution, and are presumably dependent on the intensity and spectral distribution of the solar flux in the solution. The average steady-state molar concentrations of oxidants were on the order of 10^{-13} for singlet oxygen, 10^{-9} for peroxy radicals, and 10^{-17} for hydroxyl radicals. More recent investigations have found surface concentrations of singlet oxygen from about 9×10^{-13} M down to 4×10^{-15} M (Haag and Hoigné 1986). Even at these low concentrations, singlet oxygen can be a significant factor in the environmental fate of substituted alkenes, phenols, anilines, and mercaptans (Weber 1998). Hydroxyl radical concentrations have more recently been reported to range from 10^{-15} to 10^{-18} M, with reaction with hydroxyl radical potentially accounting for as much as 15% of total carbaryl dissipation in some shallow water systems (Armbrust 2000).

Table 14. Steady-state concentration (moles/liter) of oxidants in some natural waters

Source	Singlet Oxygen ($M\times10^{13}$)	Peroxy Radical ($M\times10^{9}$)	Hydroxyl Radical ($M\times10^{17}$)
Aucilla River, FL	18	2.8	1.8
Okefenokee Swamp, GA	22		
Mississippi River, LA	5		
Coyote Creek, CA		9.1, 5.0	1.6
Boronda Lake, CA		9.5, 0.45	0.15

Carbonate radical is a secondary oxidant, produced in natural waters by reaction of hydroxyl radical with carbonate or bicarbonate ion. Steady-state concentrations in Ontario, Canada have been observed ranging from 5×10^{-15} to 10^{-13} M (Huang and Mabury 2000); in the Greifensee (Switzerland) summer carbonate radical concentrations are about 3×10^{-14}M (Larson and Zepp 1988).

Because light extinction in the water column reduces the volumetric average solar flux below that at the air-water interface, the oxidant concentrations given in **Table 14** apply only to the surface zone of natural bodies of water. The effect of light extinction can be computed from the equation:

$$I/Io = (1-\exp(-kZ))/kZ$$

where I/Io is the average light intensity expressed as a fraction of its surface value (Io), k is a diffuse attenuation coefficient (/m), and Z is the depth of the compartment (m). The factor I/Io is calculated by EXAMS for the UV light important in generating photochemical oxidants (280-395 nm), and then used to generate depth-corrected oxidant concentrations:

$$\text{OXRADL} = \text{OXRAD} \times (I/Io)$$

EXAMS allows for the entry of environmental concentrations of only one kind of oxidant other than singlet oxygen, which is treated separately (Chapter 2.2.5.2). For a compound reactive with more than one oxidant species, the rate constant and environmental concentration giving the most significant transformation rate can be entered, or a composite rate constant and environmental oxidant concentration can be computed and loaded in the data bases.

2.3.5.2 Singlet Oxygen

Singlet oxygen ($^1O_2$), an electronically excited state of the dioxygen molecule (O_2), is formed in natural waters by the transfer of solar energy from illuminated DOM. EXAMS calculates the concentration of $^1O_2$ in each surface water segment, using methods described by Zepp and coworkers (Zepp et al. 1985, Zepp 1988b), corrects for depth and couples the result to a 3×7 matrix of second-order reaction rate constants K1O2 for application in the mass balance Eq. (2-1). Generation of $^1O_2$ begins with the production of electronically excited triplet states (S^*) via absorption of sunlight energy by dissolved organic matter (S). The wavelength-specific quantum yields ϕ used in EXAMS for this process were computed from the relationship $\phi=0.015\ \exp(0.01(366-\lambda)$, where λ is the wavelength in nm. The pre-exponential factor in this relationship was derived from the average value of ϕ (0.015) reported for 11 natural waters at 366 nm (Zepp et al. 1977b), corrected as per (Haag et al. 1984a). The slope (0.01) was calculated from the observation that ϕ at 313 nm is approximately 0.025 (Haag et al. 1984b, Zepp et al. 1985). Example values are given in **Table 15**. Computation of light absorption by DOC uses the specific absorption coefficients ϵ of **Table 9**.

Table 15. Example quantum yields for production of triplet sensitizer *S from DOC**

λ (nm)	ϕ	λ (nm)	ϕ
280	0.035	400	0.011
300	0.029	450	0.006
312.5	0.026	490	0.004
350	0.016	650	0.0009

S^* decays back to its ground state by spontaneous decay (with first-order rate constant $Kdec\text{S}_3$, with units s^{-1}) and self-quenching interactions with other components of the DOM (second-order process rate constant $Kqnch$ with units $M^{-1}\ s^{-1}$). The second-order rate constant (Kox) for the production of singlet oxygen by energy transfer to dissolved oxygen from S^* is between 1×10^9 and 3×10^9 (R. G. Zepp 2000, oral comm.), for EXAMS it is taken as 2×10^9 $M^{-1}\ s^{-1}$ (Zepp et al. 1985). Singlet oxygen undergoes rapid physical quenching by water to ground state dioxygen with a pseudo-first-order rate constant $KdecO_2$ of $2.5\times10^5\ s^{-1}$ ((Rodgers and Snowden 1982) cited from (Haag et al. 1984a)). These reactions can be summarized by Eq. (2-122)-(2-124), where D is the distribution function and Iave is the average light intensity. The quantity ($\phi\ \epsilon$ Iave) is integrated across the sunlight spectrum during EXAMS' computations.

$$S \xrightarrow{\phi\varepsilon DIave} S^* \qquad (2\text{-}122)$$

$$S^* \xrightarrow{O_2,S,H_2O} S + {}^1O_2 \qquad (2\text{-}123)$$

$$^1O_2 \xrightarrow{KdecO_2} O_2 \qquad (2\text{-}124)$$

The steady-state concentration of $^1O_2$ in sunlit surface waters is given by

$$[^1O_2(ss)] = \frac{Kox[O_2]}{KdecO_2}[S^*(ss)] \qquad (2\text{-}125)$$

where

$$[S^*(ss)] = \frac{D[DOC]\int_{\lambda} \phi \varepsilon I ave}{Kox[O_2] + KdecS_3 + Kqnch[DOC]} \qquad (2\text{-}126)$$

Increasing the oxygen concentration from 2.6×10^{-4} M (air saturated) to 1.2×10^{-3} M (oxygen saturated) decreases *[S*(ss)]* by some 4× (Zepp et al. 1985). Given *Kox[O2],* the sum of the other terms in the denominator of Eq. (2-126) *($KdecS_3$* and *Kqnch[DOC]*) is 1.6×10^5. These experiments were conducted using [DOC] of about 20 mg/L (R. G. Zepp 2000, oral comm.). For EXAMS, the terms were equally partitioned, thus giving $KdecS_3 = 8.0\times10^4$ (s^{-1}) and $Kqnch = 4{,}000$ ($s^{-1}(mg/L)^{-1}$) for calculating steady-state concentrations of triplet sensitizer and singlet oxygen. Model performance can be gauged by comparison of EXAMS' calculated values to published estimates of surface concentrations of $^1O_2$ (Zepp et al. 1977b, Haag and Hoigné 1986). The calculated $^1O_2$ concentrations (**Table 16**) are acceptable except in the case of the three USA rivers with [DOC] < 15 mg/L; these waters (from the Wakulla, St. Marks, and Mississippi rivers) contained significant quantities of non-colored DOC (R. G. Zepp 2000, oral com.).

Table 16. Comparison of EXAMS' singlet oxygen estimates with literature values

Water	[DOC]	$[^1O_2]$ss $\times10^{14}$ M	
	mg/L	Lit Val	EXAMS
Lentic			
Türlersee[1]	8.3	2.8	9.7
Greifensee[1]	3.5	3.3	4.5
Lützelsee[1]	7.9	5.4	9.3
Etang de la Gruère[1]	13	11.6	14.
Okefenokee[2]	24	17.8	6.9
Lotic			
Rhine[1]	3.2	2.4	4.1
Kleine Emme[1]	3.2	4.1	4.1
Glatt[1]	4.1	4.6	5.2
Aucilla[2]	24	14.6	6.9
Ecofina[2]	41	15.4	9.0
Fenholloway[2]	77	13.8	11.
Wakulla[2]	6	0.16	2.4
St. Marks[2]	9	0.49	3.3
Mississippi[2]	14	0.41	4.8

1. June Swiss values from Haag and Hoigné 1986, corrected to full day values by day length and factor of 2/π
2. December USA values from Zepp et al. 1977b, corrected as above, normalized to flat water body by division by 2, and corrected for updated DMF rate constant via division by 1.6

2.3.5.3 Reduction

Anaerobic (reducing) environments are common in nature, including many groundwaters and saturated soils, aquatic sediments below the surface oxidized layer, waterlogged peats and marshlands, and, at least periodically, the hypolimnion of stratified lakes. Chemicals notoriously persistent in aerobic environments can be remarkably less so under anaerobic conditions (Macalady et al. 1986). In anaerobic sediments, the transformation half-lives of nitroaromatics can be from minutes to hours, with formation of aromatic amines as hazardous daughter products (Weber 1998). The responsible reducing agents may include ferrous iron, iron sulfides and dissolved sulfidic species (Simon et al. 2000), biochemical agents

produced by the benthos, and direct biolysis. Reductive transformations encompass a variety of reaction types and chemical classes, including reductive dechlorination, (or, more generally, reductive dehalogenation), reduction of nitroaromatic and azo compounds, reduction of N-nitrosamines across either the N-N or N-O bond, reduction of sulfoxides to thioethers, of quinones, and reductive dealkylation (Larson and Weber 1994). Prediction of the environmental concentrations of reducing agents has thus far proved intractable. The situation is further complicated by the observation that, although sorption inhibits reduction reactions, the velocity of the reaction increases with increasing sediment concentration. This result suggests that regeneration of the reducing agent by "electron-transfer mediators" may play in important role in governing the velocity of reduction pathways (Weber 1998), and that reducing agents maintain stable levels in the presence of low concentrations of reacting pollutants.

As with oxidants, EXAMS provides a phenomenological coupling between a reaction rate constant structure (the 3×7 matrices KRED) and an array (monthly for each environmental segment) of molar concentrations of reducing agents (REDAG). Effects of temperature are entered via a parallel matrix of Arrhenius activation energies ERED (kcal/mol), again as described in Chapter 2.3.4 for hydrolytic reactions. EXAMS does not include nominal values for REDAG.

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2.3.6 Microbial Transformations

Microbial communities are a ubiquitous constituent of almost all aquatic ecosystems. The microbiota play a central role in the remineralization of plant and animal debris; they have evolved the capacity to transform and harvest energy from an immense array of naturally occurring organic compounds. The optimistic hope that "the solution to pollution is dilution" to some extent had its origin in a naive faith in the ability of saprobic microbes to utilize any and all synthetic organic compounds in their metabolic mills.

Total faith in the ability of natural systems to absorb and detoxify synthetic chemicals was, of course, shaken by the discovery of the world-wide dispersal (and bioconcentration) of synthetic biocides, notably DDT and the related compounds DDE and DDD. It is now "axiomatic that micro-organisms are fallible and that many synthetic organic compounds are recalcitrant ... and accumulating in some environments" (Alexander 1979b). In consequence, qualitative "biodegradability" tests (Swisher 1970) are now routine in the detergent industry, and "sludge" tests have been suggested (Buzzell et al. 1969) as a routine procedure for evaluating industrial synthetic organic compounds. The latter tests can also provide some assurance that the compound will not destroy the microbial communities that serve man in sewage treatment plants, as well as providing an evaluation of the biodegradability of the compound (e.g., Baird et al. 1974).

The discovery of microbial fallibility has led to a more critical and quantitative view of microbial metabolism of synthetic organics; it no longer suffices to know that a compound is "biodegradable." Instead the rates, products, microbial populations, and environmental conditions surrounding an observed biodegradation are of increasing interest to the microbiological and ecological community. Given that the natural microbial substrates can massively accumulate in special circumstances (e.g., peat bogs and swamps), a degree of skepticism is obviously warranted toward any claim of universal, unconditional biodegradability of a synthetic organic compound. The rates at which a compound is biodegraded must depend upon both the structure of the compound, and on the metabolic capacity of the microbial community resident in the ecosystem receiving the compound.

Microbial communities derive energy for metabolism and growth from the breakdown of organic compounds, and the kinetics of growth and substrate utilization have been of interest to microbiologists for many years. Both population growth and substrate utilization rate have been described via Monod's (1942) analogy with Michaelis-Menten enzyme kinetics (Slater 1979). In this approach, the growth of a microbial population in a non-limiting environment is described by

$$\frac{dN}{dt} = \mu N \qquad (2\text{-}127)$$

where μ is called the "specific growth rate" and N is microbial biomass or population size. The Monod equation modifies Eq. (2-127) via the recognition that consumption of resources in a finite environment must at some point curtail the rate of increase (dN/dt) of the population. This fact is typically incorporated into Eq. (2-127) via

$$\mu = \mu_{\max} \frac{[S]}{K_S + [S]} \qquad (2\text{-}128)$$

in which $[S]$ is the concentration of the growth limiting substrate, μ_{max} is the "maximum specific growth rate" obtaining when $[S]$ is present in excess (i.e., non-limiting), and K_S, the "half-saturation constant" is that value of $[S]$ allowing the population to grow at rate $\mu_{max}/2$. An equation describing the behavior of the growth substrate $[S]$ over time, and thus by implication the dynamics of a biodegradable synthetic compound, follows via a simple derivation (Slater 1979): Assuming that a fixed amount of growth results from metabolism (and therefore loss from solution) of a unit quantity of S, then $dN = -Y\,dS$, where Y is the "yield coefficient" in cells or biomass produced per unit S metabolized. Taking

$$\frac{d[S]}{dt} = \frac{d[S]}{dN} \times \frac{dN}{dt} \qquad (2\text{-}129)$$

gives $dS/dt = -(\mu/Y)\,N$, or, substituting Eq. (2-128) for μ,

$$\frac{d[S]}{dt} = -\frac{\mu_{\max}}{Y} \times \frac{[S]}{K_S + [S]} N \qquad (2\text{-}130)$$

The observed microbial growth yield Y is often calculated from the amount of microbial biomass produced during the course of transformation of a measured quantity of substrate. Because a microbial population must satisfy maintenance requirements before any growth can occur, the apparent yield Y can fall quite drastically at low concentrations of S. Expressions with separated growth and maintenance yields have been developed by Pirt (1975) and it is possible to compute the separate magnitudes of growth and maintenance yields from microbial growth experiments (Slater 1979).

The Monod formulation (Eq. (2-130)) has been successfully applied to biotransformation of synthetic chemicals in a laboratory setting. These studies have demonstrated that a Monod analysis need not be restricted to single-species populations, that is, the Monod equations can serve as adequate descriptors of substrate transformation by "mixed" or "heterogeneous" (i.e., multi-species) microbial populations. In one example, Paris, Lewis, and Wolfe (1975) isolated a 4-species consortium of organisms able to use malathion as its sole source of carbon. Analysis of the growth response of the population and of concurrent malathion transformation rates then gave the Monod parameters μ_{max} = 0.37 /h, K_S = 2.17

μmol/L (0.716 mg/L), and $Y = 4.1\times10^{10}$ cells/μmol (1.2×10^{11} cells/mg). In a similar study, Smith and coworkers (1978) investigated the degradation of p-cresol by mixed microbial cultures able to use the compound as a sole carbon source. These authors expressed their results in terms of Monod parameters, finding μ_{max} = 0.62 /h, $Y = 1.8\times10^{9}$ cells/mg, and K_S = 0.84 mg/L.

Unfortunately, these elegant applications of classical microbiological methods to the biotransformation or "biolysis" of synthetic organic compounds are difficult to extrapolate to a broader ecological context. The first difficulty, which has received some attention in the microbiological literature, is primarily mechanical: The Monod formulation (Eq.(2-130)) is non-linear in its parameters, and thus imposes a high cost in computation time when used in a computer program or mathematical model. For trace concentrations of pollutants (i.e., $[S] << K_S$), however, the term ($K_S + [S]$) in the denominator of Eq.(2-130) can be approximated by K_S, giving the linear approximation

$$\frac{d[S]}{dt} = -\frac{\mu_{max}}{Y\,K_S} N[S] \qquad (2\text{-}131)$$

This formulation is similar to the "second-order" equations used to describe the kinetics of chemical reactions, and the term $\mu_{max}/(Y K_S)$ can by analogy be termed a second-order biolysis rate constant K_{B2}, with units /h/(cells/L) when population sizes N are expressed in cells/L.

The propriety of this substitution can be readily evaluated. For malathion, $\mu_{max}/(Y\ K_S)$ = $0.37/(4.1\times10^{10}\times2.17)$ $=4.16\times10^{-12}$ /h/(cells/L). Paris et al. (1975) also computed values of K_{B2} from microbial population sizes and malathion transformation rates in their experimental studies, finding a mean value for K_{B2} of $(2.6\pm0.7)\times10^{-12}$ (95% confidence interval) /h/(cells/L) for a series of 8 experimental determinations spanning a concentration range from 0.0273 to 0.33 μmol/L in malathion. The measured K_{B2} differed from $\mu_{max}/(Y K_S)$ by less than a factor of 2, suggesting that simplified kinetic experiments could be used to develop second-order rate constants, in lieu of a detailed elaboration of μ_{max}, Y, and K_S, when the region of concern is restricted to levels of compound $<< K_S$.

Furthermore, dissolved pesticide concentrations in surface waters are often very low indeed. For example, dieldrin, lindane, and DDT have been found primarily at ng/L levels both in the USA(1972) and in Britain (Brooks 1972). For industrial chemicals, however, the situation can be somewhat different. For example, the release of phenolic wastes into the St. Lawrence River results in riverine concentrations of 0.01 to 0.15 mg/L (Visser et al. 1977). Although these high concentrations are restricted to a dispersion cone immediately downstream of the effluents, K_S for p-cresol (0.84 mg/L) is uncomfortably close to the highest measured concentrations.

The need for a thorough evaluation of the propriety of Eq. (2-131) as an adequate approximation to the Monod formula (Eq. (2-130)) disappears, however, upon examination of the conceptual difficulties standing in the way of the application of either equation to environmental situations. A natural microbial community derives its energy from a large variety of organic detrital materials. A microbial species restricted to a trace-level synthetic compound as its sole carbon source would be at a severe competitive disadvantage; there is no way of predicting *a priori* the population densities the degrader could attain in real systems. Even when a synthetic compound is sufficiently similar to natural substrates that it can be indifferently degraded by the microbial community as a whole, the presence of multiple energy-yielding substrates in the environment violates a fundamental assumption underlying the Monod approach, that is, that [*S*], the synthetic compound, limits growth. In many instances, moreover, a compound may be transformed or degraded in an energy-requiring detoxification process, making the concept of cell yield (*Y*) of dubious utility. When the compound, for whatever reason, is degraded in the absence of a change in population size, the apparent zero yield forces abandonment of Eq.(2-130) and (2-131) alike. This phenomenon is sometimes called "cometabolism," e.g., (Alexander 1979a, Jacobson et al. 1980).

Despite these difficulties, the rate of transformation of organic pollutants must depend on the structure of the compound and the metabolic capacity of microbial communities. The simplest expression of this duality is the second-order equation

$$\frac{dS}{dt} = -\ K_{B2}[S] \times B \qquad (2\text{-}132)$$

which asserts that the rate of biolysis ($d[S]/dt$) is first-order in compound concentration [*S*] and in microbial activity, biomass, or population size *B*, and in which the identification of K_{B2} with $\mu_{max}/(Y\ K_S)$ is discounted. This approach requires that the second-order rate constant be determined via laboratory studies of relatively undisturbed samples drawn from natural microbial communities. It also requires demonstration that $d[S]/dt$ is linearly proportional to [*S*] for fixed levels of *B*, and that appropriate measures of *B* be found.

One conventional microbiological technique for characterizing microbial populations is simple population size, measured, for example, by colony counts on pour-plate agars (APHA 1976.). To the extent that population size is an adequate measure of community metabolic capacity, simple microbiological techniques could serve to characterize the rate of biotransformation of synthetic compounds in natural

environments. This hypothesis has been explored for three compounds – the butoxyethyl ester of 2,4-D (2,4-DBE), malathion, and chlorpropham – by Paris and coworkers (Baughman et al. 1980, Paris et al. 1981). These authors investigated biotransformation of their study compounds in samples of natural waters drawn from 40 locations in the continental USA. Ambient water temperatures at the collection points ranged from 1° to 29° C, and the laboratory studies were conducted at the observed ambient temperature of the sampled environments. Ambient bacterial populations, as measured by 48-hour incubation on TGE (tryptone glucose extract) agar at 22° C, ranged from 4×10^2 to 9×10^5 cells/ml (Paris et al. 1981). Biolysis of these chemicals was demonstrably first-order in compound concentration and in population size, and was relatively independent of temperature. The 95% confidence intervals (based on among-site variation) for K_{B2} (/h/(cell/L)) and the number of sites for these compounds were $(5.42\pm0.97)\times10^{-10}$ (2,4-DBE, 31 sites), $(4.54\pm0.74)\times10^{-11}$ (malathion, 14 sites), and $(2.63\pm0.72)\times10^{-14}$ (chlorpropham, 11 sites).

Evaluation of biolysis in such "river die-away" studies is particularly difficult when a combination of small populations and slow rates of biodegradation leads to inconveniently long biolysis halflives. In such cases population densities must be augmented via centrifugation or supplemental nutrient broth. The latter procedure can have the disadvantage of favoring opportunistic heterotrophs at the expense of organisms better equipped to degrade more recalcitrant compounds. For example, the second-order biolysis rate constant (K_{B2}) for chlorpropham is unaffected when population densities are augmented via nutrient broth supplementation, but the measured K_{B2} for phenanthrene decreases in approximate proportion with the population increase (Paris 1982, oral comm.).

Baughman, Paris, and Steen (1980) also reported second-order rate constants for biotransformation of synthetic chemicals by populations derived from aquatic sediments. The observed rate constants for 2,4-DBE and malathion were consistent with the rate of degradation by water-column populations, at K_{B2} of 2.3×10^{-10} and 4.0×10^{-11} /h/(cell/L) respectively. Aerobic biolysis of chlorpropham by the sediment-derived populations was, however, almost an order of magnitude faster ($K_{B2} = 1.42\times10^{-13}$) than biolysis by the water-column populations ($K_{B2} = 2.4\times10^{-14}$ /h/(cell/L)). By varying the sediment/water ratio, these authors also demonstrated that chlorpropham, methoxychlor, and several phthalate esters were unavailable to biolytic organisms when sorbed to suspended sediments.

Plate-count estimates of bacterial population densities are extremely selective and can underestimate total population sizes by three or more orders of magnitude (Jannasch and Jones 1959, Wetzel 1975:571, Fletcher 1979). Furthermore, although increases in pollutant flux (that is, kg m^{-3} s^{-1} or mass degraded/time) with increasing chemical concentration (consonant with pseudo-first-order kinetics) have been observed in nature (e.g., Sherrill and Sayler 1980), it is also true that, at elevated pollutant concentrations, both a reduction in the apparent first-order rate constant (Tinsley 1979:149ff), and zero-order kinetics (Visser et al. 1977) have been observed. The latter phenomena are consonant (mathematically) with Eq. (2-130). It is not clear, however, whether these kinetics are a reflection of the maximum growth rate of a specialized sub-population of degraders or result from toxic effects of elevated concentrations on the microbial community.

In any case, it is clear that the studies of second-order kinetics cited above are a useful beginning in the detailed quantitative study of rates of biotransformation of pollutant chemicals. Little more extrapolative power can be developed until such time as the environmental coupling variables that govern the metabolic capacity of natural and laboratory microbial populations have been rigorously determined and measured in both kinds of systems.

As a first approximation, EXAMS utilizes a simple second-order equation (Eq.(2-132)) to compute the rate of biotransformation of pollutant chemicals. Microbial population densities (as "colony forming units" (abbrev. cfu)) for each sector of the ecosystem enter EXAMS' environmental data base via the BACPL and BNBAC vectors. For water column compartments, BACPL has units of cfu/mL; BNBAC for benthic compartments has units cfu/100 g dry weight of sediment. (A useful summary of observed bacterial population densities in aquatic systems can be found at pp. 571-596 of (Wetzel 1975).) Second-order biolysis rate constants enter EXAMS' chemical data base via separated parameters for water-column (KBACW) and benthic (KBACS) populations. The nominal units are $h^{-1}(cfu/mL)^{-1}$ in both cases. EXAMS internally converts benthic microbial population densities to units (cfu/mL of water) commensurate with the units of the rate constant KBACS. This conversion is executed via the expression *(BNBAC × SEDMSL)/(100×WATVOL)* where SEDMSL is the mass of sediment in the compartment (kg), WATVOL is the volume of water contained in the compartment (Liters) (Eq. (2-21)), and the numerical factor (100) is a units conversion term (1000(mL/L)/10(decagrams/kg).

Despite the ruthless parsimony imposed on EXAMS' representation of biolysis kinetics, the degree of chemical detail provided by EXAMS' allowance for ionic and sorptive speciation leads to fairly substantial opportunities for the inclusion of biolytic kinetic detail. Both KBACW and KBACS are 4×7 element matrices for each chemical under study; each element represents a separate rate constant for the ionic and sorbed species of the pollutant. (The use of the matrix indices to specify chemical species is described in Chapter 2.3.4.) In addition, biolysis rate constants can be entered either as temperature-independent single values, or a Q_{10} function can be invoked to depict the

effects of temperature on biolysis rates.

The Q_{10} values (i.e., increase in biolysis rate per 10° C change in temperature) for KBACW and KBACS occur as the parallel matrices QTBAW and QTBAS, respectively. When the value of parameter QTBAW or QTBAS is non-zero, EXAMS takes the corresponding member of KBACW or KBACS as the biolysis rate constant at 25° C (in accordance with Subpart N guidelines), and recalculates the second-order rate constant via the Q_{10} equation:

$$K_{BAC,TCEL} \leftarrow K_{BAC,25} \times Q_{10}^{(TCEL-25/10)} \quad (2\text{-}133)$$

Because microbial communities frequently adapt their metabolic capacity to keep pace with slow secular (e.g. seasonal) changes in environmental temperatures, temperature responses measured in a laboratory setting do not always apply to environmental conditions. This limitation should be recognized when interpreting the results of EXAMS simulations that include temperature effects on biolysis rate constants.

Although the nominal units for bacterial numbers and for KBAC include bacterial population densities expressed as numbers/mL, clearly these variables can in both instances be redefined to encompass any environmental coupling variable of utility in estimating biodegradation rates in aquatic ecosystems. It is, however, especially important that these units be commensurate: For example, if the rate constants were determined via viable plate counts, and the natural population estimated via direct counts, biolysis rates would probably be grossly overstated. Furthermore, the simple second-order equation allows for a multiplicity of estimators of microbial capacity. For example, Neely (1980:117ff)) lists 7 commonly used estimators of microbial biomass or activity, including counting techniques, ATP and DNA analyses, and oxygen uptake. By suitable (user) redefinition of the nominal units of KBACs, BACPL, and BNBAC, EXAMS can be used to compute pseudo-first-order rate constants as a function of environmental variation in the presumed governing variable, so long as the rate constants and the bacterial population sizes are entered into EXAMS' data bases in commensurate units.

The mechanics of EXAMS' conversion of second-order biolysis rate constants and the compartment-specific environmental coupling variables to pseudo-first-order form are completely homologous with the equations used for chemical reactions. The total pseudo-first-order biolysis rate constant K is accumulated as the sum of expressions of the form $K = \alpha \times KBAC \times B$, where α is the fraction of the total pollutant concentration present in each existing ionic or sorbed chemical species, *KBAC* is the appropriate element of matrix KBACW or KBACS (corrected as needed for environmental temperatures using the Q_{10} equation), and B is the degrader population density or metabolic capacity of the microbial community in each ecosystem compartment. The sum of these pseudo-first-order (/h) expressions then becomes the biolysis contribution to the overall (compartment-specific) pseudo-first-order rate constant K of Eq. (2-1).

Biolysis rate data can alternatively be supplied as Aquatic Aerobic and Anaerobic Metabolism half-lives (in days). When no KBAC value is non-zero, these variables (AerMet and AnaerM) respectively) are converted to KBACW and KBACS.

AerMet and AnaerM are available for each chemical under study. At RUN time they are converted to internal second-order biolysis rate constants using properties of the water body. For aerobic metabolism, the average bacterioplankton population density is calculated and AerMet is converted to KBACW. For anaerobic metabolism, the average surficial benthic bacterial population density is calculated and AnaerM is converted to KBACS. In both cases, the resulting KBAC is applied to all dissolved forms (i.e., pH independence is presumed); DOC-complexes and sorbed forms are presumed to be unavailable for biolysis. In MODE 1 and MODE 2, the particular temporal element of the water body data selected for the RUN is used in the conversion (i.e., one of MONTHs 1-12 or 13 (average values)). In MODE 3, the bacterial populations of June, July, and August are considered. Aquatic metabolism inputs are only considered when user-entered second-order biolysis rates are not already present in the chemical data.

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2.4 Input Pollutant Loadings

The flux of a pollutant chemical entering an ecosystem (term "Le" in Eq. (2-1)) is a primary determinant of the ultimate exposure experienced by resident organisms. EXAMS does not compute pollutant *loadings*. Loadings may be developed via projected or measured industrial effluent fluxes, agricultural runoff, by transfer from the PRZM model, landfill seepages, etc., but these computations must be executed externally to EXAMS.

EXAMS provides input vectors for 5 kinds of loadings to each compartment of the system. These are: point-source or stream-borne loadings (STRLD), non-point-source loadings (NPSLD), contaminated ground-water seepage entering the system (SEELD), precipitation washout from the atmosphere (PCPLD), and spray-drift (or miscellaneous) loadings (DRFLD). The loadings have units of kg (of chemical)/hour in all cases. These loadings are taken as time-invariant constants in EXAMS' steady-state computations, or as monthly values when EXAMS is run in mode 3. In addition, both Mode 2 and Mode 3 provide for event loadings by specification of the date, chemical, and kg mass of the event.

Each non-zero pollutant loading must conform to the hydrologic definition of the ecosystem, or EXAMS will not implement the loading. For example, EXAMS will cancel a STRLD, NPSLD, or SEELD for a given compartment, if that compartment does not receive an appropriate carrier flow STFLO, NPSFL, or SEEPS respectively. (Definition and entry of the hydrologic variables is discussed in Chapter 2.3.1.1.) Precipitation (RAIN) is a monthly climatic variable in EXAMS; a PCPLD is therefore allowed only for compartments possessing an air-water interface. Non-zero PCPLD s are automatically canceled in the case of B (benthic) or H (hypolimnion) compartments. A PCPLD is unconditionally permitted for compartment number 1, which will always have an air-water interface if the system definition rules discussed in Chapter 2.3.1.1 are followed. For all other water-column compartments, EXAMS simply looks back at the (J-1) compartment. If this (J-1) compartment is also part of the water column, it is assumed to be directly above the current (J) compartment and any non-zero PCPLD is removed. Compartments with an air-water interface are always preceded by a benthic (B) compartment when EXAMS' system definition conventions (Chapter 2.3.1.1) are observed.

EXAMS' subroutine CKLOAD evaluates the propriety of the four kinds of loadings that enter via carrier flows. These loadings are evaluated against the volume of the carrier flows and the water quality characteristics of the target compartment. These evaluations were designed to prevent inadvertent specification of a loading outside EXAMS' operating range. In particular, EXAMS makes no provision for crystallization of the compound from solution, nor does the program allow for a gradual dissolution of chemical from a condensed (solid or liquid) phase. In addition, the non-linearities potentially present at high chemical concentrations (non-linear sorption isotherms, appreciable light absorption by the compound, zero-order biolysis, etc.) are not incorporated in the code. EXAMS' loading check computations are divided into two groups: checks based on carrier flows of water alone (PCPLD and SEELD), and checks based on carrier flows of water plus an entrained sediment loading (STRLD and NPSLD).

Ground-water seep and rainfall loadings are simply constrained to aqueous solubility. In these computations, the temperature (TCEL) and pH (PH and POH) of the compartment receiving the load are used to compute (as appropriate) the solubilities of each ionic species of the compound, and the distribution of the pollutant among its ionic species (distribution coefficients α, computed as described in Chapter 2.2). EXAMS then computes the concentration of pollutant in the carrier flow. If the solubility criterion is exceeded, EXAMS reduces the load to the extent necessary to conform to the upper limit of EXAMS' operating range, notifies the user of the modification(s), and returns control to the user without executing a simulation. The loadings are recomputed as the product of the limiting concentration and the carrier flow rate, that is,

$$Load = \frac{(Limit)(Inflow)}{\beta} \qquad (2\text{-}134)$$

where *Load* is in kg/h, *Inflow* in L/h, *Limit* (kg/L) is one-half the solubility of the least soluble chemical species, and β is the fraction of the total concentration present in the least soluble dissolved form.

Each streamflow (STFLO) or non-point-source water flow (NPSFL) entering a compartment may have an associated stream sediment (STSED) or non-point-source sediment (NPSED) loading (kg sediment/h) to the compartment. STSED and NPSED are not used in transport computations (see Chapter 2.3.1.3). In the course of evaluating stream-borne and non-point-source pollutant loadings, EXAMS computes a sorption equilibrium for capture of the pollutant by entrained sediments in the stream or non-point-source flows entering each compartment. These computations use the temperature, pH, and sediment partitioning parameters (e.g., organic carbon content (FROC) and ion exchange capacities (AEC and CEC)) of the receiving compartment. From the sediment/water ratio of the carrier flow, EXAMS computes the distribution coefficients (α) of the chemical in the carrier flow.

If the residual aqueous concentration of any dissolved species exceeds its concentration limit, the offending loading is reduced via Eq. (2-134), the simulation is aborted, and control is returned to the user for evaluation. EXAMS' method for calculating concentration limits that ensure linearity of sorption isotherms is described in Chapter 2.2.2.

After checking the loadings and making any necessary modifications, summing all external loads and units conversion from kg/h to mg/h yields term Le of Eq. (2-1).

"Drift" loadings (DRFLD) are initially implemented uncritically. If, however, EXAMS' computations result in final steady-state chemical concentrations above EXAMS' operating range, any DRFLD s are then sequentially reduced until the computationally invalid estimates are corrected. (If MODE>1, or no drift loads were specified and the results are outside the operating range, EXAMS aborts the run and returns control to the user for corrective action.)

The DRFLD vector can be used to specify miscellaneous loadings not encompassed in EXAMS' four other monthly loading types. EXAMS, for example, does not allow for entry of pollutant across the air-water interface from a polluted atmosphere (Chapter 2.3.2). The impact of a polluted atmosphere can, however, be computed from the bulk atmospheric partial pressure of the contaminant, and entered into EXAMS via the DRFLD vector. The net flux of pollutant across the air-water interface (F, moles m^{-2} h^{-1}) is given (see Eq. (2-71)) by $F = K_l (P_g/H - C_l)$ where K_l is the exchange constant (m h^{-1}), and both (P_g/H) and have C_l units of (moles m^{-3}). By assuming the bulk atmosphere to be uncontaminated ($P_g \equiv 0.0$), the term (P_g/H) was discarded in the development of EXAMS' algorithm for computing volatilization losses of pollutants from aquatic systems. In much the same way, the gross pollutant loadings imposed by a contaminated atmosphere can be computed by taking $C_l \equiv 0.0$.

Non-zero boundary conditions can be loaded into EXAMS via the DRFLD vector. EXAMS' environmental input data can include a characteristic length (CHARL), cross-sectional area (XSTUR), and dispersion coefficient (DSP) at any boundary of the system (by setting either JTURB or ITURB to zero, as described in Chapter 2.3.1.4). The exchange flow of water across the boundary is given by

FLOW (liters/h) = (1000)(DSP)(XSTUR)/(CHARL)

If the inlet exchange flow is contaminated to a level of [C] mg/L, the loading (kg/h) on the system of interest is simply:

$$LOAD = FLOW \times [C] \times 10^{-6} \text{ (kg/mg)}$$

This load can be imposed on the receptor compartment via the appropriate element of the DRFLD vector.

The final term in Eq. (2-1) is "Li," the sum of the internal loadings on the system compartments. Internal loads arise from two sources: chemical and biological transformation processes, and internal transport processes. The transport loadings arise from flows of contaminated water, sediments, and plankton among the physical sectors (compartments) of the ecosystem. Their magnitudes can be computed from the magnitudes of the flows, the distribution of the compound among its dissolved and sorbed species, and the concentration of the pollutant in the source compartments (expressed as mass/unit aqueous volume). EXAMS uses the WATFL (L/h) and SEDFL (kg/h) flow matrices (see Chapter 2.3.1.5) to compute a matrix of internal loading factors (EXAMS' internal variable INTINL), by associating carrier flows with appropriate elements of the α matrix (Chapter 2.2.4). This computation results in terms which, when multiplied by the total concentration of pollutant in the source compartments (mg/L), yield the mass loadings Li (mg/h) on the target compartments, constituents of the final term in Eq. (2-1).

2.4.1 Product Chemistry

Transformation products are an additional element in the internal loadings of some compounds. These are specified to EXAMS by setting the activity database (ADB) number of the parent and daughter within the current simulation specifications, the process generating the product, the reactive form of the parent molecule, the process yield, and, if desired, the enthalpy of the transforming process. The EXAMS input parameters are CHPAR, the chemical parent ADB number, TPROD, the transformation product ADB number, NPROC, the number of the process, RFORM, the reactive form of the parent molecule, yield, the (M/M) process yield, and EAYLD, the enthalpy (kcal).

The generating process is specified using the following codes for NPROC:

1 = specific acid hydrolysis
2 = neutral hydrolysis
3 = specific base hydrolysis
4 = direct photolysis
5 = singlet oxygen
6 = free radical oxidation (e.g., hydroxyl radical)
7 = water column bacterial biolysis
8 = benthic sediment bacterial biolysis
9 = reduction

Twenty-eight reactive forms are available for specifying RFORM, in addition to which total dissolved etc. can be specified using an RFORM of

29 = all dissolved species
30 = all sediment-sorbed species
31 = all DOC-complexed species
32 = all biosorbed species

(The complete list of RFORM specifications is given at the RFORM entry in the EXAMS data dictionary in Chapter 6 of this document.) The process YIELD may be entered as the simple mole of product per mole reacted, or as an Arrhenius function, in which case the enthalpy of the reaction is entered as EAYLD.

Entering transformation process chemisty requires specification of these parameters using a "pathway number" as the index for each complete reaction path. For example, if the parent compound (parathion) is recalled as ADB chemical 1, and the product (paraoxon) is recalled as ADB chemical 2, then a reaction scheme in which direct photolysis of DOC-complexed parathion yields a 50% generation of paraoxon , and hydroxyl radical oxidation of dissolved parathion produces paraoxon in mole-for-mole formation, would be specified to EXAMS as follows:

CHPAR	1	1
TPROD	2	2
NPROC	4	6
RFORM	3	1
YIELD	0.5	1
EAYLD	0	0
Pathway:	1	2

Given these specifications, EXAMS calculates the resultant generating flux (in this case of paraoxon, chemical number 2) from the breakdown of the parent material(s) (in this example, parathion, chemical number 1), and adds the resulting terms to the mass loadings Li (mg/h) in each segment, thus completing Eq. (2-1).

EXAMS allows for multiple transformations; any one of the chemicals being studied can generate any of the others. Among the possibilities thus available are regeneration of parent from product, generation of multiple products from a single starting material, reaction chains, etc.

2.5 Data Assembly and Solution of Equations

EXAMS includes three "modes" of operation: direct calculation of the "steady-state" outcome of long-term contamination (Mode 1), step-wise computation of the time course of contaminant exposure under a specified set of environmental conditions, (Mode 2), and computation of daily exposure concentrations using monthly updates of environmental conditions (Mode 3). The numerical integration techniques are the same, and the output summaries analogous, for each operating "mode" of the program.

2.5.1 Exposure

After computing all terms in Eq. (2-1), the resulting system of mass-balance equations can be divided through by the volume of the compartments to give a set of equations describing the rate of change of chemical concentration over time:

$$\frac{d[C]}{dt} = \frac{Le}{V} + \frac{Li}{V} - K[C]$$

(EXAMS allows the volumes of system elements to be altered by the user during the course of an analysis (except in Mode 1), and makes appropriate modifications to exposure levels. This feature is difficult to use, however, and requires care in interpretation. A version of EXAMS that includes dynamic changes in storage volumes (Mode 4) is in preparation.)

As time passes, the system evolves toward an ultimate "steady-state" condition at which the concentrations achieve stable values. This endpoint is defined by the condition d [C]/dt = 0.0 for every compartment. At steady state, then, the concentration of pollutant in each sector of the ecosystem is given by

$$[C] = \frac{\frac{Le}{V} + \frac{Li}{V}}{K} \qquad (2\text{-}135)$$

Numerical integration to steady state is notoriously profligate of computational resources, so EXAMS contains an explicit procedure (subroutine STEADY) designed to solve the equations for these concentrations, which define long-term exposure levels of the pollutant and can serve as a useful adjunct to any exposure analysis.

The logic of the situation can be illustrated via an elementary example. For the example, consider the behavior of a non-sorbing chemical, subject to neutral hydrolysis as its sole transformation process, in a static one-hectare pond. The pond is 1 meter deep, with VOL V therefore 10,000 m^3 (10^7 L). The benthic subsystem consists of a 5 cm active depth of material with a bulk density (BULKD) of 1.5 g/cc and a water content (PCTWA) of 150%. The environmental volume of the benthic zone (VOL) is 500 m^3; its aqueous volume is 250,000 liters of water (Eq. (2-21)). Defining exchange between the benthic subsystem and the water column via XSTUR = 10,000 m^2, CHARL = (1.05/2) = 0.525 m, and DSP = 10^{-4} m^2/h, the rate of exchange of fluid volume between the water column and the interstitial pore water (Chapter 2.3.1.4) is

$$WATFL = \frac{250{,}000}{500} \times \frac{10^{-4} \times 10{,}000}{0.525} = 952.4\ L/h$$

This exchange flow of water can be reduced to its pseudo-first-order effect on chemical concentrations (Kt, /h) in the water column (w) and the benthic (b) subsystem via:

$Kt(w) = 952.4/10^7 = 9.524\times10^{-5}$ /h, and

$Kt(b) = 952.4/250{,}000 = 3.810\times10^{-3}$ /h

As the compound does not sorb, transport of sediment and plankton can in this instance be ignored.

The internal loadings on the system arise from pollutant contamination of the 952.4 L/h exchange flow between the system compartments. All the compound is present in dissolved form in this example; sorbed and complexed exchange processes are here immaterial. EXAMS computes its internal load factors Li/V by dividing the elements of INTINL by the volume of the target compartment. In this instance, the load factor on the benthic subsystem resulting from contamination of the water column is

$$INTINL(b,w) \leftarrow (952.4 \times 1.00)/250{,}000 = 3.810\times10^{-3}\ /h$$

and the load factor on the water column resulting from contamination of the benthic interstitial water is

$$INTINL(w,b) \leftarrow (952.4 \times 1.00)/10^7 = 9.524\times10^{-5}\ /h$$

(INTINL and Kt are equal in this much simplified example; this is not usually the case.)

Finally, given an external load on the water column (here a DRFLD) of, say, 0.02 kg/h, and a neutral hydrolysis rate constant of 0.01 /h, the behavior of the chemical in the system is given by:

$$d[Cw]/dt=(0.02\times10^6/10^7)+9.524\times10^{-5}(Cb)-(0.01 + 9.524\times10^{-5})Cw$$

$$d[Cb]/dt= 3.810\times10^{-3}(Cw) - (0.01 + 3.810\times10^{-3})Cb$$

where Cw is the aqueous concentration in the water column and Cb is the aqueous concentration in the interstitial pore water (mg/L). At steady state, d[Cw]/dt = d[Cb]/dt = 0.0, resulting in 2 equations in 2 unknowns:

$$-0.01009524\ Cw + 0.00009524\ Cb = -0.002$$

$$0.00381\ Cw - 0.01381\ Cb = 0.0$$

This elementary example can be easily solved to give Cw = 0.1986 and Cb = 0.0548 mg/L. EXAMS solves the simultaneous linear equations that describe steady-state concentrations by Gaussian elimination (Chapter 2.3.1.2). EXAMS' output for the example system described above is given in Exams Output Table 10.

```
Ecosystem: Static 1-hectare pond, 1 meter deep
Chemical:  Unsorbed chemical subject to neutral hydrolysis
-----------------------------------------------------------------
Table 15.01.  Distribution of chemical at steady state.
-----------------------------------------------------------------
Seg  Resident Mass   ******** Chemical Concentrations *********
 #                     Total    Dissolved  Sediments    Biota
     Kilos      %      mg/*     mg/L **     mg/kg       ug/g
--- -------- ------  ---------  ---------  ---------  ---------
In the Water Column:
  1  2.0     100.00  0.199      0.199      0.00       0.00
     ======== ======
     2.0      99.32

 and in the Benthic Sediments:
  2 1.37E-02 100.00  2.740E-02  5.479E-02  0.00       0.00
     ======== ======
     1.37E-02   0.68
Total Mass (kilograms) =     2.000
-----------------------------------------------------------------
 * Units: mg/L in Water Column; mg/kg in Benthic Zone.
** Excludes complexes with "dissolved" organics.
```

Exams Output Table 10. EXAMS output tabulation of steady-state concentrations.

As Gaussian elimination is not an infallible mechanism for executing these computations, EXAMS includes a second technique for computing the solution to the system of equations (Eq. (2-135)), which is invoked in those cases for which Gaussian elimination fails. This algorithm is an iterative "linear cascade" method that applies Eq. (2-135) to each compartment in turn, and then repeats the entire process until such time as the successive estimates for each compartment change by less than 0.0001%. EXAMS allows for up to 100,000 iterations of the full "linear cascade" computation. If the linear cascade terminates without full convergence, EXAMS aborts the run; this event generally can be taken as an indication that steady-state concentrations are unbounded. For example, a non-transformable chemical in a static pond without any export pathways will accumulate indefinitely; in this situation no "steady-state" condition can be computed. The degree of convergence achieved by EXAMS for the full ecosystem can be examined in the mass balance check printed as the final entry ("Residual Accumulation Rate") in EXAMS' output table entitled "Analysis of Steady-State Fate of Organic Toxicant."

In the elementary example given above, the linear cascade solution would proceed:

Iteration 1, step 1: solve for Cw (compartment number 1)

$$Cw = (Le/V + Li/V)/K = (0.002 + 9.524\times10^{-5}(Cb)) / 0.01009524$$

giving, as Cb at the moment = 0.0,

$$Cw = 0.002/0.01009524 = 0.19811$$

Iteration 1, step 2: solve for Cb (compartment number 2)

$$Cb = (Le/V + Li/V)/K = 0.00381(Cw)/0.01381$$

$$= (0.00381\times0.19811)/0.01381 = 0.05467$$

From the initial estimates, the second iteration proceeds to compute a refined estimate of Cw and Cb:

$$Cw=(0.002+(9.524\times10^{-5}\times0.05467))/0.01009524=0.19863$$

$$Cb=(0.00381\times0.19863)/0.01381 = 0.054799$$

The convergence test is computed for each compartment by calculating the relative change in the estimate. The change in Cw was

$$1 - 0.19811/0.19863 = 0.0026$$

and the change in Cb was

$$1 - 0.05467/0.054799 = 0.0026$$

As these test values are greater than EXAMS' convergence criterion (10^{-6}), EXAMS continues with a third iteration of the linear cascade. EXAMS judges convergence to be complete only when the relative change in every compartment is less than 10^{-6}.

In mode 2, EXAMS integrates from time "TINIT" to time "TFINAL" with output and intervals of "CINT" in units specified by "TCODE." At the end of an integration ("RUN"), the simulation is paused and the user can evaluate the results and choose to "CONTINUE" the simulation to some new value of TFINAL. In Mode 3, the minimum run time is one year, with monthly updates of environmental properties. Multiple years ("NYEAR") can be run as a single unit, or the continue command can be used to run blocks of years. When EXAMS is used in conjunction with the PRZM model, EXAMS reads the climate time-series used with PRZM and build a climatic data set consistent with the PRZM data.

2.5.2 Fate

After computing exposure concentrations, EXAMS evaluates the impact of each transport and transportation process on the behavior of the compound. During the course of reducing its input data to pseudo-first-order form, EXAMS preserves the value of each process' contribution to the overall pseudo-first- order rate constant K (Eq. (2-1)) for each compartment. The flux of chemical transformed or transported (mass/time) is then given by the product of the process rate constant, the concentrations, and the aqueous volume of each compartment. In the instance under review, the chemical fluxes attributable to neutral hydrolysis are

$$Fw = Khyd \times Cw \times WATVOL(w) \times 10^{-6} \text{ (kg/mg)}$$

$$= (0.01)(0.1986)(10^{7})(10^{-6}) = 0.01986 \text{ kg/h}$$

in the water column, and

$$Fb = (0.01)(0.05479)(2.5\times10^{5})(10^{-6}) = 0.000137 \text{ kg/h}$$

in the benthic subsystem.

EXAMS sums the fluxes (by process) over the entire system, and computes the significance of the process via division of the process flux by the sum of the external loadings on the system, followed by conversion of this result to a percentage basis. In the example, the total flux is (0.01986 + 0.000137) kg/h, the total loading was 0.02 kg/h, thus hydrolytic transformation accounts for 100(0.01986 + 0.000137)/0.02 = 100% of the input loadings, as of course it must in this elementary example.

EXAMS' output table containing the results of the flux analysis, entitled "Sensitivity Analysis of Chemical Fate," also includes estimated half-lives for removal or dissipation of the chemical from the system. These half-lives are computed under the assumption that internal transport delays are insignificant, giving a supplemental view of the general significance of each process. The half-life computations are executed via division of the total process fluxes by the total mass of pollutant resident in the system to give a system-wide pseudo-first-order rate constant Kpr. The half-life is then simply

$$T½ = - \ln(0.5)/Kpr$$

In the example case, the total resident mass (computed as the sum of volumes and concentrations) is 2.00 kg (Exams Output Table 10), and the projected hydrolytic half-life is therefore

$$T½ = (0.69315 \times 2.00)/(0.01986 + 0.000137) = 69.3 \text{ hours}.$$

EXAMS does not inflexibly report fluxes and half lives in hours, for in many instances the hour is an inconveniently small reporting unit. Instead, the program makes a preliminary evaluation of the total transport and transformation flux through the ecosystem, and computes a first-order estimate of the total half-life of the compound. This preliminary estimate is then used to select the most appropriate (hours, days, months, or years) time scale for reporting the results of all succeeding time-dependent computations. This estimate of the "system-level" half-life is also used to set the time intervals for EXAMS' Mode 1 "persistence" computations, as described in Chapter 2.5.3.

EXAMS' flux computations, along with its table of compartment-specific pseudo-first-order rate constants (output table "Kinetic Profile of Synthetic Chemical") provide a sensitivity analysis of the behavior of the pollutant in the particular ecosystem under study. These tables indicate the relative strength of the transformation processes, and thereby indicate which processes are in need of the most scrupulous and exact experimental determinations of rate constants. In addition, EXAMS interactive capabilities allow a user to vary the input data over a reported error bound, and thus determine, for example, the degree of uncertainty implied for exposure concentrations.

2.5.3 Persistence

EXAMS' final round of computations deal directly with a third (after exposure and fate) aspect of exposure evaluation in aquatic systems, that of the "persistence" of the compound. (These are a feature of Mode 1 only.) It should perhaps be emphasized that EXAMS computes local, rather than global, persistence, that is, EXAMS' computations address the persistence of compounds in the specific ecosystem under review, and do not address the global issue of the persistence of a compound after it leaves the local ecosystem. Thus, for example, a compound that is not subject to any transformation processes is *ipso facto* (globally) persistent. Within the more limited context of a particular ecosystem, however, export processes will ultimately result in a "cleanup" of the system, and the time required for this cleanup process can be computed. (As the ultimate exposure concentrations for a transformationally persistent chemical in a static (closed) system are unbounded, EXAMS never encounters the resulting infinite cleanup times.)

EXAMS begins its Mode 1 persistence computations by using the steady-state concentrations of pollutant in the system as a set of starting values or "initial conditions." These initial conditions are presented to the numerical integration package (subroutine DRIVER et seq.). The relevant set of differential equations, describing the behavior of the pollutant over time, is essentially Eq. (2-1) with the external loadings (Le) set to zero or struck from the equations:

$$\frac{d[C]}{dt} = \frac{Li}{V} - K[C]$$

In Mode 1, EXAMS computes the dissipation of the compound over time, taking the time required to encompass 2 (estimated) system-level half-lives as the endpoint of the simulation. The results of this simulation are summarized in EXAMS' output table entitled "Exposure Analysis Summary."

EXAMS makes use of two integration packages (Malanchuk et al. 1980). EXAMS initially calls upon a variable step size, variable order (1-12) Adams PECE[2] method. In the event that the equations prove to be mathematically "stiff," the partially complete integration is remanded to an alternate package that integrates stiff equations by a variable-order, variable step size code employing multi-step backward differentiation methods of order 1 through 6. The Adams method code was taken from (Shampine and Gordon 1975); the stiff equations method was derived from an algorithm originally developed by Gear (Gear 1971c, b, a).

[2] So called from their successive operations of *prediction*, derivative *evaluation*, *correction*, and final derivative *evaluation*.

EXAMS limits the expense incurred in the integration via a limitation on the total number of steps which these routines are permitted to execute. EXAMS writes out the secular dissipation of the compound at 12 equally spaced times, up to the endpoint (TFINAL) defined by 2 estimated system-level half-lives. If the integrators exceed their allotted expense allowance prior to integration to TFINAL, control is relinquished by the integrator for evaluation of the situation. If the integrators have failed to reach the first output point (TFINAL/12), EXAMS aborts all further persistence computations and so notifies the user. If at least one output point has been passed, EXAMS uses the latest point reached by the integrators in its persistence computations, and notifies the user that the dissipation simulation was abbreviated.

Integration expense is also influenced by the precision demanded. This can be controlled by the user by alteration of ABSER and RELER, the absolute and relative error criteria used by the numerical integration package. The smaller their values, the greater the precision of the analysis, but the greater the performance costs incurred. These parameters cannot be made arbitrarily small due to the intrinsic limitations of digital computing machinery; upon invocation EXAMS evaluates the numerical precision limitations of the computing platform and establishes limits for ABSER and RELER. If these are too large, the integrators will encounter stability problems, so it is sometimes worth experimenting with ABSER and reler to optimize the conditions of an analysis.

In the vast majority of cases, EXAMS' dissipation simulations conclude with a successful integration to TFINAL. EXAMS' output summary of the time course of dissipation via neutral hydrolysis in the static pond used as an example in Chapter 2.5.1 is given in ?.

```
Ecosystem: Static 1-hectare pond, 1 meter deep
Chemical:  Unsorbed chemical subject to neutral hydrolysis
-----------------------------------------------------------------
Table 19.  Summary time-trace of dissipation of steady-state
  chemical mass following termination of allochthonous loadings.
-----------------------------------------------------------------
  Time     Average Chemical Concentrations    Total Chemical Mass
  -----    -------------------------------    -------------------
  Hours  Water Column      Benthic Sediments   Water Col  Benthic
     -------------------- -------------------  --------- --------
     Free-mg/L Sorb-mg/kg Pore-mg/L Sed-mg/kg  Total kg  Total kg
-----------------------------------------------------------------
     0 0.20       0.0      5.48E-02   0.0        2.0     1.37E-02
    12 0.18       0.0      5.43E-02   0.0        1.8     1.36E-02
    24 0.16       0.0      5.30E-02   0.0        1.6     1.32E-02
    36 0.14       0.0      5.11E-02   0.0        1.4     1.28E-02
    48 0.12       0.0      4.87E-02   0.0        1.2     1.22E-02
    60 0.11       0.0      4.62E-02   0.0        1.1     1.15E-02
    72 9.63E-02   0.0      4.34E-02   0.0       0.96     1.09E-02
    84 8.53E-02   0.0      4.06E-02   0.0       0.85     1.01E-02
    96 7.56E-02   0.0      3.78E-02   0.0       0.76     9.44E-03
   108 6.70E-02   0.0      3.50E-02   0.0       0.67     8.75E-03
   120 5.94E-02   0.0      3.23E-02   0.0       0.59     8.08E-03
   132 5.27E-02   0.0      2.97E-02   0.0       0.53     7.43E-03
   144 4.67E-02   0.0      2.73E-02   0.0       0.47     6.82E-03
```

Exams Output Table 11. Sample EXAMS output for dissipation of chemical after removal of external loadings.

EXAMS prints a summary of the exposure and fate information generated by the program and also estimates and reports the length of time required for cleanup of the ecosystem. EXAMS reports, in the first instance, the percentage of the initial chemical masses in the entire water column and benthic subsystem that had been dissipated by time TFINAL. EXAMS then weights these dissipations according to the initial distribution of the chemical in the system, and reports a first-order estimate of the time required for the system to cleanse itself of the chemical mass accumulated at steady state. This estimate is computed as 5 (pseudo-first-order, weighted) half-lives; in a true first-order system this would correspond to dissipation of 97% of the mass of chemical initially present in the system. (The actual (mathematical) "order" of the system is defined by the number of compartments used to describe the ecosystem. For example, when a water-body is described to EXAMS via 20 segments, EXAMS compiles 20 linked first-order differential equations, and solves this system of equations to generate its outputs. The data used in EXAMS' persistence time computations is generated by summing the residual chemical masses over compartments, thereby following the dissipation of the chemical in the entire system. The computations are in this sense reduced order approximations; thus EXAMS reports are given as "rough" estimates (e.g., Exams Output Table 12).)

This computation can be illustrated via the results of the sample simulation given in ?. At the expiration of 144 hours, the resident pollutant mass had fallen from 1.986 to 0.467 kg in the water column. This dissipation of the pollutant represents a loss of

$$100\ (1 - (0.467/1.986)$$

or 76.5% of the original material. Similarly, the benthic subsystem has lost (0.0137 - 0.00682) = 0.00688 kg or 50.2% of its original mass of chemical. (The benthic sediment exhibits a slower loss of chemical as a result of continuing recontamination (Li, Eq. 10) of this subsystem from the water column.)

In a first-order system, the decrease of an initial mass of material Qo over time is given by

$$Q(t) = Q(0)\ \exp(-k \times t), \text{ or}$$

$$\ln(Q(t)/Q(0)) = -k \times t$$

where k is the first-order rate constant and t is time. The half-life is defined as the time required for Q(t) to reach Q(0)/2 or for Q(t)/Q(0) = 0.5, that is,

$$H = -\ln(0.5)/k$$

The first-order half-lives (H) for these water-column (Hw) and benthic (Hb) subsystems are, therefore:

Hw = (0.69315)(144) / ln(0.467/1.986) = 69.0 hrs, and

Hb = (0.69315)(144) / ln(0.00682/0.0137) = 143.4 hrs

At steady state, 99.32% of the compound is present in the water column, and only 0.68% is in the benthic subsystem (Exams Output Table 10). EXAMS thus estimates the time required for dissipation of the chemical as:

Td = 5 (0.9932 (Hw) + 0.0068 (Hb))

= 5 (0.9932 (69.0) + 0.0068 (143.4)) = 347.5 hrs

or 14.5 days. EXAMS output summary for this example is given in Exams Output Table 12.

```
Ecosystem: Static 1-hectare pond, 1 meter deep
Chemical:  Unsorbed chemical subject to neutral hydrolysis
---------------------------------------------------------------
Table 20.01.  Exposure analysis summary.
---------------------------------------------------------------
Exposure (maximum steady-state concentrations):
 Water column: 0.199     mg/L dissolved; total = 0.199     mg/L
 Benthic sediments: 5.479E-02 mg/L dissolved in pore water;
   maximum total concentration = 2.740E-02 mg/kg (dry weight).
 Biota (ug/g dry weight): Plankton:          Benthos:

Fate:
 Total steady-state accumulation:  2.00     kg, with  99.32%
   in the water column and   0.68% in the benthic sediments.
 Total chemical load: 2.00E-02 kg/ hour.  Disposition: 100.00%
   chemically transformed,   0.00% biotransformed,   0.00%
   volatilized, and   0.00% exported via other pathways.

 Persistence:
  After  144.      hours of recovery time, the water column had
  lost  76.49% of its initial chemical burden; the benthic zone
  had lost  50.21%; system-wide total loss of chemical =  76.3%.
  Five half-lives (>95% cleanup) thus require ca.    14.   days.
```

Exams Output Table 12. Example summary output table (Mode 1).

If the majority of the chemical had been present in the benthic zone, EXAMS would of course have given computational precedence to dissipation in the sediment subsystem for its estimate of decontamination time.

A more detailed evaluation of the persistence of the chemical can be executed via a graphical analysis of the time course of pollutant dissipation, plotted from the results of EXAMS' numerical simulation of this phenomenon (?). In interpreting EXAMS' estimate of the time required to dissipate the chemical, it should be remembered that EXAMS' estimate represents five half-lives, or about 97% removal of the initial mass. If this removal suggests that the chemical would still occur at unacceptable concentrations, a first-order evaluation of the time required to achieve a specified reduction can be computed from EXAMS' outputs. Suppose, for example, that the time to reduce the chemical to 0.01% of its initial value were the time of interest. This time is given by the expression (-ln(Q/Q(0))/K), where Q/Q(0) is in this case 0.0001. EXAMS' estimate of decontamination time is computed as (5)(0.69315)/K, where K can be regarded as a weighted whole-system first-order decay constant. EXAMS' estimate of dissipation time Td can thus be expanded via the approximation:

$$T = \frac{-\ln(Q/Q(0))Td}{(5)(0.69315)}$$

In this instance, Q/Q(0) = 0.0001, -ln(Q/Q(0)) = 9.21, and the time to reduce the chemical to 0.01% of its steady-state value is approximately $T = \frac{(9.21)(14)}{(5)(0.69315)} = 37$ days.

Note, however, that a continued first-order decay of chemical in the benthic subsystem would, at 37 days (888 hours), result in a residual of

100 exp(888 (ln 0.5 / Hb))

or 1.4% of the original benthic pollutant mass. The system-wide dissipation of the chemical may leave pockets of higher concentration in zones of restricted physical transport.

Extrapolations of EXAMS' results beyond the designed operating range of the program are probably ill-advised. If necessary, however, a plot of the results of EXAMS' dissipation simulation should be used to evaluate the propriety of a first-order extrapolation of system self-purification times.

References for Chapter 2.5.

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3.0 Tutorials and Case Studies[3]

3.1 Tutorial 1: Introduction to Exposure Analysis with EXAMS – Laboratory 1

I. First computer run of EXAMS (the overall Lab plan)

- Follow the directions in the "Lab 1, Exercise 1: Steady-State Analysis (Mode 1)" (page 86) through line 30. This will introduce you to the basics of running the program.

- Review the principles of running the program in "Mode 1" (the default mode, steady-state analysis).

- Stop and review the inputs, outputs, and interrelationships, complete the worksheets on pages 80 and 81 , and prepare for Lab. 2 by entering the Lab. 1 data for methyl parathion chemistry and its behavior in the standard pond on pages 84 and 85.

Ia. Running the program: Inputs

EXAMS has "User Data Bases" (UDB) for Chemicals, Environments, Loads, and Products (i.e., products of transformation processes). Each entry in the UDB is accessed by its number, e.g., CHEM 11. To run a simulation, you must

- Recall an environment (ENV)
- Recall at least one chemical (CHEM)
- Recall or set an input LOAD (i.e., the amount of pesticide added over time, or an event loading from spray drift or runoff).
- Set a MODE (default is Mode 1, steady-state analysis)

The RECALL command (REC) loads data from the UDB into the Activity Data Base (ADB), and changes the UDB number to an ADB number. For example, when you RECALL CHEM 11, its number in the *ADB* becomes CHEM 1.

Only one ENVIR can be active at any time. More than one CHEM can be active; this is especially useful when you specify the generation of a transformation product, e.g., production of 2,4-D by hydrolysis of 2,4DBE, the butoxyethyl ester of 2,4-D. In addition to the continuous long-term loads of Mode 1, you can also specify load events (as direct initial conditions in Mode 2, or from PRZM transfer files in Mode 3) and piece-wise (monthly) continuous loads.

Once you have specified the required information, the RUN command executes a simulation.

[3] I thank Dr. Frieda B. Taub of the University of Washington School of Aquatic and Fishery Science for her material contributions to the development of these introductory EXAMS laboratories.

Ib. Running the program: Outputs

EXAMS produces at least 20 output tables for each simulation. For complex, multi-year studies the total output can rapidly become overwhelming. In most cases, you will want to examine the ecotoxicological exposure information in one or a few tables and graphics, as you did in the introductory tutorial. Warning: when requesting a plot, make note of the variables you have asked for and their units, because the graphic will not provide the labels. The control variable "OUTFIL" is used to specify which output files are to be produced. These may include both ecotoxicological exposure files (EcoToxC.xms or EcoToxR.xms) and ordered sets of annual maximum series of standard, or user-specified (see variable "EventD") exposure event durations (files EcoRiskC.xms or EcoRiskR.xms.)

Type LIST HELP to display a list of the available input and output tables (as at lines 18 and 19 of the first introductory exercise). On some computers, [Shift][PrintScrn] will print the list.

- Note that Table 1 is an echo of the chemical input data.
- Because transformation product chemistry was not entered, Table 2 is empty.
- Because no pulse loads were specified (and are in any case irrelevant to steady-state analyses), Table 3 is also empty.
- Tables 4 through 13 are the environmental model, again an echo of the input data although Table 12 and Table 13 contain some inferred values. You will need to examine these tables to see what kind of an environment ENV 2 is so you can label your diagram on page 4. The EXAMS "data dictionary" (pages 176 ff.) includes descriptions and units for the parameters given in the tables.
- Table 14 contains load information.
- Tables 15 through 20 are output results.

For reference, you can PRINT ALL to get a paper copy of all the input and output tables (Tables 1-20, which may in some instances have several sub-tables).

Warning: The output file "report.xms" is overwritten each time you make an EXAMS run.

Once you have completed the worksheets on pages 80 and 81 , you may return to the introductory exercises to explore Mode 2 (initial value approaches) and Mode 3 (seasonal effects).

Name _

EXAMS Lab Assignment – Introduction

1. Working from the Mode 1 analysis, make a half-page diagram of the EXAMS pond environment (on the next page). Include the compartments, their sizes, numbers, and types, and the geometry and hydrology of the system.

2. What is the water solubility of methyl parathion? _

3. What mass (kg) of chemical is resident in the littoral water column at steady state?

4. What concentration (mg/L or ppm) of the chemical is dissolved in the littoral?

5. What is the bulk mass (kg) of the chemical in the benthic sediment?

6. What is the analytical concentration (mg/kg dry weight) in the sediment?

7. What is the exposure of benthic organisms (i.e., ppm dissolved in pore water)?

Do the different locations of the chemical and its concentration in the various media (water column, benthic sediments, pore water) make sense to you? If not, please discuss with your instructor – this is an important part of the exercise.

8. Of the processes considered, which two were responsible for the greatest loss of chemical?

(1) _____

(2) _____

9. Of the processes considered, which two were least responsible for loss of chemical?

(1) _____

(2) _____

Go back and examine the properties of the chemical and the environment and determine why these processes had the relative importance they did.

Given the properties of methyl parathion and the pond environment, propose at least three questions that the model could help you study (for methyl parathion or a related chemical, for the pond or a related environment). For example, if the pond were more oligotrophic with less numerous bacteria, what would be the steady-state exposure?

Diagram of EXAMS' Constructed Farm Pond

Your questions:

(1)

(2)

(3)

3.2 Tutorial 1: Introduction to Exposure Analysis with EXAMS – Laboratory 2

EXAMS' second tutorial (beginning on page 113) is a substantial exercise in assembling chemical data, building an environmental model (of the lower basin of Lake Zurich, Switzerland), validating the model against observed data and exploring the dynamics of an environmental pollutant. Here we will use the first part of that tutorial (chemistry of 1,4 dichlorobenzene) to illustrate chemical data entry and basic studies of the environmental behavior of pesticides and other organic chemicals.

1. Restart EXAMS from the DOS prompt. (It is sometimes safer to re-start the program when beginning a new problem to ensure that all previous results are deleted.)

2. Review what you did in Lab1. Note that the only required EXAMS commands were

```
RECALL CHEM 11
RECALL ENV 2
SET STRL(1,1,13)=.01
SET OUTFIL(1)=Y
SET OUTFIL(2)=Y
```

All the other commands you used (e.g., HELP, SHOW, CATALOG CHEMICAL, etc.) were optional entries to teach you how to use the program.

3. Add another chemical to the user database (UDB) and use it in the standard pond.

Type the following series of commands (note the similarity to the first part of the Lake Zurich tutorial). Press the Enter key after each line.

```
EXAMS                                   (To re-start the program)
REC CHEM 1 (This entry in the UDB is an empty template for loading new data.)
CHEM NAME IS 1,4-Dichlorobenzene
set mwt(1)=147.0
change sol(1,1) to 73.8
set kow(1)=2340
set henry(1)=2.66e-3
cat chem      (To see how many chemicals are in the UDB)
sto chem 12   (Assuming you have no CHEM 12 now)
REC ENV 2
SET STRL(1,1,13)=.01
SET OUTFIL(1)=Y
RUN
PRINT 15
PRINT 18
PRINT 20
```

If your computer doesn't print, use the screen listings (LIST 15, etc.) to start filling out the tables on pages 84 and 85.

4. Modify (eutrophy) the pond to increase the organic carbon content of the sediment (both the suspended sediment in the water column and the benthic sediment).

```
SHOW FROC(1,13) (Write down what you see) _
SHOW FROC(2,13) (Write down what you see) _
```

Look in the EXAMS User's guide for an explanation of the FROC parameter.

```
SET FROC(1,13)=0.4
SET FROC(2,13)=0.4
```

SHOW FROC(1,13) (Write down what you see) _
SHOW FROC(2,13) (Write down what you see) _
SHOW CHEM (Check that the values you added for the chemical are there; EXAMS may have added additional properties based on its understanding of pesticide chemistry. If so, you can use the HELP function to gain an understanding of these new values.
SHOW LOAD (Check to see that the load is what you expect it to be.)
RUN
LIST 15 (Fill in some of the table data on pages 84 and 85)
LIST 6
LIST 1
LIST 18
LIST 20
ENV NAME IS Hyper-eutrophic Pond (You are naming and will store this environment)
CAT ENV (To see how many you have)
STOR ENV 6 (Assuming you have 5)
CAT ENV (To make sure it took)

5. Determine how the first chemical (methyl parathion) would behave in the hyper-eutrophic pond.

REC CHEM 11
REC ENV 6
SET STRL(1,1,13)=.01
RUN
LIST 15 (Write your answers on the Tables)
LIST 6
LIST 1
LIST 18
LIST 20

Name _

1. Compare the chemical properties of methyl parathion and p-DCB. Provide number and units.
a. In what table are these variables found?
b. Where are the units listed?
c. Fill in the table. If necessary, use EXAMS' "help" functions to generate a consistent data set.

Chemical Property	Units	Methyl Parathion	1,4-Dichlorobenzene
Molecular Weight			
Solubility			
K_{ow} (n-Octanol:water solubility ratio)			
Henry's Law Constant			
KBACW			
KBACS			

If a value has not been entered or calculated by EXAMS, the EXAMS table entry is blank and its value is zero.

d. List the major differences between these chemicals that affect their fate and exposure.
I.

II.

III.

2. Compare the standard and the hyper-eutrophic ponds.
a. Define FROC _____
(_____ , _____) units _____

Variable	Standard Pond	Hyper-Eutrophic Pond
FROC (1,13)		
FROC (2,13)		

3. Compare the distribution and transformation of the two chemicals in the two environments.

Variable	EXAMS Table No.	Methyl Parathion		1,4-DCB	
		Std. Pond	Eutr pond	Std. Pond	Eutr pond
% in water column					
Kg in water col.					
% in benthic zone					
Kg in benthic zone					
Total mass (Kg)					
Conc in plankton (µg/g)					
Conc in benthos (µg/g)					
Flux (%load) from					
Bacterioplankton					
Water-borne export					
Volatilization					
Persistence: time to 95% dissipation					

4. Using the numbers you filled in above, explain why increasing the organic carbon content of the suspended and bed sediment had a major impact on 1,4-DCB, but not on methyl parathion. Is this realistic? If you think not, re-run the analysis and revise your conclusions.

5. Which of these chemicals would have a different environmental fate and exposure if the numbers of bacteria in the water column or benthic zone were changed. Why?

3.3 Command Sequences for Tutorial 1, Lab. 1

3.3.1 Lab. 1, Exercise 1: Steady-State Analysis (Mode 1)

Introduction to EXAMS. Execute the following commands at the EXAMS prompt. The object of the exercises is to gain a basic familiarity with the EXAMS command interface.

```
HELP
HELP HELP
HELP USER
HELP PAGES
SHOW VAR
HELP MODE
SET MODE to 1
CATALOG CHEMICAL
CATALOG ENVIRONMENT
CAT
LO
HELP RECALL
REC CHEM 11
RECALL ENV 2
HELP LOAD
SHOW LOAD
SET STRL(1,1,13)=.01
SET OUTFIL(1)=Y
SET OUTFIL(2)=Y
RUN
LIST
HELP
20
LIST 18
LIST 15
HELP PLOT
PLOT
KI
PL
3
6
0
0
```

3.3.2 Lab. 1, Exercise 2: Mode 2 Analysis of Initial Value Problems – Sixty Day RUn Time

```
REC CHEM 11
REC ENV 2
SET STRLD(1,1,13)=0.01
SET MODE=2
SHOW TI FR
HELP TCODE
SET TCODE=2
SET TEND=60
SET CINT=1
SHOW TI FR
SET OUTFIL(1)=Y
SET OUTFIL(2)=Y
RUN
PLOT KI PL
3
6
0
0
SHOW LOAD
ZERO LOAD
SHOW LOAD
SET ICHEM(1)=1
SET ISEG(1)=1
SET IMASS(1)=.1
SHO PU
SET TEND=14
RUN
PL KI PL
3
6
0
0
CONTINUE
```

```
34      28
35      CONTINUE
36      60
37      PL KI PL
38      3
39      6
40      0
41      0
42      PL KI PL
43      6
44      0
45      0
```

3.3.3 Lab. 1, Exercise 3: Time-varying seasonal analysis using Mode 3

```
REC CHEM 11
SET MODE=3
REC ENV 2
SET ICHEM(1)=1
SET ISEG(1)=1
SET IMASS(1)=.1
SET IMON(1)=5
SET IDAY(1)=15
SET ICHEM(2)=1
SET ICHEM(3)=1
SET ISEG(2)=1
SET ISEG(3)=1
SET IMASS(2)=.1
SET IMASS(3)=.1
SET IMON(2)=6
SET IMON(3)=6
SET IDAY(2)=1
SET IDAY(3)=15
SHO PU LO
SET OUTFIL(1)=Y
SET OUTFIL(2)=Y
RUN
PL KI PL
3
6
0
0
PL KI PL
3
0
0
CONTINUE
PLOT KI PL
3
```

35 0

36 0

37 LIST 20

38 Y

39 QUIT

3.4 Introduction to EXAMS – Lab. 1 Exercises with Complete EXAMS Responses

These three exercises illustrate the EXAMS command line interface, data entry, and operations "modes." The commands in the summary listings are given here in ***BOLD/ITALIC***. Note that EXAMS starts in Mode 1 when it is initially invoked, i.e., the default "Mode" is 1.

3.4.1 Lab. 1, Exercise 1: Steady-State Analysis (Mode 1)

To begin, at the DOS prompt, enter

```
C:> EXAMS
                     Welcome to EXAMS Release <current release number>
                    Exposure Analysis Modeling System

               Technical Contact: Lawrence A. Burns, Ph.D.
                   U.S. Environmental Protection Agency
                         960 College Station Road
                        Athens, GA 30605-2700 USA
                   Phone: (706) 355-8119  (Fax) 355-8104
                     Internet: burns.lawrence@epa.gov

                    Latest Maintenance <date of latest maintenance>

          Type HELP and press the RETURN key for command names,
               HELP USER  for a summary of command functions,
               HELP PAGES for a list of information pages,
          or   HELP EXAMS for introductory information.

     Please stand by while EXAMS checks the computational precision
     of this computer and initializes the Activity Data Base.


EXAMS-> HELP

EXAMS includes these system commands:

AUDIT        CATALOG      CHANGE       CONTINUE     DESCRIBE
DO (@)       ERASE        HELP         LIST         NAME
PASSWORD     PLOT         PRINT        QUIT         READ
RECALL       RUN          SET          SHOW (?)     STORE
WRITE        ZERO

Help pages describe the commands and additional topics:
ADB, COMMAND, EXAMS, INPUTS, LOADS, LODNAM, NEWDAT, TABLE,
TABNUM, TUTOR, UDB, USER, WILD

Text describing the commands, and the text of the additional
topics, can be seen by entering HELP <topic>, where <topic>
is either a command, one of the additional topics above, or
the name of one of EXAMS' input data parameters.

USER  gives a summary list of EXAMS' command functions.
PAGES gives an annotated list of EXAMS' information pages.
TUTOR is an introduction to using the HELP facility.
TABNUM describes EXAMS' table numbering scheme.



EXAMS-> HELP HELP
```

The HELP command invokes EXAMS' HELP facility to display information about a particular EXAMS topic. For a tutorial explanation of the HELP command, now type HELP TUTOR and press the RETURN key. For more detail on the available information, now type HELP USER or HELP PAGES and press the RETURN key.

Related topics: DESCRIBE
Syntax: HELP [command], or [EXAMS parameter]

HELP is also available from the interior of most EXAMS commands. A list of the "parameters" available through HELP can be invoked by typing "SHOW VAR". HELP provides definitions and dimensions of all these input data and control variables.

EXAMS-> ***HELP USER***

Command	Summary Description
AUDIT	Start/Stop user notepad for recording procedures
CATALOG	List the contents of User Databases (UDBs)
CHANGE/SET	Enter/reset input data and program controls
CONTINUE	Resume integration (Modes 2 and 3 only)
DESCRIBE	Report dimensions and data type of parameter
DO	Execute file of EXAMS commands (file.EXA)
ERASE	Clear section of stored database (UDB)
HELP	Describes access to EXAMS on-line HELP facility
LIST	Show tabular results on the screen
NAME	Specify the name of a UDB, e.g., CHE NAME IS ...
PASSWORD	Restrict Recall/Store access to UDB datasets
PLOT	Plot results on the screen
PRINT	Queue tabular results for hardcopy printing
QUIT	Abort command, or End interactive session
READ/WRITE	Upload/download data from non-EXAMS disk files
RECALL	Activate data from stored database (UDB)
RUN	Begin simulation run
SHOW	Display current data values or control settings
STORE	Download current data into stored database (UDB)
ZERO	Clear loadings, pulses, or current concentration

EXAMS-> ***HELP PAGES***

ADB	defines the term "activity database"
COMMAND	tells how to use EXAMS' system commands
EXAMS	describes the scope and operation of the program
INPUTS	describes EXAMS input data and data manipulation
LOADS	explains how to specify chemical loads on the ecosystem
LODNAM	gives EXAMS' special names for the chemical loadings
NEWDAT	tells how to begin entry of a new dataset
HELP	gives more explanation of the HELP facility
TABLE	explains why your initial outputs seem to disappear
TABNUM	explains the numbering system used for EXAMS' outputs
TUTOR	introduces EXAMS' HELP utility
UDB	defines the term "user database"
USER	gives a general command summary.
WILD	describes the use of wild cards in SET/CHANGE commands

Enter HELP and the name of a topic for further information.

EXAMS-> ***SHOW VAR***

```
CHEMNA ECONAM LOADNM PRODNM TYPE   AIRTY  FIXFIL IUNIT  MCHEM
KCHEM  MODE   PRSW   MONTH  NYEAR  YEAR1  TCODE  CINT   TEND
TINIT  ABSER  RELER  SPFLG  MWT    SOL    ESOL   PK     EPK
KOC    KOW    KPB    KPDOC  KPS    KIEC   MP     HENRY  EHEN
VAPR   EVPR   QYield KDP    RFLAT  ABSOR  LAMAX  KAH    EAH
KNH    ENH    KBH    EBH    KOX    EOX    K1O2   EK1O2  KRED
ERED   KBACW  QTBAW  KBACS  QTBAS  KOUNT  JFRAD  ITOAD  ADVPR
JTURB  ITURB  XSTUR  CHARL  DSP    SUSED  BULKD  FROC   CEC
AEC    PCTWA  TCEL   PH     POH    OXRAD  REDAG  BACPL  BNBAC
PLMAS  BNMAS  KO2    DOC    CHL    CLOUD  DFAC   DISO2  OZONE
VOL    AREA   DEPTH  XSA    LENG   WIDTH  RAIN   EVAP   LAT
LONG   WIND   ELEV   RHUM   ATURB  STFLO  STSED  NPSFL  NPSED
SEEPS  STRLD  NPSLD  PCPLD  DRFLD  PRBEN  SEELD  IMASS  ISEG
ICHEM  IMON   IDAY   IYEAR  SPRAY  CHPAR  TPROD  NPROC  RFORM
YIELD  EAYLD
```

EXAMS-> ***HELP MODE***

```
MODE is an integer scalar.
MODE sets the operating "mode" of EXAMS. Three operating modes
are available; these are selected by SETting MODE to 1, 2, or 3.

 MODE              Operational characteristics of EXAMS
 ----         ---------------------------------------------------
  1           Long-term (steady-state) analysis.
  2           Pulse analysis--specifiable initial chemical mass
              (IMASS) and time frame, time-invariant environment.
  3           Monthly environmental data, daily pulse loads IMASS
              and monthly chemical loadings of other types.
```

EXAMS-> ***SET MODE to 1***

EXAMS-> ***CATALOG CHEMICAL***

```
UDB #     Name of Chemistry Dataset
=====    ==================================================
   1     Chemical Data Entry Template
   2     p-Cresol [CAS# 106-44-5]
   3     Benz[a]anthracene [CAS# 56-55-3]
   4     Benzo[a]pyrene [CAS# 50-32-8]
   5     Quinoline [CAS# 91-22-5]
   6     Benzo[f]quinoline [CAS# 85-02-9]
   7     9H-Carbazole [CAS# 86-74-8]
   8     7H-Dibenzo[c,g]carbazole [CAS# 194-59-2]
   9     Benzo[b]thiophene [CAS# 95-15-8]
  10     Dibenzothiophene [CAS# 132-65-0]
  11     Methyl Parathion [CAS# 298-00-0]
  12     Mirex [CAS# 2385-85-5]
  13     Heptachlor  [CAS# 76-44-8]
```

EXAMS-> ***CATALOG ENVIRONMENT***

```
UDB #     Name of Environmental Dataset
=====    ==================================================
   1     Environmental Data Entry Template
   2     Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
```

```
   3     Georgia OPP Farm Pond (MLRA P136, WBAN 13873)
   4     Mississippi OPP Farm Pond (MLRA P134, WBAN 03940)
   5     Index Reservoir, IL (MLRA M115, WBAN 13994)
   6     Lake Zurich (Untersee), Switzerland: annual means

EXAMS-> CAT

Enter Environment, Chemical, Load, Product,
Help, or Quit-> LO

Catalog of Chemical LOADings

UDB No.     Name of Entry Volume
=======    =======================
     1     Load Data Entry Template
     2     Test input loadings for Exams <version number>


EXAMS->  HELP RECALL

RECALL transfers data from permanent storage (UDB) to activity
databases (ADB). The data to be used by EXAMS for an analysis
are held in a foreground memory bank or ADB (activity database).
When EXAMS is started, the ADB is empty. Use the RECALL command
to transfer data from the User Databases (UDBs) to foreground
memory (ADB). Be sure to STORE all new data before you QUIT
from EXAMS: the ADB is discarded at the end of each session!!
                ==========================================
Related topics: CATALOG, ERASE, NAME, STORE

Syntax:          RECALL <datatype> <UDB#> [AS ADB#]
        where <datatype> can be CHEM, ENV, LOAD, or PRODUCT

EXAMS uses these four kinds of datasets:
 1. CHEMICAL reactivity and partitioning (up to MCHEM sectors),
   2. ENVIRONMENTal physical and chemical parameters,
     3. allochthonous chemical LOADings, and
       4. PRODUCT chemistry for generating interconversions
          among multiple chemicals in an analysis.
For more information: ADB, AS, UDB

EXAMS-> REC CHEM 11

Selected compound is "Methyl Parathion [CAS# 298-00-0]"

EXAMS-> RECALL ENV 2

Selected environment is "Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)"

EXAMS->  HELP LOAD

Enter allochthonous loadings of synthetic chemicals either as
instantaneous pulses, or as stable (or average) values that
persist for at least one month. SHOW PULSE displays pulsed
loadings; SHOW LOADS displays the steady loadings. Steady
loadings are entered by specifying the type of load (STRLD,
etc.), the segment, ADB number of the chemical, month of the
loading, and the mass loading (kg/hour). For example, command:
EXAMS-> SET STRLD(1,2,8) TO 0.01
```

sets an August load of 0.01 kg/h of chemical #2 on segment #1.

Pulse loads are entered by "event number." Each event includes the ADB # of the chemical, the month and day of the event, the target segment, and the mass (kg) of the pulse.

If, during a RUN, a loading violates assumptions of the model (e.g., by super-saturating an incoming flow), or is found to be impossible (e.g., a PCPLD to a (B)enthic segment), the load is reduced or deleted. The corrected loadings are stored in the LOADS matrix and returned to the user, i.e., the unusable loadings are discarded and the new values are substituted.

```
EXAMS-> SHOW LOAD

Name of environment: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Total number of segments (KOUNT) =   6
Segment Number:   1   2   3   4   5   6
Segment "TYPE":   L   B   L   B   L   B

Exposure Analysis Modeling System -- EXAMS Version <ver>, Mode 1
Ecosystem: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical: 1) Methyl Parathion [CAS# 298-00-0]
----------------------------------------------------------------
Mean of year 2000: allochthonous chemical loads (kg/hr).
----------------------------------------------------------------
Load data--
Seg  Streams  Rainfall    Seeps   NPS Loads   Drift
--- --------- --------- --------- --------- ---------
  1
  2
  3
  4
  5
  6
----------------------------------------------------------------

EXAMS-> SET STRL(1,1,13)=.01

Command processing complete; ready for input.

EXAMS-> SET OUTFIL(1)=Y

Command processing complete; ready for input.

EXAMS-> SET OUTFIL(2)=Y

Command processing complete; ready for input.

EXAMS-> RUN

Simulation beginning for:
Environment: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical  1: Methyl Parathion [CAS# 298-00-0]

RUN command completed.

EXAMS-> LIST
```

```
At the prompt, enter a Table number, "Quit,"
or "Help" to see a catalog of the output tables.
Enter Table Number -> HELP

  1 Chemical inputs: FATE Data
  2 Chemical inputs: PRODUCT Chemistry
  3 PULSE Chemical Loadings
  4 Environmental Input Data: BIOLOGICAL Parameters
  5 Environmental Input Data: HYDROLOGIC Parameters
  6 Environmental Input Data: SEDIMENT Properties
  7 Environmental Input Data: PHYSICAL GEOMETRY
  8 MISCellaneous Environmental Input Data: Wind, D.O., etc.
  9 Input specifications: ADVECTIVE transport field
 10 Input specifications: DISPERSIVE transport field
 11 Environmental Input Data: GLOBAL site parameters
 12 KINETIC PROFILE of Synthetic Chemical
 13 Chemical REACTIVITY PROFILE of Ecosystem
 14 Allochthonous Chemical LOADS and Pulses
 15 DISTRIBUTION of Chemical in Environment
 16 Chemical SPECIATION of Dissolved Concentrations
 17 Chemical Concentration MEANS, Maxima, and Minima
 18 Sensitivity Analysis of Chemical FATE
 19 Summary TIME-TRACE of Chemical Concentrations
 20 Exposure Analysis SUMMARY
 ALL Entire Report

At the prompt, enter a Table number, "Quit,"
or "Help" to see a catalog of the output tables.
Enter Table Number ->  20


Ecosystem: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical:  Methyl Parathion [CAS# 298-00-0]
---------------------------------------------------------------
Table 20.01.  Exposure analysis summary.
---------------------------------------------------------------
Exposure (maximum steady-state concentrations):
 Water column: 7.393E-02 mg/L dissolved; total = 7.405E-02 mg/L
 Benthic sediments: 6.586E-02 mg/L dissolved in pore water;
   maximum total concentration =  3.32     mg/kg (dry weight).
 Biota (ug/g dry weight): Plankton:  27.     Benthos:  24.

Fate:
 Total steady-state accumulation:  2.44     kg, with  62.72%
   in the water column and  37.28% in the benthic sediments.
 Total chemical load: 0.24     kg/  day.  Disposition:   2.30%
   chemically transformed,  81.86% biotransformed,   0.06%
   volatilized, and  15.78% exported via other pathways.

 Persistence:
  After  12.0       days of recovery time, the water column had
  lost  85.24% of its initial chemical burden; the benthic zone
  had lost  29.47%; system-wide total loss of chemical =  64.4%.
  Five half-lives (>95% cleanup) thus require ca.    58.   days.

EXAMS->  LIST 18
```

```
Ecosystem: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical:  Methyl Parathion [CAS# 298-00-0]
-----------------------------------------------------------------
Table 18.01. Analysis of steady-state fate of organic chemical.
-----------------------------------------------------------------
 Steady-state Values        Mass Flux    % of Load   Half-Life*
      by Process             Kg/  day                    days
---------------------       ----------   ---------   ----------
Hydrolysis                  4.0378E-03      1.68      418.6
Reduction
Radical oxidation
Direct photolysis           1.4853E-03      0.62      1138.
Singlet oxygen oxidation
Bacterioplankton            0.1686         70.23      10.03
Benthic Bacteria            2.7911E-02     11.63      60.56
Surface Water-borne Export  3.7872E-02     15.78      44.63
Seepage export
Volatilization              1.3355E-04      0.06     1.2656E+04
-----------------------------------------------------------------
Chemical Mass Balance:
   Sum of fluxes =          0.2400
   Sum of loadings =        0.2400
      Allochthonous load:                 100.0
      Autochthonous load:                   0.0
   Residual Accumulation =     0.0          0.0
-----------------------------------------------------------------
* Pseudo-first-order estimates based on flux/resident mass.

EXAMS->  LIST 15
Ecosystem: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical:  Methyl Parathion [CAS# 298-00-0]
-----------------------------------------------------------------
Table 15.01.  Distribution of chemical at steady state.
-----------------------------------------------------------------
Seg  Resident Mass   ******** Chemical Concentrations *********
 #                     Total    Dissolved  Sediments    Biota
     Kilos      %      mg/*     mg/L **     mg/kg       ug/g
--- -------- ------  ---------  ---------  ---------  ---------
In the Water Column:
  1  1.5      96.84  7.405E-02  7.393E-02   3.70       27.5
  3 1.07E-02   0.70  7.152E-02  7.140E-02   3.57       26.5
  5 3.76E-02   2.46  6.263E-02  6.253E-02   3.13       23.2
    ======== ======
     1.5      62.72

 and in the Benthic Sediments:
  2 0.61      66.71  0.898      1.783E-02  0.892       6.62
  4 6.72E-02   7.39   3.32      6.586E-02   3.29       24.5
  6 0.24      25.90   2.91      5.768E-02   2.88       21.4
    ======== ======
    0.91      37.28
Total Mass (kilograms) =     2.438
-----------------------------------------------------------------
 * Units: mg/L in Water Column; mg/kg in Benthic Zone.
** Excludes complexes with "dissolved" organics.

EXAMS->  HELP PLOT

Use the PLOT command to display results of the current analysis.
Three kinds of PLOTs are available on-line from EXAMS: POINT,
```

PROFILE, and KINETIC. Each PLOT requires the specification of several options; these can either be entered on the system command line or entered in response to EXAMS' prompts. You can enter HELP in response to any of these prompts; EXAMS will then describe the available options.

Related topics: LIST, PRINT

Syntax: PLOT <option1 option2 option3>

For more information on option1: type HELP POINT,
HELP PROFILE, or
HELP KINETIC

HELP for options 2 and 3 is available inside the PLOT command.

EXAMS-> ***PLOT***

The following options are available:

```
POint   - Vertical concentration profile
PRofile - Longitudinal concentration profile
Kinetic - List or plot kinetic outputs
Help    - This message
Quit    - Return to the EXAMS program prompt
```

Option-> ***KI***

The following KINETIC options are available:

```
List - lists selected KINETIC output parameters
Plot - plots selected KINETIC output parameters
Help - this message
Quit - return to the EXAMS prompt
```

Option-> ***PL***

Chemical: Methyl Parathion [CAS# 298-00-0]
Environment: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)

```
Simulation units:   Days
Number of segments:    6
Segment Number:  1  2  3  4  5  6
Segment "TYPE":  L  B  L  B  L  B
```

The following parameters are available for time-trace plotting of values averaged over the ecosystem space:

```
1 - Water Column: average dissolved  (mg/L)
2 -               average sorbed     (mg/kg)
3 -               total mass         (kg)
4 - Benthic:      average dissolved  (mg/L)
5                 average sorbed     (mg/kg)
6                 total mass         (kg)
```

Enter parameters, one per line;
enter "0" to end data entry and proceed.

```
Parameter-> 3
Parameter-> 6
Parameter-> 0

The following parameters are available for each segment:
1 -  Total concentration   (Water Column, mg/L; benthic, mg/kg)
2 -  Dissolved             (mg/liter of fluid volume)
3 -  Sorbed                (mg/kg of sediment)
4 -  Biosorbed             (ug/g)
5 -  Mass                  (grams/square meter of AREA)

Enter segment-parameter number pair, one number per line;
enter 0 when data entry is complete; or Quit to cancel.

Enter segment number---> 0

System:   Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical: Methyl Parathion [CAS# 298-00-0]
  1.53     I*
           I
           I    *
           I
           I        *
  1.02     I
           I+   +   +    +
           I                 +   +   +   +
           I                     *           +    +   +   +
           I                         *                        +
 0.510     I                             *
           I                                 *
           I                                      *   *   *
           I                                                   *
           I
  0.00     I
            +----+----+----+----+----+----+----+----+----+----+
           0.00      2.40      4.80      7.20      9.60      12.0
                1.20      3.60      6.00      8.40      10.8
                                Time, Days
```

3.4.2 Lab. 1, Exercise 2: EXAMS in Mode 2

Using EXAMS to solve initial value problems. Mode 2 can be used to study details of exposure during brief (60 days in the example) periods, or through a series of episodic contaminant releases. If you have not continued on directly from Exercise 1, after starting EXAMS you should first issue the commands to "**RECALL CHEM 11**" (methyl parathion), "**REC ENV 2**", "**SET STRLD(1,1,13)=0.01**", **"SET OUTFIL(1)=Y", SET OUTFIL(2)=Y"**, and "**RUN**" to begin this exercise.

```
EXAMS-> SET MODE=2
Command processing complete; ready for input.

EXAMS-> SHOW TI FR
A RUN will integrate from      0 to      1 Days
with output at intervals of      1 Days.

CINT =      1, TINIT =      0
TEND =      1, TCODE =    2

EXAMS-> HELP TCODE
TCODE is an integer scalar.
The value of Time_CODE sets the units of TINIT, TEND, and CINT
SET TCODE to 1 (hours), 2 (days), 3 (months), or 4 (years).

TCODE is under full user control only in Mode 2. In mode 2 TCODE
controls the time frame of the study: e.g., given TINIT=0, TEND=
24, and CINT=2; CHANge TCODE from 1 to 3 to convert a 0-24 hour
study into 0-24 months (bimonthly reports). In mode 1, EXAMS
selects the units for reporting results from the probable half-
life of the study chemical(s). In mode 3, a RUN encompasses one
year or longer, and the timing is set to produce standard output

EXAMS-> SET TCODE=2
Command processing complete; ready for input.
EXAMS-> SET TEND=60
Command processing complete; ready for input.
EXAMS-> SET CINT=1
Command processing complete; ready for input.
EXAMS-> SHOW TI FR

A RUN will integrate from      0 to     60 Days
with output at intervals of      1 Days.

CINT =      1, TINIT =      0
TEND =     60, TCODE =    2

EXAMS-> RUN
Simulation beginning for:
Chemical: Methyl Parathion [CAS# 298-00-0]
Environment: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
RUN command completed.

EXAMS-> PLOT KI PL
Chemical: Methyl Parathion [CAS# 298-00-0]
Environment: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)

Simulation units:   Days
Number of segments:    6
Segment Number:  1  2  3  4  5  6
```

```
Segment "TYPE":  L  B  L  B  L  B


The following parameters are available for time-trace plotting
of values averaged over the ecosystem space:

1 - Water Column: average dissolved  (mg/L)
2 -               average sorbed     (mg/kg)
3 -               total mass         (kg)
4 - Benthic:      average dissolved  (mg/L)
5                 average sorbed     (mg/kg)
6                 total mass         (kg)

Enter parameters, one per line;
enter "0" to end data entry and proceed.

Parameter-> 3
Parameter-> 6
Parameter-> 0

The following parameters are available for each segment:
1 -  Total concentration   (Water Column, mg/L; benthic, mg/kg)
2 -  Dissolved             (mg/liter of fluid volume)
3 -  Sorbed                (mg/kg of sediment)
4 -  Biosorbed             (ug/g)
5 -  Mass                  (grams/square meter of AREA)


Enter segment-parameter number pair, one number per line;
enter 0 when data entry is complete; or Quit to cancel.

Enter segment number---> 0

System:   Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical: Methyl Parathion [CAS# 298-00-0]
  1.52     I                    ******************************
           I             *******
           I          ***
           I        **
           I       *
  1.02     I      *
           I     *
           I    *                               +++++++++++++++
           I   *                        ++++++++
           I   *                  ++++++
 0.508     I                 +++++
           I  *          ++++
           I          ++++
           I *      ++
           I    ++++
  0.00     I++++
            +----+----+----+----+----+----+----+----+----+----+
           0.00      12.0      24.0      36.0      48.0      60.0
                6.00      18.0      30.0      42.0      54.0
                                Time, Days
```

```
EXAMS-> SHOW LOAD

Name of environment: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Total number of segments (KOUNT) =   6
Segment Number:   1   2   3   4   5   6
Segment "TYPE":   L   B   L   B   L   B

Exposure Analysis Modeling System -- EXAMS Version <ver>, Mode 2
Ecosystem: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical: 1) Methyl Parathion [CAS# 298-00-0]
---------------------------------------------------------------
Mean of year 2000: allochthonous chemical loads (kg/hr).
---------------------------------------------------------------
Load data--
Seg  Streams  Rainfall    Seeps   NPS Loads   Drift
--- --------- --------- --------- --------- ---------
  1 1.000E-02
  2
  3
  4
  5
  6
---------------------------------------------------------------

EXAMS-> ZERO LOAD

All allochthonous loads removed.

EXAMS-> SHOW LOAD

Name of environment: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Total number of segments (KOUNT) =   6
Segment Number:   1   2   3   4   5   6
Segment "TYPE":   L   B   L   B   L   B

Exposure Analysis Modeling System -- EXAMS Version <ver>, Mode 2
Ecosystem: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical: 1) Methyl Parathion [CAS# 298-00-0]
---------------------------------------------------------------
Mean of year 2000: allochthonous chemical loads (kg/hr).
---------------------------------------------------------------
Load data--
Seg  Streams  Rainfall    Seeps   NPS Loads   Drift
--- --------- --------- --------- --------- ---------
  1
  2
  3
  4
  5
  6
---------------------------------------------------------------

EXAMS-> SET ICHEM(1)=1
Command processing complete; ready for input.

EXAMS-> SET ISEG(1)=1
Command processing complete; ready for input.

EXAMS-> SET IMASS(1)=.1
```

```
Command processing complete; ready for input.

EXAMS->  SHO PU
Exposure Analysis Modeling System -- EXAMS Version <ver>, Mode 2
Ecosystem: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical: 1) Methyl Parathion [CAS# 298-00-0]
---------------------------------------------------------------
Table 3.  Chemical input data: pulse loadings.*
---------------------------------------------------------------
Load Entry--

ICHEM-ADB#     1
ISEGment       1
IMASS (kg) 0.100
Event Number   1

---------------------------------------------------------------
* N.B.: Input data only; may be revised during simulation.

EXAMS-> SET TEND=14
Command processing complete; ready for input.
EXAMS-> RUN
Simulation beginning for:
Environment: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical  1: Methyl Parathion [CAS# 298-00-0]
RUN command completed.

EXAMS-> PL KI PL
Chemical: Methyl Parathion [CAS# 298-00-0]
Environment: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Simulation units:   Days
Number of segments:    6
Segment Number:  1  2  3  4  5  6
Segment "TYPE":  L  B  L  B  L  B

The following parameters are available for time-trace plotting
of values averaged over the ecosystem space:

1 - Water Column: average dissolved  (mg/L)
2 -               average sorbed     (mg/kg)
3 -               total mass         (kg)
4 - Benthic:      average dissolved  (mg/L)
5                 average sorbed     (mg/kg)
6                 total mass         (kg)

Enter parameters, one per line;
enter "0" to end data entry and proceed.

Parameter-> 3
Parameter-> 6
Parameter-> 0

The following parameters are available for each segment:
1 -  Total concentration   (Water Column, mg/L; benthic, mg/kg)
2 -  Dissolved             (mg/liter of fluid volume)
3 -  Sorbed                (mg/kg of sediment)
4 -  Biosorbed             (ug/g)
5 -  Mass                  (grams/square meter of AREA)
```

```
Enter segment-parameter number pair, one number per line;
enter 0 when data entry is complete; or Quit to cancel.

Enter segment number---> 0

System:   Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical: Methyl Parathion [CAS# 298-00-0]
 0.100     I*
           I
           I    *
           I
           I       *
 6.667E-02 I
           I           *
           I              *
           I                  *
           I                     *
 3.333E-02 I                         *
           I                             *
           I                                *   *  *
           I                     +   +   +  +   +  +   +  +   +
           I       +   +  +   +
  0.00     I+   +
            +----+----+----+----+----+----+----+----+----+----+
           0.00      2.80      5.60      8.40      11.2      14.0
                1.40      4.20      7.00      9.80      12.6
                                Time, Days

EXAMS-> CONTINUE

Initial time for integration will be    14 Days
Enter ending time of integration, Help, or Quit-> 28
Simulation continuing for:
Environment: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical  1: Methyl Parathion [CAS# 298-00-0]

CONTINUE command completed.

EXAMS-> CONTINUE
Initial time for integration will be           28.0 Days
Enter ending time of integration, Help, or Quit-> 60
Simulation continuing for:
Environment: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical  1: Methyl Parathion [CAS# 298-00-0]

CONTINUE command completed.

EXAMS-> PL KI PL

Chemical: Methyl Parathion [CAS# 298-00-0]
Environment: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)

Simulation units:   Days
Number of segments:    6
Segment Number:  1  2  3  4  5  6
Segment "TYPE":  L  B  L  B  L  B

The following parameters are available for time-trace plotting
of values averaged over the ecosystem space:
```

```
1 - Water Column: average dissolved  (mg/L)
2 -               average sorbed     (mg/kg)
3 -               total mass         (kg)
4 - Benthic:      average dissolved  (mg/L)
5                 average sorbed     (mg/kg)
6                 total mass         (kg)

Enter parameters, one per line;
enter "0" to end data entry and proceed.
Parameter-> 3
Parameter-> 6
Parameter-> 0

The following parameters are available for each segment:
1 -  Total concentration   (Water Column, mg/L; benthic, mg/kg)
2 -  Dissolved             (mg/liter of fluid volume)
3 -  Sorbed                (mg/kg of sediment)
4 -  Biosorbed             (ug/g)
5 -  Mass                  (grams/square meter of AREA)

Enter segment-parameter number pair, one number per line;
enter 0 when data entry is complete; or Quit to
cancel.
Enter segment number---> 0
```

Notice how the pulse is repeated on each "continue" if it is not explicitly removed.

```
System:   Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical: Methyl Parathion [CAS# 298-00-0]
 0.112     I            *          *
           I
           I*            *          *
           I *
           I             *           *
 7.467E-02 I  *
           I              *           *
           I   *           *           *
           I   *            *           *
           I    *            *          *
 3.733E-02 I     *            *          *
           I      **          *           **
           I        *        +++++  +++++++++++++++
           I        +++* ++++     ++         ***  ++++++++++
           I  ++++++   ++                     *******     +++
  0.00     I++                                         ********
            +----+----+----+----+----+----+----+----+----+----+
           0.00      12.0      24.0      36.0      48.0      60.0
                6.00      18.0      30.0      42.0      54.0
                                Time, Days

EXAMS-> PL KI PL

Chemical: Methyl Parathion [CAS# 298-00-0]
Environment: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
```

```
Simulation units:   Days
Number of segments:    6
Segment Number:  1  2  3  4  5  6
Segment "TYPE":  L  B  L  B  L  B


The following parameters are available for time-trace plotting
of values averaged over the ecosystem space:

1 - Water Column: average dissolved  (mg/L)
2 -               average sorbed     (mg/kg)
3 -               total mass         (kg)
4 - Benthic:      average dissolved  (mg/L)
5                 average sorbed     (mg/kg)
6                 total mass         (kg)

Enter parameters, one per line;
enter "0" to end data entry and proceed.

Parameter-> 6
Parameter-> 0

The following parameters are available for each segment:
1 -  Total concentration   (Water Column, mg/L; benthic, mg/kg)
2 -  Dissolved             (mg/liter of fluid volume)
3 -  Sorbed                (mg/kg of sediment)
4 -  Biosorbed             (ug/g)
5 -  Mass                  (grams/square meter of AREA)


Enter segment-parameter number pair, one number per line;
enter 0 when data entry is complete; or Quit to cancel.

Enter segment number---> 0

System:   Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical: Methyl Parathion [CAS# 298-00-0]
 2.395E-02 I                           *****
           I                          *     **
           I                        *        **
           I                ******  *           ***
           I               *      **              **
 1.597E-02 I              *                         **
           I             *                            **
           I             *                              **
           I      *******                                ***
           I    **                                         ***
 7.983E-03 I   *
           I   *
           I  *
           I *
           I
  0.00     I*
            +----+----+----+----+----+----+----+----+----+----+
           0.00      12.0      24.0      36.0      48.0      60.0
                6.00      18.0      30.0      42.0      54.0
                                Time, Days
```

3.4.3 Lab. 1, Exercise 3: EXAMS in Mode 3

Mode 3 is used for exposure over a minimum period of one year, with monthly updates of the properties of the environment. It can be used with PRZM to examine the exposure pattern arising from use of a pesticide over many years. In this exercise the load is entered manually to illustrate the structure of the data.

```
EXAMS-> REC CHEM 11

Selected compound is Methyl Parathion [CAS# 298-00-0]

EXAMS-> SET MODE=3

Command processing complete; ready for input.

EXAMS-> REC ENV 2

Selected environment is "Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)"

EXAMS-> SET OUTFIL(1)=Y
Command processing complete; ready for input.

EXAMS-> SET OUTFIL(2)=Y
Command processing complete; ready for input.

EXAMS-> SET ICHEM(1)=1
Command processing complete; ready for input.

EXAMS-> SET ISEG(1)=1
Command processing complete; ready for input.

EXAMS-> SET IMASS(1)=.1
Command processing complete; ready for input.

EXAMS-> SET IMON(1)=5
Command processing complete; ready for input.

EXAMS-> SET IDAY(1)=15
Command processing complete; ready for input.

EXAMS-> SET ICHEM(2)=1
Command processing complete; ready for input.

EXAMS-> SET ICHEM(3)=1
Command processing complete; ready for input.

EXAMS-> SET ISEG(2)=1
Command processing complete; ready for input.

EXAMS-> SET ISEG(3)=1
Command processing complete; ready for input.

EXAMS-> SET IMASS(2)=.1
Command processing complete; ready for input.

EXAMS-> SET IMASS(3)=.1
Command processing complete; ready for input.
```

```
EXAMS-> SET IMON(2)=6
Command processing complete; ready for input.

EXAMS-> SET IMON(3)= 6
Command processing complete; ready for input.

EXAMS-> SET IDAY(2)=1
Command processing complete; ready for input.

EXAMS-> SET IDAY(3)=15
Command processing complete; ready for input.

EXAMS->  SHO PU LO

Exposure Analysis Modeling System -- EXAMS Version <ver>, Mode 3
Ecosystem: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical: 1) Methyl Parathion [CAS# 298-00-0]
----------------------------------------------------------------
Table 3.  Chemical input data: pulse loadings.*
----------------------------------------------------------------
Load Entry--

IMONth         5         6         6
IDAY          15         1        15
ICHEM-ADB#     1         1         1
ISEGment       1         1         1
IMASS (kg) 0.100     0.100     0.100
Event Number   1         2         3

----------------------------------------------------------------
* N.B.: Input data only; may be revised during simulation.

EXAMS-> RUN

Simulation beginning for:
Environment: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical  1: Methyl Parathion [CAS# 298-00-0]

RUN command completed.

EXAMS-> PL KI PL

Chemical: Methyl Parathion [CAS# 298-00-0]
Environment: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)

Simulation units:   Days
Number of segments:    6
Segment Number:  1  2  3  4  5  6
Segment "TYPE":  L  B  L  B  L  B

The following parameters are available for time-trace plotting
of values averaged over the ecosystem space:

1 - Water Column: average dissolved  (mg/L)
2 -               average sorbed     (mg/kg)
3 -               total mass         (kg)
4 - Benthic:      average dissolved  (mg/L)
5                 average sorbed     (mg/kg)
6                 total mass         (kg)
```

```
Enter parameters, one per line;
enter "0" to end data entry and proceed.
Parameter-> 3
Parameter-> 6
Parameter-> 0

The following parameters are available for each segment:
1 -  Total concentration   (Water Column, mg/L; benthic, mg/kg)
2 -  Dissolved             (mg/liter of fluid volume)
3 -  Sorbed                (mg/kg of sediment)
4 -  Biosorbed             (ug/g)
5 -  Mass                  (grams/square meter of AREA)


Enter segment-parameter number pair, one number per line;
enter 0 when data entry is complete; or Quit to cancel.

Enter segment number---> 0

System:   Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical: Methyl Parathion [CAS# 298-00-0]
 0.111     I                       *
           I                  *  *
           I                       *
           I                   * *
           I                       *
 7.384E-02 I                   * *
           I                     * *
           I                   *   *
           I                   * * *
           I                   * * *
 3.692E-02 I                   *  * *
           I                   ** * *
           I                    * *+++
           I                    *+++*++
           I                   +++ * *+++++
  0.00     I+++++++++++++++++++      ****+++++++++++++++++++++++
            +----+----+----+----+----+----+----+----+----+----+
           0.00      73.2      146.      220.      293.      366.
                36.6      110.      183.      256.      329.
                                Time, Days

EXAMS-> PL KI PL

Chemical: Methyl Parathion [CAS# 298-00-0]
Environment: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)

Simulation units:   Days
Number of segments:    6
Segment Number:  1  2  3  4  5  6
Segment "TYPE":  L  B  L  B  L  B

The following parameters are available for time-trace plotting
of values averaged over the ecosystem space:

1 - Water Column: average dissolved  (mg/L)
2 -               average sorbed     (mg/kg)
3 -               total mass         (kg)
4 - Benthic:      average dissolved  (mg/L)
```

```
5                 average sorbed     (mg/kg)
6                 total mass         (kg)

Enter parameters, one per line;
enter "0" to end data entry and proceed.

Parameter-> 3
Parameter-> 0

The following parameters are available for each segment:
1 -  Total concentration   (Water Column, mg/L; benthic, mg/kg)
2 -  Dissolved             (mg/liter of fluid volume)
3 -  Sorbed                (mg/kg of sediment)
4 -  Biosorbed             (ug/g)
5 -  Mass                  (grams/square meter of AREA)

Enter segment-parameter number pair, one number per line;
enter 0 when data entry is complete; or Quit to cancel.

Enter segment number---> 0

System:   Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical: Methyl Parathion [CAS# 298-00-0]
 0.111     I                       *
           I                  *  *
           I                       *
           I                   * *
           I                       *
 7.384E-02 I                   * *
           I                     * *
           I                   *   *
           I                   * * *
           I                   * * *
 3.692E-02 I                   *  * *
           I                   ** * *
           I                    * * *
           I                    * ****
           I                    ** * **
  0.00     I*******************       *************************
            +----+----+----+----+----+----+----+----+----+----+
           0.00      73.2      146.      220.      293.      366.
                36.6      110.      183.      256.      329.
                              Time, Days

EXAMS->  CONTINUE
CONTinuing integration through 31 December 2001.

Simulation continuing for:
Environment: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical  1: Methyl Parathion [CAS# 298-00-0]

CONTINUE command completed.

EXAMS-> PLOT KI PL

Chemical: Methyl Parathion [CAS# 298-00-0]
Environment: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Simulation units:   Days
Number of segments:    6
```

```
Segment Number:  1  2  3  4  5  6
Segment "TYPE":  L  B  L  B  L  B

The following parameters are available for time-trace plotting
of values averaged over the ecosystem space:

1 - Water Column: average dissolved  (mg/L)
2 -               average sorbed     (mg/kg)
3 -               total mass         (kg)
4 - Benthic:      average dissolved  (mg/L)
5                 average sorbed     (mg/kg)
6                 total mass         (kg)

Enter parameters, one per line;
enter "0" to end data entry and proceed.

Parameter-> 3
Parameter-> 0

The following parameters are available for each segment:
1 -  Total concentration   (Water Column, mg/L; benthic, mg/kg)
2 -  Dissolved             (mg/liter of fluid volume)
3 -  Sorbed                (mg/kg of sediment)
4 -  Biosorbed             (ug/g)
5 -  Mass                  (grams/square meter of AREA)

Enter segment-parameter number pair, one number per line;
enter 0 when data entry is complete; or Quit to cancel.

Enter segment number---> 0
System:   Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical: Methyl Parathion [CAS# 298-00-0]
 0.111     I           *                       *
           I         **                      **
           I           *                       *
           I         **                      **
           I           *                       *
 7.384E-02 I         * *                     **
           I           **                      **
           I         *  *                    *  *
           I          ***                    * **
           I          ***                     ***
 3.692E-02 I          ***                     ***
           I          ***                     ***
           I          ***                     ***
           I          ***                     ***
           I          ****                    ****
  0.00     I**********   **********************   *************
            +----+----+----+----+----+----+----+----+----+----+
           0.00      146.      292.      439.      585.      731.
                73.1      219.      366.      512.      658.
                                Time, Days


EXAMS->  LIST 20
```

```
Exposure Analysis Modeling System -- EXAMS Version <ver>, Mode 3
Ecosystem: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical:  Methyl Parathion [CAS# 298-00-0]
Table 20.01.  Exposure analysis summary: Maximum Events of 2000.
-----------------------------------------------------------------------------
Event Duration           96-hour    21-day     60-day     90-day      2000
====================  =========  =========  =========  =========  =========
         ***** Ecotoxicological Direct Exposure Concentrations ******
Water Column      Min.  2.781E-03  5.128E-04  7.040E-05  7.664E-06   0.00
 dissolved mg/L   Mean  3.995E-03  2.423E-03  1.487E-03  9.994E-04  2.581E-04
                  Peak  5.505E-03  5.505E-03  5.505E-03  5.505E-03  5.505E-03
Benthic Sediment  Min.  1.617E-03  1.165E-03  5.834E-04  1.578E-04   0.00
 mg/L dissolved   Mean  1.640E-03  1.446E-03  1.108E-03  8.522E-04  7.716E-05
   in pore water  Peak  1.650E-03  1.650E-03  1.650E-03  1.650E-03  1.650E-03
         ***** Ecotoxicological Trophic Exposure Concentrations *****
Water Column      Min.   1.03      0.191      2.615E-02  2.847E-03   0.00
 ug/g dry weight  Mean   1.48      0.900      0.552      0.371      9.588E-02
   of plankton    Peak   2.04       2.04       2.04       2.04       2.04
Benthic Sediment  Min.  0.601      0.433      0.217      5.864E-02   0.00
 ug/g dry weight  Mean  0.609      0.537      0.411      0.317      2.867E-02
   of benthos     Peak  0.613      0.613      0.613      0.613      0.613
         ***** Total Media Concentrations ***************************
Water Column      Min.  2.785E-03  5.137E-04  7.051E-05  7.677E-06   0.00
 total mg/L       Mean  4.002E-03  2.427E-03  1.489E-03  1.001E-03  2.585E-04
                  Peak  5.514E-03  5.514E-03  5.514E-03  5.514E-03  5.514E-03
Benthic Sediment  Min.  8.145E-02  5.867E-02  2.938E-02  7.951E-03   0.00
 total mg/kg      Mean  8.262E-02  7.284E-02  5.579E-02  4.293E-02  3.887E-03
   dry weight     Peak  8.313E-02  8.313E-02  8.313E-02  8.313E-02  8.313E-02

More? (Yes/No/Quit)->  Y

Exposure Analysis Modeling System -- EXAMS Version <ver>, Mode 3
Ecosystem: Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
Chemical:  Methyl Parathion [CAS# 298-00-0]
Table 20.01.  Exposure analysis summary: Maximum Events of 2001.
-----------------------------------------------------------------------------
Event Duration           96-hour    21-day     60-day     90-day      2001
====================  =========  =========  =========  =========  =========
         ***** Ecotoxicological Direct Exposure Concentrations ******
Water Column      Min.  2.781E-03  5.128E-04  7.040E-05  7.664E-06  2.018E-12
 dissolved mg/L   Mean  3.995E-03  2.423E-03  1.487E-03  9.994E-04  2.588E-04
                  Peak  5.505E-03  5.505E-03  5.505E-03  5.505E-03  5.505E-03
Benthic Sediment  Min.  1.617E-03  1.165E-03  5.834E-04  1.578E-04  9.304E-12
 mg/L dissolved   Mean  1.640E-03  1.446E-03  1.108E-03  8.522E-04  7.737E-05
   in pore water  Peak  1.650E-03  1.650E-03  1.650E-03  1.650E-03  1.650E-03
         ***** Ecotoxicological Trophic Exposure Concentrations *****
Water Column      Min.   1.03      0.191      2.615E-02  2.847E-03  7.499E-10
 ug/g dry weight  Mean   1.48      0.900      0.552      0.371      9.613E-02
   of plankton    Peak   2.04       2.04       2.04       2.04       2.04
Benthic Sediment  Min.  0.601      0.433      0.217      5.864E-02  3.456E-09
 ug/g dry weight  Mean  0.609      0.537      0.411      0.317      2.874E-02
   of benthos     Peak  0.613      0.613      0.613      0.613      0.613
         ***** Total Media Concentrations ***************************
Water Column      Min.  2.785E-03  5.137E-04  7.051E-05  7.677E-06  2.022E-12
 total mg/L       Mean  4.002E-03  2.427E-03  1.489E-03  1.001E-03  2.592E-04
                  Peak  5.514E-03  5.514E-03  5.514E-03  5.514E-03  5.514E-03
EXAMS-> QUIT
```

3.5 Tutorial 2: Chemical & Environmental Data Entry

This tutorial example illustrates the entry of EXAMS chemical and environmental data and the exploration of alternative process models and parameters. The EXAMS session duplicates the problem analysis in the text beginning on page 38; it should be executed using that text as a guide. Note that the environmental data are not a complete characterization of Lake Zurich; they include only a simple geometry plus the parameters needed to construct a volatilization model for EXAMS. The data entry sequence contains some errors; these are intended as illustrations of error recovery methods.

3.5.1 Exercise 4: p-DCB in Lake Zurich

```
    ! Commands for Lake Zurich analysis of p-DCB
1   REC CHEM 1
2   CHEM NAME IS 1,4-Dichlorobenzene
3   set mwt(1)=147.0
4   change sol(1,1) to 73.8
5   set kow(1)=2340
6   set henry(1)=2.66e-3
7   cat chem
8   stor chem 20
9   rec env 1
10  env name is Lake Zurich - central basin (Untersee)
11  set elev=431
12  set airty(*)=r
13  set lat=47.48
14  set lon=8.53
15  SET KO2(1,13)=2.5
16  SET WIND(13)=1.38
17  HELP WIND
18  SET WIND(1,13)=1.38
19  SHOW KOUNT
20  SET KOUNT=3
21  SET TYPE(1)=E
22  SET TYPE(2)=H
23  SET TYPE(3)=B
24  SET DEPTH(1)=10
25  SET VOL(1)=6.8E8
26  SET DEPTH(2)=40
27  SET VOL(2)=2.72E9
28  SET DEPTH(3)=0.02
```

```
29    SET VOL(3)=1.36E6
30    SET AREA(*)=6.8E7
31    SET TCEL(1,13)=11
32    SET TCEL(2,13)=5.6
33    SET TCEL(3,13)=5.6
34    SET DSP(1,13)=0.2
35    SET DSP(2,13)=1.E-4
36    SET XST(*)=6.8E7
37    SET JTUR(1)=1
38    SET ITUR(1) TO 2
39    CHA JTUR(2)=2
40    SET ITUR(2)=3
41    SHO DISP
42    HELP CHARL
43    SET CHARL(1)=25
44    SET CHARL(2)=20.01
45    SHO DISP
46    SET SUSED(*,13)=5
47    SET BULKD(3,13)=1.5
48    SET PCTWA(3,13)=150
49    SET FROC(*,13)=.02
50    SET STRFL(1,13)=3.E5
51    HELP STFL
52    SET STF(1,13)=3.E5
53    SET STSED(1,13)=1500
54    SET STRLD(1,1,13)=0.01
55    SET OUTFIL(1)=Y
56    RUN
57    SET JFR(1)=1
58    SET ITO(1)=0
59    SET ADVPR(1)=1.0
60    SHO AD
61    RUN
62    LI 15
63    list 18
64    list 20
65    CAT ENV
66    ERA ENV 5
67    STOR ENV 5
68    SET DRFL(2,1,13)=1.5E-3
```

```
SET STRL(1,1,13)=8.5E-3
ENV NAME IS Lake Zurich with partial load to hypolimnion
run
li 15
list 18
li 20
zero load
set strl(1,1,13)=0.01
cat chem
rec chem 20
rec env 6
env name is Lake Zurich with oceanic wind and reaeration
show ko2(1,13)
set ko2(1,13)=20
sho wind(1,13)
set wind(1,13)=2.6245
run
list 15
list 18
era chem 20
quit
```

3.5.2 Exercise 4 (Lake Zurich) with Complete EXAMS Responses

```
                 Welcome to EXAMS Release <current release number>
                  Exposure Analysis Modeling System

             Technical Contact: Lawrence A. Burns, Ph.D.
                 U.S. Environmental Protection Agency
                       960 College Station Road
                      Athens, GA 30605-2700 USA
                Phone: (706) 355-8119  (Fax) 355-8104
                  Internet: burns.lawrence@epa.gov

                 Latest Maintenance <date of latest maintenance>

          Type HELP and press the RETURN key for command names,
               HELP USER  for a summary of command functions,
               HELP PAGES for a list of information pages,
          or   HELP EXAMS for introductory information.

     Please stand by while EXAMS checks the computational precision
     of this computer and initializes the Activity Data Base.


EXAMS->  REC CHEM 1
Selected compound is "Chemical Data Entry Template"

EXAMS->  CHEM NAME IS 1,4-Dichlorobenzene
EXAMS->  set mwt(1)=147.0
EXAMS->  change sol(1,1) to 73.8
EXAMS->  set kow(1)=2340
EXAMS->  set henry(1)=2.66e-3
EXAMS->  cat chem

UDB #     Name of Chemistry Dataset
=====    ==================================================
   1     Chemical Data Entry Template
   2     p-Cresol [CAS# 106-44-5]
   3     Benz[a]anthracene [CAS# 56-55-3]
   4     Benzo[a]pyrene [CAS# 50-32-8]
   5     Quinoline [CAS# 91-22-5]
   6     Benzo[f]quinoline [CAS# 85-02-9]
   7     9H-Carbazole [CAS# 86-74-8]
   8     7H-Dibenzo[c,g]carbazole [CAS# 194-59-2]
   9     Benzo[b]thiophene [CAS# 95-15-8]
  10     Dibenzothiophene [CAS# 132-65-0]
  11     Methyl Parathion [CAS# 298-00-0]
  12     Mirex [CAS# 2385-85-5]
  13     Heptachlor  [CAS# 76-44-8]


EXAMS->  store chem 20
Chemical stored: "1,4-Dichlorobenzene"

EXAMS->  rec env 1
```

```
Selected environment is "Environmental Data Entry Template"

EXAMS->  env name is Lake Zurich - central basin (Untersee)
EXAMS->  set elev=431
EXAMS->  set airty(*)=r
EXAMS->  set lat=47.48
EXAMS->  set lon=8.53
EXAMS->  SET KO2(1,13)=2.5
EXAMS->  SET WIND(13)=1.38
Invalid number of subscripts.

EXAMS->  HELP WIND

WIND is a Real Matrix with 32 rows and 13 columns.
WINDspeed (segment,month)                    Units: meters/second
Average wind velocity at a reference height of ten centimeters
above the water surface.  Parameter is used to compute a piston
velocity for water vapor (Liss 1973, Deep-Sea Research 20:221)
in the 2-resistance treatment of volatilization losses.


EXAMS->  SET WIND(1,13)=1.38
EXAMS->  SHOW KOUNT
KOUNT  is           1

EXAMS->  SET KOUNT=3

EXAMS->  SET TYPE(1)=E
EXAMS->  SET TYPE(2)=H
EXAMS->  SET TYPE(3)=B
EXAMS->  SET DEPTH(1)=10
EXAMS->  SET VOL(1)=6.8E8
EXAMS->  SET DEPTH(2)=40
EXAMS->  SET VOL(2)=2.72E9
EXAMS->  SET DEPTH(3)=0.02
EXAMS->  SET VOL(3)=1.36E6

EXAMS->  SET AREA(*)=6.8E7

EXAMS->  SET TCEL(1,13)=11
EXAMS->  SET TCEL(2,13)=5.6
EXAMS->  SET TCEL(3,13)=5.6

EXAMS->  SET DSP(1,13)=0.2
EXAMS->  SET DSP(2,13)=1.E-4
EXAMS->  SET XST(*)=6.8E7
EXAMS->  SET JTUR(1)=1
EXAMS->  SET ITUR(1) TO 2
EXAMS->  CHA JTUR(2)=2
EXAMS->  SET ITUR(2)=3

EXAMS->  SHO DISP
```

```
Name of environment: Lake Zurich - central basin (Untersee)
Total number of segments (KOUNT) =   3
Segment Number:  1  2  3
Segment "TYPE":  E  H  B
-----------------------------------------------------------------
Table 10.13.  Mean dispersive transport field.
-----------------------------------------------------------------

J TURB            1         2
I TURB            2         3
XS TUR m2     6.800E+07 6.800E+07
CHARL m        1.00     0.000
DSP m2/h*    0.200     1.000E-04
 Path No.:        1         2
-----------------------------------------------------------------
* Average of 12 monthly mean values.
```

EXAMS-> ***HELP CHARL***

```
CHARL is a real vector with 300 elements.
CHARacteristic_Length or mixing length (path)      Units: meters
Average of segment dimensions normal to the exchange interface
linking segment numbers JTURB(p) and ITURB(p). The matching ("p"
subscript) members of JTURB, ITURB, CHARL, DSP, and XSTUR define
define a dispersive transport pathway. N.B.: A given segment
may have different mixing lengths at different interfaces.
CHARL can also be calculated from the distance along a path that
connects the centers of segments JTURB(p) and ITURB(p), passing
through the interface whose area is XSTURG(p).
See also: DSP, ITURB, JTURB, XSTUR
```

EXAMS-> ***SET CHARL(1)=25***
EXAMS-> ***SET CHARL(2)=20.01***
EXAMS-> ***SHO DISP***

```
Name of environment: Lake Zurich - central basin (Untersee)
Total number of segments (KOUNT) =   3
Segment Number:  1  2  3
Segment "TYPE":  E  H  B
-----------------------------------------------------------------
Table 10.13.  Mean dispersive transport field.
-----------------------------------------------------------------

J TURB            1         2
I TURB            2         3
XS TUR m2     6.800E+07 6.800E+07
CHARL m        25.0      20.0
DSP m2/h*    0.200     1.000E-04
 Path No.:        1         2
-----------------------------------------------------------------
* Average of 12 monthly mean values.
```

EXAMS-> ***SET SUSED(*,13)=5***
EXAMS-> ***SET BULKD(3,13)=1.5***
EXAMS-> ***SET PCTWA(3,13)=150***
EXAMS-> ***SET FROC(*,13)=.02***
EXAMS-> ***SET STRFL(1,13)=3.E5***
Option not identified.

```
EXAMS->  HELP STFL
STFLO is a real matrix with 100 rows and 13 columns.
STream_FLOws (segment,month)            Units: cubic meters/hour
Flow into head reach of river or estuary; segment tributaries
and creeks or other streamflows entering a lake or pond. Note
that STFLO represents stream flow entering system segments from
external sources ONLY. EXAMS itself computes hydrologic flows
among segments that are part of the waterbody being studied, via
the specified advective and dispersive flow patterns (see JFRAD,
JTURB, etc.). Therefore, DO NOT compute net water balances for
each segment and enter these into the database--enter ONLY those
flows entering the system across external boundaries!

EXAMS->  SET STF(1,13)=3.E5
EXAMS->  SET STSED(1,13)=1500
EXAMS->  SET STRLD(1,1,13)=0.01
EXAMS-> SET OUTFIL(1)=Y
EXAMS->  RUN

Simulation beginning for:
Environment: Lake Zurich - central basin (Untersee)
Chemical  1: 1,4-Dichlorobenzene

Hydrologic definition of segment    1 is improper.
There is a net advected flow leaving this segment,
but the flow pathway has not been specified. Simulation aborted.
RUN command completed.

EXAMS->  SET JFR(1)=1
EXAMS->  SET ITO(1)=0
EXAMS->  SET ADVPR(1)=1.0

EXAMS->  SHO AD

Name of environment: Lake Zurich - central basin (Untersee)
Total number of segments (KOUNT) =   3
Segment Number:  1  2  3
Segment "TYPE":  E  H  B
----------------------------------------------------------------
Table 9.  Input specifications -- advective transport field.
----------------------------------------------------------------

J FR AD        1
I TO AD        0
ADV PR      1.00
 Path No.:     1
----------------------------------------------------------------

EXAMS->  RUN

Simulation beginning for:

Environment: Lake Zurich - central basin (Untersee)
Chemical  1: 1,4-Dichlorobenzene

RUN command completed.

EXAMS->  LI 15
```

```
Ecosystem: Lake Zurich - central basin (Untersee)
Chemical:  1,4-Dichlorobenzene
-----------------------------------------------------------------
Table 15.01.  Distribution of chemical at steady state.
-----------------------------------------------------------------
Seg  Resident Mass   ******** Chemical Concentrations *********
 #                     Total    Dissolved  Sediments    Biota
     Kilos      %      mg/*     mg/L **     mg/kg       ug/g
--- -------- ------  ---------  ---------  ---------  ---------
In the Water Column:
  1  7.3      20.00  1.074E-05  1.074E-05  1.759E-04   0.00
  2  29.      80.00  1.074E-05  1.074E-05  1.759E-04   0.00
    ======== ======
     37.      99.33

 and in the Benthic Sediments:
  3 0.24     100.00  1.798E-04  1.065E-05  1.744E-04   0.00
    ======== ======
    0.24       0.67
Total Mass (kilograms) =     36.75
-----------------------------------------------------------------
 * Units: mg/L in Water Column; mg/kg in Benthic Zone.
** Excludes complexes with "dissolved" organics.
```

EXAMS-> ***list 18***

```
Ecosystem: Lake Zurich - central basin (Untersee)
Chemical:  1,4-Dichlorobenzene
-----------------------------------------------------------------
Table 18.01. Analysis of steady-state fate of organic chemical.
-----------------------------------------------------------------
 Steady-state Values        Mass Flux    % of Load   Half-Life*
      by Process             Kg/  day                   days
---------------------       ----------   ---------   ----------
Hydrolysis
Reduction
Radical oxidation
Direct photolysis
Singlet oxygen oxidation
Bacterioplankton
Benthic Bacteria
Surface Water-borne Export  7.7314E-02     32.21      329.5
Seepage export
Volatilization              0.1627         67.79      156.6
-----------------------------------------------------------------
Chemical Mass Balance:
   Sum of fluxes =          0.2400
   Sum of loadings =        0.2400
      Allochthonous load:                 100.0
      Autochthonous load:                   0.0
   Residual Accumulation =    2.24E-08      0.0
-----------------------------------------------------------------
* Pseudo-first-order estimates based on flux/resident mass.
```

EXAMS-> ***list 20***

```
Ecosystem: Lake Zurich - central basin (Untersee)
Chemical:  1,4-Dichlorobenzene
-------------------------------------------------------------
Table 20.01.  Exposure analysis summary.
-------------------------------------------------------------
Exposure (maximum steady-state concentrations):
 Water column: 1.074E-05 mg/L dissolved; total = 1.074E-05 mg/L
 Benthic sediments: 1.065E-05 mg/L dissolved in pore water;
   maximum total concentration = 1.798E-04 mg/kg (dry weight).
 Biota (ug/g dry weight): Plankton:          Benthos:

Fate:
 Total steady-state accumulation:  36.8     kg, with  99.33%
   in the water column and   0.67% in the benthic sediments.
 Total chemical load: 0.24     kg/  day.  Disposition:   0.00%
   chemically transformed,   0.00% biotransformed,  67.79%
   volatilized, and  32.21% exported via other pathways.

 Persistence:
  After  216.       days of recovery time, the water column had
  lost  50.52% of its initial chemical burden; the benthic zone
  had lost  19.55%; system-wide total loss of chemical =  50.3%.
  Five half-lives (>95% cleanup) thus require ca.    35. months.
```

EXAMS-> ***CAT ENV***

```
UDB #     Name of Environmental Dataset
=====    ==================================================
   1     Environmental Data Entry Template
   2     Georgia Piedmont Farm Pond (WBAN 13873, MLRA P136)
   3     Georgia OPP Farm Pond (MLRA P136, WBAN 13873)
   4     Mississippi OPP Farm Pond (MLRA P134, WBAN 03940)
   5     Index Reservoir, IL (MLRA M115, WBAN 13994)
```

EXAMS-> ***STORE ENV 6***

Environment stored: "Lake Zurich - central basin (Untersee)"

EXAMS-> ***SET DRFL(2,1,13)=1.5E-3***

EXAMS-> ***SET STRL(1,1,13)=8.5E-3***

EXAMS-> ***ENV NAME IS Lake Zurich with partial load to hypolimnion***

EXAMS-> ***run***

```
Simulation beginning for:
Environment: Lake Zurich with partial load to hypolimnion
Chemical  1: 1,4-Dichlorobenzene
RUN command completed.
```

EXAMS-> ***li 15***

```
Ecosystem: Lake Zurich with partial load to hypolimnion
Chemical:  1,4-Dichlorobenzene
-----------------------------------------------------------------
Table 15.01.  Distribution of chemical at steady state.
-----------------------------------------------------------------
Seg  Resident Mass   ******** Chemical Concentrations *********
 #                     Total    Dissolved  Sediments    Biota
     Kilos      %      mg/*     mg/L **     mg/kg       ug/g
--- -------- ------  ---------  ---------  ---------  ---------
In the Water Column:
  1  7.3      16.59  1.074E-05  1.074E-05  1.759E-04   0.00
  2  37.      83.41  1.350E-05  1.349E-05  2.210E-04   0.00
    ======== ======
     44.      99.31

 and in the Benthic Sediments:
  3 0.31     100.00  2.260E-04  1.338E-05  2.192E-04   0.00
    ======== ======
    0.31       0.69
Total Mass (kilograms) =     44.32
-----------------------------------------------------------------
 * Units: mg/L in Water Column; mg/kg in Benthic Zone.
** Excludes complexes with "dissolved" organics.
```

EXAMS-> ***list 18***

```
Ecosystem: Lake Zurich with partial load to hypolimnion
Chemical:  1,4-Dichlorobenzene
-----------------------------------------------------------------
Table 18.01. Analysis of steady-state fate of organic chemical.
-----------------------------------------------------------------
 Steady-state Values        Mass Flux    % of Load   Half-Life*
      by Process             Kg/  day                   days
---------------------       ----------   ---------   ----------
Hydrolysis
Reduction
Radical oxidation
Direct photolysis
Singlet oxygen oxidation
Bacterioplankton
Benthic Bacteria
Surface Water-borne Export  7.7314E-02     32.21      397.3
Seepage export
Volatilization              0.1627         67.79      188.8
-----------------------------------------------------------------
Chemical Mass Balance:
   Sum of fluxes =          0.2400
   Sum of loadings =        0.2400
      Allochthonous load:                 100.0
      Autochthonous load:                   0.0
   Residual Accumulation =     0.0          0.0
-----------------------------------------------------------------
* Pseudo-first-order estimates based on flux/resident mass.
```

EXAMS-> ***li 20***

```
Ecosystem: Lake Zurich with partial load to hypolimnion
Chemical:  1,4-Dichlorobenzene
-------------------------------------------------------------
Table 20.01.  Exposure analysis summary.
-------------------------------------------------------------
Exposure (maximum steady-state concentrations):
 Water column: 1.349E-05 mg/L dissolved; total = 1.350E-05 mg/L
 Benthic sediments: 1.338E-05 mg/L dissolved in pore water;
   maximum total concentration = 2.260E-04 mg/kg (dry weight).
 Biota (ug/g dry weight): Plankton:          Benthos:

Fate:
 Total steady-state accumulation:  44.3     kg, with  99.31%
   in the water column and   0.69% in the benthic sediments.
 Total chemical load: 0.24     kg/  day.  Disposition:   0.00%
   chemically transformed,   0.00% biotransformed,  67.79%
   volatilized, and  32.21% exported via other pathways.

 Persistence:
  After  252.       days of recovery time, the water column had
  lost  54.37% of its initial chemical burden; the benthic zone
  had lost  25.71%; system-wide total loss of chemical =  54.2%.
  Five half-lives (>95% cleanup) thus require ca.    37. months.

EXAMS->  zero load
All allochthonous loads removed.

EXAMS->  cat chem
UDB #     Name of Chemistry Dataset
=====    ==================================================
   1     Chemical Data Entry Template
   2     p-Cresol [CAS# 106-44-5]
   3     Benz[a]anthracene [CAS# 56-55-3]
   4     Benzo[a]pyrene [CAS# 50-32-8]
   5     Quinoline [CAS# 91-22-5]
   6     Benzo[f]quinoline [CAS# 85-02-9]
   7     9H-Carbazole [CAS# 86-74-8]
   8     7H-Dibenzo[c,g]carbazole [CAS# 194-59-2]
   9     Benzo[b]thiophene [CAS# 95-15-8]
  10     Dibenzothiophene [CAS# 132-65-0]
  11     Methyl Parathion [CAS# 298-00-0]
  12     Mirex [CAS# 2385-85-5]
  13     Heptachlor  [CAS# 76-44-8]
  20     1,4-Dichlorobenzene
EXAMS->  rec chem 20
Selected compound is "1,4-Dichlorobenzene"
EXAMS->  rec env 6
Selected environment is "Lake Zurich - central basin (Untersee)"
EXAMS->  env name is Lake Zurich with oceanic wind and reaeration
EXAMS->  show ko2(1,13)
KO2(1,13) is   2.500
EXAMS->  set ko2(1,13)=20
EXAMS->  sho wind(1,13)
WIND(1,13) is   1.380
```

In this study, we wish to set V_w to 3000 cm/h. Use Eq. (2-82) (On page 36) to calculate the required value for WIND.

```
EXAMS->  set wind(1,13)=2.6245
EXAMS->  set strl(1,1,13)=0.01
```

```
EXAMS->  run
Simulation beginning for:
Environment: Lake Zurich with oceanic wind and reaeration
Chemical  1: 1,4-Dichlorobenzene
RUN command completed.
EXAMS->  list 15
Ecosystem: Lake Zurich with oceanic wind and reaeration
Chemical:  1,4-Dichlorobenzene
----------------------------------------------------------------
Table 15.01.  Distribution of chemical at steady state.
----------------------------------------------------------------
Seg  Resident Mass   ******** Chemical Concentrations *********
 #                     Total    Dissolved  Sediments    Biota
     Kilos      %      mg/*     mg/L **     mg/kg       ug/g
--- -------- ------  ---------  ---------  ---------  ---------
In the Water Column:
  1  1.3      20.00  1.952E-06  1.952E-06  3.198E-05   0.00
  2  5.3      80.00  1.952E-06  1.952E-06  3.198E-05   0.00
    ======== ======
     6.6      99.33

 and in the Benthic Sediments:
  3 4.45E-02 100.00  3.269E-05  1.936E-06  3.172E-05   0.00
    ======== ======
    4.45E-02   0.67
Total Mass (kilograms) =     6.683
----------------------------------------------------------------
 * Units: mg/L in Water Column; mg/kg in Benthic Zone.
** Excludes complexes with "dissolved" organics.

EXAMS->  list 18
Ecosystem: Lake Zurich with oceanic wind and reaeration
Chemical:  1,4-Dichlorobenzene
----------------------------------------------------------------
Table 18.01. Analysis of steady-state fate of organic chemical.
----------------------------------------------------------------
 Steady-state Values        Mass Flux    % of Load   Half-Life*
      by Process             Kg/  day                   days
---------------------       ----------   ---------   ----------
Hydrolysis
Reduction
Radical oxidation
Direct photolysis
Singlet oxygen oxidation
Bacterioplankton
Benthic Bacteria
Surface Water-borne Export  1.4058E-02      5.86      329.5
Seepage export
Volatilization              0.2259         94.14      20.50
----------------------------------------------------------------
Chemical Mass Balance:
   Sum of fluxes =          0.2400
   Sum of loadings =        0.2400
      Allochthonous load:                 100.0
      Autochthonous load:                   0.0
   Residual Accumulation =     0.0          0.0
----------------------------------------------------------------
* Pseudo-first-order estimates based on flux/resident mass.
EXAMS->  quit
```

4.0 EXAMS Command Language Interface (CLI) User's Guide

Introduction This Chapter describes the EXAMS command language, including usage and reference information. The first part provides an overview of the command language and its grammar. The second part contains detailed descriptions of each command. The commands are listed in alphabetical order.

4.1 Conventions Used in this Chapter

Convention	Meaning
CTRL/X	The phrase CTRL/X indicates that you must press the key labeled CTRL while simultaneously pressing another key, for example, CTRL/Q.
-> LIST 7	Vertical series of periods, or ellipsis, mean that not all the data EXAMS would display in response to the particular command is shown, or that not all the data a user would enter is shown.
keyword, ...	Horizontal ellipsis indicates that additional key-words, command parameters, or data can be entered in a command sequence, or that EXAMS displays additional data as part of the sample output line.
[keyword]	Square brackets indicate that the item enclosed is optional, that is, the entity can be omitted from the command line altogether.
<option>	Angle brackets indicate that a command requires a choice among two or more options.

4.2 Overview

The EXAMS command language provides a set of commands for

- Entering, storing, and manipulating data describing the reaction chemistry of synthetic compounds, the environmental parameters governing their transport and transformation in aquatic systems, patterns of allochthonous loadings, and product chemistry.

- Studying the results of an analysis by listing tabular output on a terminal, plotting the concentration data ("Expected Environmental Concentrations" or EECs) computed during simulations, and printing paper copy.

- Choosing among analytical frameworks for investigating exposure to chemicals in a particular case study. EXAMS includes three operational modalities or "MODEs"

MODE	Analytical Methodology
1	Long-term consequences of continued releases of chemicals; steady-state analysis.
2	Detailed examination of immediate consequences of chemical releases; initial-value problems.
3	Intermediate-scale resolution of events over several years, including effects of seasonal environmental variability; analysis of time-series data.

4.3 Entering Commands

EXAMS commands are composed of English-language words (mostly verbs) that describe what you want EXAMS to do. Some commands require qualifiers and parameters. These give EXAMS more information on how to execute the command. Command parameters describe the object to be acted upon by the command. In some cases, the object is a keyword (as in the HELP command); in others, it is an EXAMS data element (SET command) or a section of a file of input data or analysis results to manipulate (STORE and LIST commands).

Throughout this Chapter, EXAMS commands are printed in uppercase letters for the sake of clarity. However, EXAMS will accept commands entered in uppercase, lowercase, or a mixture of uppercase and lowercase letters. Most EXAMS commands and keywords can be abbreviated to the least number of characters needed to uniquely distinguish them from other options available. For example, to end EXAMS you can enter "QUIT", "QUI", "QU", or "Q". The least number of required characters depends on the context, however, but is never more than three. For example, the SHOW command includes among its options both <QUALITY> and <QUIT>; in this case you must enter three characters for EXAMS to distinguish between them. In EXAMS' "help fields" and prompts, capitalization is used to show you how many characters are required for uniqueness.

The following example shows an AUDIT command and EXAMS' response, as they would appear on a terminal.

```
EXAMS-> AUDIT ON

All input will now be copied into the file
named "AUDOUT" on Fortran Unit Number  4
```

EXAMS-> ! This Command File should be renamed file.EXA

EXAMS->

EXAMS analyzes the parts of the above example as follows.

EXAMS-> The EXAMS system prompt for command input; a greater-than (->) means that EXAMS' command interpreter is ready for a command to be entered.

AUDIT The command name, requesting that EXAMS enable/disable the User Notepad/Command File Creation facility.

ON An option of the AUDIT command, requesting that the Notepad/Create facility be enabled.

All input will now be copied into the file named "AUDOUT" on Fortran Unit Number 4

A message from the AUDIT command, indicating that the command completed successfully. The command interpreter used the value of AUDOUT (4) to establish communication with an external file.

EXAMS-> The next system command prompt, confirming that the command has completed its operations (AUDIT has opened communications with an external file and started recording terminal inputs), and EXAMS is ready for additional input.

! This Command File should be renamed file.EXA

A comment entered by the user. Comment lines must begin with an exclamation point (!) or an asterisk (*). You can use comments, as needed, to document EXAMS analysis sessions or command procedures.

EXAMS-> The next EXAMS system command prompt, confirming that the comment has been recorded in the Notepad/Command file and EXAMS is ready to accept another command.

4.4 Command Prompting

When you enter a command at the terminal, you need not enter the entire command on a single line. If you enter a command that requires that you specify its range or the object of the requested action, and you do not include the needed information, EXAMS' command interpreter prompts you for all missing information. For example:

EXAMS-> AUDIT

The following AUDIT options are available

ON -- begins a new Audit file,
OFF -- ends Audit recording of input commands,
Help -- this message,
Quit -- return to the EXAMS prompt.

AUDIT-> ON

All input will now be copied into the
file named "AUDOUT" on Fortran unit number 4

In this example, no AUDIT option was entered, so EXAMS prompts for a more complete specification of the intended action. The line ending with a -> indicates that EXAMS is waiting for the additional input.

In many cases, EXAMS' prompts do not include an automatic description of the full range of possible response options. Often, however, entering HELP in response to the prompt will display a list of available choices, as in the following example.

EXAMS-> LIST

At the prompt, enter a Table number, "Quit," or "Help" to see a catalog of the output tables.

Enter Table Number -> HELP

1 Chemical inputs: FATE Data
2 Chemical inputs: PRODUCT Chemistry
3 PULSE Chemical Loadings
.
.
.
20 Exposure Analysis SUMMARY
ALL Entire Report

At the prompt, enter a Table number, "Quit,"
or "Help" to see a catalog of the output tables.

Enter Table Number -> 18

```
Ecosystem: Name of Water body
Chemical:  Name of chemical
----------------------------------------
Table 18.01. Analysis of steady-state fate
----------------------------------------
       .
       .  (body of table)
       .
----------------------------------------
```

In the example above, LIST is entered without the number of the output table to be displayed. EXAMS prompts for the missing

information; typing HELP in response to the LIST prompt displays a catalog of EXAMS output tables.

4.5 EXAMS Messages

When a command is entered incorrectly, EXAMS displays a descriptive error message indicating what is wrong. For example, if a data subscript larger that the maximum available is entered, EXAMS will respond

Subscript out-of-range.

You can then retype the command correctly.

Other error messages may be produced during the execution of a command, or during a simulation or data display sequence. These messages indicate such things as incomplete environmental data, character data entered where numeric data are required, or typographic errors during entry of commands. EXAMS will respond to typographic errors in command entries by displaying:

Command not recognized. Type HELP for command information.

Because the messages are descriptive, it is usually possible to determine what corrective action is required in order to proceed. When this is not the case, EXAMS' HELP facility contains a large body of additional and supplementary information available through the HELP, DESCRIBE, and SHOW commands.

4.6 The HELP Command

Consulting a printed guide is not the most convenient way to get a summary of the syntax of a command or a definition of an input datum. EXAMS' HELP command provides this information in EXAMS' interactive environment. For example, you can type the command:

```
EXAMS-> HELP LIST
```

EXAMS responds by displaying a description of the LIST command, its syntax, and the options needed to specify the range of the command.

The HELP facility also provides on-line assistance for EXAMS' input data, e.g.,

```
EXAMS-> HELP QYIELD
```

will display the subscript ranges, their meanings, the physical dimensions, and the English definition of EXAMS chemical input datum "QYIELD". This information is available online for all EXAMS' input data and control parameters. The names of all of EXAMS' input variables were selected as mnemonics for their English-language names. (For example, QYIELD is the photochemical quantum yield.) These mnemonics are used in EXAMS' output tables; definitions are given in the Data Dictionary (pages 176 ff.) as well as in the on-line HELP.

EXAMS' HELP facility supplies lists of individual topics and subtopics. The HELP command is described in more detail later in this Chapter, and a tutorial explanation of the command is available online by entering

```
EXAMS-> HELP TUTOR
```

4.7 Command Procedures

A command procedure is a file that contains a sequence of EXAMS commands, optionally interspersed with descriptive comments (lines with "!" or "*" in column one). By placing sets of frequently-used commands and/or response options in a command procedure, all the commands in it can be executed as a group using a single command. For example, suppose a file called START.EXA were to contain these command lines and comments:

```
SET MODE TO 3
SET KCHEM TO 4
SET NYEAR TO 5
RECALL LOAD 7
! Loadings UDB Sector 7 is the spray drift study
```

The four commands in this file can be executed by entering the command

```
EXAMS-> DO START
```

or

```
EXAMS-> @START
```

You do not have to specify the file type of a command procedure when you use the @ command, so long as the file type is ".EXA"--the default file type for EXAMS' @ command. You can use another file suffix, if you so inform EXAMS when you enter the command request. For example, to execute commands in a file named START.UP

```
EXAMS-> @START.UP
```

4.8 Wild Card Characters

Some EXAMS commands accept a "wild card" character in the input command specifications. The asterisk (*) is the only symbol having this function in EXAMS. Wild card characters are used to refer to a range of data subscripts, or other entities, by a general name, rather than having to enter a specific name for each member of the group. Particular uses of wild cards in EXAMS vary with the individual commands. The command

descriptions later in this Chapter indicate where wild cards are allowed and describe their effects.

4.9 Truncating Command Names and Keywords

All keywords and names of input data that are entered as command input can be abbreviated. Only enough characters to uniquely distinguish a keyword or datum from others with similar names need be entered (often only one).

4.10 Summary Description of EXAMS' System Commands

EXAMS Command	Summary Description
AUDIT	Start/Stop user notepad for recording procedures
CATALOG	List the contents of User Databases (UDBs)
CHANGE/SET	Enter/reset input data and program controls
CONTINUE	Resume integration (Modes 2 and 3 only)
DESCRIBE	Report dimensions and data type of parameter
DO or @	Execute file of EXAMS commands (file.EXA)
ECHO	Control command echoing
ERASE	Clear section of stored database (UDB)
HELP	Describes access to EXAMS on-line HELP facility
LIST	Show tabular results on the screen
NAME	Specify the name of a UDB, e.g., CHEM NAME IS ...
PLOT	Plot results on the screen
PRINT	Queue tabular results for hardcopy printing
QUIT	Abort command, or End interactive session
READ	Upload data from non-EXAMS ASCII disk file
RECALL	Activate data from stored database (UDB)
RUN	Begin simulation run
SHOW	Display current data values or control settings
STORE	Download current data into stored database (UDB)
WRITE	Download data to ASCII disk file
ZERO	Clear chemical loadings, pulses, or residuals

5.0 System Command Descriptions

A U D I T

Creates a copy of user input commands and responses in an external file.

Related: Control variables: AUDOUT
Commands: DO

Syntax: AUDIT <option>

Options

ON
OFf

Prompt: The following AUDIT options are available

ON -- begins a new Audit file,
OFf -- ends Audit recording of input commands,
Help -- this message,
Quit -- return to the EXAMS prompt.

AUDIT->

Options: O Ff
Ends copying of EXAMS commands to the external file.

ON
Begins copying of EXAMS commands to an external file.

Description: The AUDIT command starts copying inputs typed at the terminal, into an external file. These inputs include EXAMS commands, and user responses to EXAMS prompts and option selections. The output terminus for the copy is a file named "AUDOUT." The resulting output file can be used to record an analysis procedure, or as a general notepad. The output file can be renamed "file.EXA" and used as an EXAMS command (DO) file.

Examples:

1. EXAMS-> AUDIT

   The following AUDIT options are available:

   ON -- begins a new Audit file,
   OFf -- ends Audit recording of input commands,
   Help -- this message,
   Quit -- return to the EXAMS prompt.

   AUDIT-> ON

   All input will now be copied into file "AUDOUT.XMS".

This command begins recording of input from the terminal into an external file. The output will go to a disk file named "AUDOUT.XMS". After leaving EXAMS, this file can be printed to give a permanent record of the analysis.

2. EXAMS-> AUDIT OFF

   The AUDIT option has been terminated.

This command ends copying of EXAMS commands and responses to the external medium (usually a disk file).

3. EXAMS-> AUDIT ON

   All input will now be copied into the
   file named "AUDOUT" on Fortran Unit Number 4

   EXAMS-> RECALL ENV 2

   Selected environment is: Phantom Inlet

   EXAMS-> RECALL CHEM 2

   Selected compound is: Dichloroexample

   EXAMS-> RECALL CHEM 4 AS 2

   Selected compound is: Tetrabromoexample

   EXAMS-> AUDIT OFF

These commands build a file (AUDOUT) that can later be used as a command file upon entering the EXAMS system. In this instance, the file would be renamed (e.g., MYCOMAND.EXA) and used to execute the above series of commands as a unit--

EXAMS-> DO MYCOMAND

C A T A L O G

Lists, by accession number, the title of all current entries in the specified User Database (UDB).

Related: Control variables: none
Commands: ERASE, NAME, RECALL, STORE

Syntax: CATALOG <option>

Options: CHEMICAL, ENVIRONMENT, LOAD, PRODUCT

Prompt: Enter Environment, Chemical, Load, Product, Help, or Quit->

Options: CHEMICAL
Lists the titles, by access number, of chemical databases currently in the User Database. Each entry corresponds to a single chemical, and contains the laboratory data describing ionization and (species-specific) partitioning and reaction kinetics.

ENVIRONMENT
List the titles, by access number, of environmental databases currently in the User Database. Each entry contains a "canonical" physical and chemical model of an aquatic system, including the environmental data needed to compute reactivity and transport of synthetic chemicals in the system.

LOAD
Lists the titles, by access number, of allochthonous chemical loading patterns stored in the User Database. These data include monthly values (kg/hour) for stream-loads, non-point-source loads, groundwater seepage loads, precipitation loads, and drift loads of chemicals entering the aquatic environment, plus specification of pulse loadings. The pulse load data include the magnitude (kg), target environmental segment, and scheduling (month and day) of pulses of synthetic chemicals entering the system.

PRODUCT
Lists the titles, by access number, of reaction or transformation product chemistries stored in the User Database. These data include the Activity Database numbers of chemical parent and product compounds, the number of the process responsible for the transformation, and the yield efficiency (mole/mole) as an (optional) function of temperature.

Description: The CATALOG command inventories the contents of the specified User Database (UDB) and lists the titles of active entries on the terminal screen. Four types of UDBs are available, corresponding to the four options available to the CATALOG command. The titles are listed by accession number; this number is used to STORE, RECALL, or ERASE database entries.

Examples:

1. EXAMS-> CATALOG HELP

   The CATALOG command requires that you specify either:
   1. Environment,
   2. Chemical,
   3. Load,
   4. Product,
   5. Help (this option), or
   6. Quit.

   Enter Environment, Chemical, Load, Product, Help, or Quit-> CHEMICAL

```
Catalog of CHEMICAL parameter sets
UDB No.        Name of Entry Volume

    1          Chemical Data Entry Template
    2          p-Cresol
    3          Benz[a]anthracene
    .
    .
    .
EXAMS->
```

This example use of the CATALOG command lists the contents of the current User Database for chemical data. Any of these datasets can be loaded into the Activity Database (ADB) for study, using the RECALL command and the appropriate access number. The first entry ("Chemical Data Entry Template") is a blank data area reserved for entering new chemical data.

2.
```
EXAMS-> CATALOG ENVIRON
Catalog of ENVIRONMENTal models
UDB No.        Name of Entry Volume
1              Environmental Data Entry Template
2              Pond -- code test data
3              Connecticut River estuary
.
.
```

This example CATALOG command generates a listing of the environmental datasets present in the User Database. Any of these can be retrieved for study using a RECALL command and the accession number. The first entry ("Environmental Data Entry Template") is a template for entering a new environmental model.

C H A N G E

Use to enter data into the activity database (synonymous with SET).

Related: Commands: DESCRIBE, HELP, SET

Syntax: CHANGE <name of variable> TO <new value>
or SET <name of variable> = <new value>

Prompt: Enter name=value command->

Variable: The data entry or variable to be entered can be specified either as a single datum or, using wild cards (*), as an entire vector, row/column of a matrix, etc.

Description: Use the CHANGE command to specify the values of data in the activity database. "Value" can be any numerical quantity or literal characters, as appropriate. "Variable" specifies an individual element of input data or a program control parameter. Entire vectors, rows/columns of matrices, etc. can be set to a single uniform value using wild cards (*).

Examples:

1. EXAMS-> CHANGE VOL(153) TO 7E5

   Subscript out-of-range.

   EXAMS-> DESCRIBE VOL

   VOL is a Real Vector with 100 elements.

   EXAMS> CHANGE VOL(2) TO E

   Invalid numeric quantity after TO or =.

   EXAMS-> CHANGE VOL(2) TO 7E5

This command sets the environmental volume of segment 2 to 7.0E+05 cubic meters. The initial attempt to set the volume of segment 153 was rejected by EXAMS because the version in use was set up for environmental models of 100 segments at most. The DESCRIBE command was used to check the number of subscripts and the dimensional size of the variable "VOL". The accidental entry of an alphabetic character ("E") for the volume was trapped by the CHANGE command; VOL(2) was not altered.

2. EXAMS-> HELP TCEL

   TCEL is a Real Matrix with 100 rows and 13 columns.
   Temperature-CELsius (segment, month) Units: degrees C.
   Average temperature of ecosystem segments. Used (as enabled by input data) to compute effects of temperature on transformation rates and other properties of chemicals.

EXAMS-> CHANGE TCEL(2,7) TO 24

This command changes the July temperature in segment 2 to 24° C. The HELP command was used to check subscript dimensions, maximum values, the meaning of the subscripts (subscript #1 denotes the segment, subscript #2, the month), and the proper units for the input datum (degrees Celsius).

3. EXAMS-> HELP POH

POH is a Real Matrix with 100 rows and 13 columns.
pOH (segment, month) Units: pOH units
The negative value of the power to which 10 is raised in order to obtain the temporally averaged concentration of hydroxide [OH^-] ions in gram-equivalents per liter.

EXAMS-> CHANGE POH(*,13) TO 6.2

This command sets the average pOH (sector 13) of every segment to 6.2. Note use of wild card "*" to specify that all segments are to be changed. As in the previous example, HELP was used to check subscript dimensions, units, etc. This step, of course, is optional.

C O N T I N U E

The CONTINUE command resumes EXAMS' simulation analysis of chemical dynamics beginning from the current state of the system.

Related: Control variables: CINT, TINIT, TEND, TCODE, NYEAR
Commands: RUN, SHOW_TIME_FRAME

Syntax: CONTINUE

Prompt: (In Mode 2 only:)
Initial time for integration will be (nn.n) units
Enter ending time of integration, Help, or Quit->

Options: None. Reply to prompt with a value greater than (nn.n).

Description: The CONTINUE command resumes EXAMS' simulation analysis of chemical dynamics, beginning from the current state of the system. Chemical loadings and other input data can be altered (CHANGEd or SET) between simulation time segments; EXAMS will re-evaluate equation parameters as needed to incorporate the changed conditions into the analysis. CONTINUE cannot be invoked from Mode 1, where it is not appropriate. The SHOW TIME FRAME (abbreviate to SH T F) command can be used to examine the current state of the integrator timer controls. In Mode 2, the Communications INTerval CINT can be used to vary the temporal resolution in different segments of the analysis (see Example 1). In Mode 3, NYEAR, the number of years in a simulation time segment, can similarly be altered.

Examples:

1. EXAMS-> SET MODE=2

   EXAMS-> SHOW TIME FRAME

   A RUN will integrate from 0. to 24. Hours
   with output at intervals of 2.00 Hours

   EXAMS-> SET TCODE=2

   EXAMS-> SET TEND=10

   EXAMS-> SET CINT=1

   EXAMS-> SH TI F

   A RUN will integrate from 0 to 10 Days
   with output at intervals of 1 Days

   EXAMS-> RUN

   Simulation beginning for:
   Environment: Pond -- code test data
   Chemical 1: Dichloroexample

   Run complete

   EXAMS-> PLOT KIN PL (3,0,0 -- see PLOT command)

```
System:  Pond -- code test data
Chemical:  Dichloroexample

  2.00          I** ***
                I      * **** ****
                I                   **** **** ***
                I                                * **** **** **
                I                                              ** ***
  1.33          I
                I
                I
                I
                I
  0.667         I
                I
                I
                I
                I
  0.000         I
                 +----+----+----+----+----+----+----+----+----+----+
                0.000     2.00      4.00      6.00      8.00      10.0
                     1.00      3.00      5.00      7.00      9.00
                                  Time, Days
```

EXAMS-> CONTINUE
Initial time for integration will be 10.0 Days
Enter ending time of integration, Help, or Quit-> 30

Simulation beginning for:
Environment: Pond -- code test data
Chemical 1: Dichloroexample
Run complete.

EXAMS-> SET CINT=10
EXAMS-> ZERO PULSE LOAD
EXAMS-> CONTINUE

Initial time for integration will be 30.0 Days
Enter ending time of integration, Help, or Quit-> 90

Simulation beginning for:
Environment: Pond -- code test data
Chemical 1: Dichloroexample

Run complete.

EXAMS-> PLOT KINETIC PLOT (3,0,0)

```
System:   Pond -- code test data
Chemical: Dichloroexample

  3.49     I      *
           I      **
           I       **
           I         *
           I          **
  2.33     I            **
           I*             **
           I***             ***
           I   ***
           I     **               *
  1.16     I                            *
           I                                 *
           I                                       *    *     *
           I
           I
  0.000    I
            +----+----+----+----+----+----+----+----+----+----+
           0.000     18.0      36.0      54.0      72.0      90.0
                9.00      27.0      45.0      63.0      81.0
                                Time, Days
```

These commands show the use of the CONTINUE command in Mode 2. The objective of the analysis was to introduce two pulses of chemical separated by 10 days and to follow exposure over 90 days. Note the phased increase in the Communications INTerval CINT from 1 to 10 days. Note the use of the ZERO command to clear the pulse load ADB before the simulation of dissimilation from day 30 through day 90. If this were not done, EXAMS would introduce an additional pulse on day 30.

2. EXAMS-> SET MODE=3

EXAMS-> SHO TI FR

A RUN will integrate from 1 January 1989
through 31 December 1989.
(YEAR1 = 1989, and NYEAR = 1.)

EXAMS-> RUN

Simulation beginning for:
Environment: Pond -- code test data
Chemical 1: Dichloroexample

Run complete.

EXAMS-> SHO TI FR

A RUN will integrate from 1 January 1989
through 31 December 1989.
(YEAR1 = 1989, and NYEAR = 1.)

CONTinuation will proceed through 31 December 1990
(NYEAR = 1.)

EXAMS-> SET NYEAR=3
EXAMS-> SH TI F

```
A RUN will integrate from  1 January  1989
     through 31 December 1991.
(YEAR1 = 1989, and NYEAR =   3.)

CONTinuation will proceed through 31 December 1992
(NYEAR =    3.)

EXAMS-> CONTINUE

CONTinuing integration through 31 December 1992.

Simulation beginning for:
Environment: Pond -- code test data
Chemical  1: Dichloroexample

Run complete.

EXAMS->
```

These commands illustrate the use of the CONTINUE command in Mode 3. "SHOW TIME FRAME" is used to check the state of the integrator timer controls.

D E S C R I B E

Reports the data type, dimensionality, and maximum UDB storage size of parameters.

Related: Control variables:
Commands: HELP

Syntax: DESCRIBE <parameter>

Parameters:

Any "system parameter"--any chemical or environmental input datum, control parameter (e.g., MODE, CINT), etc.

Prompt: Enter name of input parameter->

Options: Any parameter accessible to the CHANGE and SET commands.

Description: The DESCRIBE command returns information about EXAMS' input data and control parameters. All variables whose values can be altered using the CHANGE and SET commands can be inspected by the DESCRIBE command. The information returned by DESCRIBE includes the data type (real, integer, character), dimensionality (scalar, vector, matrix (2-dimensional), table (3-dimensional matrix)) and the maximum size that can be STOREd in the UDB (file "EXAMS.DAF") of the version of EXAMS in use. When a SET or CHANGE command fails, the DESCRIBE command can help diagnose the problem by indicating the structure and dimensionality of the variable.

Examples:

1. EXAMS-> DESR MODE

   Command not recognized. Type HELP for command information.

   EXAMS-> DESCR

   Enter name of input parameter-> MODE

   MODE is an Integer Scalar.

   These commands establish that "MODE" is an integer scalar. Note that the initial typing error (DESR) resulted in a "not recognized" error message followed by return to the EXAMS prompt.

2. EXAMS-> CHANGE VOL(133) TO 7E5

   Subscript out-of-range.

   EXAMS-> DESCRIBE VOL

   VOL is a Real Vector with 100 elements.

This command reports that VOL is a real variable, a vector of 100 elements. In this example, the number of segments (NPX) of an aquatic system model to be STOREd in the UDB of the version of EXAMS currently in use is set for 100 at most. The number of computational elements of the current model in the ADB is controlled by the user's setting of "KOUNT." Any (intentional or accidental) attempt to enter a value for the VOLume of a segment > the current value of KOUNT (e.g., VOL(133)) will fail, as illustrated above. Similarly, an attempt to STORE an environment with >100 segments will be rejected, with the suggestion that the WRITE command be used to store the data in a separate file. DESCRIBE can be used to check the reason for a failure of the STORE command when a problem with dimension sizes is suspected.

3. EXAMS-> DESCRIBE QYIELD

QYIELD is a Real Table with dimensions (3,7,5)

EXAMS-> HELP QYIELD

QYIELD is a Real Table with dimensions (3,7,5)
Quantum_YIELD (form, ion, chemical) Units: dimensionless
Reaction quantum yield for direct photolysis of chemicals--fraction of the total light quanta absorbed by a chemical that results in transformations. Separate values (3×7=21) for each potential molecular type of each chemical allow the effects of speciation and sorption on reactivity to be specified in detail. Matrix of 21 values specifies quantum yields for the (3) physical forms: (1) dissolved, (2) sediment-sorbed, and (3) DOC-complexed; of each of (7) possible chemical species: neutral molecules (1), cations (2-4), and anions (5-7). (QYIELD is an efficiency, hence dimensionless.)

These commands report the data type and UDB storage capacity of EXAMS' input "QYIELD" (result of "DESCRIBE QYIELD") and then report the meaning of the dimensions and the physical units of the variable (result of "HELP QYIELD"). The local implementation of EXAMS used in this example has the capacity to store load patterns and product chemistries of no more than five chemicals simultaneously. Thus, QYIELD was DESCRIBEd as consisting of a set of five matrices, each of (fixed) size (3,7). Note, however, that EXAMS can accommodate an unlimited number of chemicals in any given study (e.g., 25 separate organophosphorus pesticides, a suite of 12 PCB congeners, etc.) by SETting the value of KCHEM. Loading patterns or product chemistries of dimensionalities >5 cannot be stored in the UDB, however, but must be written to external files (see documentation for the WRITE command).

D O

Executes a command procedure; requests that EXAMS read subsequent input from a specific file.

Related: Control variables:
Commands: AUDIT

Syntax: DO <name of command file>

Prompt: Enter name of file (no more than nn characters), Help, or Quit->

Parameters: name of file

Specifies the file from which to read a series of EXAMS commands. If you do not specify a file type suffix, EXAMS uses a default file type of EXA (e.g., "filename.EXA"). Wild cards are not allowed in the file specification.

Description: Use command procedures to catalog frequently used sequences of commands. An EXAMS command procedure can contain

- Any valid EXAMS command. The command line can include all the necessary options and data to build a complete command (exception: kinetic plots).
- Parameters or response options for a specific command. When the currently executing command requires additional parameters, the next line of the command file is searched for appropriate input.
- Data. When the currently executing command requires numerical or character data entry, the next line of the command file is searched for input.
- Comment lines. Any line that contains an exclamation point (!) or asterisk (*) in column one is ignored by EXAMS' command interpreter. These lines can be used as needed to document the command procedure.

Command procedures must not contain a request to execute another command procedure. (In other words, a DO file must not contain a DO (@) command; EXAMS' DO commands cannot be nested.) Command procedures can be constructed as external files using your favorite editor, or they can be constructed interactively through the EXAMS system command processor, as illustrated below. The default file type is "EXA", but files of any type (suffix) can be used if the entire file name is specified when entering the DO command.

Examples: 1. EXAMS-> AUDIT ON

All input will now be copied into the
file named "AUDOUT" on Fortran Unit Number 4

EXAMS-> RECALL

Enter Environment, Chemical, Load, Product, Help or Quit-> ENV
Enter environment UDB catalog number, Help, or Quit-> 2
Selected environment is: Phantom Inlet

EXAMS-> RECALL CHEM 2

Selected compound is: Dichloroexample

EXAMS-> RECALL LOAD 2

Selected load is: Aedes control spray drift

EXAMS-> ! Load 2 is the Phantom Inlet salt marsh study
EXAMS-> SET KCHEM TO 2
EXAMS-> RECALL CHEM 4 AS 2

Selected compound is: Tetrabromoexample

EXAMS-> AUDIT OFF

These commands build a file (AUDOUT.DAT) that can later be used as a command file upon entering the EXAMS system. In this instance, the file could be renamed (e.g., SETUP.EXA) and used to execute the above series of commands as a unit:

EXAMS-> DO SETUP
or, EXAMS-> @SETUP

The completed command file appears as follows

```
RECALL
ENV
2
RECALL CHEM 2
RECALL LOAD 2
! Load 2 is the Phantom Inlet salt marsh study
SET KCHEM TO 2
RECALL CHEM 4 AS 2
AUDIT OFF
```

Note that command files that are constructed interactively will include "AUDIT OFF" as the final instruction. This can, of course, be removed by editing the file if it is undesirable.

2. EXAMS-> DO

Enter name of file (no more than nn characters), Help, or Quit-> HELP

The "DO" or "@" command provides a means of executing stored EXAMS commands. In response to the prompt, enter the name of the file that contains the stored commands. A three-character filename extension of "EXA" is added to the name if no period is present in the name as entered. The maximum length for file names is nn characters; this limit includes the .EXA suffix.

Enter name of file (no more than nn characters), Help, or Quit-> AUDOUT

EXAMS/DO-> ! Audit trail of input sequence from EXAMS.
EXAMS/DO-> RECALL

Enter Environment, Chemical, Load, Product, Help, or Quit->
EXAMS/DO-> ENV

Enter environment UDB catalog number, Help, or Quit->
EXAMS/DO-> 2

Selected environment is: Phantom Inlet
EXAMS/DO-> RECALL CHEM 2

Selected compound is: Dichloroexample
EXAMS/DO-> RECALL LOAD 2

```
Selected load is: Aedes control spray drift
EXAMS/DO-> ! Load 2 is the Phantom Inlet salt marsh study
EXAMS/DO-> SET KCHEM TO 2
EXAMS/DO-> RECALL CHEM 4 AS 2

Selected compound is: Tetrabromoexample
EXAMS/DO-> AUDIT OFF
The AUDIT option has been terminated.
```

This command requests execution of the command procedure constructed in Example 1 above. The default name (AUDOUT) was not altered, so the complete file specification was given to the DO command as the entry parameter. The DO file transfers a set of two chemicals, an environmental model, and a load pattern from the stored UDB to the ADB for study and analysis.

E C H O

The ECHO command turns echoing of command inputs on and off.

Related: Control variables: None
Commands: None

Syntax: ECHO ON/OFF

Prompt: The following Echo options are available
ON – begins command echo,
Off – turns off echo of input commands,
Help – this message
Quit – return to the EXAMS prompt

Options: OFF
End echoing of commands

ON
Begins echoing of commands

Description: If ECHO is entered from the EXAMS prompt command level, EXAMS stops echoing commands on the interactive terminal. This feature is primarily useful for batch processing, in which case it serves to limit the size of resulting output files.

Examples:

1. EXAMS-> ECHO OFF

   This command terminates echoing of EXAMS commands at the terminal or in the log file.

2. EXAMS-> ECHO ON

   This command resumes echoing of EXAMS commands at the terminal or in the log file.

E R A S E

Deletes, by accession number, the data stored at a single sector of a User Database (UDB) library (chemical, environmental, loadings, product chemistry).

Related: Control variables:
Commands: CATALOG, RECALL, STORE

Syntax: ERASE <option> <accession number>

Options

CHEMICAL
ENVIRONMENT
LOAD
PRODUCT

Prompt: Enter Environment, Chemical, Load, Product, Help, or Quit->

Options: CHEMICAL
Deletes the contents, by entry access number, of chemical databases currently in the User Database. Each entry corresponds to a single chemical, and contains the laboratory data describing ionization and (species-specific) partitioning and reaction kinetics.

ENVIRONMENT
Deletes the contents, by entry access number, of environmental databases currently in the User Database. Each entry contains a canonical physical and chemical model of an aquatic system, including the environmental data needed to compute the reactivity and transport of synthetic chemicals in the system.

LOAD
Deletes the contents, by entry access number, of chemical loading patterns stored in the User Database. These data include monthly values (kg/hour) for stream loads, non-point-source loads, groundwater seepage loadings, precipitation loads, and drift loads of chemicals entering the aquatic environment, plus the magnitude (kg), target environmental sector, and scheduling (month and day) of chemical pulse loads.

PRODUCT
Deletes the contents, by entry access number, of chemical product data stored in the User Database (UDB). These data include the Activity Database numbers of reactants and products, the number code of the chemical process, and yield efficiencies (mole/mole) as an (optional) function of temperature.

Description: ERASE deletes the contents of a single sector of the specified User Database (UDB) library (chemical, environmental, loads, or product chemistry). The data to be deleted are selected by choosing the appropriate accession number. (If you work in a multi-user environment, be sure to avoid erasing others' data.)

Examples:

1. EXAMS-> ERASE ENV 20

Environment 20 erased.

This command erases the data stored at Environmental UDB sector number twenty. The space is now available for storing another dataset.

2. EXAMS-> ERASE

Enter Environment, Chemical, Load, Product, Help, or Quit-> HELP

The ERASE command requires that you specify either:

1. Environment,
2. Chemical,
3. Load,
4. Product,
5. Help (this option), or
6. Quit.

Enter Environment, Chemical, Load, Product, Help, or Quit-> LOAD

Enter allochthonous loading UDB catalog number, Help, or Quit-> 10

Load 10 erased.

This command erases the data stored at Loadings UDB sector number ten. The space is now available for another dataset.

E X I T

EXIT can be used as a synonym for QUIT to end an interactive session.

Related: Control variables:
Commands: QUIT is used to abort commands in progress.

Syntax: EXIT

Prompt: None

Options: None

Description: If EXIT is entered from the EXAMS prompt command level, EXAMS stops and returns control to the computer operating system.

Examples:

1. EXAMS-> EXIT

   This command terminates an interactive EXAMS session.

H E L P

Displays, on the terminal, information available in EXAMS' help files. EXAMS provides descriptions of its commands, input data, control parameters, and general concepts and analysis procedures.

Related: Control variables:
Commands: DESCRIBE

Syntax: HELP [keyword]

Prompt: None

Keyword: Specifies a keyword (a topic or an element of EXAMS input data) that tells EXAMS what information to display.

- None--if HELP is typed with no keyword, EXAMS lists the keywords that can be specified to obtain information about other topics.
- Topic-name--describes either a basic EXAMS command, an information page, or a "system parameter." System parameters include chemical and environmental input data, system control parameters (e.g., CINT), and parameters that control the current analysis (e.g., IMASS).

Ambiguous abbreviations result in a failure to achieve a match on the keyword, and an error message is displayed.

Description: The HELP command provides access to EXAMS' collection of on-line user aids and information texts. This material includes

- Brief discussions of the syntax and function of each of EXAMS' command words (RECALL, RUN, etc.)
- Definitions, physical dimensions, and meanings of subscripts for EXAMS' chemical and environmental input data and control parameters.
- A series of information pages providing orientation to the concepts implemented in the EXAMS program, the range of capabilities and analyses that can be executed with the program, and brief expositions on data structures and program control options.

Examples:

1. EXAMS-> HELP

   EXAMS includes these system commands:
   .
   . HELP message text and list of command and
   . information topics

   Issuing the HELP command without any keywords produces a list of the HELP topics in EXAMS main command library. When responding to one of the topics on the list, EXAMS displays a HELP message on that topic, and a list of subtopics (if any).

2. EXAMS-> HELP QUOIT

No information available for this request.

EXAMS->

When you request information for a topic not on file, EXAMS displays a message to that effect and returns you to the EXAMS-> prompt.

3. EXAMS-> HELP QYIELD

QYIELD is a Real Table with dimensions(3,7,4)
QUANTUM_YIELD (form, ion, chemical) Units: dimensionless
Reaction quantum yield for direct photolysis of chemicals--fraction of the total light quanta absorbed by a chemical that results in transformations. Separate values (3×7=21) for each potential molecular type of each chemical allow the effects of speciation and sorption on reactivity to be specified in detail. Matrix of 21 values specifies quantum yields for the (3) physical forms: (1) dissolved, (2) sediment-sorbed, and (3) DOC-complexed; of each of (7) possible chemical species: neutral molecules (1), cations (2-4), and anions (5-7). (QYIELD is an efficiency.)

You can request information about any input datum (chemical, environmental, control parameters, analysis parameters) accessible to the CHANGE and SET commands. EXAMS then displays on the screen the characteristics of the variable (equivalent to the results of DESCRIBE), followed by a discussion of the variable that echoes the entry in the Data Dictionary (page 176).

L I S T

Displays an EXAMS output table on the terminal screen.

Related: Control variables: FIXFIL
Commands: PLOT, PRINT

Syntax: LIST <option>

Options

table-#
ALL
HELP

Prompt: Enter Table Number -> option

Options:

table-#	specifies the number of an EXAMS output table to be displayed.
ALL	Sequential display of all current output tables.
HELP	Displays a list of titles of EXAMS output tables.

Description: The LIST command displays EXAMS' output tables at the terminal. To temporarily halt the output and resume it at the line where it was interrupted, use CTRL/S followed by CTRL/Q.

When you request a primary table number (that is, an integer from 1 to 20) EXAMS displays the first table of that number present in the analysis file. If additional tables of that type are present in the file, EXAMS will display the first, and then search for more tables of that type and, if any are found, ask if you want to see them.

Examples:

1. EXAMS-> LIST

   A PRINT, LIST, or PLOT command was issued before executing a RUN. If results exist from a previous simulation, these can be accessed after issuing the command: SET FIXFIL TO 1

   EXAMS-> SET FIXFIL TO 1

   EXAMS-> LIST

   Enter Table Number -> HELP

   1 Chemical inputs: FATE Data
   2 Chemical inputs: PRODUCT Chemistry
   3 PULSE Chemical Loadings
   .

```
    .
    .
18 Sensitivity Analysis of Chemical FATE
19 Summary TIME-TRACE of Chemical Concentrations
20 Exposure Analysis SUMMARY
ALL Entire Report

Table-> 18

Ecosystem: Name of Water body
Chemical:  Name of chemical
-------------------------------------------------------
TABLE 18.01.  Analysis of steady-state fate ...
-------------------------------------------------------
    .
    .  (body of table)
    .
-------------------------------------------------------
```

The LIST command requests that output Table 18 from an EXAMS results file be displayed on the terminal. For illustrative purposes, it was assumed that the user had left EXAMS and then returned to inspect Table 18 generated in the previous session.

2. EXAMS-> LIST 20

```
Ecosystem: Name of Water body
Chemical:  Name of FIRST chemical
-------------------------------------------------------
TABLE 20.01.  Exposure analysis summary: 1983--1985.
-------------------------------------------------------
    .
    .  (body of table)
    .

More? (Yes/No/Quit)-> Y

Ecosystem: Name of Water body
Chemical:  Name of SECOND chemical
-------------------------------------------------------
TABLE 20.02.  Exposure analysis summary: 1983--1985.
-------------------------------------------------------
    .
    .  (body of table)
    .
```

In this example, EXAMS was used to investigate the behavior of two chemicals over a period of several years, using Mode 3 simulations. The analysis began with year 1983, and NYEAR was set to 3 to produce an analysis of the period 1983 through 1985. The LIST command requests that all versions of Table 20 in the analysis file be displayed, with a pause between each for inspection of the results. In the example, the analyst chose to examine the output for both chemicals. If the analysis is now CONTINUEd, the current set of tables will be replaced with new results. The PRINT command should be used to make copies of all intermediate results you want to save.

The sub-table numbers of EXAMS' output tables identify the ADB number of the chemical, the indexes of any ions (see SPFLG in the Data Dictionary on page 176), and the month of the year, as follows.

Table	Sub-tables	Examples	Sub-table Meaning
1	1.cc.i	1.01.1	Table.chemical.ion
4-6, 8, 10,11,13	NN.mm	4.01 10.13	Table.month (13 = annual mean)
12	12.cc.mm	12.01.12	Table.chemical.month
14 (Mode ½) 14 (Mode 3)	14.cc 14.cc.mm	14.01 14.01.12	Table.chemical Table.chemical.month
15-18,20	NN.cc	18.01 20.01	Table.chemical

N A M E

Use the NAME command to attach unique names to datasets.

Related: Control Variables: MCHEM
Commands: CATALOG, ERASE, STORE, RECALL

Syntax: <datatype> NAME IS a[aa...] (up to 50 characters), where <datatype> can be CHEmical, ENvironment, LOad, or PROduct

Prompt: Options available are:

Help - this message.
Quit - return to EXAMS command mode.
<carriage return> = Help
<any other response> - accepted as the new name.

Enter new name->

<datatype>: EXAMS uses these four kinds of datasets:

1. CHEMICAL reactivity and partitioning,

2. ENVIRONMENTal physico/chemical parameters,

3. allochthonous chemical LOADings, and

4. PRODUCT chemistry for generating interconversions among multiple chemicals in an analysis

Description: The NAME command is used to associate unique names with datasets in the UDB. These names can be STOREd in the CATALOGs; they are printed in the headers of EXAMS' output tables. When naming CHEMICAL datasets, the ADB number of the chemical to be named is given by MCHEM; use "SET MCHEM TO n" before naming dataset "n".

Examples:

1. EXAMS-> CHEM NAME IS Tetrachloroexample

   The NAME command associates the name "Tetrachloro..." with the chemical data in the sector of the activity database (ADB) given by the current value of MCHEM. This name will be printed on all subsequent appropriate output tables, and it will be used as a title for the database if the STORE command is used to download the data into the User Database (UDB).

2. EXAMS-> SET MCHEM = 2

   EXAMS-> CHEM NAME IS Dichloroexample

   The chemical name command always addresses the MCHEM sector of the chemical ADB, thus, this example names chemical number 2 to "Dichloro...".

3. EXAMS-> ENVIR NAME IS Pogue Sound

   This command names the current environmental dataset "Pogue Sound". The name will now appear on output tables, and remain with the dataset if it is downloaded to the UDB permanent files.

P L O T

Used to plot character graphics for the chemical state of the ecosystem.

Related: Control Variables: MCHEM
Commands: LIST, PRINT

Syntax: PLOT <Option1, Option2, Option3>

Options

POINT
PROFILE
KINETIC

Prompt: The following options are available:

POint - Vertical concentration profile
PRofile - Longitudinal concentration profile
Kinetic - List or plot kinetic outputs
Help - This message
Quit - Return to the EXAMS program prompt

Option->

Plot options: POINT

"POINT" plots are generalized profiles of chemical concentrations. These also require selection of a variable to be displayed (total concentration, dissolved concentration, etc.) and a "statistical" class (average values, minima, or maxima).

PROFILE

"PROFILE" plots are longitudinal profiles of chemical concentrations. These require selection of a concentration variable (total concentration, dissolved concentration, etc.) and an environmental sector (water column or benthic sediments). The abscissa of the resulting plot is set up by increasing segment number, which in most cases should represent an upstream-downstream progression. When the aquatic model includes both longitudinal and vertical segmentation, each section of the plot begins at the air-water or water/benthic interface and proceeds vertically downward (the bars are presented along the abscissa).

KINETIC

"KINETIC" plots display the results of integration of the governing equations over the time spans selected for simulation. These plots also require selection of concentration variables and either particular segments, or summary "statistics," for display. Time is used as the abscissa for the plot. The "LIST" option produces numerical output which, when re-directed to an external file, can be used as a data source for any graphics package that can assimilate ASCII files.

Description: Use the PLOT command to display results of the current analysis. Three kinds of character graphic PLOTs are available on-line from EXAMS: POINT, PROFILE, and KINETIC. Each PLOT requires the specification of several options; these can either be entered on the system command line or entered in response to EXAMS prompts. The available second- and third-level

options are illustrated in the examples below. The results available to POINT and PROFILE plots depend on the Mode used in the simulation. In Mode 1, the outputs are steady-state concentrations. In Mode 2, the results are a snap-shot of concentrations as of the end of the current temporal simulation segment. In Mode 3, the results are time-averaged concentrations over the most recent temporal simulation segment of length NYEAR.

Examples:

1. EXAMS-> PLOT POINT

The following concentration options are available:

Total	-	mg/L in Water Column
	-	mg/kg in Benthic Sediments
Dissolved	-	"Dissolved" (mg/L)
	(aqueous + complexes with "dissolved" organics)	
Particulate	-	Sediment-sorbed (mg/kg dry weight)
Biota	-	Biosorbed (ug/g dry weight)
Mass	-	Chemical mass as grams/square meter AREA
Help	-	This message
Quit	-	Return to the EXAMS prompt

Option-> DISSOLVED

The following statistical options are available:

MAX - Maximum concentration
MIN - Minimum concentration
AVE - Average concentration
Help - This message
Quit - Return to the EXAMS prompt

Option-> AVERAGE

```
                    9.00E-04   -I
                                I
                                I AAAAAAAAAAA
                                I A|||||||||A
                  C             I A|||||||||A
                  O  8.00E-04   -I A|||||||||A
                  N             I A||||D||||A      D
                A C             I A||||I||||A      I
                V E             I A||||S||||A      S
                E N             I A||||S||||A      S
                R T  7.00E-04   -I A||||O||||A      O
                A R             I A||||L||||A      L
                G A             I A||||V||||A      V
                E T             I A||||E||||A      E
                  I             I A||||D||||A      D
                  O  6.00E-04   -I A|||| ||||A
                  N             I A||||M||||A      M
                                I A||||G||||A AAAAAGAAAAA
                                I A||||/||||A A||||/||||A
                                I A||||L||||A A||||L||||A
                    5.00E-04   -+_AAAAAAAAAAA_AAAAAAAAAAA
                                    Water Col    Benthic
```

EXAMS-> SET MCHEM=2

EXAMS-> PL PO DI AV

```
          4.00E-04   -I
                      I
                      I
                      I
      C               I
      O   3.50E-03   -I
      N               I      D           D
    A C               I      I           I
    V E               I      S           S
    E N               I      S      AAAAASAAAAA
    R T   3.00E-03   -I      O      A||||O||||A
    A R               I      L      A||||L||||A
    G A               I AAAAAVAAAAA A||||V||||A
    E T               I A||||E||||A A||||E||||A
      I               I A||||D||||A A||||D||||A
      O   2.50E-03   -I A||||  ||||A A||||  ||||A
      N               I A||||M||||A A||||M||||A
                      I A||||G||||A A||||G||||A
                      I A||||/||||A A||||/||||A
                      I A||||L||||A A||||L||||A
          2.00E-03   -+_AAAAAAAAAAA_AAAAAAAAAAA
                         Water Col    Benthic
```

This example illustrates EXAMS' internal prompting for POINT plots. Note that the analysis included two chemicals; the plot for chemical number two was obtained by first SETting MCHEM=2. The second plot was requested via a single command line, thus bypassing the PLOT prompts.

2. EXAMS-> PLOT PROF
   The following concentration options are available:

Total	-	mg/L in Water Column
	-	mg/kg in Benthic Sediments
Dissolved	-	"Dissolved" (mg/L)
	(aqueous + complexes with "dissolved" organics)	
Particulate	-	Sediment-sorbed (mg/kg dry weight)
Biota	-	Biosorbed (ug/g dry weight)
Mass	-	Chemical mass as grams/square meter AREA
Help	-	This message
Quit	-	Return to the EXAMS prompt

   Option-> TOTAL
   The following options are available:

WATER	-	Water Column concentrations
SEDIMENTS	-	Benthic Sediment concentrations
Help	-	This message
Quit	-	Return to the EXAMS prompt

   Option-> WATER

```
     8.00E-01   -I
                 I
                 I
                 I
  C              I
T O  6.00E-01   -I
O N              I
T C              I                                                        015
A E              I                                                        H|H
L N              I                                                    014 H|H
  T  4.00E-01   -I                                                    H|H H|H
M R              I                                                    H|H H|H
G A              I                                                013 H|H H|H
/ T              I                                                E|E H|H H|H
L I              I                                            012 E|E H|H H|H
  O  2.00E-01   -I                                       010 011 E|E E|E H|H H|H
  N              I                                   009 E|E E|E E|E E|E H|H H|H
                 I                               008 E|E E|E E|E E|E E|E H|H H|H
                 I                       005 006 007 E|E E|E E|E E|E E|E E|E H|H H|H
                 I     002 003 004 E|E E|E E|E E|E E|E E|E E|E E|E E|E E|E H|H H|H
     0.00E+00   -+_001_EEE_EEE_EEE_EEE_EEE_EEE_EEE_EEE_EEE_EEE_EEE_EEE_HHH_HHH
                                     WATER COLUMN
```

The above example illustrates EXAMS' internal prompts for a PROFILE plot. As with the POINT option, this entire command could be entered on a single line:

EXAMS-> PLOT PROF TOT WAT

3. EXAMS-> PLOT KIN

The following KINETIC options are available:

List - lists selected KINETIC output parameters
Plot - plots selected KINETIC output parameters
Help - this message
Quit - return to the EXAMS prompt

Option-> PLOT

Chemical: Methyl Parathion
Environment: Pond -- code test data

Simulation units: Days
Number of segments: 2
1 2
Type of segment (TYPE): L B

The following parameters are available for time-trace plotting
of values averaged over the ecosystem space:
("Dissolved" = aqueous + complexes with "dissolved" organics.)
1 - Water Column: average "dissolved" (mg/L)
2 - average sorbed (mg/kg)
3 - total mass (kg)

4 - Benthic: average "dissolved" (mg/L)

5 average sorbed (mg/kg)
6 total mass (kg)

Enter parameters, one per line;
enter 0 to end data entry and proceed.

Parameter-> 3
Parameter-> 6
Parameter-> 0

The following parameters are available for each segment:

1	-	Total concentration	(Water Column, mg/L; benthic, mg/kg)
2	-	"Dissolved"	(mg/liter of fluid volume)
3	-	Sorbed	(mg/kg of sediment)
4	-	Biosorbed	(ug/g)
5	-	Mass	(grams/square meter of AREA)

Enter segment-parameter number pair, one number per line;
enter 0 when data entry is complete; Quit to abort.

Enter segment number---> 0

```
System:   Monthly pond -- code test data
Chemical: Methyl Parathion


 0.160     I                        **
           I                       *
           I                      ** *
           I                      *
           I                      * *
 0.106     I                      * *
           I                      * *
           I                     *   *
           I                     *    +++
           I                     * ++* +++
 5.322E-02 I               *       ++ *   +++
           I               **     * + **    +++
           I                *      ++   *      ++++
           I                * * *+     **       +++++
           I                *+++++++       ****       ++++++++++
 0.000     I+++++++++++++++++******           *****************+
            +----+----+----+----+----+----+----+----+----+----+
          0.000      73.0      146.      219.      292.     365
                                Time, Days
```

This example illustrates EXAMS' prompting in KINETIC plots. The numerical options cannot be entered on the command line, but must be entered in response to the prompts.

P R I N T

Use the PRINT command to export an output table to a file for hardcopy printing or incorporation into a document.

Related: Control variables: FIXFIL
Commands: LIST

Syntax: PRINT <option>

Options:

table-#
ALL
Help
Quit

Prompt: Enter Table Number->

Options:		
	table-#	specifies the number of an EXAMS output table to be displayed.
	ALL	Sequential printing of all current output tables.
	HELP	Displays a list of titles of EXAMS output tables.

Description: The PRINT command transfers EXAMS results tables to an output file for subsequent printing. The command functions much like the LIST command, except that output is saved for later hardcopy printing or incorporation into a report, rather than being routed to your interactive terminal. Should the PRINT command result in output at your terminal, you may need to consult with site ADP personnel to properly direct the print stream to a file.

Examples: See the documentation for the LIST command.

Q U I T

Use QUIT to abort a command in progress or to end an interactive EXAMS session.

Related: Control variables:
Commands: EXIT

Syntax: QUIT

Prompt: None

Options: None

Description: Entering QUIT at the EXAMS prompt command level will terminate an interactive session, returning control to the computer's operating system. QUIT is included as an option of many EXAMS commands to allow the command to be aborted.

Examples:

1. EXAMS-> AUDIT

   The following AUDIT options are available

ON	--	begins a new audit file,
OFf	–	ends Audit recording of input commands,
Help	--	this message,
Quit	--	return to the EXAMS prompt.

   AUDIT-> QUIT

   EXAMS->

This command terminates processing of the AUDIT command and returns control to the EXAMS prompt command level. The current status of AUDIT is not altered.

2. EXAMS-> QUIT

This command terminates an interactive EXAMS session.

R E A D

Use the READ command to transfer data from a properly organized non-EXAMS file into the Activity Data Base (ADB).

Related: Control variables: MODE, MCHEM, PRBEN
Commands: WRITE

Syntax: READ <datatype> <name of file>

Prompt: Enter Environment, Chemical, PRZM, Meteorology, Help, or Quit->

Description: The READ command provides a facility for up-loading EXAMS datasets from external ASCII sequential files. These non-EXAMS files can be stored entirely separately from the main EXAMS User Data Base (UDB), which is contained in a direct access file named "EXAMS.DAF". Data are transferred directly to the Activity Data Base (foreground memory ADB) rather than to the User Data Base (UDB) file area, so the STORE command must be used to transfer data to the UDB from the ADB after invoking READ or they will be discarded when you exit from EXAMS.

Under the ENVIRONMENT option of READ, the entire ADB dataset ("months" 1 through 13) will be uploaded from the external file called <name of file>.

Under the CHEMICAL option of READ, the chemical dataset to be uploaded from <name of file> is put into the MCHEM sector of the Activity Data Base (ADB).

In the PRZM option of the READ command, EXAMS acquires a set of external loadings generated by the Pesticide Root Zone Model (PRZM). This facility transfers chemicals exported from the land surface into an adjacent aquatic system. The PRZM transfer file is a MODE 3 construct, in which the first set of loadings contains the application rate of the pesticide, and the succeeding loadings contain runoff events generating water-borne and sediment-borne chemical transfers to the aquatic system. The parameter PRBEN (c.f.) controls EXAMS' treatment of sediment-borne materials. When PRBEN is zero, all sediment-borne materials are equilibrated with the water column upon entry into the system. When PRBEN is 1.0, all sediment-borne materials are routed directly to the benthic zone. PRBEN has a default value of 0.5, based on the observation that, in general, about 50% of sorbed chemical is usually labile, and about 50% recalcitrant, to rapid re-equilibration in water. Runoff from PRZM is translated into monthly non-point-source water and sediment input.

The METEOROLOGY option reads a PRZM meteorology file. These files contain daily values of precipitation, pan evaporation, temperature, and wind speed. If (*and only if*) an EXAMS environment has been selected, the period-of-record monthly averages are transferred to the corresponding EXAMS variables. In addition, a digest of monthly mean values is prepared for each year of data in the file; when a PRZM transfer file is read, the weather data for that year is loaded into EXAMS.

Examples:

1. Transfer an environmental dataset from a file called "INLET.DAT" on the default directory; the dataset can then be then STOREd in EXAMS' direct access UDB file.

EXAMS-> READ

Enter Environment, Chemical, Load, Help, or Quit-> EN

Enter name of file, Help, or Quit-> INLET.DAT

2. Read precipitation, pan evaporation, temperature, and wind speed from a meteorology file. Note that a directory other than the default can be specified as part of the READ command <name of file> option; the default suffix for meteorology files is ".met".

EXAMS-> SET MODE=3

EXAMS-> READ MET C:\EXAMS\PROJECTX\W13873

3. To read a PRZM transfer file, first set MODE to 3, and then read the dataset. Note the convention for naming of PRZM transfer files--the base name is always "PRZM2EXA" or "P2E-Cn" and the suffix indicates the year--in this case data from 1989 ("D89"). Because EXAMS will accept any file name for acquisition by the READ command, these files can be renamed to any convenient file name for archiving or to prevent subsequent PRZM runs from over-writing them.

EXAMS-> READ PRZM PRZM2EXA.D89

R E C A L L

Use RECALL to upload data from the permanent database (UDB) into current foreground memory (ADB).

Related: Control Variables: MCHEM

Commands: CATALOG, ERASE, NAME, STORE

Syntax: RECALL <datatype> <UDB#> [AS ADB#]

Prompt: Enter Environment, Chemical, Load, Product, Help, or Quit->

Command parameters:

<datatype> can be Chemical, Environment, Load, or Product
(EXAMS uses these four kinds of datasets.)

AS ADB# is an optional explicit specification of MCHEM (see Example 1).

UDB# specifies the accession number or location in the User Database for the source data for transfer to the ADB (Example 2).

Description: RECALL transfers data from permanent storage (UDB) to activity databases (ADBs). The data in active use by EXAMS are held in a foreground memory bank (Activity DataBase or ADB) with four sectors, one for each datatype required by EXAMS--

<C>hemical reactivity and partitioning,

<E>nvironmental physical and chemical parameters,

allochthonous chemical <L>oadings, and

<P>roduct chemistry for generating interconversions among multiple chemicals in an analysis.

When EXAMS is started, the ADB is empty. Use the RECALL command to transfer data from the permanent User Databases (UDBs) to foreground memory (ADB). When an analysis session is ended (QUIT or EXIT), ADBs are discarded. Use the STORE command to transfer new data from the ADB to the UDB sector of the same datatype for permanent retention of the data.

Examples:

1. Because EXAMS can process several chemicals in a single analysis, the target sector of the chemical activity database should be specified when using the RECALL command to activate CHEMICAL data. (This section of the command should be omitted for other data types.) When the ADB# (an integer between 1 and KCHEM) is omitted, the chemical data are transferred to the sector of the activity database given by the current value of MCHEM. For example, to activate data from the chemical UDB, putting UDB dataset number 9 into ADB sector 1, and UDB #14 into sector 2:

Either:

EXAMS-> SET MCHEM TO 1

EXAMS-> RECALL CHEMICAL 9

EXAMS-> SET MCHEM TO 2

EXAMS-> RECALL CHEMICAL 14

or, equivalently:

EXAMS-> RECALL CHEMICAL 9 AS 1

EXAMS-> RECALL CHEMICAL 14 AS 2

2. Long-term retention of data required by EXAMS is provided by storage in the "User Database" (UDB, generally resident on a physical device--e.g., a hard disk) for Chemicals, Environments, Loads, or Products. Within each UDB sector, each dataset is catalogued via a unique accession number (UDB#). When transferring data to foreground memory (the activity database or ADB) from a UDB, the source location must be specified by the name of the UDB sector and the accession number within the sector. For example, to RECALL an environmental dataset:

EXAMS-> RECALL ENVIR 2

Selected environment is: Phantom Inlet, Bogue Sound

EXAMS->

R U N

The RUN command begins a simulation analysis.

Related: Control Variables: MODE
Commands: CONTINUE

Syntax: RUN

Prompt: None

Description: The RUN command executes an analysis and creates the output files accessed by the LIST and PLOT commands. The activity database (ADB) must be loaded, either via entry of new data or by RECALL from the UDB, before a RUN can be started.

Examples:

1. EXAMS-> RECALL CHEMICAL 22

   Selected compound is: Dibromoexample

   EXAMS-> RECALL ENVIRON 17

   Selected environment is: Albemarle Sound--Bogue Bank

   EXAMS-> SET STRL(1,1,13)=.01

   EXAMS-> RUN

   Simulation beginning for:
   Environment: Albemarle Sound--Bogue Bank
   Chemical 1: Dibromoexample

   Run complete.

   EXAMS->

   In this example, a steady-state (MODE=1) analysis is conducted by selecting a chemical and an environment, imposing a loading of chemical 1 on segment 1 under average conditions (i.e., data sector 13, EXAMS initial default value) and invoking EXAMS' simulation algorithms with the RUN command.

S E T

Use SET to specify the values of data in the activity database.

Related: Commands: CHANGE (synonym), DESCRIBE, HELP

Syntax: SET <name of variable> TO <new value>
or
SET <name of variable> = <new value>

Prompt: Enter name=value command->

Variable: The data entry or variable to be SET can be specified either as a single datum or, using wild cards (*), as an entire vector, row/column of a matrix, etc.

Description: Use the SET command to specify the values of data in the activity database. "Value" can be any numerical quantity or literal, as appropriate. "Variable" specifies an individual element of input data or a program control parameter. Entire vectors, rows/columns of matrices, etc. can be set to single values using wild cards (*).

Examples:

1. EXAMS-> SET VOL(167) TO 7E5

   Subscript out-of-range.

   EXAMS-> DESCRIBE VOL

   VOL is a Real Vector with 100 elements.

   EXAMS> SET VOL(2) TO E

   Invalid numeric quantity after TO.

   EXAMS-> SET VOL(2) TO 7E5

This command sets the environmental volume of segment 2 to 7.0E+05 cubic meters. The initial attempt to set the volume of segment 67 was rejected by EXAMS because the version in use was set up for environmental models of 100 segments at most. The DESCRIBE command was used to check the number of subscripts and the dimensional size of the variable "VOL". The erroneous entry of an alphabetic for the volume was trapped by the SET command; the initial value of VOL(2) was not altered.

2. EXAMS-> HELP TCEL

   TCEL is a Real Matrix with 100 rows and 13 columns.
   Temperature-CELsius (segment, month) Units: degrees C.
   Average temperature of ecosystem segments. Used (as enabled by input data) to compute effects of temperature on transformation rates and other properties of chemicals.

EXAMS-> SET TCEL(2,7)=24

This command changes the July temperature in segment 2 to 24°C. The HELP command was used to check subscript dimensions, maximum values, the meaning of the subscripts (subscript #1 denotes the segment; subscript #2, the month), and the proper units for the input datum (degrees Celsius).

3. EXAMS-> HELP POH

POH is a Real Matrix with 100 rows and 13 columns.
pOH (segment, month) Units: pOH units
The negative value of the power to which 10 is raised in order to obtain the temporally averaged concentration of hydroxide [OH^-] ions in gram-molecules per liter.

EXAMS-> SET POH(*,13) TO 6.2

This command sets the average pOH (sector 13) of every segment to 6.2. Note use of wild card "*" to specify that all segments are to be changed. As in the previous example, HELP was used to check subscript dimensions, units, etc. This step, of course, is optional.

S H O W

Use SHOW to display current data values or control settings.

Related: Control Variables: MCHEM, MONTH

Commands: CHANGE, SET

Syntax: SHOW <option> [range]

Prompt: The following options are available:

Advection,	Chemistry,	Dispersion,	GEometry,
GLobals,	Loads,	PLot,	PUlse Loads,
PRoducts,	QUAlity,	Time Frame,	Variables,
Help, or	QUIt->		

Command parameters:

Range: Some options of the SHOW command accept the specification of a range of values to define the scope of the data to be displayed (see Example 1). Use MCHEM to delimit the range of SHOW Chemistry, and MONTH for GEometry, QUAlity, etc.

Options:

ADVECTION

SHOW ADVECTION gives the advective hydrologic flow structure of the current aquatic system. A single element in a dataset might typically look like the following example.

J FR AD	1	J FRom ADvection: Source Segment
I TO AD	3	I TO ADvection: Terminus
ADV PR	1.00	ADVection Proportion: Percent of total JFRAD flow on path
Path No.:	1	Vector index for SETting data

No more than NCON hydrologic pathways can be specified. If more are needed, special versions of EXAMS can be produced. Specify export pathways by entering a zero (0) for the number of the segment to receive the flow (ITOAD). Do not specify a hydrologic source term by entering zero in the JFRAD vector; instead use stream flows, non-point-source flows, etc.

DISPERSION

SHOW DISPERSION displays the input data describing transport in the active (loaded in the ADB) Environmental dataset. The index vectors (JTURB, ITURB) define the existence of inter-segment dispersive transport paths. A zero in either vector, when paired with a non- zero value at the corresponding position in the other index vector, is taken as a boundary condition with an uncontaminated body of water. A single element in a dataset might typically be displayed like the following example.

J TURB	1	Segment number for dispersion
I TURB	2	Segment number for dispersion
XS TUR m^2	5.000E+04	Cross-sectional area of path
CHARL m	2.53	CHARacteristic_Length of path

DSP m^2/h	4.676E-05	Eddy DiSPersion coefficient
Path No.:	1	Vector index for data entry

No more than NCON hydrologic pathways can be specified. If more are needed, this number can be increased and EXAMS recompiled.

CHEMISTRY

SHOW CHEMISTRY displays the chemical output data currently in the ADB (foreground memory bank). The sector of the ADB denoted by the current value of MCHEM is displayed. Within each sector of the ADB (that is, for each chemical under active review), the data for each ionic species are presented separately, and photochemical data are presented on separate screens.

GEOMETRY

SHOW GEOMETRY returns a segment-by-segment description of the geometry (volumes, areas, etc.) of the current ecosystem. The segment number reported with each block of data is the first subscript for modifying the datum using CHANGE or SET. The month to be displayed is set by the current value of MONTH (explicit mean values are denoted by MONTH number 13): the month is the second subscript of such data as WIND, STFLO, etc.

GLOBALS

SHOW GLOBALS displays the input data that are "global" in extent, that is, "global" data apply to all segments of the current ecosystem.

LOADS

SHOW LOADS displays the current state of allochthonous chemical loadings. The form of the display depends on the current operational MODE: initial values are ignored in Mode 1 as they have no effect on the analysis results. The value of PRSW also affects the display: when PRSW is 0, SHOW LOADS returns a summary of annual loadings; when PRSW=1, a month-by-month tabulation is displayed as well. This display may not represent the final values used in the analysis, because EXAMS will modify loads that result in violation of the linearizing assumptions used to construct the program. After a RUN has been executed, however, SHOW LOADS will display the corrected values.

PRODUCTS

SHOW PRODUCTS displays the specifications for product chemistry currently in the ADB. Each entry is identified and loaded according to a unique "pathway number." A single element of a dataset might look like this:

CH PAR	1	ADB number of CHemical PARent
T PROD	2	ADB number of Transformation PRODuct
N PROC	7	Number of transforming PROCess
R FORM	29	Reactive FORM (dissolved, etc.)
YIELD M/M	0.100	Mole/Mole YIELD of product
EAYLD Kcal	0.000	Enthalpy of yield (if appropriate)
Pathway:	1	Number of the pathway

More detail as to the numbering of NPROC and RFORM is given in the Data Dictionary (page 176), which can also be accessed on-line using the HELP command. No more than NTRAN transformation pathways can be specified. If more are needed, a special version of EXAMS can be created.

PLOT

SHOW PLOT examines the contents of the concentration time-series and steady-state files, and reports the names of the chemicals and ecosystem used in the analysis.

PULSE LOADS

SHOW PULSE LOADS displays the specifications for allochthonous pulses of chemicals entering the system. This display may not represent the final values used in the analysis, because EXAMS will modify loads that result in violation of the linearizing assumptions used to construct the program. Although faulty pulse loads are discarded, EXAMS does not correct the input pulse load data, because the occurrence of load constraint violations depends on the context (i.e., the size of current stream loadings, etc.). Thus, unlike SHOW LOADS, the SHOW PULSE display following execution of a RUN does not display corrected data. The pulses actually used during an analysis are instead entered into EXAMS' output tables, where they can be examined using the LIST and PRINT commands.

QUALITY

SHOW QUALITY returns a segment-by-segment display of the canonical water-quality data included in the current Environmental ADB dataset. The month to be displayed is set by the current value of MONTH (explicit mean values are denoted by MONTH number 13). The month is the second subscript of such data as pH, pOH, etc. The first subscript is the segment number; thus these data are entered (CHANGE/SET) as "datum(segment,month)".

TIME FRAME

SHOW TIME FRAME displays the current status of the parameters needed to control the temporal aspects of a Mode 2 or Mode 3 simulation.

VARIABLES

SHOW VARIABLES displays a list of the names of EXAMS input data and control parameters. These names must be used to SET/CHANGE, SHOW values, HELP/DESCRIBE, etc.

Description: Use the SHOW command to examine the current contents of the ADB, that is, the foreground datasets used for the current analysis. The SHOW command can be used to examine clusters of similar data, the values of individual parameters, or the data contained in entire vectors. Typing SHOW without an option will display a list of the available options.

Examples: 1. The SHOW command can be used to examine the value of single parameters. For example, the pH of segment 7 of the current ecosystem during September could be inspected by entering:

```
EXAMS-> SHOW PH(7,9)
```

Using wild cards (*), the SHOW command can also be used to display the data in an entire vector or row/column of a data matrix. For example, the pH in every segment of the current ecosystem during September could be displayed by entering:

```
EXAMS-> SHOW PH(*,9)
```

and the pH of segment 7 through the year could be displayed by:

```
EXAMS-> SHOW PH(7,*)
```

S T O R E

Use STORE to download current (ADB) data into the permanent database (UDB).

Related: Control Variables: MCHEM

Commands: CATALOG, ERASE, NAME, RECALL

Syntax: STORE <datatype> [ADB# IN] <UDB#>

Prompt: Enter Environment, Chemical, Load, Product, Help, or Quit->

Command parameters:

<datatype> can be Chemical, Environment, Load, or Product
(EXAMS uses these four kinds of datasets.)

ADB# IN is an optional explicit specification of MCHEM (see Example 1).

UDB# specifies the accession number or location in the User Database for storage of the current ADB sector (Example 2).

Description: STORE downloads data from activity databases (ADBs) into the permanent User DataBases (UDBs). The data in active use by EXAMS are held in a foreground memory bank (Activity DataBase or ADB) with four sectors, one for each datatype required by EXAMS:

CHEMICAL reactivity and partitioning,

ENVIRONMENTal physical and chemical parameters,

allochthonous chemical LOADings, and

PRODUCT chemistry for generating interconversions among multiple chemicals in an analysis.

When an analysis session is ended (QUIT or EXIT), these data are discarded. Use the STORE command to transfer data from the ADB to the UDB sector of the same datatype for permanent retention of the data.

Examples: 1. Because EXAMS can process several chemicals in a single analysis, the source sector of the chemical activity database should be specified when using the STORE command to download CHEMICAL data. (This section of the command should be omitted for other data types.) When the ADB# (an integer from 1 to KCHEM) is omitted, the chemical data are taken from the sector of the activity database given by the current value of MCHEM. For example, to STORE data in the UDB, putting ADB sector 1 into the chemical UDB under catalog/accession 9 and ADB sector 2 into UDB sector 14:

Either:

EXAMS-> SET MCHEM TO 1

EXAMS-> STORE CHEMICAL 9

EXAMS-> SET MCHEM TO 2

EXAMS-> STORE CHEMICAL 14

or, equivalently:

EXAMS-> STORE CHEMICAL 1 IN 9

EXAMS-> STORE CHEMICAL 2 IN 14

2. Long-term retention of data required by EXAMS is provided by storage in the "User Database" (UDB, generally resident on a physical device--e.g., a hard disk) for Chemicals, Environments, Loads, or Products. Within each of these UDB sectors, each dataset is CATALOGued via a unique accession number (UDB#). When transferring data between foreground memory (the activity database or ADB) and a UDB, the target location must be specified by the name of the UDB sector and the accession number within the sector. For example, to STORE the current environmental dataset:

   EXAMS-> STORE ENVIR 2

   Environment record 2 is in use with
   Pond -- code test data
   Replace?-> no

   Nothing changed.

   EXAMS-> STORE ENVIR 14

   Environment stored: Phantom Inlet-Bogue Sound Study Data

   EXAMS->

   Note that EXAMS provides a measure of protection against accidental overwriting of existing datasets, an important courtesy in a multi-user environment.

W R I T E

Use the WRITE command to transfer data from the Activity Data Base (ADB) to an external (outside EXAMS' UDB direct access file EXAMS.DAF) sequential file.

Related: Control variables: MODE, MCHEM
Commands: READ

Syntax: WRITE <datatype> <name of file>

Prompt: Enter Environment, Chemical, Load, Help, or Quit->

Description: The WRITE command provides a facility for off-loading EXAMS datasets into external ASCII sequential files. These files are stored separately from the main EXAMS User Data Base (UDB). Data are transferred from the Activity Data Base (foreground memory ADB) rather than directly from the User Data Base (UDB) file, so the RECALL command must be used to transfer data from the UDB to the ADB prior to invoking WRITE, when the intention is to transfer data from the UDB to an external file. The write command must be used to store problem scenarios (load patterns, product chemistries) or datasets in which the number of environmental segments exceeds 100 or the number of chemicals being studied exceeds five.

Under the CHEMICAL option of WRITE, the chemical dataset to be downloaded to <name of file> is chosen from the MCHEM sector of the Activity Data Base (ADB).

In the LOAD option of WRITE, a set of external chemical loadings are written to an ASCII file. The setting of MODE affects the amount of data written to the file. In Mode 1, only monthly data and mean values are written from the ADB, pulse loadings are deleted as they are of no relevance to a steady-state analysis. in Mode 2, initial conditions are added, and in Mode 3 a full set of monthly loads and daily pulse loads are written from the ADB to the external file. Using EXAMS' WRITE facility to manage chemical loading scenarios thus requires some care when moving across operational modes. For example, a MODE 3 pulse load scenario can be read by EXAMS operating in MODE 2, but when the scenario is RUN, the daily values are accumulated into a single set of initial mass loadings for each segment.

In the PRODUCT option of WRITE, product chemistry specifications are written to an external file; the file contains internal character fields documenting the data structure.

Examples:

1. In this example, the environmental data is RECALLed from the UDB, and the data are downloaded to a file called "INLET.DAT" on the default directory.

   EXAMS-> RECALL ENVIRONMENT 12

   Selected environment is: Chinquoteague Inlet

   EXAMS-> WRITE
   Enter Environment, Chemical, Load, Product, Help, or Quit-> EN
   Enter name of file, Help, or Quit-> INLET.DAT

2. To continue the above example, an entire loadings dataset could be stored in another file by changing the MODE to 3. Note that a directory other than the default can be specified as part of the WRITE command <name of file> option.

   EXAMS-> SET MODE=3
   EXAMS-> WRITE LOAD C:\EXAMS\PROJECTX\INLET.LOD

Z E R O

Use the ZERO command to initialize (set to zero) loadings databases or the concentration of pollutant chemicals throughout the ecosystem.

Related: Control variables: MODE
Commands: CONTINUE, RUN

Syntax: ZERO <option>

Options:

PULSE LOADS
LOADS
RESIDUALS

Prompt: The following options are available:

Pulse Loads	-	zero all pulse loads,
Loads	-	zero all other loads,
Residuals	-	zero all pollutant concentrations,
Help	-	this message, or
Quit	-	return to command mode with no action.

ZERO->

Description: The ZERO command initializes (sets to zero) the entire suite of allochthonous chemical pulse loadings (IMASS), longer term loadings (stream loads, drift loads, etc.), or the current values of pollutant chemical concentrations throughout the ecosystem. The ZERO command is designed primarily for use during the course of temporally segmented simulation studies. The same effect can be achieved with multiple applications of the CHANGE/SET command; ZERO is a block-mode implementation that reduces the work needed to remove loadings datasets. (See Example 1 in the documentation of the CONTINUE command.)

Examples:

1. EXAMS-> SET MODE=2

   EXAMS-> RECALL CHEMICAL 22

   Selected compound is: Dibromoexample

   EXAMS-> RECALL ENVIRON 17

   Selected environment is: Albemarle Sound--Bogue Bank

   EXAMS-> SET STRL(1,1,13)=.01

   EXAMS-> SET IMASS(1)=2.0

   EXAMS-> SET ISEG(1)=14

```
EXAMS-> SET ICHEM(1)=1

EXAMS-> RUN

Simulation beginning for:
Environment: Albemarle Sound--Bogue Bank
Chemical  1: Dibromoexample

Run complete.

      .
      .
      .

EXAMS-> ZERO PULSE LOADS

EXAMS-> CONTINUE
```

In this example, an initial-value (MODE=2) analysis is begun by selecting a chemical and an environment, imposing an allochthonous load of chemical 1 on segment 1 under average conditions (i.e., data sector 13, EXAMS' initial default value), and specifying the initial presence (or introduction at time zero) of 2.0 kg of material in segment 14. At the end of the initial RUN segment, one might want to examine the output tables, plot the results, etc. Then, before CONTINUing, the ZERO command is used to remove the pulse load specifications. If this were not done, EXAMS would introduce a second 2.0 kg pulse into segment 14 at the beginning of the continuation segment. Alternatively, the other loadings could have been removed, and the effect of a series of pulse loads could be studied by issuing a sequence of CONTINUE commands.

6.0 EXAMS Data Dictionary

ABSER

ABSolute ERror tolerance of integrators

When the characteristics of the chemical and ecosystem are such as to result in "stiff" equations, numerical errors may lead to small negative numbers in the time series. If desired, the value of ABSER and RELER can be decreased in order to achieve greater precision in the simulation outputs.

ADB

Activity DataBase

EXAMS provides for long-term storage of CHEMical, ENVironmental, transformation PRODuct chemistry, and allochthonous LOADings databases in a User DataBase or UDB. The actual analyses are conducted on particular datasets drawn from these files (or entered via SET/CHANGE). Particular cases are loaded from the UDB into the foreground transient memory of your computer in an Activity DataBase or ADB, using the RECALL command. Because EXAMS simulates the behavior of several (MCHEM) chemicals simultaneously, the ADB for chemicals has MCHEM separate sectors. These data are lost when you EXIT from EXAMS, so be sure to STORE any new or corrected datasets before leaving EXAMS.

ABSOR

ABSORption spectra (wavelength, ion, chemical)
Units: $cm^{-1}(mole/L)^{-1}$ (**N.B.**: When entering data, "w" is the index number for λ, not the wavelength *per se*. See page 196 for the mapping between ABSOR entries and λ.)
Mean decadic molar light extinction coefficients in 46 wavelength intervals over 280 – 825 nm. For wavelength "w" and chemical "c":

ABSOR(w,1,c) is molar absorption coefficient of RH_3 (neutral molecule)
ABSOR(w,2,c) is molar absorption coefficient of RH_4^+ (+1 cation)
ABSOR(w,3,c) is molar absorption coefficient of RH_5^{2+} (+2 cation)
ABSOR(w,4,c) is molar absorption coefficient of RH_6^{3+} (+3 cation)
ABSOR(w,5,c) is molar absorption coefficient of RH_2^- (−1 anion)
ABSOR(w,6,c) is molar absorption coefficient of RH^{2-} (−2 anion)
ABSOR(w,7,c) is molar absorption coefficient of R^{3-} (−3 anion)

ADVPR

ADVection PRoportion (path)
Units: n/a Range: > 0 – 1.0

PRoportion of flow ADVected from segment JFRAD that enters ITOAD. The matching (same subscript) members of JFRAD, ITOAD, and ADVPR define an advective hydrologic flow pathway. Although usually 1, ADVPR lets one enter braided channels, etc. The total of ADVPRs for each segment must sum to either 0 or 1, failing which, EXAMS aborts the RUN. The flow data can be inspected by typing SHOW ADV; path numbers are given above each active dataset. Enter data via CHANGE or SET commands.

Additional information available: JFRAD, ITOAD

AEC

Anion Exchange Capacity (segment, month)
Units: meq/100 g (dry)

Anion exchange capacity of sediment phase of each segment. Useful in relating sediment sorption (partitioning) of anions to a variable characteristic of system sediments.

AerMet

Aquatic Aerobic Metabolism Half-Life (chemical)
Units: days

Aquatic aerobic metabolism half-life of each study chemical.
When biolysis rate constants are zero, AerMet is used to calculate biolysis rate constants for water-column bacterio-plankton. In making this computation, the planktonic populations are averaged for the entire water body. In Mode 1 and Mode 2, the single temporal value in use at RUN time is used. For other Modes, the mid-Summer populations are used.

AIRTY

AIR mass TYpe (month)
Units: letter codes

Select: Rural (default), Urban, Maritime, or Tropospheric

AnaerM

Aquatic Anaerobic Metabolism half-life (chemical)
Units: Days
Aquatic anaerobic metabolism half-life of each study chemical. When biolysis rate constants are zero, AnaerM

is used to calculate biolysis rate constants for the benthic microbiota. This computation uses a population number for benthic bacteria calculated as the average for all surficial sediments. In Mode 1 and Mode 2, the single temporal value in use at RUN time is used. For other Modes, the mid-Summer populations are used.

AREA

AREA (segment)
Units: m^2

Top plan area of each model segment of the water body. For Epilimnion and Littoral segments, AREA is the area of the air-water interface; for Hypolimnion segments AREA is the area of the thermocline; for Benthic segments it is the surface area of the bottom. In the latter case AREA may differ from XSTUR in a dispersive exchange pair because of reduction in exchanging area due to rock outcrops, etc.

ATURB

Atmospheric TURBidity (month)
Units: km

Equivalent aerosol layer thickness.

BACPL

BACterioPLankton population (segment, month)
Units: cfu/mL

Population density of bacteria capable of degrading xenobiotics. The abbreviation "cfu" stands for a "colony forming unit."

BNBAC

BeNthic BACteria (segment, month)
Units: cfu/100g dry sediment

Population density of benthic bacteria that degrade xenobiotics. The abbreviation "cfu" stands for a "colony forming unit."

BNMAS

BeNthic bioMASs (segment, month)
Units: g(dry)/m^2

Biomass of small benthos – infauna subject to biosorption.

BULKD

BULK Density (segment, month)
Units: g/cm^3

Fresh weight per unit volume of benthic sediments.

CEC

Cation Exchange Capacity (segment, month)
Units: meq/100g (dry)

Cation exchange capacity of sediment phase in each segment. Useful in relating sediment sorption (partitioning) of cations to a variable characteristic of system sediments.

CHARL

CHARacteristic Length or mixing length (path)
Units: m

Average of segment dimensions normal to the exchange interface linking segment numbers JTURB(p) and ITURB(p). The matching (same "p" subscript) members of JTURB, ITURB, CHARL, DSP, and XSTUR together define a dispersive transport pathway. A given segment may have different mixing lengths at different interfaces. CHARL can also be calculated from the distance along a path that connects the centers of segments JTURB(p) and ITURB(p), passing through the interface whose area is XSTUR(p).

See also: DSP, ITURB, JTURB, XSTUR

CHEMNA

CHEMical NAme of compounds (50 characters, chem)
Units: n/a

Do *not* use "CHANGE" or "SET" to enter names! The NAme for a CHEMical is entered into the database via the command sequence:

EXAMS-> CHEMICAL NAME IS nnn...

where "nnn... " can include as many as 50 characters. This name is associated with chemical library entries and is printed in the header information of the appropriate output tables.

CHL

CHLorophylls + pheophytins (segment, month)
Units: mg/L

Concentration of chlorophyll plus chlorophyll-like pigments. Used to compute spectral light absorption coefficients due to pigments which absorb light from the water column and thus compete with photolysis of synthetic chemicals.

CHPAR

CHemical PARent compound (path)
Units: n/a Range: 1– KCHEM

CHPAR(p) gives the ADB location of the parent source of TPROD(p). The matching (same transformation path

number "p") members of CHPAR and TPROD give the location numbers in the active database of the parent chemical and the transformation product for pathway "p". For example, "SET CHPAR(p) TO 1", and TPROD(p) TO 4, to show that the chemical in ADB sector 4 is produced via transformation of the chemical in ADB sector 1, via process data defined by the remaining members of product chemistry sector "p".

See also: EAYLD, NPROC, RFORM, TPROD, YIELD

CINT

Communications INTerval for dynamic simulations.
Units: see TCODE

CINT is the interval between output cycles from the integrators. In Mode 2, CINT can be set to produce any desired output frequency, so long as the resulting reporting interval is >1 hour. When CINT is set to 0, EXAMS (Mode 2) sets CINT to report at the 12 equal-increment periods most closely matching the duration specified by (TEND - TINIT). CINT is under full user control only in Mode 2; in Modes 1 and 3 EXAMS itself sets the value of CINT according to the needs of the analysis.

CLOUD

CLOUDiness (month)
Units: dimensionless Range: 0 – 10

Mean monthly opaque cloudiness in tenths of full sky cover.

DEPTH

DEPTH (segment)
Units: m

Average vertical depth of each segment.

DFAC

Distribution FACtor (segment, month)
Units: dimensionless ratio

Ratio of optical path length to vertical depth, range 1.0 – 2.0. A vertical light beam has a DFAC of 1.0; a fully diffused light field has a DFAC of 2.0. For whole days, a value of 1.19 is often adequate; EXAMS defaults to this value when the entry for DFAC is outside the range 1.0 – 2.0.

DISO2

DISsolved O2 (segment, month)
Units: mg/L

Concentration of dissolved oxygen (O_2) in each segment of ecosystem.

DOC

Dissolved Organic Carbon (segment, month)
Units: mg/L

Used for computing spectral light absorption, singlet oxygen concentrations, and complexation.

DRFLD

DRiFt LoaD (segment, chemical, month)
Units: kg/hour

Drift loadings: aerial drift, direct applications, stack fallout (etc.) of chemical on each system element.

DSP

DiSPersion coefficient (path, month)
Units: m^2/hour

Eddy diffusivity to be applied to dispersive exchange pairing "p". The matching (same "p" subscript) members of JTURB, ITURB, CHARL, and XSTUR together define a dispersive transport pathway. In the case of horizontal mixing, DSP is the longitudinal dispersion coefficient; for vertical mixing it may represent exchange across the thermocline or exchanges with bottom sediments. In the latter case DSP is a statistical kinetic composite incorporating direct sorption to the sediment surface, mixing of the sediments by benthos (bioturbation), stirring by demersal fishes, etc.

See also: CHARL, ITURB, JTURB, XSTUR

EAH

E_a for Acid Hydrolysis (form, ion, chemical)
Units: kcal/mol

Arrhenius activation energy E_a of specific-acid-catalyzed hydrolysis of chemicals. Matrix indices match those of KAH, giving, for each chemical, data for 3 forms (1: dissolved, 2: solids-sorbed, 3: DOC-complexed) of 7 ionic species (1: neutral; 2, 3, 4: cations; 5, 6, 7: anions). When EAH is non-zero, the second-order rate constant K ($M^{-1}h^{-1}$) is calculated from:

$$\log K = KAH(f,i,c) - \frac{1000 \times EAH(form, ion, chemical)}{4.58(TCEL(segment, month) + 273.15)}$$

EAYLD

E_A YieLD (path)
Units: kcal

EAYLD(p) is activation energy E_a to compute transformation

product yield as a function of environmental temperatures (TCEL). When EA_YIELD(p) is zero, YIELD(p) gives the dimensionless molar product yield. A non-zero EAYLD(p) invokes a re-evaluation in which YIELD(p) is interpreted as the Briggsian logarithm of the pre-exponential factor in an Arrhenius-type function, giving product yield as a function of temperature (varying with position and time) (TCEL(segment, month)):

$$\log Yield(p) = Yield(p) - \frac{1000 \times EAYLD(p)}{4.58(TCEL(segment, month) + 273.15)}$$

See also: CHPAR, NPROC, RFORM, TPROD, YIELD

EBH

E_a for Base Hydrolysis (form, ion, chemical)
Units: kcal/mol

Arrhenius activation energy E_a of specific-base catalyzed hydrolysis of chemicals. Matrix indices match those of KBH, giving, for each chemical, data for 3 forms (1: dissolved, 2: solids-sorbed, 3: DOC-complexed) of 7 ionic species (1: neutral, 2, 3, 4: cations, 5, 6, 7: anions). When EBH is non-zero, the second-order rate constant K ($M^{-1}h^{-1}$) is calculated from:

$$LogK = KBH(f,i,c) - \frac{1000 \times EBH(form, ion, chemical)}{4.58(TCEL(segment, month) + 273.15)}$$

EHEN

Enthalpy term for HENry's law (chemical)
Units: kcal/mol

Used to compute Henry's law constants as a function of TCEL (environmental temperature). When EHEN is non-zero, the Henry's law constant (H) affecting volatilization at a particular (segment, month) is computed from TCEL:

$$\log H = HENRY(chemical) - \frac{1000 \times EHEN(chemical)}{4.58(TCEL(segment, month) + 273.15)}$$

EK1O2

E_a K1O2 (singlet oxygen) (form, ion, chemical)
Units: kcal/mol

Arrhenius activation energy for singlet oxygen photo-oxygenation of chemicals. Matrix indices match those of K1O2, giving, for each chemical, data for 3 forms (1: dissolved, 2: solids-sorbed, 3: DOC-complexed) of 7 ionic species (1: neutral, 2, 3, 4: cations, 5, 6, 7: anions). When EK1O2 is non-zero, the second-order rate constant K ($M^{-1}h^{-1}$) is calculated as:

$$\log K = K1O2(f,i,c) - \frac{1000 \times EK1O2(form, ion, chemical)}{4.58(TCEL(segment, month) + 273.15)}$$

ELEV

ELEVation
Units: meters above mean sea level

Ground station elevation.

ENH

E_a for Neutral Hydrolysis (form, ion, chemical)
Units: kcal/mol

Arrhenius activation energy for neutral hydrolysis of chemicals. Matrix indices match those of KNH, giving, for each chemical, data for 3 forms (1: dissolved, 2: solids-sorbed, 3: DOC-complexed) of 7 ionic species (1: neutral, 2, 3, 4: cations, 5, 6, 7: anions). When ENH is non-zero, the pseudo-first-order rate constant (h^{-1}) is calculated from:

$$\log K = KNH(f,i,c) - \frac{1000 \times ENH(form, ion, chemical)}{4.58(TCEL(segment, month) + 273.15)}$$

EOX

E_a OXidation (form, ion, chemical)
Units: kcal/mol

Arrhenius activation energy for oxidative transformations of chemicals. Matrix indices match those of KOX, giving, for each chemical, data for 3 forms (1: dissolved, 2: solids-sorbed, 3:DOC-complexed) of 7 ionic species (1: neutral, 2, 3, 4: cations, 5, 6, 7: anions). When EOX is non-zero, the second-order rate constant K ($M^{-1}h^{-1}$) is calculated from:

$$\log K = KOX(f,i,c) - \frac{1000 \times EOX(form, ion, chemical)}{4.58\ (\mathrm{TCEL(segment, month)} + 273.15)}$$

EPK

Enthalpy term for pK (ion, chemical)
Units: kcal/mol

When EPK is non-zero, pK is computed as a function of temperature via:

$$\log PK = PK(i,c) - \frac{1000 \times EPK(ion, chemical)}{4.58(TCEL(segment, month) + 273.15)}$$

The vector indices for EPK ("c" denotes the chemical) are

EPK(1,c) contains datum for generation of RH_4^+ from RH_3
EPK(2,c) contains datum for generation of RH_5^{2+} from RH_4^+
EPK(3,c) contains datum for generation of RH_6^{3+} from RH_5^{2+}
EPK(4,c) contains datum for generation of RH_2^- from RH_3
EPK(5,c) contains datum for generation of $RH^=$ from RH_2^-
EPK(6,c) contains datum for generation of R^{3-} from $RH^=$

ERED

E_a REDuction (form, ion, chemical)
Units: kcal/mol

Arrhenius activation energy for reductive transformations of chemicals. Matrix indices match those of KRED, giving, for each chemical, data for three forms (1: dissolved, 2: solids-sorbed, 3: DOC-complexed) of seven ionic species (1: neutral, 2, 3, 4: cations, 5, 6, 7: anions). When ERED is non-zero, the second-order rate constant K ($M^{-1}h^{-1}$) is calculated as:

$$\log K = KRED(f,i,c) - \frac{1000 \times ERED(form, ion, chemical)}{4.58(TCEL(segment, month) + 273.15)}$$

ESOL

Enthalpy term for SOLubility (ion, chemical)
Units: kcal/mol

ESOL describes chemical solubility as a function of temperature (TCEL). The matrix indices ("c" denotes the chemical) denote:

ESOL(1,c) is datum for solubility of neutral molecules RH_3
ESOL(2,c) is datum for solubility of singly charged cations RH_4^+
ESOL(3,c) is datum for solubility of doubly charged cations RH_5^{2+}
ESOL(4,c) is datum for solubility of triply charged cations RH_6^{3+}
ESOL(5,c) is datum for solubility of singly charged anions RH_2^-
ESOL(6,c) is datum for solubility of doubly charged anions $RH^=$
ESOL(7,c) is datum for solubility of triply charged anions R^{3-}

EVAP

EVAPoration (segment, month)
Units: mm/month

(Monthly) evaporative water losses from ecosystem segments.

EVPR

Molar hEat of VaPoRization (chemical)
Units: kcal/mol

Enthalpy term for computing vapor pressure as a function of TCEL (environmental temperature (segment,month)). When EVPR is non-zero, vapor pressure Va is computed from:

$$\log Va = VAPR(chemical) - \frac{1000 \times EVPR(chemical)}{4.58(TCEL(segment, month) + 273.15)}$$

EVENTD

Event Duration (5)
Units: days Range: 1–364

In Mode 3, Exams reports period average, minimum, and peak concentrations, and the minimum, average, and peak concentration of the largest (as defined by their mean values) 96-hour, 21-day, 60-day, and 90-day events during each time segment (one or more years) of the simulation. Up to five additional averaging periods can be specified; these are reported in an addendum to Table 20.

FIXFIL

FIXFIL signals the existence of output data for LISTs and PLOTs.

To access results from a prior run, "SET FIXFIL TO 1." FIXFIL is set to zero when EXAMS is invoked, so that the LIST and PLOT commands are protected from attempts to access non-existent output data files. When results exist from a previous simulation, you can reset FIXFIL to 1 in order to gain access to them.

FROC

FRaction Organic Carbon (segment, month)
Units: dimensionless

Organic carbon content of solids as fraction of dry weight. FROC is coupled to KOC to generate the sediment partition coefficient for neutral chemicals ($R\text{-}H_3$) as a function of a property (organic carbon content) of the sediment.

HENRY

HENRY's law constant (chemical)
Units: atmosphere-m^3/mole

Used in computation of air/water exchange rates (volatilization). If parameter EHEN is non-zero, HENRY is used as the pre-exponential factor in computing the Henry's law constant H as a function of environmental temperatures (TCEL):

$$\log H = HENRY(chemical) - \frac{1000 \times EHEN(chemical)}{4.58(TCEL(segment, month) + 273.15)}$$

ICHEM

I CHEMical (event)
Units: n/a Range: 1--KCHEM

Event "e" is a pulse of chemical number ICHEM(e) in the active database ICHEM identifies the location in the Activity Database (ADB) of the chemical entering the ecosystem via pulse load event "e". When, for example, chemical data are loaded into ADB sector 3 (whether RECALLed from the User

Database Library (UDB) (via, for example, the command sequence "RECALL CHEM 7 AS 3") or entered as new data), ICHEM(e) can be SET to 3 to create a pulse load event of that chemical.

See also: IDAY, IMASS, IMON, ISEG

IDAY

I DAY (event)
Units: n/a Range: 1–31

Pulse load event "e" takes place on day IDAY(e) of month IMON(e). The pulse load data are organized by vertical event columns, that is, the set of pulse load variables (IMASS(e), ICHEM(e), ISEG(e), IMON(e), and IDAY(e)) with the same vector subscript describes a single chemical pulse event. Thus a pulse of chemical ICHEM(e), of magnitude IMASS(e), is released into segment ISEG(e) on day IDAY(e) of month IMON(e). During mode 2 simulations, IDAY and IMON are inoperative.

See also: ICHEM, IMASS, IMON, ISEG

IMASS

Initial MASS (event)
Units: kg

IMASS gives the magnitude of chemical pulse load event "e". In mode 2, pulses are entered at time 0 (i.e., as initial conditions), and at the outset of each CONTINUation of the simulation. In mode 3, IMON and IDAY specify the date of the load events. An event recurs in each year of the RUN or CONTINUed simulation. The pulse load data are organized by vertical event columns; that is, the series of pulse load variables (IMASS, ICHEM, ISEG, IMON, and IDAY) with the same vector subscript describes a single event.

See also: ICHEM, IDAY, IMON, ISEG

IMON

I MONth (event)
Units: n/a Range: 1--12

Pulse load event "e" takes place on day IDAY(e) of month IMON(e). The pulse load data are organized by vertical event columns; that is, the set of pulse load variables (IMASS(e), ICHEM(e), ISEG(e), IMON(e), and IDAY(e)) with the same vector subscript describes a single chemical pulse event. Thus a pulse of chemical ICHEM(e), of magnitude IMASS(e), is released into segment ISEG(e) on day IDAY(e) of month IMON(e). During mode 2 simulations, IDAY and IMON are inoperative.

See also: IDAY, ICHEM, IMASS, ISEG

ISEG

I SEGment (event)
Units: n/a Range: 1--KOUNT

Pulse load event "e" loads chemical ICHEM(e) on segment ISEG(e). Any segment can receive a pulse load. Should the pulse loads increase the *free* concentration of unionized chemical above 10^{-5} M (or half its aqueous solubility, whichever is less), the size of the event is reduced, to avoid violating the linearizing assumptions used to create EXAMS. The pulse load data are organized by vertical event columns; that is, the pulse load variables having the same vector subscript define a single chemical pulse event.

See also: ICHEM, IDAY, IMASS, IMON

ITOAD

I TO ADvection (path)
Units: n/a Range: 0--KOUNT (0 = export)

Chemicals are advected to segment ITOAD(p) from segment JFRAD(p). The matching (same subscript) members of JFRAD, ITOAD, and ADVPR define an advective hydrologic flow pathway carrying entrained chemicals and solids through the water body. When ITOAD(p) is 0, the pathway advects water and entrained substances across system boundaries, i.e., ITOAD(p) = 0 specifies an export pathway. The flow data can be inspected by typing "SHOW ADV"; path numbers are given above each active dataset. Enter data with SET or CHANGE commands.

See also: JFRAD, ADVPR

ITURB

I TURBulent dispersion (path)
Units: n/a Range: 0--KOUNT

Segments ITURB(p) and JTURB(p) exchange via turbulent dispersion. The matching (same "p" subscript) members of ITURB, JTURB, CHARL, DSP, and XSTUR together define a dispersive transport pathway; ITURB(p) and JTURB(p) indicate which segments are linked by dispersive transport pathway "p". A "0" in ITURB paired with a non-zero segment number in JTURB denotes a boundary condition with a pure (zero chemical) water-body. The input data can be examined via SHOW TURBULENCE; pathway numbers are shown with each dataset.

See also: CHARL, DSP, JTURB, XSTUR

IUNIT

IUNIT controls the printing of diagnostics from the integrators.

Normally zero (off), it may be turned on when problems occur. To manually set IUNIT to generate integrator diagnostic messages, SET IUNIT TO 1. The message generator can be disabled at any time by SETting IUNIT to 0.

JFRAD

J FRom ADvection (path)
Units: n/a Range: 1– KOUNT

Chemicals are advected from segment JFRAD(p) to segment ITOAD(p). The matching (same subscript) members of JFRAD, ITOAD, and ADVPR define an advective hydrologic flow pathway. EXAMS computes the total net flow available for advection from segment JFRAD(p). Of the total flow, the fraction ADVPR(p) flows from segment JFRAD(p) into segment ITOAD(p). The hydrologic flow carries an entrained mass of chemical along the pathway. The flow specifications can be inspected by typing SHOW ADV; pathway numbers are given above each active dataset. Enter data with SET or CHANGE commands.

See also: ITOAD, ADVPR

JTURB

J TURBulent dispersion (path)
Units: n/a Range: 0--KOUNT

Segments JTURB(p) and ITURB(p) exchange via turbulent dispersion. The matching (same "p" subscript) members of JTURB, ITURB, CHARL, DSP, and XSTUR together define a dispersive transport pathway; JTURB(p) and ITURB(p) indicate which segments are linked by dispersive transport pathway "p". A "0" in JTURB paired with a non-zero segment number in ITURB denotes a boundary condition with a pure (zero chemical) water-body. The input data can be examined via SHOW TURBULENCE; pathway numbers are shown with each dataset.

See also: CHARL, DSP, ITURB, XSTUR

KAH

K Acid Hydrolysis (form, ion, chemical)
Units: per mole [H^+] per hour

Second-order rate constant for specific-acid-catalyzed hydrolysis of chemicals. When the matching (same subscripts) Arrhenius activation energy (EAH) is zero, KAH is interpreted as the second-order rate constant. When the matching entry in EAH is non-zero, KAH is interpreted as the (Briggsian) logarithm of the frequency factor in an Arrhenius equation, and the 2nd-order rate constant is computed as a function of segment temperatures TCEL. Matrix indices refer to three forms--1: aqueous, 2: solids-sorbed, and 3: DOC-complexed; by seven ions--1: neutral, 2-4: cations, and 5-7: anions.

KBACS

K BACteria benthoS (form, ion, chemical)
Units: $(cfu/mL)^{-1}$ $hour^{-1}$

Second-order rate constants--benthic sediment bacterial biolysis of chemicals normalized by "colony forming units" (cfu) per mL of test medium. When the matching (same subscripts) Q_{10} (QTBAS) is zero, KBACS is interpreted as the second-order rate constant. When the matching entry in QTBAS is non-zero, KBACS is interpreted as the numerical value of the second-order rate constant at 25°C, and local values of the rate constant are computed as a function of temperature (TCEL) in each ecosystem segment. Indices refer to four forms--1: aqueous, 2: solids-sorbed, 3: DOC-complexed, and 4: bio-sorbed; by seven ions--1: neutral, 2-4: cations, and 5-7: anions.

KBACW

K BACterioplankton Water (form, ion, chemical)
Units: $(cfu/mL)^{-1}$ $hour^{-1}$

Second-order rate constants K for water column bacterial biolysis of chemicals normalized by "colony forming units" (cfu) per mL of test medium. When the matching (same subscripts) Q_{10} (QTBAW) is zero, KBACW is interpreted as the second-order rate constant. When the matching entry in QTBAW is non-zero, KBACW is interpreted as the numerical value of the second-order rate constant at 25°C, and local values of the rate constant are computed as a function of temperature (TCEL) in each ecosystem segment. Indices refer to four forms--1: aqueous, 2: solids-sorbed, 3: DOC-complexed, and 4:bio-sorbed; by seven ions--1: neutral, 2-4: cations, and 5-7: anions.

KBH

K Base Hydrolysis (form, ion, chemical)
Units: per mole [OH^-] per hour

Second-order rate constant for specific-base-catalyzed hydrolysis of chemicals. When the matching (same subscripts) Arrhenius activation energy (EBH) is zero, KBH is interpreted as the second-order rate constant. When the matching entry in EBH is non-zero, KBH is interpreted as the (Briggsian) logarithm of the frequency factor in an Arrhenius equation, and the 2nd-order rate constant is computed as a function of segment temperatures TCEL. Matrix indices refer to three forms--1: aqueous, 2: solids-sorbed, and 3: DOC-complexed; by seven ions--1: neutral, 2-4: cations, and 5-7: anions.

KCHEM

Number of chemicals under review in current study.

Units: n/a

KDP

K Direct Photolysis (ion, chemical)
Units: $hour^{-1}$

Estimated photolysis rates--use only when ABSOR, the actual light absorption spectra of the compound in pure water, are unavailable. KDP is an annual average pseudo-first-order photolysis rate constant under cloudless conditions at RFLAT, where

KDP(1,c) are pseudo-first-order photolysis rate constants of neutral molecules RH_3
KDP(2,c) are pseudo-first-order photolysis rate constants of singly charged cations RH_4^+
KDP(3,c) are pseudo-first-order photolysis rate constants of doubly charged cations RH_5^{2+}
KDP(4,c) are pseudo-first-order photolysis rate constants of triply charged cations RH_6^{3+}
KDP(5,c) are pseudo-first-order photolysis rate constants of singly charged anions RH_2^-
KDP(6,c) are pseudo-first-order photolysis rate constants of doubly charged anions $RH^=$
KDP(7,c) are pseudo-first-order photolysis rate constants of triply charged anions R^{3-}

KIEC

Kp for Ion Exchange Capacity (ion, chemical)
Units: Kp $(meq/100g\ dry)^{-1}$

Coefficient relating sediment partition coefficient Kp of ions to exchange capacity of sediments. KIEC times the cation exchange capacity CEC(seg, month) (or anion exchange capacity AEC for anionic species) gives the Kp for sorption of ions with solid phases. This computation is overridden by explicit (non-zero) values of KPS, i.e., a non-zero value of KPS takes precedence over a Kp computed by EXAMS using KIEC.

KIEC(1,c) is datum for relating CEC and sorption of singly charged cation RH_4^+
KIEC(2,c) is datum for relating CEC and sorption of doubly charged cation RH_5^{2+}
KIEC(3,c) is datum for relating CEC and sorption of triply charged cation RH_6^{3+}
KIEC(4,c) is datum for relating AEC and sorption of singly charged anion RH_2^-
KIEC(5,c) is datum for relating AEC and sorption of doubly charged anion $RH^=$
KIEC(6,c) is datum for relating AEC and sorption of triply charged anion R^{3-}

KNH

K Neutral Hydrolysis (form, ion, chemical)
Units: $hour^{-1}$

Pseudo-first-order rate constants for neutral hydrolysis of chemicals. When the matching (same subscripts) Arrhenius activation energy (ENH) is zero, KNH is interpreted as the first-order rate constant. When the matching entry in ENH is non-zero, KNH is interpreted as the (Briggsian) logarithm of the frequency factor in an Arrhenius equation, and the 1st-order rate constant is computed as a function of segment temperatures TCEL. Matrix indices refer to three forms--1: aqueous, 2: solids-sorbed, and 3: DOC-complexed; by seven ions--1: neutral, 2-4: cations, and 5-7: anions.

KOC

KOC (chemical)
Units: $[(mg/kg)/(mg/L)]\ (organic\ carbon\ fraction)^{-1}$

KOC is partition coefficient (Kp) keyed to organic carbon content FROC(s, m) of the sediment solids in each (s) segment, during each (m) month of simulation of chemical behavior in the system. Multiplication of KOC by the organic carbon fraction FROC(s) of the solids in each segment yields the partition coefficient (Kp) for sorption of unionized (R-H3) species with those solids:

Kp(chemical, segment, month)=
KOC(chemical) × FROC(segment, month)

KOUNT

Number of segments used to define current ecosystem.
Units: n/a

KOW

Octanol-Water partition coefficient (chemical)
Units: (mg/L)/(mg/L)

Kow is an experimentally determined chemical descriptor. Kow (KOW(c)) can be used to estimate Koc (c.f.), and thus relate the Kp of a chemical to the organic carbon content of sediments.

KOX

K OXidation (form, ion, chemical)
Units: per mole [OXRAD] per hour

Second-order rate constants for free-radical (OXRAD) oxidation of chemicals. When the matching (same subscripts) Arrhenius activation energy (EOX) is zero, KOX is interpreted as the second-order rate constant. When the matching entry in EOX is non-zero, KOX is interpreted as the (Briggsian) logarithm of the frequency factor in an Arrhenius equation, and the 2nd-order rate constant is

computed as a function of segment temperatures TCEL. Matrix indices refer to three forms--1: aqueous, 2: solids-sorbed, and 3: DOC-complexed; by seven ions--1: neutral, 2-4: cations, and 5-7: anions.

KO2

KO2 (segment, month)
Units: cm/hour

Oxygen exchange constant or piston velocity at 20 degrees C in each ecosystem segment. When explicit values of KO2 are not present as environmental descriptors, EXAMS calculates KO2 from windspeed.

KPB

KP for Biomass (ion, chemical)
Units: (ug/g) / (mg/L)

Partition coefficient (Kp) for computing equilibrium biosorption. The "c" subscript denotes the chemical; the "ion" subscripts identify:

KPB(1,c) datum for biosorption of neutral molecules RH_3
KPB(2,c) datum for biosorption of singly charged cations RH_4^+
KPB(3,c) datum for biosorption of doubly charged cations RH_5^{2+}
KPB(4,c) datum for biosorption of triply charged cations RH_6^{3+}
KPB(5,c) datum for biosorption of singly charged anions RH_2^-
KPB(6,c) datum for biosorption of doubly charged anions $RH^=$
KPB(7,c) datum for biosorption of triply charged anions R^{3-}

KPDOC

KP Dissolved Organic Carbon (ion, chemical)
Units: (ug/g)/(mg/L)

Partition coefficient (Kp) for equilibrium complexation with DOC. The "c" subscript denotes the chemical; the "ion" subscripts identify:

KPDOC(1,c) datum for complexation of neutral molecules RH_3
KPDOC(2,c) datum for complexation of singly charged cations RH_4^+
KPDOC(3,c) datum for complexation of doubly charged cations RH_5^{2+}
KPDOC(4,c) datum for complexation of triply charged cations RH_6^{3+}
KPDOC(5,c) datum for complexation of singly charged anions RH_2^-
KPDOC(6,c) datum for complexation of doubly charged anions $RH^=$
KPDOC(7,c) datum for complexation of triply charged anions R^{3-}

KPS

KP for Sediment solids (ion, chemical)
Units: (mg/kg)/(mg/L)

Partition coefficients (Kp) for computing sorption with sediments. The "c" subscript denotes the chemical; the "ion" subscripts identify:

KPS(1,c) datum for sorption of neutral molecules RH_3
KPS(2,c) datum for sorption of singly charged cations RH_4^+
KPS(3,c) datum for sorption of doubly charged cations RH_5^{2+}
KPS(4,c) datum for sorption of triply charged cations RH_6^{3+}
KPS(5,c) datum for sorption of singly charged anions RH_2^-
KPS(6,c) datum for sorption of doubly charged anions $RH^=$
KPS(7,c) datum for sorption of triply charged anions R^{3-}

KRED

K REDuction (form, ion, chemical)
Units: per mole [REDAG] per hour

Second-order rate constants for REDucing AGent chemical reduction of compounds. When the matching (same subscripts) Arrhenius activation energy (ERED) is zero, KRED is interpreted as the second-order rate constant. When the matching entry in ERED is non-zero, KRED is interpreted as the (Briggsian) logarithm of the frequency factor in an Arrhenius equation, and the 2nd-order rate constant is computed as a function of segment temperatures TCEL. Matrix indices refer to three forms--1: aqueous, 2: solids-sorbed, and 3: DOC-complexed; by seven ions--1: neutral, 2-4: cations, and 5-7: anions.

K1O2

K1O2 (singlet oxygen) (form, ion, chemical)
Units: per M [$^1O_2$] per hour

Second-order rate constants for singlet oxygen photo-oxygenation of chemicals. When the matching (same subscripts) Arrhenius activation energy (EK1O2) is zero, K1O2 is interpreted as the second-order rate constant. When the matching entry in EK1O2 is non-zero, K1O2 is interpreted as the (Briggsian) logarithm of the frequency factor in an Arrhenius equation, and the 2nd-order rate constant is computed as a function of segment temperatures TCEL. Matrix indices refer to three forms--1: aqueous, 2: solids-sorbed, and 3: DOC-complexed; by seven ions--1: neutral, 2-4: cations, and 5-7: anions.

LAMAX

LAMbda MAXimum (ion, chemical)
Units: nanometers

Wavelength of maximum absorption of light by each ionic species, or wavelength of maximum overlap of solar spectrum and chemical's absorption spectrum (of each ion). Indices match with KDP matrix. LAMAX selects the wavelengths used to compute light extinction factors for photochemical transformation, in those cases where the absorption spectrum of the compound is not available, but the results of simple photochemical experiments can be used as a coarse estimate of rates of photochemical transformations (i.e., KDP > 0.0). When set to zero, LAMAX defaults to 300 nm.

LAT

LATitude
Units: degrees and tenths (e.g., 37.24)

Geographic latitude of the ecosystem. EXAMS uses latitude and longitude for retrieving data and for calculating climatological parameters. When entering latitude and longitude of a study site, enter south latitude as a negative number; north latitude as a positive number.

LENG

LENGth (segment)
Units: m

Length of a reach – used to compute volume, area, depth.

LOADNM

LOADings database NaMe (50 characters)
Units: n/a

Do *not* use "CHANGE" or "SET" to enter names! The NaMe for a LOADings database is entered via the command sequence:

EXAMS-> LOAD NAME IS nnn...

where "nnn... " can include as many as 50 characters. This name is associated with chemical loadings database library entries, so that load patterns can be found in the catalog. The Ith character can be corrected with a CHANGE or SET command. For example, to repair the 7th character, "SET LOADNM(7) TO ... ."

LONG

LONGitude
Units: degrees and tenths (e.g., -83.2)

Geographic longitude of the ecosystem. EXAMS uses longitude and latitude for retrieving data and for calculating climatological parameters. When entering longitude and latitude of a study site, enter west longitude as a negative number; east longitude as a positive number.

MCHEM

M CHEMical
Units: n/a

Number of chemical in activity data base.

MODE

MODE sets the operating "mode" of EXAMS.

Three operating modes are available; these are selected by SETting MODE to 1, 2, or 3:

MODE	Operational characteristics of EXAMS
1	Long-term (steady-state) analysis.
2	Pulse analysis -- specifiable initial chemical mass (IMASS) and time frame, time-invariant environment.
3	Monthly environmental data, daily pulse loads IMASS and monthly chemical loadings of other types.

MONTH

MONTH
Units: n/a

Set MONTH to inspect a specific block of environmental data. Months 1--12 correspond to January--December; month 13 is average data.

MP

MeltingPoint (chemical)
Units: degrees Celsius

Melting point of the chemical – used for calculating linear range of sorption isotherm.
Melting Point is used in the calculation of the maximum concentrations within the range of linear isotherms. When computing the crystal energy term for chemicals that are solids at the ambient temperature (Karickhoff 1984, J. Hydraulic Eng. 110:707-735) the solute entropy of fusion is taken as 13 eu.

MWT

Gram Molecular WeighT (chemical)
Units: g/mole

Molecular weight of the neutral species of each study chemical. Changes in molecular weight due to ionization are neglected.

NPROC

Number of PROCess (path)

Units: n/a Range: 1--9

Signals the type of process transforming CHPAR(p) into TPROD(p). NPROC can be set to the following:

1 --> specific acid hydrolysis
2 --> neutral hydrolysis
3 --> specific base hydrolysis
4 --> direct photolysis
5 --> singlet oxygen reactions
6 --> free radical oxidation
7 --> water column bacterial biolysis
8 --> benthic sediment bacterial biolysis
9 --> reductions, e.g., reductive dechlorination

See also: CHPAR, EAYLD, RFORM, TPROD, YIELD

NPSED
Non-Point-Source SEDiment (segment, month)
Units: kg/hour

Non-point-source sediment loads entering ecosystem segments.

NPSFL
Non-Point-Source FLow (segment, month)
Units: m^3/hour

Non-point-source water flow entering ecosystem segments.

NPSLD
Non-Point-Source LoaD (segment, chemical, month)
Units: kg/hour

Chemical loadings entering segments via non-point sources.

NYEAR
Number of YEARs
Units: n/a

NYEAR is number of years to be simulated for a mode 3 run.

OXRAD
OXidant RADicals (month)
Units: moles/L

Concentration of environmental oxidants in near-surface waters (e.g., peroxy radicals). EXAMS computes segment-specific oxidant concentrations using ultra-violet light extinction in the system.

OUTFIL
OUTput FILe controls (10)

Units: "Y" or "N"

Control the production of output files. Set the corresponding member to "Y" to produce the file(s); set it to "N" to suppress file production.

1: standard report file (report.xms)
2: standard plotting files (ssout.plt, kinout.plt)
3: BASS data transfer file (bassexp.xms)
4: FGETS data transfer files (fgetscmd.xms and fgetsexp.xms)
5: HWIR data transfer file (HWIRExp.xms)
6: compartment-oriented EcoTox exposure data file (EcoToxC.xms)
7: compartment-oriented event analysis and report file (EcoRiskC.xms)
8: reach-oriented EcoTox exposure data file (EcoToxR.xms)
9: reach-oriented event analysis and report file (EcoRiskR.xms)
10: full Exams compartment file of time-varying concentrations (FullOut.xms)

OZONE
OZONE (month)
Units: centimeters NTP Typically 0.2--0.4 cm

Mean (monthly) ozone (O_3) content of atmosphere. EXAMS includes a database (ozone.daf) of total column ozone data summarized from the Total Ozone Mapping Spectrometer (TOMS) that flew on the Nimbus7 spacecraft from 11/Nov/78 through 06/May/93. From the latitude and longitude of the environment, EXAMS finds its position in a 1 degree latitude by 1.25 degree longitude grid of the Earth and retrieves monthly mean ozone for the site. In this grid, south latitude is negative, north latitude positive; west longitude is negative, east longitude positive.

PCPLD
PreCiPitation LoaD (segment, chemical, month)
Units: kg/hour

Chemical loadings entering each segment via rainfall.

PCTWA
PerCenT WAter (segment, month)
Units: dimensionless

Percent water in bottom sediments of benthic segments. Elements of these vectors that correspond to water column segments are not used (dummy values). PCTWA should be expressed as the conventional soil science variable (the fresh weight : dry weight ratio times 100); all values must be greater than or equal to 100. An entry in PCTWA that is

less than 100.0 for a benthic segment raises an error condition, and control is returned to the user for correction of the input data.

PH

pH (segment, month)
Units: pH units

The negative value of the power to which 10 is raised in order to obtain the temporally averaged concentration of hydronium ions [H_3O^+] in gram-equivalents per liter.

PK

pK (ion, chemical)

Negative of base-10 logarithm of acid/base dissociation constants. When the matching value in the EPK matrix is zero, PK(I, c) is taken as the pK value. (To "match" is to have the same subscript values.) When EPK(I, c) is non-zero, PK is taken as the base-10 logarithm of the pre-exponential factor in the equation for pK as a function of environmental temperature TCEL.

The vector indices for PK ("c" denotes the chemical) are

PK(1,c) contains datum for generation of $R\text{-}H_4^+$ from RH_3
PK(2,c) contains datum for generation of $R\text{-}H_5^{2+}$ from RH_4^+
PK(3,c) contains datum for generation of $R\text{-}H_6^{3+}$ from RH_5^{2+}
PK(4,c) contains datum for generation of $R\text{-}H_2^{-1}$ from RH_3
PK(5,c) contains datum for generation of $R\text{-}H^-$ from RH_2^-
PK(6,c) contains datum for generation of R^{3-} from RH^-

PLMAS

PLanktonic bioMASs (segment, month)
Units: mg (dry weight)/L

Total plankton subject to biosorption of synthetic chemicals.

POH

pOH (segment, month)
Units: pOH units

The negative value of the power to which 10 is raised in order to obtain the temporally averaged concentration of hydroxide [OH^-] ions in gram-equivalents per liter.

PRBEN

PRoportion of sorbed chemical delivered to BENthic zone
Unitless

The PRZM model generates an output file that can be read by the READ command in EXAMS. PRZM reports, for each runoff date, contaminant dissolved in the flow, and contaminant sorbed to entrained particulate matter. Use PRBEN (SET to a value between 0.0 and 1.0) to indicate how much of the sorbed material is to sink through the water column and become incorporated into the benthic sediments. Based on the generalization that about 50% of sorbed contaminant is typically quite labile, and 50% is refractory, the default value of PRBEN is set to 0.50.

PRODNM

PRODuct chemistry database NaMe (50 characters)
Units: n/a

Do *not* use "CHANGE" or "SET" to enter names! The NaMe for a PRODuct chemistry database is entered via the command sequence:

EXAMS-> PRODUCT NAME IS nnn...

where "nnn... " can include as many as 50 characters. This name is associated with product chemistry database library entries, so that databases can be found in the catalog. Use a CHANGE or SET command to repair single characters in the name. For example, to repair character seven, enter "SET PRODNM(7) TO ... ."

PRSW

PRint SWitch
Units: n/a

PRSW is a switch for controlling printing options. In mode 3, when PRSW is set to 0 (the default), average values of the environmental parameters are recorded in the run log. When PRSW is 1, a separate table is produced for each (monthly) data set, except for those values which are invariant (VOL etc.).

QTBAS

Q Ten BActeria benthoS (form, ion, chemical)
Units: dimensionless

Q_{10} values for benthic bacterial biolysis (see KBACS) of chemical. "Q_{10}" is the increase in the second-order rate constant due to a 10°C increase in temperature. Indices refer to 28 molecular spp: 4 forms--1:aqueous, 2:solids-sorbed, 3:DOC-complexed, and 4: bio-sorbed; by 7 ions--1:neutral, 2-4:cations, and 5-7:anions. When QTBAS is non-zero, the matching (same subscripts) rate constant is computed as:

$$KBACS(f,i,c)=QTBAS(f,i,c)^{(TCEL(seg,month)-QTBTS)/10} \times KBACS(f,i,c)$$

QTBAW

Q Ten BActeria Water (form, ion, chemical)
Units: dimensionless

Q_{10} values for bacterioplankton biolysis (see KBACW) of chemical. "Q_{10}" is the increase in the second-order rate constant due to a 10°C increase in temperature. Indices refer to 28 molecular spp: 4 forms--1:aqueous, 2:solids-sorbed, 3:DOC-complexed, and 4: bio-sorbed; by 7 ions--1:neutral, 2-4:cations, and 5-7:anions. When QTBAW is non-zero, the matching (same subscripts) rate constant is computed as:

$$KBACW(f,i,c)=QTBAW(f,i,c)^{(TCEL(seg,month)-QTBTW/10} \times KBACW(f,i,c)$$

QTBTW

Q_Ten_Base_Temperature_Water (form,ion,chemical)
Units: °C

Temperature of aerobic limnetic metabolism study.

QTBTS

Q_Ten_Base_Temperature_Sediment (form,ion,chemical)
Units: °C

Temperature of anaerobic benthic metabolism study.

QYIELD

Quantum_YIELD (form, ion, chemical)
Units: dimensionless

Reaction quantum yield for direct photolysis of chemicals--fraction of the total light quanta absorbed by a chemical that results in transformations. Separate values (3×7=21) for each potential molecular type of each chemical allow the effects of speciation and sorption on reactivity to be specified in detail. Matrix of 21 values specifies quantum yields for the (3) physical forms: (1) dissolved, (2) sediment-sorbed, and (3) DOC-complexed; of each of (7) possible chemical species: neutral molecules (1), cations (2-4), and anions (5-7). (QYIELD is an efficiency.)

RAIN

RAINfall (month)
Units: mm/month

Average (monthly) rainfall in geographic area of system.

REDAG

REDucing AGents (segment, month)
Units: moles/L

Molar concentration of reducing agents in each system segment.

RELER

RELative ERror tolerance for integrators.

When the characteristics of the chemical and ecosystem are such as to result in "stiff" equations, numerical errors may lead to small negative numbers in the time series. If desired, the value of ABSER and RELER can be decreased in order to achieve greater precision in the simulation outputs.

RFLAT

ReFerence LATitude (ion, chemical)
Units: degrees (e.g., 40.72)

(RFLAT - LAT) corrects for North or South displacement of the ecosystem LATitude from the location (RFLAT) of a photochemical study used to develop a matched (same subscript) KDP pseudo-first-order rate constant.

RFLAT(1,c) refer to photolysis of neutral molecules RH_3
RFLAT(2,c) refer to photolysis of singly charged cations RH_4^+
RFLAT(3,c) refer to photolysis of doubly charged cations RH_5^{2+}
RFLAT(4,c) refer to photolysis of triply charged cations RH_6^{3+}
RFLAT(5,c) refer to photolysis of singly charged anions RH_2^-
RFLAT(6,c) refer to photolysis of doubly charged anions $RH^=$
RFLAT(7,c) refer to photolysis of triply charged anions R^{3-}

RFORM

Reactive FORM (path)
Units: n/a Range: 1--32

RFORM gives the reactive molecular form (ionic species in each of the possible sorptive states) of CHPAR(p) resulting in product TPROD(p). The following table shows the value of RFORM for each molecular entity, including values for total dissolved (29), solids-sorbed (30), *etc*.

See also: CHPAR, EAYLD, NPROC, TPROD, YIELD

	Ionic species	Neutral	Cations			Anions			Total
	Valence	0	1+	2+	3+	1-	2-	3-	(all)
Forms:	Dissolved	1	5	9	13	17	21	25	29
	Solids-sorbed	2	6	10	14	18	22	26	30
	DOC-complexed	3	7	11	15	19	23	27	31
	Biosorbed	4	8	12	16	20	24	28	32

RHUM

Relative HUMidity (month)
Units: %, i.e., saturation = 100% R.H.

Mean (monthly) relative humidity during daylight hours. Data typical of daylight hours are needed because their primary use is to characterize light transmission in the atmosphere.

SEELD

SEEpage LoaD (segment, chemical, month)
Units: kg/hour

Chemical loadings entering the system via "interflows" or seepage (all sub-surface water flows entering the system, (usually) via a benthic segment).

SEEPS

SEEPage flowS (segment, month)
Units: m^3/hour

Interflow (subsurface water flow, seepage) entering each segment. SEEPS usually enter via a benthic segment. SEEPS are assumed to lack an entrained sediment flow; that is, they are flows of water only.

SOL

SOLubility (ion, chemical)
Units: mg/L

Aqueous solubility of each species (neutral molecule + all ions). When the matching value in the ESOL matrix is zero, SOL(I, c) is taken as the aqueous solubility in mg/L. (To "match" is to have the same subscript values.) When ESOL(I, c) is non-zero, SOL(I, c) is taken as the base-10 logarithm of the pre-exponential factor of the equation describing the *molar* solubility of the species as a function of environmental temperature (TCEL). The vector indices for SOL are given in the text describing ESOL. Solubility must be specified, because it is used as a constraint on loads.

SPFLG

SPecies FLaGs (ion, chemical)
Takes on values of "1" (exists) or "0"

This vector of "flags" or "switches" shows which ions exist. Set the flags ("SET SPFLG(I, c)=1") when entering chemical data in order to show EXAMS the ionic structure of the chemical. When EXAMS starts, only SPFLG(1,*) are set, i.e., the default chemical structure is a neutral (non-ionizing) molecule. As additional SPFLG are set, EXAMS displays the additional chemical data tables needed to display the properties of the ionic species.

set SPFLG(1,c)=1 to signal existence of a neutral molecule RH_3
set SPFLG(2,c)=1 to signal existence of a singly charged cation RH_4^+
set SPFLG(3,c)=1 to signal existence of a doubly charged cation RH_5^{2+}
set SPFLG(4,c)=1 to signal existence of a triply charged cation RH_6^{3+}
set SPFLG(5,c)=1 to signal existence of a singly charged anion RH_2^-
set SPFLG(6,c)=1 to signal existence of a doubly charged anion $RH^=$
set SPFLG(7,c)=1 to signal existence of a triply charged anion R^{3-}

SPRAY

SPRAY drift from agricultural chemicals
Unitless percentage

The PRZM model generates an output file that can be read by the READ command in EXAMS. PRZM3 reports, for each application date, the application rate and the percentage drift to adjacent aquatic ecosystems. Use SPRAY to set a drift percentage for earlier versions of PRZM. EXAMS defaults SPRAY to 10%. Note that values of SPRAY are entered as percentages rather than as fractions.

STFLO

STream FLOws (segment, month)
Units: m^3/hour

Flow into head reach of river or estuary; segment tributaries and creeks or other stream flows entering a lake or pond. Note that STFLO represents stream flow entering system segments from external sources *only*. EXAMS itself computes hydrologic flows among segments that are part of the water body being studied, via the specified advective and dispersive flow patterns (see JFRAD, JTURB, etc.). Therefore, *do not* compute net water balances for each segment and enter these into the database--enter *only* those flows entering the system across external boundaries!

STRLD

STReam LoaD (segment, chemical, month)
Units: kg/hour

Chemical loadings entering ecosystem segments via stream flow.

STSED

STream-borne SEDiment (segment, month)
Units: kg/hour

Stream-borne sediment load entering ecosystem segments.

SUSED

SUspended SEDiment (segment, month)
Units: mg/L

Suspended particulate matter – applicable to the water column only.

SYSTYP

Name of aquatic ecoSYStem TYPe (50 characters)
Units: n/a

Do *not* use "CHANGE" or "SET" to enter names! The name of a water body is entered into the database via the command sequence:

EXAMS-> ENVIRONMENT NAME IS nnn...

where "nnn... " can include as many as 50 characters. This name is associated with environmental library entries (the UDB catalog) and is printed in the header information of the appropriate output tables. Use SET and CHANGE to correct single characters in the name. For example, to correct the seventh character in a name,

EXAMS-> CHAN SYSTYP(7) TO ...

TCEL

Temperature in CELsius (segment, month)
Units: degrees C

Average temperature of ecosystem segments. Used (as enabled by input data) to compute effects of temperature on transformation rates and other properties of chemicals.

TCODE

The value of Time CODE sets the units of TINIT, TEND, and CINT.

TCODE can be SET to 1 (hours), 2 (days), 3 (months), or 4 (years). TCODE is under full user control only in Mode 2. In mode 2, TCODE controls the time frame of the study. For example, given TINIT=0., TEND=24., and CINT=2.; CHANging TCODE from 1 to 3 converts a 0-24 hour study into 0-24 months, with bimonthly reports. In mode 1, EXAMS selects the units for reporting results, from the probable half-life of the study chemical(s). In mode 3, a RUN encompasses one year or longer, and the timing is set to produce standard outputs.

TEND

Time END for a dynamic simulation segment.
Units: see TCODE

A simulation segment encompasses the period TINIT through TEND. At the end of each integration, TINIT is reset to TEND. The simulation can be extended by invoking the "CONTINUE" command; EXAMS will then request a new value of TEND. Pulse loads (IMASS) and longer-term chemical loads (STRLD, NPSLD, etc.) can be modified or deleted during the pause between simulation segments.

TINIT

Time INITial for a dynamic simulation segment.
Units: see TCODE

A simulation RUN encompasses the period TINIT through TEND. At the end of each integration, TEND is transferred to TINIT. The simulation results can be evaluated, and the study continued via the "CONTINUE" command. EXAMS will note the new value of TINIT and request a new endpoint. Pulse and other chemical loadings can be modified or deleted between simulation segments.

TPROD

Transformation PRODuct (path)
Units: n/a Range: 1-KCHEM

TPROD(p) – ADB location of the transformation product of CHPAR(p). The matching (same transformation path number "p") members of CHPAR and TPROD give the

location numbers in the active database of the parent chemical and the transformation product for pathway "p". For example, SET CHPAR(p) TO 1, and TPROD(p) to 4, to show that the chemical in ADB sector 4 is produced via transformation of the chemical in ADB sector 1, via process data defined by the remaining members of product chemistry sector "p".

See also: CHPAR, EAYLD, NPROC, RFORM, YIELD

TYPE

Segment TYPE (segment)
Units: letter codes

Letter codes designating segment types used to define ecosystems.

Available types: Littoral, Epilimnion, Hypolimnion, and Benthic.

UDB

User DataBase

Long-term retention of data required by EXAMS is provided by storage in the "User Database" (UDB, generally resident on a physical device, e.g., a hard disk) for CHEMICALs, ENVIRONMENTs, LOADs, or PRODUCTs. Within each of these UDB sectors, each dataset is CATALOGued via a unique accession number (UDB#). When transferring data between foreground memory (the activity database or ADB) and a UDB, the target location must be specified by the name of the UDB sector and the accession number within the sector. For example, to STORE the current pattern of chemical loadings: STORE LOAD 7. Similarly, to retrieve or RECALL data from a UDB into the ADB for use in an analysis, one could enter: RECALL LOAD 7.

VAPR

VAPoR pressure (chemical)
Units: Torr

Used to compute Henry's law constant when HENRY datum is zero (0) but VAPR is non-zero:

HENRY = (VAPR/760) / (SOL/MWT)

If the associated molar heat of vaporization (EVPR) is non-zero, VAPR is taken as the base-10 logarithm of the pre-exponential factor in an exponential function describing vapor pressure as a function of temperature (TCEL).

VOL

VOLume (segment)
Units: m^3

Total environmental volume of ecosystem segments.

WIDTH

WIDTH (segment)
Units: m

Average bank-to-bank distance–for computing volume, area, depth of lotic systems described via length, width, and cross-sectional areas.

WIND

WINDspeed (segment, month)
Units: meters/second

Average wind velocity at a reference height of ten centimeters above the water surface. Parameter is used to compute a piston velocity for water vapor (Liss 1973, Deep-Sea Research 20:221) in the 2-resistance treatment of volatilization losses.

XSA

Cross-sectional (XS) Area (segment)
Units: m^2

Area of water body in section along advective flowpath.

XSTUR

X Section for TURbulent dispersion (path)
Units: m^2

XSTUR is cross-sectional area of a dispersive exchange interface at the boundary between segments JTURB(p) and ITURB(p). The matching (same "p" subscript) members of JTURB, ITURB, CHARL, DSP, and XSTUR collectively define a dispersive transport pathway. The exchange constant E(p) is computed as:

$$E(p)\ (m^3/hour) = DSP(p) \times XSTUR(p) / CHARL(p)$$

See also: CHARL, DSP, ITURB, JTURB

YEAR1

YEAR 1
Units: n/a
Starting year for mode 3 simulation (e.g., 1985).

YIELD

YIELD of product (path)
Units: mole per mole

YIELD(p) is the product yield from the transformation pathway "p" with dimensions mole of transformation product TPROD(p) produced per mole of parent compound CHPAR(p) reacted (dimensionless).

See also: CHPAR, EAYLD, NPROC, RFORM, TPROD

Appendices

Appendix A

Partitioning to Natural Organic Colloids

EXAMS uses the octanol:water partition coefficient (Kow) to estimate binding constants (Kpdoc) for "dissolved" (i.e., colloidal) organic matter (DOC). The calculation factor is a simple ratio to Kow (Seth et al. 1999). For developing the EXAMS factor, values of partitioning on water samples containing complete DOC (only) were tabulated, i.e., studies on chemically separated fractions were not utilized. Measurement methods included, *inter alia*, dialysis (Carter and Suffet 1982), reversed-phase separation (Landrum et al. 1984) and solubility enhancement (Chiou et al. 1986); values developed using fluorescence quenching methods (Gauthier et al. 1986) were excluded because this method is subject to interferences that often lead to over-estimates of Koc ((Laor and Rebhun 1997), (Danielson et al. 1995), (Tiller and Jones 1997)).

Compound	CAS #	Reference	Log Kow[1]	log Kpdoc and Kpdoc/Kow ratios			
				limnetic	ratio	benthic	ratio
1,3,6,8-TCDD	33423-92-6	(Servos and Muir 1989)	7.13[2]	5.50	0.023	6.06	0.085
1,3,6,8-TCDD	33423-92-6	(Servos et al. 1989)	7.13[2]	5.12	0.010		
H7CDD	37871-00-4	(Servos et al. 1989)	8.20[2]	6.85	0.045		
O8CDD	3268-87-9	(Servos et al. 1989)	8.60[2]	5.78	0.002		
p,p'-DDT	50-29-3	(Carter and Suffet 1982)	6.36	4.84	0.030		
p,p'-DDT	50-29-3	(Landrum et al. 1984)	6.36	4.52	0.014		
p,p'-DDT	50-29-3	(Chiou et al. 1987)	6.36	4.39	0.011		
p,p'-DDT	50-29-3	(Eadie et al. 1990)	6.36	4.36	0.010		
p,p'-DDT	50-29-3	(Kulovaara 1993)	6.36	3.81	0.003		
Benzo[a]pyrene	50-32-8	(Landrum et al. 1984)	5.97	4.56	0.039		
Benzo[a]pyrene	50-32-8	(Alberts et al. 1994)	5.97	4.80	0.068		
Benzo[a]pyrene	50-32-8	(Landrum et al. 1985)	5.97			5.56	0.389
Benzo[a]pyrene	50-32-8	(Morehead et al. 1986)	5.97	4.80	0.068		
Benzo[a]pyrene	50-32-8	(Kukkonen et al. 1989)	5.97	5.33	0.229		
Benzo[a]pyrene	50-32-8	(McCarthy et al. 1989)	5.97	5.16	0.155		
Benzo[a]pyrene	50-32-8	(Kukkonen et al. 1990)	5.97	5.18	0.162		
Benzo[a]pyrene	50-32-8	(Eadie et al. 1990)	5.97	4.57	0.040		
Benzo[a]pyrene	50-32-8	(Kukkonen and Oikari 1991)	5.97	5.00	0.107		
Benzo[a]pyrene	50-32-8	(Kulovaara 1993)	5.97	4.36	0.025		

Compound	CAS #	Reference	Log Kow[1]	log Kpdoc and Kpdoc/Kow ratios			
				limnetic	ratio	benthic	ratio
Dehydroabietic acid	1740-19-8	(Kukkonen and Oikari 1991)	4.80[3]	2.70	0.008		
Dieldrin	60-57-1	(Kosian et al. 1995)	5.25[3]			4.43	0.151
Fluoranthene	206-44-0	(Brannon et al. 1995)	4.95			3.83	0.076
Mirex	2385-85-5	(Yin and Hassett 1989)	6.89[4]	6.08	0.155		
Naphthalene	91-20-3	(Kukkonen et al. 1990)	3.30	3.00	0.501		
Phenanthrene	85-01-8	(Landrum et al. 1985)	4.46			4.18	0.525
Phenanthrene	85-01-8	(Landrum et al. 1987)	4.46			4.04	0.380
Phenanthrene	85-01-8	(Chin and Gschwend 1992)	4.46			4.19	0.537
4-PCB	2051-62-9	(Eadie et al. 1990)	4.40	4.02	0.417		
2,4,4'-PCB	7012-37-5	(Chiou et al. 1987)	5.62	3.55	0.009		
2,4,2',4'-PCB	2437-79-8	(Landrum et al. 1987)	6.29			5.49	0.158
2,4,2',4'-PCB	2437-79-8	(Caron and Suffet 1989)	6.29			5.21	0.083
2,4,2',4'-PCB	2437-79-8	(Kukkonen et al. 1990)	6.29	4.30	0.010		
2,4,2',4'-PCB	2437-79-8	(Hunchak-Kariouk and Suffet 1994)	6.29			4.68	0.025
2,5,2',5'-PCB	35693-99-3	(Landrum et al. 1984)	6.09	3.88	0.006		
2,5,2',5'-PCB	35693-99-3	(Eadie et al. 1990)	6.09	3.88	0.006		
2,5,2',5'-PCB	35693-99-3	(Kukkonen et al. 1990)	6.09	4.60	0.032		
3,4,3',4'-PCB	32598-13-3	(Kukkonen et al. 1990)	5.62[5]	4.90	0.191		
3,4,3',4'-PCB	32598-13-3	(Kukkonen and Oikari 1991)	5.62	4.00	0.024		
2,4,5,2',5'-PCB	37680-73-2	(Chiou et al. 1987)	6.11	4.05	0.009		
2,4,5,2',4,5'-PCB	35065-27-1	(Kukkonen et al. 1990)	7.75[5]	5.54	0.006		
2,4,5,2',4,5'-PCB	35065-27-1	(Eadie et al. 1990)	7.75	4.42	0.0005		
Pyrene	129-00-0	(Landrum et al. 1987)	5.18			4.71	0.339
Pyrene	129-00-0	(Eadie et al. 1990)	5.18	3.76	0.038		
Pyrene	129-00-0	(Chin and Gschwend 1992)	5.18			4.73	0.355
6 PAH		(Lüers and ten Hulscher 1996)					3.326
37 Compounds		(Ozretich et al. 1995)					0.072
				Averages	0.074		0.46

1. Kow from ChemFate database (http://esc.syrres.com/efdb.htm) except as otherwise indicated.

2. (Govers and Krop 1998)
3. Kow cited by author
4. (Devillers et al. 1996)
5. (Rapaport and Eisenreich 1984)

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Appendix B
EXAMS data entry template for chemical molar absorption spectra (ABSOR)

Waveband					Waveband			
No.	Center nm	Band-width nm	ABSOR cm^{-1} M^{-1}		No.	Center nm	Band-width nm	ABSOR cm^{-1} M^{-1}
1	280.0	2.5			24	380.0	10.0	
2	282.5	2.5			25	390.0	10.0	
3	285.0	2.5			26	400.0	10.0	
4	287.5	2.5			27	410.0	10.0	
5	290.0	2.5			28	420.0	10.0	
6	292.5	2.5			29	430.0	10.0	
7	295.0	2.5			30	440.0	10.0	
8	297.5	2.5			31	450.0	10.0	
9	300.0	2.5			32	460.0	10.0	
10	302.5	2.5			33	470.0	10.0	
11	305.0	2.5			34	480.0	10.0	
12	307.5	2.5			35	490.0	10.0	
13	310.0	2.5			36	503.75	17.5	
14	312.5	2.5			37	525.0	25.0	
15	315.0	2.5			38	550.0	25.0	
16	317.5	2.5			39	575.0	25.0	
17	320.0	2.5			40	600.0	25.0	
18	323.1	3.75			41	625.0	25.0	
19	330.0	10.0			42	650.0	25.0	
20	340.0	10.0			43	675.0	25.0	
21	350.0	10.0			44	706.25	37.5	
22	360.0	10.0			45	750.0	50.0	
23	370.0	10.0			46	800.0	50.0	

Appendix C
Implementing the microcomputer runtime EXAMS

Exams program files are installed from a self-unpacking archival compressed format (Install_EXAMS.exe). The files require a total of about 1.5 Mb of mass storage for transfer to a hard disk, plus an additional 20 megabytes for storage of the files as they are retrieved from the Archives, plus additional working space for the files produced while Exams runs.

The files include

The file for installing the EXAMS program, in file Install_EXAMS.EXE, within which is contained:

- o The task image in file EXAMS.EXE, which allows space for five simultaneous chemicals (or one chemical and two degradation products, etc.), and environmental models of up to one hundred segments.

- o The unformatted direct access data- and help-file EXAMS.DAF, with space for 25 chemical datasets, 10 environmental datasets, 5 external chemical load series, and 5 product chemistries.

- o A global database of total column ozone (ozone.daf) from the TOMS (Total Ozone Mapping Spectrometer) flown on the Nimbus-7 spacecraft.

- o An EXAMS command file for testing the installation, in TEST.EXA.

- o TESTOUT.XMS, a sample output for comparison with the results of the installation test run.

The User's Guide for EXAMS (file ExamsRevF.pdf) in Adobe PDF (Portable Document Format), archived in the separate 1.5 Mb file "Examsdoc.exe". Executing file "Examsdoc.exe" de-compresses the .pdf file, which in turn can be read and printed using the Adobe Acrobat reader, available gratis from http://www.adobe.com/products/acrobat/readstep.html

EXAMS accesses extended memory through Windows services; under the Windows console all virtual memory is available to the program. Under Windows 95/98, best performance can be achieved by setting memory properties of the DOS console to "none" for Expanded (EMS) and all others to "Auto" except DPMI memory. Set DPMI memory to 65535.

First, make sure that your IBM PC/AT 386/486/Pentium or "Compatible" measures up to the following minimum hardware and software specifications.

o 20 megabyte available mass storage (hard disk)

o 80x87 math co-processor

o Windows 95/98/NT/2000 operating system

If your machine does not conform to these minimum specifications, the EXAMS program WILL NOT execute properly.

- more -

Then, to install the program

1. Transfer the file "Install_EXAMS.EXE" to your hard disk in some suitable subdirectory or partition and install Exams. From a Windows console:

   a. Set the default drive to the mass storage device (e.g., hard disk "C"): C:

   b. Create an EXAMS directory: (BUT, if installing as part of PIRANHA, the PIRANHA\EXAMS directory already exists. Do NOT create another EXAMS directory) MKDIR EXAMS

   c. Request verification of copy results: VERIFY ON

   d. Change default directory to EXAMS, or to PIRANHA EXAMS subdirectory CD\EXAMS CD\PIRANHA\EXAMS

   e. Execute the file Install_EXAMS.EXE to recover files from the archives: and follow the directions provided. Install_EXAMS

2. Start the EXAMS program from the EXAMS directory.

   a. Start the EXAMS program: EXAMS

   b. When you reach the EXAMS system prompt, start the test command file: EXAMS-> DO TEST

3. When the test run finishes compare the outcome (in file REPORT.XMS) with the file TESTOUT.XMS supplied with the program:

```
FC   REPORT.XMS TESTOUT.XMS
```

Files TESTOUT.XMS and TEST.EXA are not needed for routine operation of EXAMS and can be deleted, as can files Install_EXAMS.EXE and EXAMSDOC.EXE.

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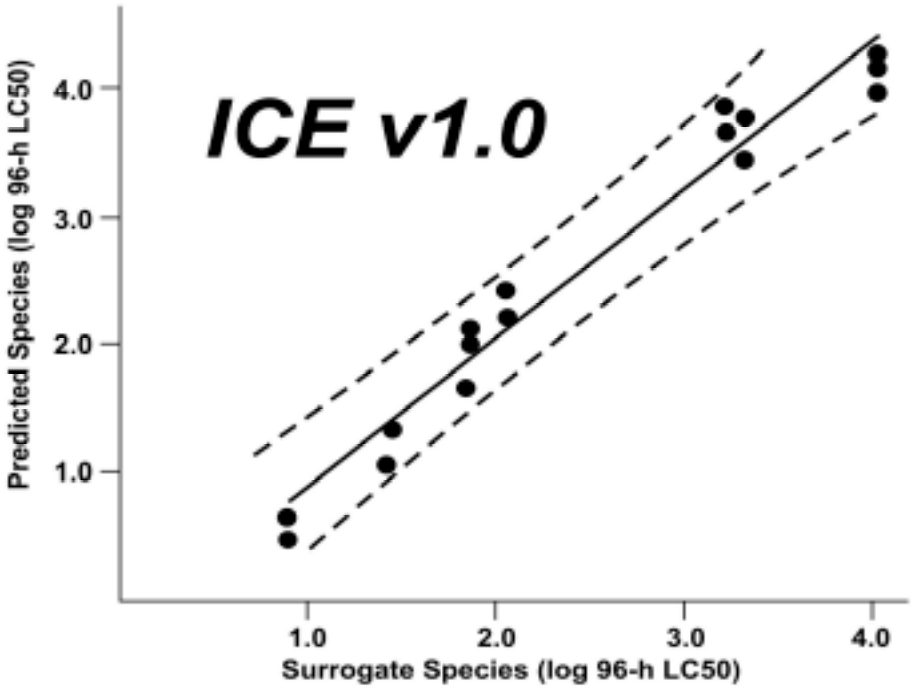
Interspecies Correlation Estimations (ICE) for Acute Toxicity to Aquatic Organisms and Wildlife

II. User Manual and Software



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November 2003

Interspecies Correlation Estimations (ICE) for Acute Toxicity To Aquatic Organisms and Wildlife

II. User Manual and Software

By

Amha Asfaw, Mark R. Ellersieck and Foster L. Mayer*

University of Missouri-Columbia
College of Agriculture, Food and Natural Resources
Agricultural Experiment Station-Statistics
Columbia, MO 65211

*U.S. Environmental Protection Agency
Office of Research and Development
National Health and Environmental Effects Research Laboratory
Gulf Ecology Division
Gulf Breeze, FL 32561

U.S. Environmental Protection Agency
Office of Research and Development
1200 Pennsylvania Avenue, N.W.
Washington, DC 20460

Notice

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Abstract

Predictive toxicological models, including estimates of uncertainty, are necessary to address probability-based ecological risk assessments. A method and software (ICE) were developed for estimating acute toxicity of chemicals to species, genera, and families when data are lacking. Interspecies correlation models for acute toxicity (4082 models) were derived for 143 aquatic and terrestrial organisms using Model II least squares regression, where both variables are independent and subject to measurement error ($\log X_2 = a + b\ [\log X_1]$). Toxicity of a chemical to one species can be predicted from toxicity to another species with known certainty. Correlations are generally best within a taxonomic family, decreasing with increasing taxonomic distance. However, certain species (e.g., rainbow trout) were found to be the most useful of all species for acute estimations among taxa, including families. Correlations for wildlife species were not as good, in general, as those for aquatic species, but routes of exposure are different - - oral or dietary versus respiratory, respectively.

Introduction

Acute and chronic toxicity testing of several species is required for protection of the numerous species represented in environmental habitats. Realistically, the number of species tested is limited by test procedure, species availability, time and expense. Thus, environmental managers must frequently perform risk analyses and make decisions regarding chemicals, mixtures, and effluents for which even acute data are minimal or do not exist. This is of particular concern for the protection of endangered species that are unavailable to test, other species that have not been tested or are not feasible to test, and when minimal data sets exist for a chemical.

To address this problem, interspecies correlations with selected organisms were conducted relating acute toxicity of a chemical for one species that of another (Mayer et al. 1987, 2004). The approach integrates species sensitivity to chemicals with species taxonomic similarities (physiology, biochemistry) using correlation methodology. This allows for estimation of acute toxicity of a chemical to many species from toxicity values of only one or a few species. However, application of this methodology is extremely time consuming without automation and software.

This software program, Interspecies Correlation Estimation (ICE), described herein, allows the user to estimate acute toxicity for a species or higher taxa (genus, family) having no acute toxicity data from a species having acute data. ICE will, therefore, greatly enhance the use of probability-based risk assessments for chemicals having minimal data sets and will extend the utility of quantitative structure-activity relationships QSAR (Lipnick 1995), from one species (i.e., fathead minnow, *Pimephales promelas*) to many species. Also, if an acute toxicity test is to be conducted, ICE can be used to more accurately identify the range of exposure concentrations required. ICE is based on the Windows platform and is specifically designed for estimating acute toxicity to aquatic and terrestrial organisms and providing graphical and tabular presentation of results.

Data Base

Three data sets (aquatic, wildlife, wildlife subacute) were used for correlation analyses. The aquatic data set was a compilation of Mayer (1987), Mayer and Ellersieck (1986), ECOTOX (U.S. Environmental Protection Agency 2002), and the U.S. Environmental Protection Agency's Office of Pesticide Programs (OPP) aquatic data (247 species, 661 chemicals, 4778 tests). Data used were based mainly on tests conducted with technical-grade chemicals, and water temperature, pH, hardness, and salinity generally conforming to requirements of ASTM (2002). Nominal or measured concentrations (µg/L) were based on active ingredients ($\geq$90%), with the exception of metal salts, which were based on metal content. The data set was standardized additionally by using only static tests. The chemicals represent all major pesticides, as well as numerous industrial and inorganic chemicals. The aquatic data set was used to compare species, species versus genera, and species versus families. Two wildlife sets, single oral dose or *per os* (47 species, 316 chemicals, 893 tests) and 5-day dietary (19 species, 214 chemicals, 493 tests) were analyzed. The two data sets consisted of data from: 1) acute *per os* tests with data (mg chemical/kg of body weight) from Hudson et al. (1984), 2) 5-day dietary subacute tests with data (mg chemical/kg dry weight of diet) from Hill et al. (1975), and 3) the OPP data base of both *per os* and 5-day dietary tests. Wildlife data sets, mainly birds and mammals, were partially standardized by using only tests with technical-grade chemicals. No correlations could be derived for wildlife species versus genera. Detailed descriptions of the data sets can be found in Buckler et al. (2003) and Mayer et al. (2004).

Software Language

The ICE software is based on a Windows platform and written in Visual Basic (Microsoft Visual Basic 2000). Subroutines (Fortran programs) in Visual Basic are required to call Fortran IMSL routines necessary in certain calculations (Compaq Fortran, Visual Numeric 1999). **See Software Development** and **Interpretation of Statistics** for detailed methodology.

Installing ICE

System Requirements

- Operates on Microsoft® Windows 95, 98, 2000, NT and XP (Windows® 98 or later is suggested).
- Minimum 16MB RAM (64 MB or greater is suggested).
- CPU speed of over 200 MHz is suggested; ICE will work with less, but is very slow acquiring equations.
- 6MB hard disk space.
- Mouse or pointing device.
- Printer (optional).

Remove any existing versions of ICE before installing the new one or malfunctions may occur.

To remove old ICE software:

1. Double click **My Computer.**
2. Double click **Control Panel.**
3. Double click **Add/Remove Programs.**
4. Click **ICE.**
5. Click **Delete** or **Change/Remove.**
6. Install new ICE software.

To install new ICE software:

1. Place the ICE CD in the CD ROM drive.
2. Click **Start** button.
3. Select **Run** from the menu.
4. Select **Browse** from the **Run** window.
5. Select the drive letter associated with the CD drive from the Browse window (or ICE July 17 2003) [D:]).
6. Double-click **Setup** or **D:\Setup.EXE** file.
7. Click **OK.**
8. Windows now walks you through the installation process.
9. Following installation, the ICE program can be accessed by clicking **Start, Programs**, and then **ICE**. You can create an icon on the Desktop screen by placing the mouse pointer on the ICE icon, holding down the control button, and dragging the icon to desired location on the screen.

Using ICE in Windows

To start the program, double click the ICE icon and select a surrogate species for which you have an acute value (ICE window 1, Fig. 1). Select data sets in **Options** (See Options and Model sections for available data sets). Enter the toxicity value in μg/L for aquaticspecies (mg chemical/kg of body weight for wildlifespecies and wildlifefamily; mg chemical/kg dry weight of

diet for wildlifesubacute) where the value of 100 (default value) is the X_1 row; press Enter. After a surrogate species is chosen, a second list of species or taxa (X_2) will appear for which you can select and estimate the acute toxicity value (ICE window 2, Fig. 2). Also at this time, the logo will disappear and be replaced with a line graph and confidence limits. Click on an X_2 taxa to estimate its acute toxicity value; additional X_2 taxa may be selected from this window. Click on the **Back** command located in the upper left corner to select another surrogate (X_1) species; this will produce a different listing of X_2 species or taxa. After choosing the X_1 and X_2 species, the program lists statistics and a graph; as you go from one X_2 species to another, difference statistics and graphics are produced for that particular model.

Model Selection

The following is recommended to provide the best confidence in the estimates made with the ICE program:

1. Use equations for species within the same genus or family.
2. Use equations that have degrees of freedom (df) $\geq$3 (n$\geq$ 5).
3. Use equations that have a significant (p$\leq$ 0.05) correlation (slope, *b*).
4. If data for more than one potential surrogate species (X_1) exists:
   a. If n for surrogate$_1$ = n for surrogate$_2$, use equation with the highest *r* value.
   b. If n for surrogate$_1$ $\neq$ n for surrogate$_2$, use equation with smallest error mean square (EMS).
5. If equations for species do not exist in aquaticspecies or wildlifespecies, search for its genus or family in aquaticgenus, aquaticfamily, or wildlifefamily. Generally, species within a genus or family will have more similar sensitivities to the same chemicals than more distantly related taxa.

ICE Application Windows

When first opened, the program will appear with the ICE logo to the right and a list of surrogate species (X_1) in the upper left box (Fig. 1). Scroll down to find the surrogate species of interest and click on it. The screen will automatically go to ICE window 2 (Fig. 2); see following numbers for explanation.

1. List of species (X_2) or taxa for which acute toxicity values can be estimated from a known surrogate species value (X_1). Click on X_2 species or taxa of interest. The X_2 species list changes depending on which surrogate species is chosen. If a specific surrogate and X_2 species or taxa have three or more chemicals in common, then a regression equation will be presented.

2. Level of statistical Type 1 Error (α) used to determine specifice t values (e.g., 1%, 5%, etc.) and confidence bands and may be changed in the **Options** window by user.

3. $\boldsymbol{X_1}$ is the acute toxicity value associated with the surrogate species under the column Actual. The number to the right (under the column **Log-Base 10**) is the same number, but the log base 10 ($\log_{10}$) of that number. The number 100 (default value) will first appear under the **Actual** column. To change the 100 value to the acute value of the surrogate species, click on the light green box and enter the surrogate species acute value (µg/L for aquatic species [aquaticspecies, aguaticgenus, aquaticfamily]; mg chemical/kg body weight [wildlifespecies, wildlifefamily] or mg chemical/kg dry weight of diet [wildlifesubacute] for wildlife).

4. $\boldsymbol{X_2}$ is the estimated acute value for species or taxa

5. **Upper** and **Lower** confidence limits for the estimated acute toxicity value – Note the two sets of confidence limits listed; one not associated with **P** (pooled) and one associated with **P**. The confidence limits not associated with **P** represent the confidence limits for that particular

Figure 1. ICE window 1

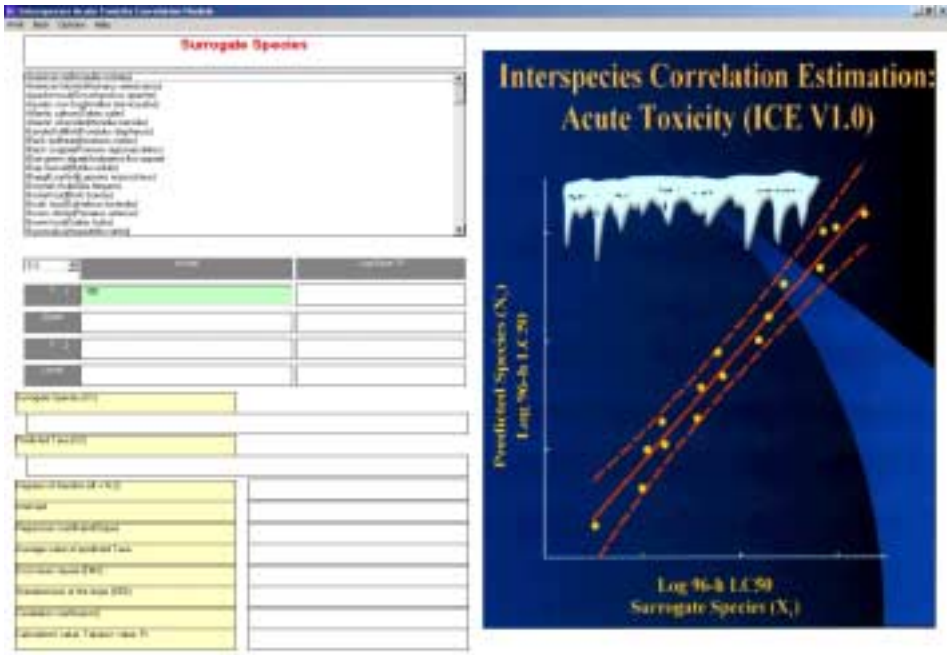
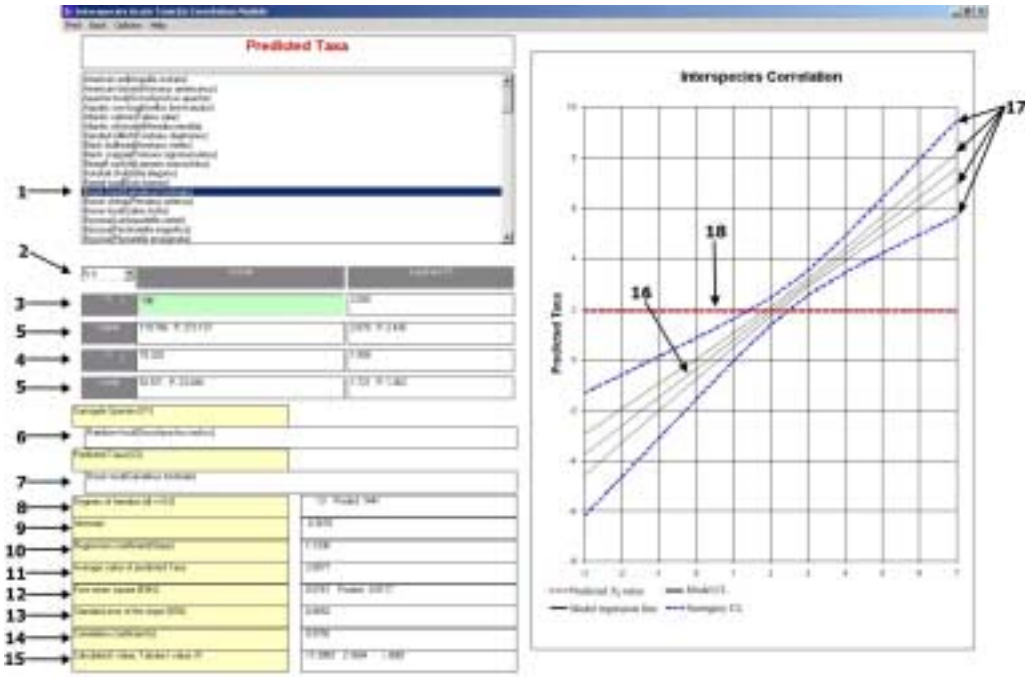


Figure 2. ICE window 2



species-species (or taxa) equation (uncertainty due to model). The confidence limits associated with **P** represent a pooled variance for that surrogate species with all other species equations (uncertainty due to surrogacy).

6. **Surrogate Species** (X_1) is name of the selected surrogate species.
7. **Predicted Taxa** (X_2) is name of the species or taxa for which acute toxicity is being estimated.
8. **Degrees of freedom** (**df = n – 2**) associated with each equation. The first **df** is based on the number of chemicals that X_1 and X_2 have in common. The second **df** (Pooled) represents the sum of df for that specific surrogate species and its equations among all other species.
9. **Intercept** (*a*) is the $\log_{10}$ EC/LC/LD50 for the X_2 species or taxa when the $\log_{10}$ value for the surrogate species (X_2) is equal to 0.
10. **Regression coefficient** (**Slope**) or *b* represents the $\log_{10}$ change in X_2 for every 1.0 $\log_{10}$ change in X_1.
11. **Average value of predicted taxa** is the average acute toxicity value for X_2 species or taxa based on df + 2 (or n).
12. **Error mean square** (**EMS**) represents the variance associated with the regression line. The **Pooled** value represents the sum of the error sum of squares associated with each equation divided by the pooled df.
13. **Standard error of slope** (**SEB**) is the standard error of the regression coefficient (slope or *b*).
14. **Correlation coefficient** (*r*) is the mutual linear association between X_1 and X_2 species or taxa.
15. This window contains two t values (**Calculated t value, Tabular t value**) and the actual level of significance (**Pr**). The **Calculated t value** is a calculated t statistic to test the significance of the relationship between X_1 and X_2. It is calculated by dividing the slope by the standard error of the slope (calculated t = *b*/SEB). The **Tabular t value** is a two-tailed tabulated t value from a standard t table. If the **Calculated t value** is ≥ **Tabular t value**, a significant relationship exists between the X_1 and X_2 species (i.e., regression line is significantly different from 0). A specific α level may be selected by changing the % for a Type 1 error rate (see 2 above) or the actual level of significance (**Pr**) may be used.
16. Graphic representation of the regression line from the statistics (see 9-13 above), with all values expressed as $\log_{10}$.
17. Curved lines represent confidence bands based on values for X_2 species or taxa. Two sets of confidence bands exist: solid and broken lines. The solid lines are derived for that specific species to species/genus/family equation (uncertainty due to model) and broken lines represent uncertainty due to surrogacy (see 5 and 12 above).
18. The horizontal line identifies the estimated $\log_{10}$ acute toxicity value where it crosses the X_2 axis.

Menu Bar

The menu bar (Fig. 3) contains four commands: **Print, Back, Options,** and **Help**.

Figure 3. Menu bar

- **Print** – To print, click **Print**. There are two options: 1) click **Single** and the present screen is printed, or 2) click **All** and all equations associated with the surrogate species and the selected data set are printed. Printing is accomplished on the default printer. If the printer supports zooming, the screen will be enlarged or reduced to fit in a landscape orientation. An alternative method of printing is to copy the screen displayed by simultaneously pressing ALT and Print Screen on the keyboard. This output can then be pasted to another program such as Microsoft® Word or Power Point, then printed from one of those programs.
- **Back –** Returns to ICE window 1 to select another surrogate species.
- **Options** – Allows setting program options (Fig. 4). The first option is choosing a data set.
- **Data Sets (Common names)** offers selection of data sets with species common name first followed by scientific name and **Data Sets (Scientific names)** provides the same data sets with species scientific name first followed by the common name. Click on the data set desired (Fig. 5), then **Open** (bottom right of window), followed by **Select** in the Options window. You can now work with the data set in the ICE program. The default data set is aquatic species versus a variety of aquatic species (aquaticspecies). As described in the following Graphics section, the captions for the graph can be changed in the Options window. At the bottom center of the Options window is the significance level (α) in % for confidence bands and t tests; it can be changed here or at item 2 on the main screen. The **Select** command will save all changes, and **Cancel** will only eliminate changes made while in the Options window. Changes made at the end of a session will remain when the ICE program is started again. Click **Default** to return everything back to the default settings.
- **Help** – A narrative of the documentation. It is outlined according to major subjects. Print documentation by clicking on the subject and then clicking **print**.

Graphics

Double click on the graph to fill the screen; double click again to return to the original size. The graph can be manipulated by clicking on the **Options** command (upper left). Click on the appropriate box in the Options window (Fig. 4) and type in desired caption changes for the X_1 and X_2 axes and the title. Then click on the **Select** command to install the changes. If the new captions do not fit on the graph, click on each caption and drag to fit the allowable space. Click **Default** to return all altered captions on the graph back to default settings. To exit the Options screen, click the upper right **X** on the Options window.

Exit

To exit the ICE program, click the **X** in the upper right corner of the screen.

Figure 4. Options window

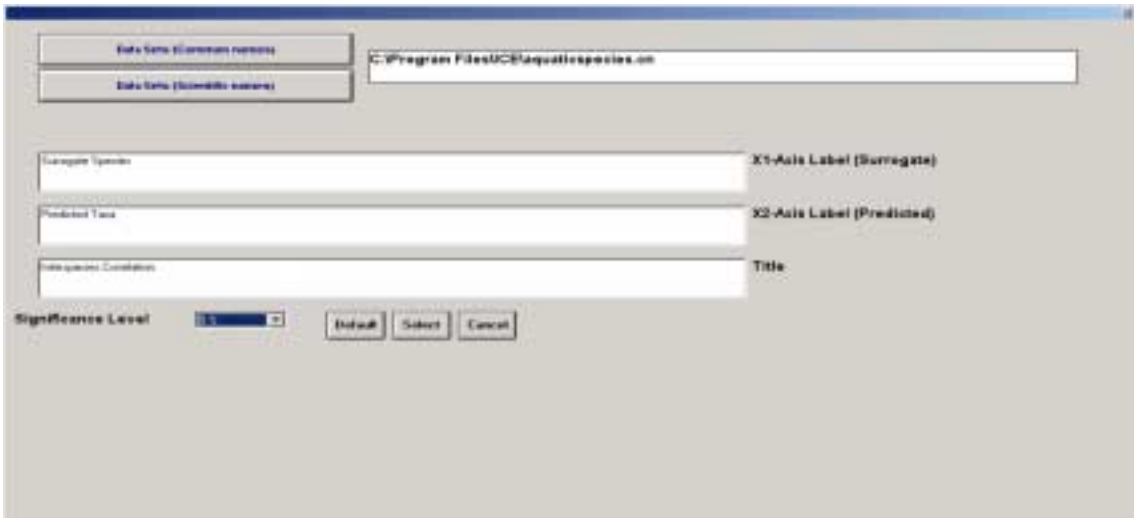
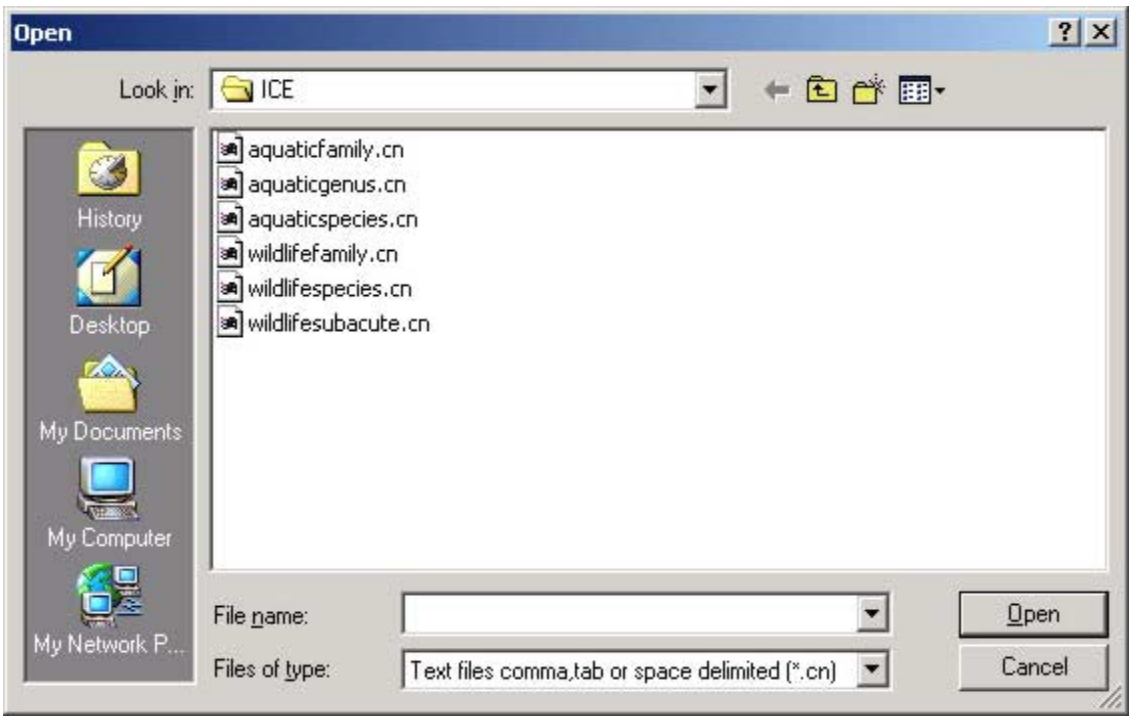


Figure 5. Data sets window



Software Development

Model

Interspecies correlations ($Y = a + bX$) were conducted using Model II least squares methodology (Snedecor and Cochran 1980) where both variables are random (both variables are independent and subject to measurement error). Different notations are used for model $Y = a + bX$ (i.e., $X_2 = a + bX_1$), because intertaxa toxicity comparisons are true correlations. For that reason, the correlation coefficient r, a measure of the mutual linear association between two variables (X_1 and X_2), is used instead of the coefficient of determination r^2 (the proportion of the variability of the dependent variable Y that is caused or explained by the independent variable X).

Slopes (b), intercepts (a), and other statistics were derived from the equation $\log X_2 = a + b(\log X_1)$, where X_1 equals the acute toxicity value for a surrogate species and X_2 equals the acute toxicity value for another species (or genus or family). Species with paired tests on three or more chemicals were the minimum requirement for inclusion in each analysis, although five or more are recommended (Mayer and Ellersieck 1986). When either of the paired species included more than one acute value (EC, LC, or LD50), the geometric mean was used (Fig. 6). For genus and family, a surrogate species was compared to all genera and families having acute geometric mean values for two or more individual species. These individual values were used for analyses (i.e., a genus or family geometric mean was not used, Fig. 7). The surrogate species was not included in its own genus or family when those comparisons were made. A rough estimate of surrogate species/genus or surrogate species/family can be made with aquaticspecies, with the understanding that you are using only one species to represent a genus or family. In summary, six equation data sets exist for ICE with aquaticspecies being the default data set for the software program; they are:

1. aquaticspecies – Aquatic species; 2914 models; 119 species versus 119 species; EC or LC50 in µg/L
2. aquaticgenus – Aquatic species; 371 models; 96 species versus 14 genera; EC or LC50 in µg/L
3. aquaticfamily – Aquatic species; 490 models; 102 species versus 13 families; EC or LC50 in µg/L
4. wildlifespecies – Wildlife species; 278 models; 25 species versus 25 species; LD50 in mg chemical/kg of body weight
5. wildlifefamily – Wildlife species; 61 models; 23 species versus 5 families; LD50 in mg chemical/kg of body weight
6. wildlifesubacute – Wildlife species; 14 models; 6 species versus 6 species; LC50 in mg chemical/kg dry weight of diet

Statistical Analyses and Equation Formation Procedures

All equations were generated using SAS (1999). An algorithm was written to pair every species with every other species (or genus or family) by common chemical. PROC GLM was then used to calculate the regression equation of $\log_{10}$ predicted taxa = $a + b^*\log_{10}$ surrogate species where $a = X_2$ intercept and b = regression coefficient (slope).

Another computer procedure was written to capture the necessary statistics to generate the equation for the data sets above. This is the same procedure to be used when data sets not

Figure 6. Species versus species correlation.

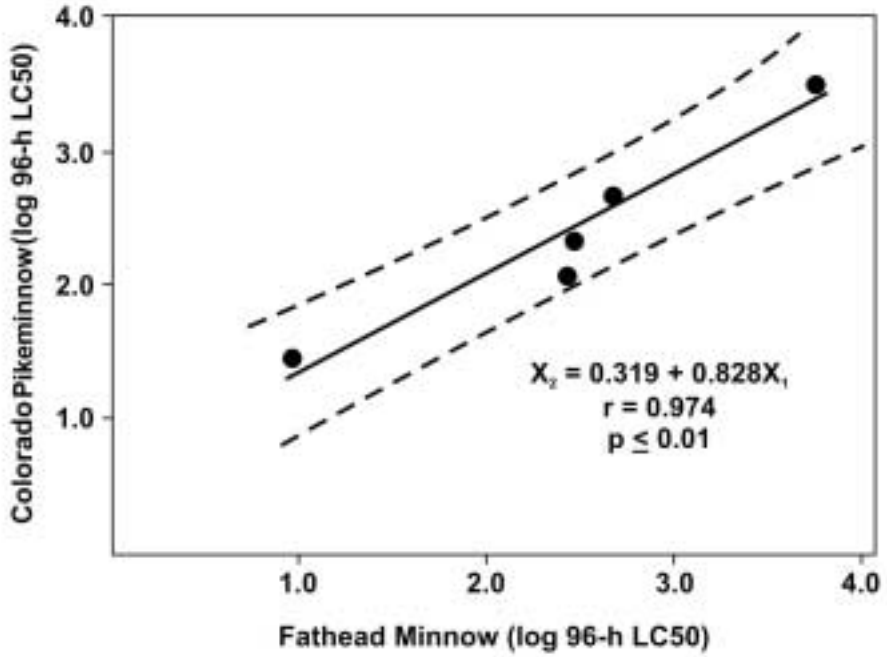
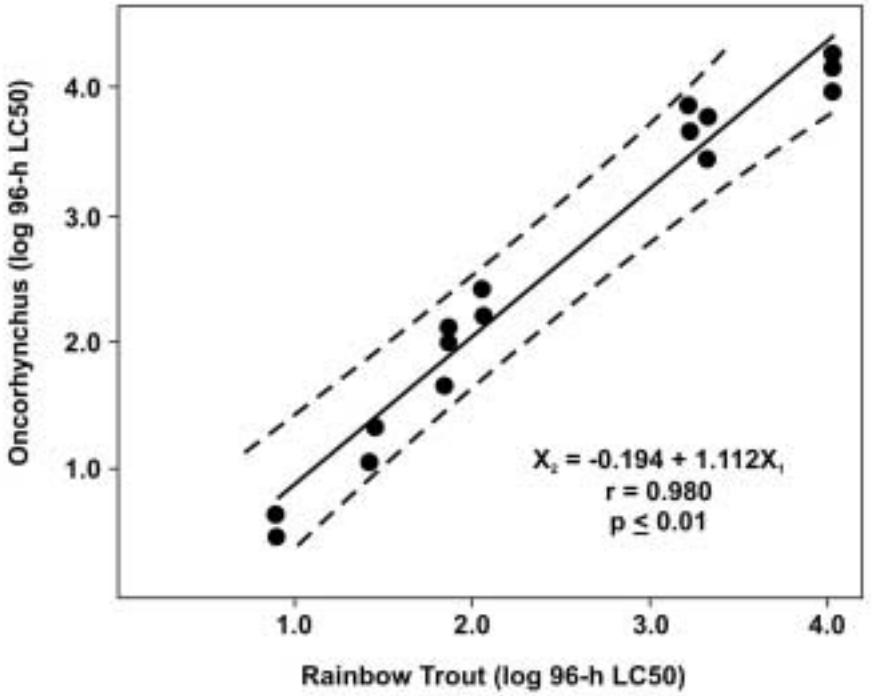


Figure 7. Species versus genus correlation.



included in ICE are of interest. In order for ICE to be able to read data, the procedure performs the following functions:

1. From the SAS output, capture the following parameters: surrogate species (X_1) name, predicted species or taxa (X_2) name, sample size, intercept, regression coefficient (slope), predicted species mean, error mean square, standard error of the slope, correlation coefficient (*r*), and probability that slope is significant.
2. Enter the parameters in Microsoft® Excel and save them as comma, tab or space delimited files. If space delimited files are used, a data value can not contain spaces. For this reason comma or tab delimited files are preferred.
3. If more than one equation is calculated, sort the file by X_1 and X_2.

All equation data sets can be viewed in Microsoft® Excel or other spreadsheet software that can read ASCII text files. All files supplied are comma delimited. The order of the parameters is as follows, which each letter representing a column in the spreadsheet.

A = Surrogate species (X_1)
B = Predicted taxa (X_2)
C = Sample size (n) for which each equation is based (df = n - 2)
D = Intercept (*a*)
E = Regression coefficient (slope *b*)
F = Average value of the predicted taxa
G = Error mean square (EMS)
H = Standard error of the regression coefficient (SEB)
I = Correlation coefficient (*r*)
J = Probability (Pr) that the slope is not equal to 0

Interpretation of Statistics

The purpose of the ICE software is to estimate an acute toxicity value for an untested species or taxa ($\boldsymbol{X_2}$) from an actual test value for the surrogate species ($\boldsymbol{X_1}$). If a model for the $\boldsymbol{X_2}$ species does not exist, an estimate may be made by using higher taxonomic levels (genus or family) containing that $\boldsymbol{X_2}$ species. The accuracy of the estimated value can be judged visually by the closeness of the confidence bands to the regression line. The closer the confidence bands are to the estimated value, the higher the confidence in the estimate. In certain cases, where the correlation may be less than acceptable, the confidence in accuracy may be enhanced by the correlative strength of the surrogate species selected. This occurs when the confidence bands for uncertainty due to surrogacy is smaller than the uncertainty due to the specific model.

ICE provides a number of other statistics that estimate the accuracy of prediction. The first statistic to evaluate is the significance of the correlation between $\boldsymbol{X_1}$ and $\boldsymbol{X_2}$ or when slope (*b*) $\neq 0$ (see 15, Fig. 2). This is accomplished by a t test and comparing the **Calculated t value** to the **Tabular t value** or by using the actual significance level (**Pr**). If the **Calculated t value** is equal to or greater than the **Tabular t value**, then the correlation is significant at the α level selected. The **Pr** value should be ≤ 0.05 for the correlation (slope, *b*) to be significant. When the regression coefficient (slope *b*) is close to 1.0, chemicals affect the $\boldsymbol{X_1}$ and $\boldsymbol{X_2}$ species in a similar fashion. The **Intercept** (*a*) can be used to determine if chemicals are generally more or less toxic to one species or taxa than another: negative intercept, the $\boldsymbol{X_2}$ species or taxa are generally more sensitive; positive intercept, the $\boldsymbol{X_1}$ species are generally more sensitive.

The next statistic to assess is the **Correlation coefficient** (***r***). The larger the ***r*** value and the closer it is to 1.0, the stronger the acute toxicity relationship is between the two taxa selected. However, *r* can sometimes be misleading in that it can be very high, but the t-test statistic may not show a significant relationship. This most frequently occurs when the degrees of freedom (df) are low and/or the slope is close to zero. We recommend that the degrees of freedom be at least 3 (or n ≥ 5) in order to increase confidence in the equations (Mayer and Ellersieck 1986). However, all equations having degrees of freedom of ≥ 1 (n ≥ 3) were included, because many species do not have existing or acceptable data available. These equations are intended to show the relationship, based on the available data. For further information on calculation and interpretation of linear regression analysis, see Ellersieck and LaPoint (1995).

Be aware that the prediction of sensitivity of one species from another by a regression equation is not the same equation if reversed. This is why two different equations are needed. The only time an equation can predict in either direction is if $r^2 = 1.0$. The following is a proof to demonstrate.

Let:
$\bar{y}$ = average value of Y
$\bar{x}$ = average value of X
$\hat{y}$ = predicted value Y
$\hat{x}$ = predicted value of X
Y_c = *substitute value of* Y

The linear regression of Y on X with slope *b*:

$$\hat{y} = \bar{y} + b\,(x - \bar{x})$$

$$\hat{y} = (\bar{y} - b\,\bar{x}) + bx \quad (\hat{y} = \text{intercept} + \text{slope [x]})$$

Substitute a particular $Y = Y_c$ *for* $\hat{y}$ and solve for $\hat{x}$.

This is the predicted *X* when $Y = Y_c$

$$\hat{x} = (Y_c - \bar{y} + b\,\bar{x})/b = (Y_c - \bar{y})/b + \bar{x} \qquad (1)$$

The linear regression of *X* on Y with slope *g*:

$$\hat{x} = (\bar{x} - g\,\bar{y}) + gY \quad (\hat{x} = \textit{intercept} + \textit{slope}\ [Y])$$
$$\hat{x} = (\bar{x} - g\,\bar{y}) + gY_c$$

Substitute *g* from $r = \sqrt{bg} \Rightarrow g = r^2/b$ in the above equation.

$$\hat{x} = (\bar{x} - r^2\,\bar{y}/b) + r^2\,Y_c/b = (Y_c - \bar{y})\,r^2/b + \bar{x} \qquad (2)$$

Compare equation (1) and (2); the two will be equal only when $r^2 = 1$.

If there is no variance around the regression line, the error mean square will equal zero; thus, all points will fit exactly on the regression line. This is the only time that $r^2 = 1$.

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Quick Reference

1. **Installing ICE**
   - Insert disk into CD ROM drive
   - Click **Start** button.
   - Select **Run** from menu.
   - Select **Browse** from the **Run** window.
   - Select drive letter associated with CD Drive from the **Browse** window (or **ICE July 17, 2003 [D:]**).
   - Double Click **Setup** or **D:\SETUP.EXE** file.
   - Click **OK**.
   - Windows now walks you through installation process.
   - Following installation, click **Start, Programs**, and then **ICE**; drag ICE icon to desired screen location.

2. **Using ICE**
   - Open ICE program.
   - Select data set in **Options** (**Data Sets**, select data set, **Open**, then **Select**); aquaticspecies = aquatic surrogate species vs. estimated species (aquaticgenus, species vs. genus; aquaticfamily, species vs. family), wildlifespecies = wildlife surrogate species vs. estimated species (wildlifefamily, species vs. family; per os), wildlifesubacute = wildlife surrogate species vs. estimated species (dietary).
   - Select Surrogate Species (X_1) having an acute toxicity value.
   - Enter surrogate species acute toxicity value at the 100 default value (µ*g*/L for aquaticspecies, aquaticgenus, aquaticfamily; mg/kg body weight for wildlifespecies and wildlifefamily; mg/kg diet for wildlifesubacute).
   - Select Predicted Taxa (X_2) to estimate acute toxicity.
   - Select **Back** in menu bar to choose another surrogate species; select **Options** to choose another data set.
   - Select **Print** then **Single** to print that frame or **All** to print all correlations for the chosen surrogate species within that data set.

3. **Choosing best correlations**
   - Use equations for surrogate and predicted taxa within same genus or family.
   - Use equations having df ≥ 3 ($n \geq 5$).
   - Use equations having a significant ($p \leq 0.05$) correlation (slope, *b*).
   - If data for more than one surrogate exists:
     $n_1 = n_2$, use equation having highest *r* value
     $n_1 \neq n_2$, use equation having smallest error mean square value.
   - If equations for the species to be estimated do not exist in aquaticspecies or wildlifespecies, search for its genus or family in aquaticgenus, aquaticfamily, or wildlifefamily.