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November 2003

California Environmental Protection Agency
California Department of Pesticide Regulation
Environmental Monitoring Branch
P.O. Box 4015 Sacramento, CA 95812-4015

EH 03-03

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[1] Environmental Monitoring Branch, California Department of Pesticide Regulation
[2] Center for Analytical Chemistry, California Department of Food and Agriculture

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Abstract

The California Department of Pesticide Regulation (CDPR) collected weekly surface water samples at four monitoring sites in the San Joaquin basin (San Joaquin, Stanislaus and Merced counties) between July 2 and September 30, 2002. Samples were analyzed for the pyrethroid insecticides permethrin and esfenvalerate, the herbicides metolachlor and alachlor and their degradation products, and other selected herbicides and organophosphate (OP) insecticides. The results of this study will be used to aid in the development of priorities for future monitoring and/or mitigation efforts.

Analytical concentrations are compared to aquatic toxicity benchmarks, including water quality criteria (WQC) established to protect aquatic organisms. Quantifiable pesticide concentrations are referred to as detections, while the presence of analytes at concentrations too low to be quantified are termed "trace" concentrations. A total of 14 pesticides and pesticide degradation products were detected in 56 water samples. This total included five OP insecticides, six herbicides and three herbicide degradation products. The most commonly detected compounds were dimethoate, diuron, metolachlor, and two metolachlor degradation products, metolachlor ethanesulfonic acid and metolachlor oxanilic acid (metolachlor ESA and metolachlor OXA, respectively).

Dimethoate, diuron and metolachlor were detected at concentrations well below those expected to impact aquatic organisms. Metolachlor ESA was detected in nearly 60% of all samples and was present at trace concentrations in an additional 30% of samples. Metolachlor OXA was detected in approximately 40% of all samples and was present at trace concentrations in an additional 35% of samples. Aquatic toxicity data are not available for the metolachlor degradation products; therefore, the significance of those detections could not be evaluated.

Three insecticides (chlorpyrifos, diazinon and malathion) were each detected in at least one sample at concentrations exceeding established WQC. Chlorpyrifos was detected in about 5% of all samples, with trace concentrations in an additional 7%. WQC for chlorpyrifos range from 0.014 to 0.041 µg/L. While chlorpyrifos concentrations exceeded established WQC in three samples, the analytical chlorpyrifos reporting limit of 0.040 µg/L was greater than certain WQC so that some additional exceedances may have occurred. The detection frequency for diazinon was similar to that of chlorpyrifos. Diazinon WQC range from 0.05 to 0.09 µg/L; the detected diazinon concentration exceeded established WQC in one sample. Malathion was detected in one sample and found at trace concentration in one sample (< 2% of samples each). The single malathion detection exceeded the established WQC of 0.1 µg/L.

The remaining detections (methyl parathion, simazine, hexazinone, norflurazon, prometryn, and alachlor ESA) were both infrequent and well below concentrations expected to impact aquatic organisms. There were no detections of the pyrethroid insecticides permethrin and esfenvalerate.

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Introduction

The San Joaquin Valley of California is one of the most productive agricultural areas in the United States. In 1987, approximately 5 percent of the total value of agricultural production in the U.S. was generated in the San Joaquin Valley (USGS, 1998).

In this area during the arid summer months, cultivation of crops such as vegetables, hay and grains, fruit and nuts, and cotton is made possible through the use of extensive irrigation. A wide variety of pesticides are applied throughout the summer irrigation season (CDPR, 2001a). Through runoff or draining of irrigation water, the potential exists for pesticide contamination of adjacent surface water bodies. Relatively little recent surface water monitoring for pesticides has been conducted in the San Joaquin basin during the summer irrigation season. Such monitoring data are needed to characterize the current summer distribution and concentrations of pesticides in the San Joaquin River and tributaries.

The objective of this study was to determine if select pesticides used in the summer irrigation season in the San Joaquin Valley are present in surface waters in measurable amounts, and if so, what typical range of concentrations may be observed. The results presented here will be used to aid in the development of priorities for future monitoring and/or mitigation efforts.

Materials and Methods

Pesticides of interest

Pesticides were selected for monitoring in this study based on (a) physiochemical properties indicating potential mobility, (b) their relatively high use, (c) potential aquatic toxicity, and/or (d) a lack of current monitoring data.

Pyrethroid insecticides

Permethrin and esfenvalerate are used on a variety of crops in the San Joaquin basin. During May through August of 2000, the reported use of permethrin and esfenvalerate in the five-county San Joaquin basin area comprised of Fresno, Madera, Merced, San Joaquin, and Stanislaus counties was 56,463 and 6,478 pounds of active ingredient, respectively (CDPR, 2001a). Permethrin use is shown in Figure 1. These pyrethroids were chosen for monitoring in this study because of a lack of summer monitoring data for these compounds in the San Joaquin Valley, and because of their potential for aquatic toxicity (Table 1). Analytical method information for the pyrethroid screen is given in Table 2.

Metolachlor and degradates

Metolachlor has been classified as a possible human carcinogen by U.S. Environmental Protection Agency Office of Pesticide Program's Carcinogenicity Peer Review Committee (U.S. EPA, 1996). Although the toxicological significance of the metolachlor degradation products (metolachlor ethanesulfonic acid and metolachlor oxanilic acid) is unknown at present, they appear to be mobile, having been frequently detected in the surface water of other states (Kalkhoff et al., 2000; Frey 2001).

During the summer there is relatively high use of metolachlor in the San Joaquin basin, primarily for control of broadleaf and annual grassy weeds in corn and beans. During May through August 2000, 63,899 pounds of metolachlor were applied in the five county San Joaquin River basin area (Figure 2). Metolachlor has been detected in California surface water (CDPR, 2001b), and degradation products of metolachlor have been detected in California groundwater (CDPR, 2001c). The Department of Pesticide Regulation is unaware of the existence of any other monitoring data for metolachlor degradation products in California surface water. While alachlor use is much less than metolachlor, alachlor and its degradates are included in the analytical method for metolachlor and degradates (Table 3) and those results are included here.

Other potential surface water contaminants

A wide variety of herbicides and OP insecticides are applied in the San Joaquin basin during the summer season (CDPR, 2001a), and several have been detected in San Joaquin Valley surface water (CDPR, 2001b). These include several of the pesticides in the OP and herbicide analytical screens shown in Tables 4 and 5, such as diazinon and chlorpyrifos. Consequently all water samples were analyzed using these two additional analytical methods to provide current information on the presence during summer months of these known contaminants. Over 85,000 pounds of chlorpyrifos was applied in Stanislaus and Merced counties from June through September, 2000 (Figure 3). During the same period, less than 5,000 pounds of diazinon was applied in those two counties.

Sampling site descriptions

Four surface water monitoring sites were selected in geographical locations with high historical use of permethrin, metolachlor, and a variety of OP insecticides during the summer irrigation season (Table 6). Additional factors which were also considered in evaluating the appropriateness of sampling sites for this study included the identification of previous irrigation season surface water detections of metolachlor and/or OP insecticides and the amount of agricultural drainage /irrigation return water flowing into the water body.

Sample Collecting and Handling

Sampling began on July 2, 2002, and continued throughout the summer until September 30, 2002. Each site was sampled once per week.

For each sampling event, four 1-liter samples were collected at each sampling site and submitted for chemical analysis. One 1-liter sample was submitted for each of the following analyses: pyrethroid insecticides, metolachlor/alachlor and degradates, OP insecticide screen, and herbicide screen.

All water samples were collected directly into 1-liter amber glass bottles using an extendable sampling pole, except for samples collected at the San Joaquin River

(Vernalis) site. At the San Joaquin River site, a weighted sampling container holding a single 1-liter bottle was lowered from the bridge to the river to collect the pyrethroid sample. The additional samples (metolachlor/alachlor, OP, and herbicide screen samples) were collected using a D-77 integrated-depth sampling device with a 3-liter Teflon bottle. The bulk samples collected in this manner were immediately transferred to three 1-liter amber glass bottles.

Water Quality Measurements

At each sampling event, temperature, dissolved oxygen (DO), pH, and electrical conductivity (EC) were measured in situ at each sampling site. DO, EC and temperature were measured with a Yellow Springs Instruments (YSI) multi-meter (model 85). Water pH was measured using a YSI model 60 pH meter or an IQ Scientific Instruments model IQ150 pH meter.

Chemical Analysis

Chemical analysis was performed by the CDFA's Center for Analytical Chemistry. The following methods (Appendix 1) were used to determine the concentrations of pesticides in whole water samples:

- OPs - gas chromatography/flame photometric detector (GC/FPD)
- pyrethroids - gas chromatography/electron capture detector (GC/ECD)
- herbicide screen - atmospheric pressure chemical ionization / liquid chromatography/ mass spectrometry/mass spectrometry (APCI/LC/MS/MS)
- metolachlor/alachlor - atmospheric pressure chemical ionization / liquid chromatography/ mass spectrometry/mass spectrometry (APCI/LC/MS/MS).

Method detection limits (MDL) and reporting limits (RL) are presented in Tables 2 through 5. The MDL is defined as in the U.S. EPA definition (40 CFR, Part 136, Appendix B): "the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater that zero and is determined from analysis of a sample in a given matrix..." The RL is generally

established as 1-5 times the MDL depending on analytical method and matrix, and accounts for the practical decrease in analytical sensitivity due to sample matrix effects. The RL is the lowest level at which concentrations are reported.

Residues determined to be present in a sample at or above the RL are reported here as detections. Residue concentrations between the RL and MDL that are determined by the analytical chemist to be likely due to the analyte of interest are reported as trace detections. The analytical chemist uses his/her best professional judgment to make this determination. No attempt is made to quantitate trace detections. Samples with no residue above the MDL are reported as non-detections (nd).

For pyrethroid analyses (permethrin and esfenvalerate), the whole samples, including any suspended sediment, were extracted and the sample bottle rinsed with extraction solvent for analysis. The pyrethroid analysis results are reported on a whole sample basis (water plus suspended sediment). At the time of this study, the performing laboratory did not yet have available an analytical method for the determination of pyrethroid insecticides in stream bed sediment; therefore, bed sediment samples were not collected.

Quality Control (QC) for the chemical analysis portion of this study was conducted in accordance with Standard Operating Procedure QAQC001.00 (Segawa, 1995).
Data generated during the analytical method validation process were used to assess the subsequent study results. The method validation recovery data were used to set warning and control limits. Warning limits were established at the mean percent recovery plus/minus 1-2 times the standard deviation. Control limits were established at the mean percent recovery plus/minus 2-3 times the standard deviation.

Blank-matrix spike samples were analyzed with each extraction set. Blank-matrix spikes are blank water samples fortified with an analyte or analytes at a known concentration and extracted and analyzed with an extraction set. Blind spike samples were also added to some analytical sets. A blind spike is a blank-matrix sample which has been spiked and submitted to the lab disguised as a field sample.

Data Analysis - Toxicity Benchmarks

In order to interpret the significance of the detections in this study, the concentrations of pesticide detections are compared to a variety of aquatic toxicity "benchmarks". These benchmarks and their sources are described below.

The concentrations presented in this report are instantaneous. Comparison of these concentrations to toxicity benchmarks are for illustrative purposes. Such comparisons are not quantitative since instantaneous concentrations do not consider the duration of exposure, and the benchmarks are based on a known exposure time (i.e., 96-hour exposure in a 96-hour LC50 toxicity test). As such, the acute toxicity criteria presented in this report are to be considered general benchmarks for evaluating relative concentration levels (Spurlock, 2001).

All water samples collected in this study consisted of untreated surface water; no samples of drinking water were collected. Sample sites were not adjacent to drinking water intakes, and in general the water bodies sampled are not primary sources of drinking water. As such, the focus in this report is the comparison of detected pesticide concentrations to toxicity data for aquatic organisms and not comparison to drinking water standards developed for the protection of human health.

Water Quality Criteria (WQC)

The U.S. EPA has developed guidelines for the development of Water Quality Criteria for the protection of aquatic organisms and their uses (U.S. EPA 1985). For a chemical under consideration, information is gathered concerning the material's toxicity to aquatic organisms. The data are reviewed for acceptability and, if enough acceptable data are available, they are used to develop WQC. As described in the EPA guidelines, the WQC provide an estimate of the highest one-hour concentration (Criterion Maximum Concentration, acute exposure) and the highest four-day average concentration (Criterion Continuous Concentration, chronic exposure) that, if not exceeded more than once every three years on average, should not cause unacceptable effects on aquatic organisms and

their uses (U.S. EPA 1985). The U.S. EPA and the California Department of Fish and Game (CDFG) have both developed Water Quality Criteria (WQC) for pesticides detected in this study.

CDFG conducts pesticide aquatic hazard assessments, and when possible, develops numerical WQC for the protection of aquatic organisms. CDFG follows the U.S. EPA guidelines for the development of WQC.

For the purpose of this report, the U.S. EPA and CDFG WQC are considered the most relevant and reliable of the available toxicity benchmarks.

Canadian Water Quality Guidelines for the Protection of Aquatic Life (Canadian Aquatic Guidelines)

These are guidelines developed by Environment Canada, the Canadian federal agency responsible for environmental protection (Environment Canada, 2003). The guidelines are developed based on toxicity data for the most sensitive species of plants and animals found in Canadian waters. They act as science-based benchmarks for the protection of the aquatic life species in Canada, and should be treated only as general benchmarks for evaluating relative concentrations in U.S. waters such as those described in this report. Data are included to provide some guide to aquatic toxicity where WQC do not exist. These guidelines are available for only a few of the detected pesticides considered in this report.

EPA ECOTOX Database

The U.S. Environmental Protection Agency maintains a database of chemical toxicity information compiled from peer-reviewed literature and U.S. and international government agencies (U.S. EPA 2003). EPA ECOTOX data are included in this report to provide a range of aquatic toxicity data for three selected species (*Ceriodaphnia dubia, Daphnia magna,* and *Oncorhynchus mykiss*). The first two organisms are freshwater arthropods, while the common name of the latter is rainbow trout. Individual studies were not reviewed. Data are included primarily to provide some guide to aquatic toxicity

where WQC or other aquatic guidelines do not exist. In order to provide a conservative estimate of the significance of detections, the lowest LC_{50} for the most sensitive of the three species is used as the toxicity benchmark in this report.

Results

Water quality measurements

Water quality measurement results are shown in Tables 7 through 10.

Orestimba Creek at River Road

Over the course of the study, the pH at Orestimba Creek ranged from 7.1 to 7.8. Measured water temperature ranged from 16 to 25.4 °C. DO and EC had ranges of 6.21 to 8.28 mg/L and 641 to 887 µS/cm, respectively.

Salt Slough at Highway 165

The pH at Salt Slough ranged from 6.49 to 7.66. Measured water temperature ranged from 18.9 to 26.9 °C. DO and EC had ranges of 5.14 to 7.37 mg/L and 877 to 1188 µS/cm, respectively.

San Joaquin River near Vernalis

The pH at Vernalis ranged from 7.01 to 9.03 . Measured water temperature ranged from 19.3 to 25.7 °C. DO and EC had ranges of 7.79 to 12.5 mg/L and 454 to 870 µS/cm, respectively.

Tuolumne River at Shiloh

The pH at the Tuolumne River site ranged from 6.96 to 8.4. Measured water temperature ranged from a low of 19.3 to a high of 26.7 °C. DO and EC had ranges of 6.44 to 10.0 mg/L and 165 to 285 µS/cm, respectively.

Chemical analysis results

Pesticide analysis results by sampling site are shown in Tables 11 through 14. Graphical representation of the results are given in Figures 4 through 7. Blind spike and continuing QC results for each of the analytical screens are presented in Appendix 5.

Sampling Sites

Salt Slough at Highway 165

Diuron and metolachlor were the most commonly detected pesticides at Salt Slough, with detection frequencies of 79 and 64 percent, respectively Table 11). These two pesticides also displayed high concentrations relative to other detected pesticides, with maximum concentrations of 0.582 and 0.951 µg/L for diuron and metolachlor, respectively. Other pesticides that were detected during the fourteen sampling events at Salt Slough were dimethoate (1 detection), chlorpyrifos (1 detection), hexazinone (4 detections), metolachlor ESA (5 detections), and metolachlor OXA (2 detections).

The single chlorpyrifos detection of 0.046 µg/L at Salt Slough exceeded both the CDFG chronic and CDFG acute WQC of 0.014 and 0.02 µg/L, as well as other toxicity benchmarks shown in Table 15. Chlorpyrifos was also found at trace concentrations in two additional samples. Diazinon was not detected above the RL at Salt Slough, but was present at trace concentrations in two samples. No other pesticide detections exceeded any of the toxicity benchmarks.

Orestimba Creek at River Road

Diazinon and chlorpyrifos were detected at concentrations exceeding toxicity benchmarks (Table 12, Table 15). Of the 14 samples collected at Orestimba Creek, diazinon was detected three times (21% detection frequency), with concentrations of 0.043, 0.046, and 0.276 µg/L. The two lowest detected concentrations were just below the CDFG chronic WQC of 0.05 µg/L. The 0.276 µg/L detection exceeded all three of the established WQC (Table 15). The three samples with quantifiable diazinon detections were taken from consecutive sampling events at Orestimba Creek (8/5, 8/12

and 8/19, 2002). This could indicate an extended period of diazinon presence in the creek.

Chlorpyrifos was detected in one sample at 0.0705 µg/L, and found at trace concentrations in one additional sample. The detection exceeds several of the toxicity benchmarks presented here, including both the acute and chronic CDFG WQC. Malathion was detected in one sample, at 0.111 µg/L. This concentration exceeded the U.S. EPA WQC of 0.1 µg/L, but was well below the CDFG acute WQC of 0.43 µg/L. Diazinon, chlorpyrifos and malathion detections were confirmed by gas chromatography/mass spectroscopy (GC/MS). No other pesticides detected at Orestimba Creek exceeded the toxicity benchmarks.

Both metolachlor degradation products were found at concentrations above the RL more frequently than the parent compound. Metolachlor ESA and metolachlor OXA were detected in 100% and 64% of samples, respectively; metolachlor was detected in 57%.

Dimethoate was detected in 86% of samples, and diuron in 43%, with maximum detections of 0.696 µg/L and 0.354 µg/L, respectively. Additional compounds detected were simazine (3 detections) and methyl parathion, hexazinone, and alachlor ESA (1 detection each).

Tuolumne River at Shiloh

There were fewer detections of sampled pesticides at Shiloh than at the other three sampled sites (Table 13, Figure 6).

Chlorpyrifos was detected at Shiloh in one sample, at 0.056 µg/L. This detection, confirmed by GC/MS, exceeded several toxicity benchmarks, including both the acute and chronic CDFG WQC (Table 15). Diazinon was not detected above the RL, but was found at trace concentrations in two samples.

Dimethoate and diuron both had detection frequencies of 21%. Maximum detected concentrations were 0.223 and 0.07 µg/L, respectively. Norflurazon was detected in one sample, at 0.281 µg/L

There were no detections of metolachlor or either of its degradates. A trace concentration of metolachlor was found in one sample, and trace concentrations of metolachlor ESA were present in 8 of 14 samples.

San Joaquin River near Vernalis

Metolachlor and its two degradation products, metolachlor ESA and OXA, were the most commonly detected compounds at Vernalis; at least trace concentrations of all three were found in every sample collected there (Table 14). Concentrations above the RL were more frequent for the degradates than for the parent compound, with detection frequencies of 100 and 79% for metolachlor ESA and OXA, respectively, and 21% for the parent compound.

Dimethoate and diuron were detected in 50% and 64% of Vernalis samples, respectively, with maximum detections of 0.073 µg/L and 0.124 µg/L, respectively. Prometryn was detected in two samples, chlorpyrifos and hexazinone were found at trace concentrations in one sample each. Diazinon was not found in any sample taken at Vernalis.

None of the detections at Vernalis exceeded any of the toxicity benchmarks.

Pesticides

Chlorpyrifos

The RL for the chlorpyrifos analytical method used in this study is 0.040 µg/L, greater than both the CDFG acute WQC of 0.02 µg/L and the CDFG chronic WQC of 0.014 µg/L. The MDL for the method is 0.0109 µg/L. Consequently WQC exceedances may have occurred that could not be detected by the analytical method. A more sensitive analytical method for chlorpyrifos is needed in order to assess more accurately how frequently the WQC are exceeded.

The CDFG acute WQC for chlorpyrifos was exceeded one time at each of the sampling sites except for Vernalis; trace concentrations were found at Vernalis in one sample (Table 16). Chlorpyrifos was found at trace concentrations or higher in two samples at Orestimba (ca. 15% of samples) and 3 samples at Salt Slough (> 20% of samples). The three samples from Salt Slough that contained chlorpyrifos were collected at three consecutive sampling events: 0.046 µg/L on 8/19/02, and trace amounts on 8/26/02 and 9/3/02. This may be an indication that the concentrations of chlorpyrifos in this water body were high enough to impact aquatic organisms for an extended period of time.

Diazinon

Diazinon was detected above the reporting limit three times at Orestimba Creek (> 20% of Orestimba Creek samples) and was present at trace concentrations at Salt Slough and Shiloh two times each (Table 16). No diazinon was detected in any sample taken during this study at Vernalis. Established diazinon WQC were exceeded once, at Orestimba Creek.

In previously reported studies, toxicities of diazinon and chlorpyrifos to *Ceriodaphnia dubia* have shown additivity (Bailey et al. 1997, CDFG 1999, 2001a). In this study there were no instances of detectable concentrations of both diazinon and chlorpyrifos co-occurring in a single sample.

Dimethoate

Dimethoate was detected in 23 samples (41% of all samples collected), with a maximum concentration of 0.696 µg/L. The CDFG conducted a hazard assessment of dimethoate (CDFG, 1996) but was unable to issue a WQC due to insufficient data. Of the data that CDFG reviewed and found acceptable in this assessment, the most acutely sensitive freshwater species tested was the stonefly *Pteronarcys californica*, with a mean 96-hour LC_{50} for this organism of 43 µg/L. Of nine values listed in the U.S. EPA's ECOTOX database, the lowest 48 hour LC50 for *Daphnia magna* was 580 µg/L. The Canadian

Aquatic Guideline for dimethoate is 6.2 µg/L. None of these benchmarks levels were exceeded in the samples collected during the study.

Malathion

Malathion was detected in one sample at 0.111 µg/L (Orestimba Creek); this concentration exceeded the U.S. EPA WQC of 0.1 µg/L. The CDFG acute WQC of 0.43 µg/L for malathion was not exceeded during the study. Additionally, EPA's ECOTOX database show the LC50's for three aquatic species (Table 1) to be on the order of 1.1 µg/L and higher, at least one order of magnitude above the highest malathion concentration.

Diuron

Diuron was detected in 29 samples (> 50% of samples), with a maximum concentration of 0.582 µg/L. No WQC or Canadian Aquatic Guideline exist for diuron. The herbicide has a low aquatic toxicity, with a reported 96-hour LC50 for *Daphnia magna* of 400 µg/L (Table 1).

Metolachlor

Throughout the study, metolachlor, metolachlor ESA, and metolachlor OXA were detected in approximately 35%, 59% and 39% of samples collected, respectively. For all three of these compounds, trace concentrations were found in an additional 30 to 40% of samples. Of the 56 total samples collected, 51 (90%) had at least trace detections of either metolachlor or a metolachlor degradation product.

The maximum concentration of metolachlor detected was 0.951 µg/L. No WQC have been issued for metolachlor; the Canadian Aquatic Guideline for metolachlor is 7.2 µg/L. The lowest metolachlor 48 hour LC50 for *daphnia magna* listed in the U.S. EPA ECOTOX database is 15400 µg/L. The U.S. EPA Lifetime Exposure Health Advisory for metolachlor is 100 µg/L (U.S. EPA 2002). This is the concentration of metolachlor in drinking water not expected to cause any adverse effects for a lifetime of exposure, including an adjustment for possible carcinogenicity.

The maximum concentrations for metolachlor ESA and OXA were 0.502 and 0.113 µg/L, respectively. Metolachlor ESA was detected above the RL in 100% of samples taken at both Orestimba Creek and Vernalis. Metolachlor OXA was detected above the RL in nearly 80% of samples taken from Vernalis, and in over 60% of samples collected at Orestimba Creek. Additional samples at both of these sites had trace concentrations of this compound. No WQC have been issued for the metolachlor degradation products, and no aquatic toxicity information is available for these compounds.

Other pesticides

Methyl parathion was detected in one sample at 0.048 µg/L, which did not exceed the CDFG interim WQC of 0.080 µg/L, or any of the other toxicity benchmarks presented in Table 15. Alachlor ESA was detected in one sample and found at trace concentrations in 7 samples. The remaining pesticides that were detected in this study, simazine, hexazinone, norflurazon, and prometryn, were detected infrequently and at concentrations well below the toxicity benchmark levels. There were no detections of permethrin, esfenvalerate, alachlor, or alachlor OXA in any sample at any of the four sampling sites. Precipitation during the time period of the study was negligible, so the off-site movement of pesticides observed in this study was not caused by storm-induced run off.

Quality Control

All QC sample results are listed in Appendix 5.

Pyrethroid Insecticide Screen

For the pyrethroid screen, a total of 16 QC samples were analyzed during the study period. Of those, 14 were blank-matrix spikes, and two were blind spikes. Recoveries for all of these samples were within the control limits.

Metolachlor/degradates screen

For the metolachlor / metolachlor degradates screen, a total of 19 QC samples were analyzed during the study period. Of those, 17 were blank-matrix spikes, and two were blind spikes. Recoveries for all of these samples were within the control limits.

OP screen

For the organophosphate screen, a total of 17 QC samples were analyzed during the study period. Of those, 14 were blank-matrix spikes, and three were blind spikes.

Chlorpyrifos, diazinon and malathion were detected at concentrations above the WQC (Table 17); all associated QC samples for these analytes were within control limits.

Two blank-matrix spike samples had several analytes with recoveries exceeding the upper control limits (UCL) only. No other OP QC samples had recoveries outside of the control limits. These two samples were the first OP QC samples analyzed at the start of the study, extracted on 7/3/2002 and 7/9/2002. The associated field samples analyzed with these QC samples were collected in the field on 7/2/2002 and 7/8/2002, respectively.

The analytes affected were the seven late-eluting compounds (see Appendix 3), dichlorvos, (7/9 QC sample only), phorate, fonofos, dimethoate, methyl parathion, tribufos, and profenofos. Dimethoate and methyl parathion were the only detections of these seven analytes in the 7/2 and 7/8 OP field samples. Because recoveries in both of the blank-matrix samples were greater than the UCL, the reported dimethoate and methyl parathion concentrations on these two dates may be biased upwards.

Herbicide screen

Sixteen herbicide screen blank-matrix spike samples and two blind spike samples were analyzed throughout the study. Recoveries were generally within control limits; the exceptions are discussed below.

Recoveries of prometryn exceeded the lower control limit (LCL) in six blank-matrix spike samples. There were no detections of prometryn in the field samples associated with these QC samples. In these field samples, concentrations of prometryn may be slightly underestimated; however, given the low aquatic toxicity of this pesticide (Table 15), concentrations of significance would not have been undetected.

The UCL was exceeded for six of the 12 analytes in QC samples extracted on 8/13/2002 (atrazine, simazine, prometryn, DEA, DACT, and norflurazon). The field samples analyzed with this set were collected in the field on 8/5/2002 and 8/12/2002. None of the six were detected in the field samples analyzed with these QC samples.

The LCL was exceeded for bromacil in one blind spike sample. There were no detections of bromacil in any sample throughout the study. While the low recovery may indicate that concentrations in field samples could be slightly underestimated, it is unlikely that concentrations of toxicological significance would have remained undetected as a result.

The exceedances of the control limits in these analyses have no impact on the conclusions of the study.

Conclusion

Chlorpyrifos, diazinon and malathion were detected at concentrations above established Water Quality Criteria. Although the frequency of detection of chlorpyrifos was not high, the insecticide was found during the summer irrigation season at concentrations potentially harmful to aquatic species at each of the sites sampled. Based on the WQC for chlorpyrifos and the relatively high reporting limit of the analytical method used in this study, even trace concentrations (as defined in this report) of this pesticide could pose a threat to aquatic organisms. A lower Reporting Limit/Method Detection Limit for chlorpyrifos is needed in order to assess more accurately how frequently the WQC are exceeded.

Diazinon and malathion were both detected infrequently. A single diazinon detection exceeded all three established WQC for diazinon. Malathion was detected in one sample, at 0.111 µg/L. This concentration exceeds the U.S. EPA WQC of 0.1 µg/L, but does not exceed the CDFG acute WQC of 0.43 µg/L. Based on the data and criteria considered here, use of diazinon and malathion in this area during the summer irrigation season does

not appear to commonly result in concentrations that are harmful to the aquatic environment.

Although dimethoate, diuron and metolachlor were detected frequently (> 35% detection rate each), based on available toxicity data the concentrations detected did not have the potential to cause acute toxicity to aquatic organisms.

The authors are not aware of any existing aquatic toxicity test data for the metolachlor degradation products, metolachlor OXA and metolachlor ESA. These degradates were frequently detected in this study; nearly 70% of all samples collected had detections of at least one degradation product. In order to interpret the relevance of these detections, reliable aquatic toxicity information is needed.

The CDFG interim acute WQC of 0.03 µg/L for permethrin is below the RL of the analytical method used in this study. A more sensitive analytical method for permethrin is needed in order to assess more accurately how frequently the WQC are exceeded. Additionally, due to the hydrophobicity of the pyrethroid insecticides, steam bed sediment analysis should be considered in the design of future efforts to assess the potential impacts of these compounds on aquatic systems.

Acknowledgments

We would like to thank the following for their contributions to this project:

Staff at CDPR, Environmental Monitoring Branch, especially Nina Bacey, Heather Casjens, Heather Imgrund, Adriana Moncada and Amy Washburn for sample collection/handling and Jesse Ybarra for technical assistance; Staff at the Center for Analytical Chemistry, CDFA, especially Catherine Cooper, Adriana Moncada, Janice Temple, Ryan Wichert and Teresa Woroneicka; Pat Dunn for early contributions to project formulation; Carissa Ganapathy for serving as the laboratory liaison.

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Table 1. Toxicity of pesticides to aquatic invertebrates and rainbow trout (*O. Mykiss*) [A].

Pesticide	*Ceriodaphnia dubia*	*Daphnia magna*	*Oncorhynchus mykiss*
Chlorpyrifos	0.053 to 0.060 (3)	0.6 to 1.0 (2) [B]	< 1 to 51 (10)
Diazinon	0.32 to 0.47 (4)	0.21 (1)	20 to 6200 (13)
Dimethoate	NA	580 to 6400 (9) [B]	6200 to 8600 (4)
Diuron	NA	400 (1)	4900 to 23800 (16)
Esfenvalerate	NA	0.27 (1) [B]	0.07 (1)
Ethoprop	NA	NA	700 to 13800 (6)
Hexazinone	NA	151000 [E]	146,000 to 1964000 (8)
Malathion	1.14 to 2.12 (2) [B]	1.6 to 33 (3) [B]	2.8 to 234 (22)
Methidathion	NA	7.2 (1) [B, D]	10 to 80 (5)
Methyl Parathion	2.6 to 3.5 (3) [B]	12 (48h) (1)	2200 to 3700 (9)
Metolachlor	15930 (1) [B]	15400 to 25100 (4) [B]	3900 (1)
Norflurazon	NA	15000 [C]	8100 (1)
Permethrin	0.55 (1) [B]	0.3 to 21.8 (9)	0.62 to 20.9 (22)
Prometryn	NA	35000 (1)	12000 to 20000 (5)
Simazine	NA	10000 to 94000 (3)	10000 to 100000 (11)

NA = data not available

A. Data are from US EPA 2003, 96-hour LC50 data, in µg/L, unless otherwise indicated. Number of records shown in parentheses.

B. 48-hour LC50 data in µg/L.

C. 48-hour acute No Observable Effect Limit (NOEL) in µg/L.

D. Data from Department of Pesticide Regulation database, in µg/L.

E. Weed Society of America, 1994.

Table 2. Analytical limits for pyrethroid insecticides in surface water.

Pyrethroid Pesticides in Surface Water Method: GC/EC		
Compound	**Reporting Limit (µg/L)**	**Method Detection Limit (µg/L)**
Esfenvalerate	0.05	0.028
Permethrin	0.05	0.0049

Table 3. Analytical limits for metolachlor and degradates in surface water.

Metolachlor/Alachlor and degradates in Surface Water by LC/MS Method: APCI/LC/MS/MS		
Compound	**Reporting Limit (µg/L)**	**Method Detection Limit (µg/L)**
Metolachlor	0.05	0.0207
Alachlor	0.05	0.0169
Metolachlor OXA	0.05	0.0235
Metolachlor ESA	0.05	0.0434
Alachlor OXA	0.05	0.0108
Alachlor ESA	0.05	0.0331

Table 4. Analytical limits for OP insecticides in surface water.

Organophosphate Pesticides in Surface Water by GC Method: GC/FPD		
Compound	**Reporting Limit (µg/L)**	**Method Detection Limit (µg/L)**
Azinphos methyl	0.05	0.0099
Chlorpyrifos	0.04	0.0109
Diazinon	0.04	0.011
Dichlorvos	0.05	0.0098
Dimethoate	0.04	0.0079
Disulfoton	0.04	0.0093
Ethoprop	0.05	0.0098
Fenamiphos	0.05	0.0125
Fonofos	0.04	0.008
Malathion	0.04	0.0117
Methidathion	0.05	0.0111
Methyl Parathion	0.03	0.008
Phorate	0.05	0.0083
Profenofos	0.05	0.0114
Tribufos	0.05	0.0142

Table 5. Analytical limits for herbicides in surface water.

Triazines/Herbicides in Surface Water by LC/MS Method: APCI/LC/MS/MS		
Compound	**Reporting Limit (µg/L)**	**Method Detection Limit (µg/L)**
Atrazine	0.05	0.02
Bromacil	0.05	0.031
Diuron	0.05	0.042
Hexazinone	0.05	0.04
Metribuzin	0.05	0.025
Norflurazon	0.05	0.019
Prometon	0.05	0.016
Prometryn	0.05	0.016
Simazine	0.05	0.013
DEA [A]	0.05	0.0157
ACET [B]	0.05	0.0173
DACT [C]	0.05	0.027

A. 2-amino-4-chloro-6-isopropylamino-s-triazine, a triazine degradate

B. 2-amino-4-chloro-6-ethylamino-s-triazine, a triazine degradate

C. 2,4-diamino-6-chloro-s-triazine, a triazine degradate

Table 6 Surface water sampling site locations in the San Joaquin Valley, California.

Site Name	Description	County	Latitude	Longitude
Vernalis	San Joaquin River at Vernalis	San Joaquin	37.67611	-121.265
Salt Slough	Salt Slough at Highway 165	Merced	37.24778	-120.851
Orestimba	Orestimba Creek at River Road	Stanislaus	37.41361	-121.015
Shiloh	Tuolumne River at Shiloh	Stanislaus	37.60333	-121.131

Coordinates are decimal degrees, 1927 North American Datum (NAD27).

Table 7. Water quality measurements [A], Salt Slough, California.

Salt Slough

Date	Time	DO (mg/L)	Temp °C	EC (µS/cm)	pH
02-Jul-02	1040	5.4	26.9	1112	6.61
08-Jul-02	1035	5.6	24	1179	6.81
15-Jul-02	1105	5.65	26.2	1185	7.66
22-Jul-02	1135	NA	NA	NA	7.3
29-Jul-02	1020	5.14	23.5	877	6.95
05-Aug-02	1015	5.72	20.4	1103	7.25
12-Aug-02	1030	7.37	23	1029	NA
19-Aug-02	1105	5.28	23	916	7.07
26-Aug-02	1115	6.15	22.3	1043	7.34
03-Sep-02	1030	5.47	25.2	1063	6.49
09-Sep-02	1042	5.75	20.5	885	7.4
16-Sep-02	1045	6.74	20.8	1188	7.1
23-Sep-02	1045	5.61	22.6	1027	NA
30-Sep-02	1030	6.17	18.9	1139	7.47

A. DO = dissolved oxygen, EC = electrical conductivity

Table 8. Water quality measurements, Orestimba Creek, California.

Orestimba

Date	Time	DO (mg/L)	Temp °C	EC (µS/cm)	pH
02-Jul-02	1135	6.35	25.4	777	7.8
08-Jul-02	1140	7.1	23	656	7.4
15-Jul-02	1200	7.05	23.3	722	7.75
22-Jul-02	1225	6.21	24.4	645	7.09
29-Jul-02	1100	7.08	22.7	681	7.79
05-Aug-02	1104	7.49	21.5	662	7.65
12-Aug-02	1130	7.35	22.3	872	NA
19-Aug-02	1150	8.28	21.1	838	7.72
26-Aug-02	1200	7.58	20.4	641	7.1
03-Sep-02	1115	7.15	21.4	844	NA
09-Sep-02	1120	7.65	17.5	856	7.7
16-Sep-02	1130	7.1	19.2	887	7.7
23-Sep-02	1127	7.08	21.2	839	7.7
30-Sep-02	1115	7.91	16	755	7.8

Table 9. Water quality measurements, San Joaquin River at Vernalis, California.

Vernalis

Date	Time	DO (mg/L)	Temp °C	EC (µS/cm)	pH
02-Jul-02	1130	12.5	25.7	NA	8.26
08-Jul-02	1100	9.26	23.1	678	9.03
15-Jul-02	NA	9.74	24.4	791	8.72
22-Jul-02	1115	7.8	24	678	8.56
29-Jul-02	1100	7.79	24	730	7.73
05-Aug-02	1100	12.35	23.2	803	8.18
12-Aug-02	1130	10.93	25	764	8.68
19-Aug-02	1125	7.93	23.2	678	8.48
26-Aug-02	1230	10.65	23	802	8.38
03-Sep-02	1130	11.73	24.9	870	8.56
09-Sep-02	1145	10.4	21.3	801	8.34
16-Sep-02	1105	9.13	21.1	770	8.31
23-Sep-02	1115	8.99	22.7	454	7.85
30-Sep-02	1140	9.45	19.3	775	7.01

Table 10. Water quality measurements, Tuolumne River at Shiloh, California.

Shiloh

Date	Time	DO (mg/L)	Temp °C	EC (µS/cm)	pH
02-Jul-02	1021	8.41	26.7	NA	6.96
08-Jul-02	1015	6.68	23.7	205.6	7.59
15-Jul-02	1030	6.44	24.7	197.1	7.31
22-Jul-02	1015	6.92	24.8	276.7	8.31
29-Jul-02	1000	8.37	24.8	218.6	8.4
05-Aug-02	1000	9.54	23.2	285.5	7.48
12-Aug-02	1030	8.51	24.5	193.7	7.44
19-Aug-02	1025	7.36	24.7	269.1	8.4
26-Aug-02	1130	6.93	23	196.8	8.24
03-Sep-02	1030	7.23	24.4	226	7.54
09-Sep-02	1030	7.77	21	249	7.78
16-Sep-02	1000	7.76	20.8	255.6	7.66
23-Sep-02	1015	8.2	22.9	165	7.43
30-Sep-02	1030	10	19.3	NA	7.73

Table 11. Pesticide concentrations in surface water samples collected at Salt Slough, California. Includes only those analytes for which there was a quantified detection or trace detection.

	Concentration (µg/L) [A]								
Sample Date	chlorpyrifos	diazinon	dimethoate	diuron	hexazinone	metolachlor	metolachlor ESA	metolachlor OXA	prometryn
7/2/02	nd	nd	nd	0.582	0.072	0.373	0.05	tr	nd
7/8/02	nd	nd	nd	0.294	0.075	0.915	tr	tr	tr
7/15/02	nd	nd	nd	0.184	0.07	0.951	tr	tr	nd
7/22/02	nd	tr	nd	0.202	nd	0.203	tr	tr	nd
7/29/02	nd	tr	0.046	0.183	nd	0.343	0.063	0.054	nd
8/5/02	nd	nd	nd	0.247	nd	0.77	tr	tr	nd
8/12/02	nd	nd	nd	0.241	nd	0.104	tr	tr	nd
8/19/02	0.046	nd	nd	0.182	nd	0.115	0.054	tr	nd
8/26/02	tr	nd	nd	0.124	nd	0.094	0.06	0.059	nd
9/3/02	tr	nd	nd	0.140	tr	tr	0.063	tr	nd
9/9/02	nd	nd	nd	0.207	0.052	tr	tr	tr	nd
9/16/02	nd	nd	nd	tr	nd	tr	tr	tr	nd
9/23/02	nd	nd	nd	tr	nd	tr	tr	tr	nd
9/30/02	nd	nd	nd	tr	nd	tr	tr	tr	nd
number detections	**1**	**0**	**1**	**11**	**4**	**9**	**5**	**2**	**0**
detection frequency (%)[B]	**7**	**0**	**7**	**79**	**29**	**64**	**36**	**14**	**0**
maximum conc.	**0.046**	**tr**	**0.046**	**0.582**	**0.075**	**0.951**	**0.063**	**0.059**	**tr**

A. nd = nondetection, tr = trace detection (see text for definition)

B. Percent of samples with detections above the reporting limit.

Table 12. Pesticide concentrations in surface water samples collected at Orestimba Creek, California. Includes only those analytes for which there was a quantified detection or trace detection.

Concentration (µg/L)													
Sample Date	alachlor ESA	chlorpyrifos	diazinon	dimethoate	diuron	ethoprop	hexazinone	malathion	methyl parathion	metolachlor	metolachlor ESA	metolachlor OXA	simazine
7/2/02	tr	nd	nd	0.167	0.354	tr	0.154	nd	0.048	0.689	0.147	0.093	nd
7/8/02	nd	nd	nd	nd	0.074	nd	tr	nd	nd	0.407	0.138	0.065	nd
7/15/02	nd	nd	nd	0.675	tr	nd	nd	nd	nd	0.393	0.148	0.087	nd
7/22/02	nd	tr	nd	0.132	tr	tr	nd	nd	nd	0.135	0.083	tr	nd
7/29/02	nd	nd	nd	0.134	tr	nd	nd	tr	nd	0.262	0.196	0.069	nd
8/5/02	tr	nd	0.276	0.696	tr	nd	nd	nd	nd	0.223	0.182	0.113	nd
8/12/02	tr	nd	0.046	0.124	0.065	nd	nd	nd	nd	0.069	0.212	0.061	nd
8/19/02	tr	nd	0.043	0.504	nd	nd	nd	0.111	nd	0.088	0.348	0.093	nd
8/26/02	tr	nd	nd	0.226	0.104	nd	nd	nd	nd	tr	0.219	0.057	0.05
9/3/02	nd	nd	nd	0.0485	0.061	nd	tr	nd	nd	tr	0.234	tr	0.053
9/9/02	nd	0.0705	nd	0.132	0.074	nd	nd	nd	nd	tr	0.282	tr	0.082
9/16/02	0.064	nd	nd	0.058	nd	nd	nd	nd	nd	tr	0.502	0.077	nd
9/23/02	tr	nd	nd	0.11	tr	nd	nd	nd	nd	nd	0.332	tr	nd
9/30/02	tr	nd	nd	nd	tr	nd	nd	nd	nd	tr	0.154	tr	nd
number detections	**1**	**1**	**3**	**12**	**6**	**0**	**1**	**1**	**1**	**8**	**14**	**9**	**3**
detection frequency (%)	**7**	**7**	**21**	**86**	**43**	**0**	**7**	**7**	**7**	**57**	**100**	**64**	**21**
maximum conc.	**0.064**	**0.0705**	**0.276**	**0.696**	**0.354**	**tr**	**0.154**	**0.111**	**0.048**	**0.689**	**0.502**	**0.113**	**0.082**

Table 13. Pesticide concentrations in surface water samples collected at Tuolumne River at Shiloh, California. Includes only those analytes for which there was a quantified detection or trace detection.

	Concentration (µg/L)								
Sample date	chlorpyrifos	diazinon	dimethoate	diuron	ethoprop	methyl parathion	metolachlor	metolachlor ESA	norflurazon
7/2/02	nd	nd	tr	tr	nd	nd	nd	nd	nd
7/8/02	0.056	nd	0.04	0.05	tr	tr	nd	nd	0.281
7/15/02	nd	nd	0.223	tr	nd	nd	nd	tr	nd
7/22/02	nd	nd	tr	tr	nd	nd	nd	tr	nd
7/29/02	nd	nd	tr	tr	nd	nd	nd	tr	nd
8/5/02	nd	nd	0.068	0.07	nd	nd	nd	nd	nd
8/19/02	nd	nd	nd	nd	nd	nd	nd	tr	nd
8/26/02	nd	tr	nd	0.05	nd	nd	nd	tr	nd
9/3/02	nd	nd	nd	tr	nd	nd	tr	tr	nd
9/9/02	nd	nd	nd	tr	nd	nd	nd	tr	nd
9/30/02	nd	tr	nd	nd	nd	nd	nd	tr	nd
number detections	**1**	**0**	**3**	**3**	**0**	**0**	**0**	**0**	**1**
detection frequency (%)	**7**	**0**	**21**	**21**	**0**	**0**	**0**	**0**	**7**
maximum conc	**0.056**	**tr**	**0.223**	**0.07**	**tr**	**tr**	**tr**	**tr**	**0.281**

No detections or trace detections at this site on 8/12/02, 9/16/02 or 9/23/02.

Table 14. Pesticide concentrations in surface water samples collected at San Joaquin River at Vernalis, California. Includes only those analytes for which there was a quantified detection or trace detection.

	Concentration (µg/L)							
Sample Date	chlorpyrifos	dimethoate	diuron	hexazinone	metolachlor	metolachlor ESA	metolachlor OXA	prometryn
7/2/02	nd	tr	0.089	nd	0.062	0.09	tr	nd
7/8/02	nd	tr	0.096	nd	0.05	0.095	0.05	nd
7/15/02	nd	0.041	0.062	nd	0.055	0.088	tr	nd
7/22/02	tr	0.044	0.068	nd	tr	0.089	0.062	nd
7/29/02	nd	0.048	tr	nd	tr	0.116	0.062	nd
8/5/02	nd	0.052	tr	nd	tr	0.113	0.064	nd
8/12/02	nd	0.073	0.05	nd	tr	0.105	0.061	nd
8/19/02	nd	0.048	0.085	nd	tr	0.092	0.054	0.057
8/26/02	nd	0.043	0.078	nd	tr	0.128	0.065	0.129
9/3/02	nd	nd	0.058	nd	tr	0.151	0.062	nd
9/9/02	nd	nd	0.124	tr	tr	0.141	0.062	nd
9/16/02	nd	nd	tr	nd	tr	0.113	0.058	nd
9/23/02	nd	nd	tr	nd	tr	0.129	0.079	nd
9/30/02	nd	nd	nd	nd	tr	0.093	tr	nd
number detections	**0**	**7**	**9**	**0**	**3**	**14**	**11**	**2**
detection frequency (%)	**0**	**50**	**64**	**0**	**21**	**100**	**79**	**14**
maximum conc.	**tr**	**0.073**	**0.124**	**tr**	**0.062**	**0.151**	**.079**	**0.129**

Table 15. Freshwater toxicity benchmarks cited for comparison purposes.

Benchmark Type	Concentration (µg/L)	Source
chlorpyrifos		
CDFG chronic WQC [A]	0.014	CDFG, 2000a, 1994a
CDFG acute WQC	0.02	CDFG, 2000a, 1994a
U.S. EPA chronic WQC	0.041	U.S. EPA, 1986
U.S. EPA acute WQC	0.083	U.S. EPA, 1986
U.S. EPA ECOTOX database	0.053 (*Ceriodaphnia dubia*)	U.S. EPA, 2003
diazinon		
CDFG chronic WQC	0.05	CDFG, 2000a, 1994b
CDFG acute WQC	0.08	CDFG, 2000a, 1994b
U.S. EPA draft acute WQC	0.09	U.S. EPA, 1998
U.S. EPA ECOTOX database	0.21 (*daphina magna*)	U.S. EPA, 2003
dimethoate		
CDFG WQC	insufficient data	CDFG, 1996
Canadian Aquatic Guideline	6.2	Environment Canada, 2003
U.S. EPA ECOTOX database	580 (*daphnia magna*)	U.S. EPA, 2003
diuron		
U.S. EPA ECOTOX database	400 (*daphnia magna*)	U.S. EPA, 2003
ethoprop		
U.S. EPA ECOTOX database	700 *(O. mykiss)*	U.S. EPA, 2003
hexazinone		
U.S. EPA ECOTOX database	146000 (*O. mykiss*)	U.S. EPA, 2003

A. WQC = Water Quality Criteria

Table 15 (continued). Freshwater toxicity benchmarks cited for comparison purposes.

Benchmark Type	Concentration (µg/L)	Source
malathion		
CDFG acute WQC	0.43	CDFG, 1998
EPA WQC	0.1	U.S. EPA, 1986
U.S. EPA ECOTOX database	1.14 (*Ceriodaphnia dubia*)	U.S. EPA, 2003
methyl parathion		
CDFG interim chronic WQC	0.08	CDFG, 1992
U.S. EPA ECOTOX database	2.6 (*Ceriodaphnia dubia*)	U.S. EPA, 2003
metolachlor		
Canadian Aquatic Guideline	7.2 (interim guideline)	Environment Canada, 2003
U.S. EPA ECOTOX database	3900 (*Oncorhynchus mykiss*)	U.S. EPA, 2003
norflurazon		
U.S. EPA ECOTOX database	8100 (*Oncorhynchus mykiss*)	U.S. EPA, 2003
prometryn		
U.S. EPA ECOTOX database	35000 (*Daphnia magna*)	U.S. EPA, 2003
permethrin		
CDFG acute WQC	0.03 interim	CDFG, 2000b
U.S. EPA ECOTOX database	0.3 (*Daphnia magna*)	U.S. EPA, 2003
simazine		
Canadian Aquatic Guideline	10	Environment Canada, 2003
U.S. EPA ECOTOX database	10000 (*Daphnia magna*)	U.S. EPA, 2003

No data available for metolachlor ESA or OXA.

Table 16. Detections and trace detections, chlorpyrifos, diazinon and malathion.

Concentration detected	Sampling date	Sampling site
Chlorpyrifos		
trace [A]	7/22/02	Orestimba
0.0705	9/9/02	Orestimba
0.046	8/19/02	Salt Slough at Highway 165
trace	8/26/02	Salt Slough at Highway 165
trace	9/3/02	Salt Slough at Highway 165
trace	7/22/02	San Joaquin River near Vernalis
0.056	7/8/02	Tuolumne River at Shiloh
Diazinon		
0.276	8/5/02	Orestimba
0.046	8/12/02	Orestimba
0.043	8/19/02	Orestimba
trace [B]	7/22/02	Salt Slough at Highway 165
trace	7/29/02	Salt Slough at Highway 165
trace	8/26/02	Tuolumne River at Shiloh
trace	9/30/02	Tuolumne River at Shiloh
Malathion		
trace [C]	7/29/02	Orestimba
0.111	8/19/02	Orestimba

A. For chlorpyrifos, 0.0109 µg/L < trace < 0.04 µg/L
B. For diazinon, 0.011 µg/L < trace < 0.04 µg/L
C. For malathion, 0.0117 µg/L < trace < 0.04 µg/L

Table 17. Exceedances [A] of toxicity benchmarks.

Benchmark Type	**Level (µg/L)**	**Number of Exceedances per Sampling Site**			
		Salt Slough	Orestimba	Shiloh	Vernalis
Chlorpyrifos					
CDFG chronic WQC	0.014	1	1	1	0
CDFG acute WQC	0.02	1	1	1	0
U.S.EPA chronic WQC	0.041	1	1	1	0
U.S. EPA ECOTOX database	0.053 (*C. dubia*)	0	1	1	0
Diazinon					
CDFG WQC - acute	0.08	0	1	0	0
CDFG WQC - chronic	0.05	0	1	0	0
U.S. EPA WQC - draft acute	0.09	0	1	0	0
U.S. EPA ECOTOX data	0.21 (*D. magna*)	0	1	0	0
Malathion					
U.S. EPA WQC	0.1	0	1	0	0

A. Only detections above the Reporting Limit were included in the tabulation of exceedances. Trace detections were not included.

Figures 1-7

Figure 1. Sampling Sites and Permethrin Use in the San Joaquin Valley, California, June - August 2000

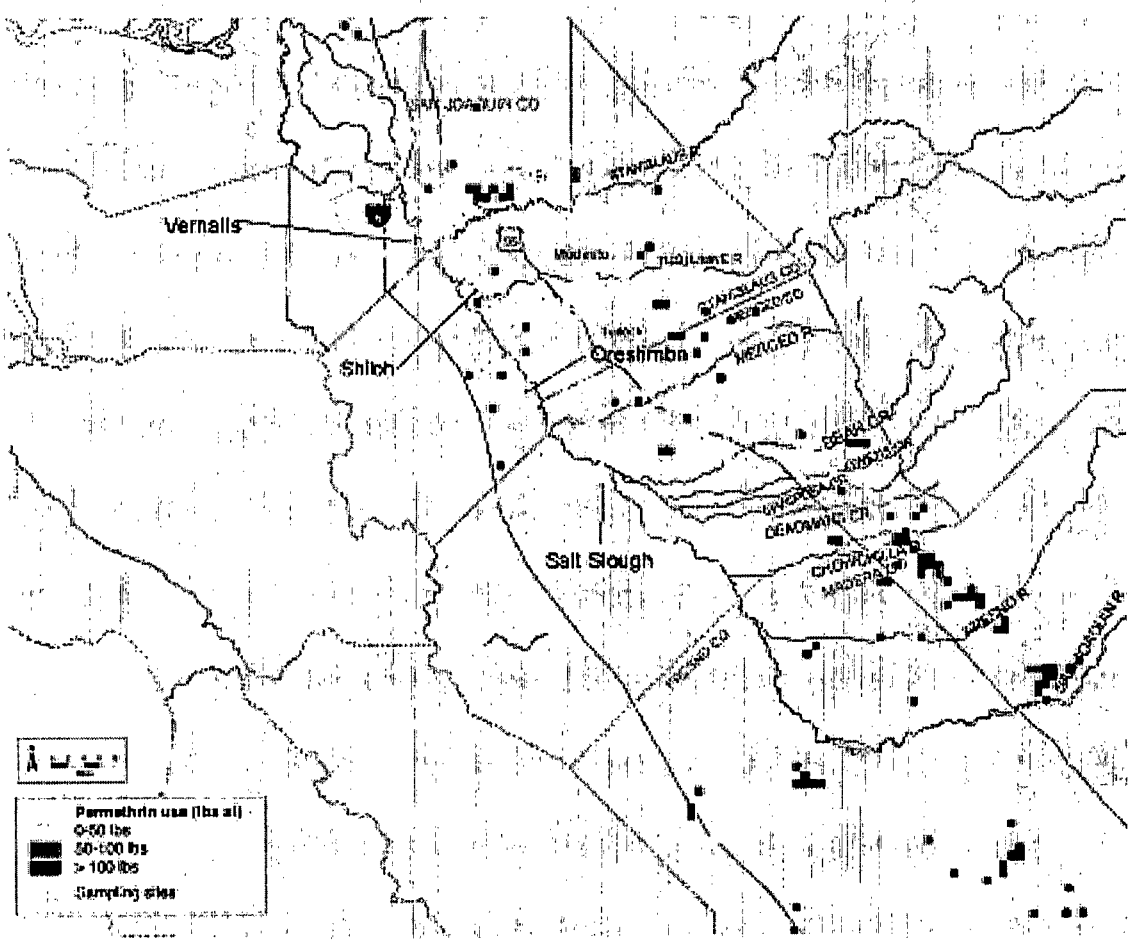


Figure 2. Sampling Sites and Metolachlor Use in the San Joaquin Valley, California, May - August 2000

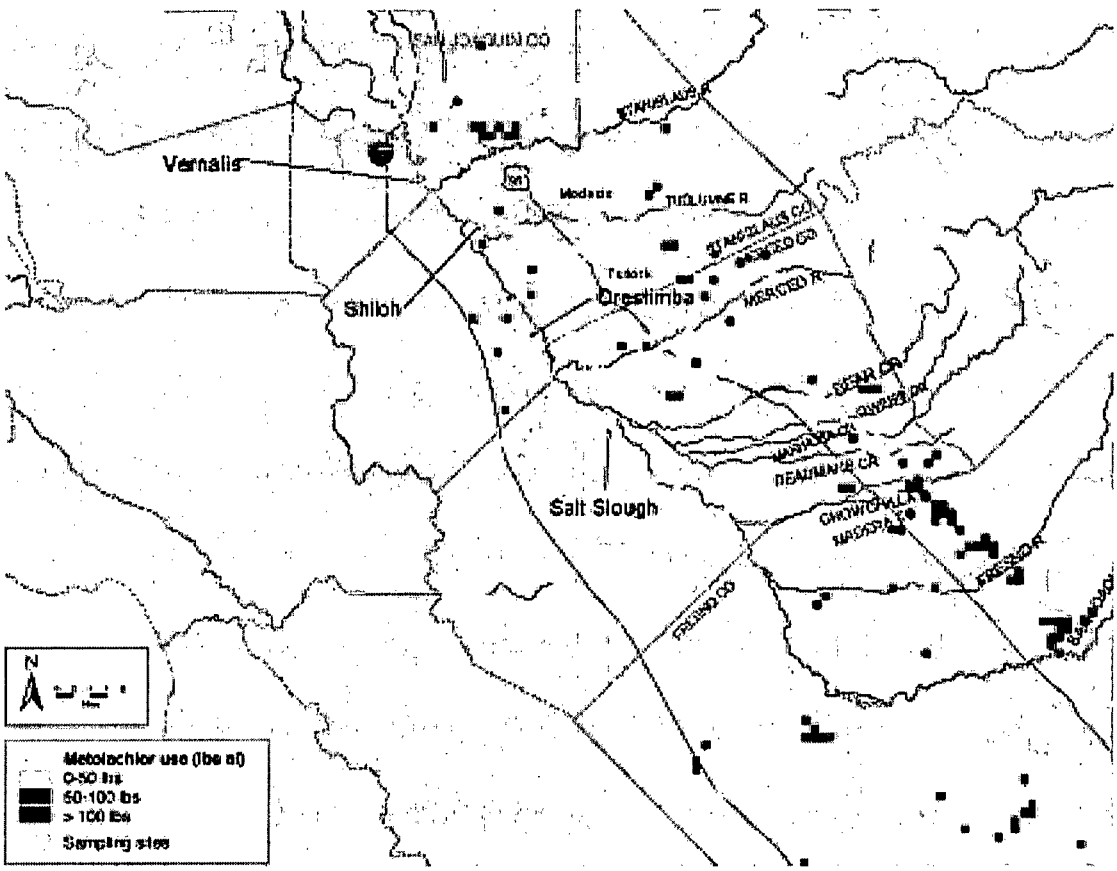


Figure 3. Sampling Sites and Chlorpyrifos Use in the San Joaquin Valley, California, May - August 2000

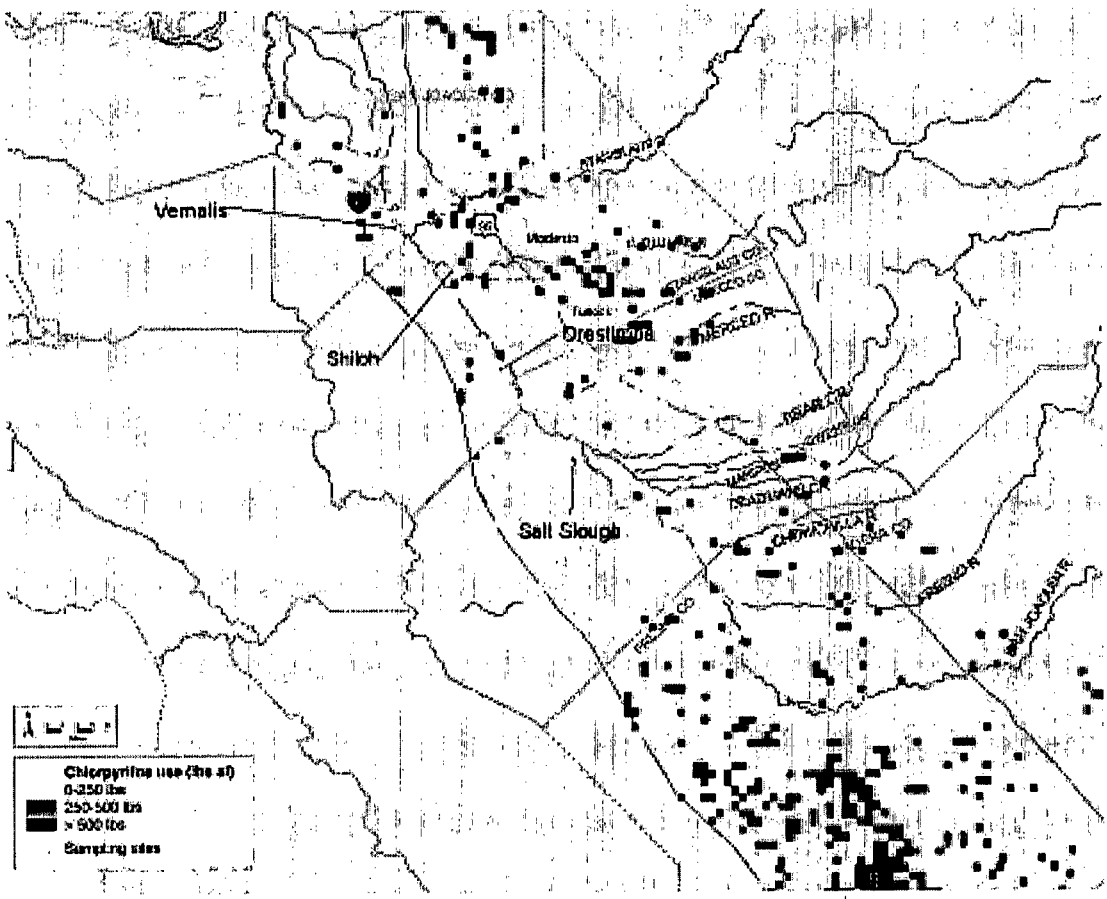
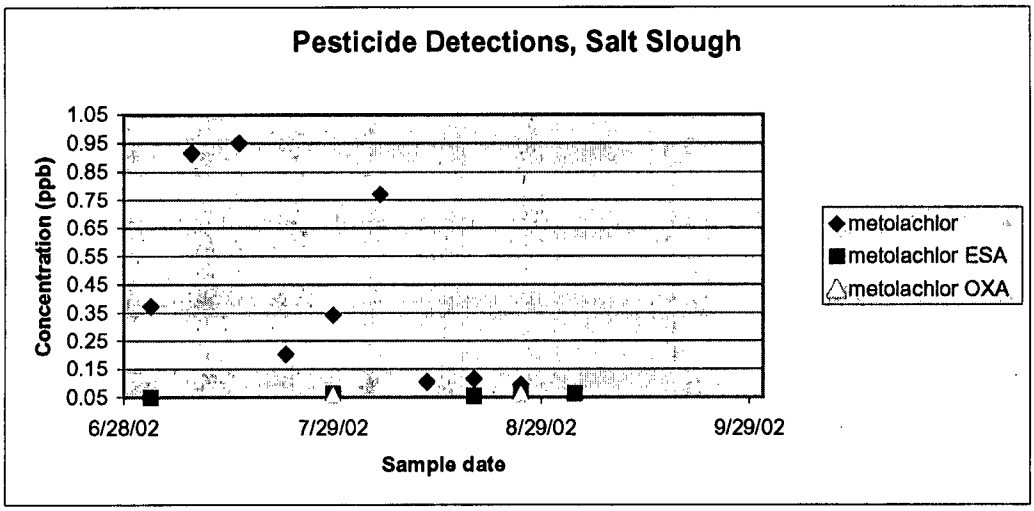


Figure 4. Pesticide detections in surface water samples collected weekly from Salt Slough, California.



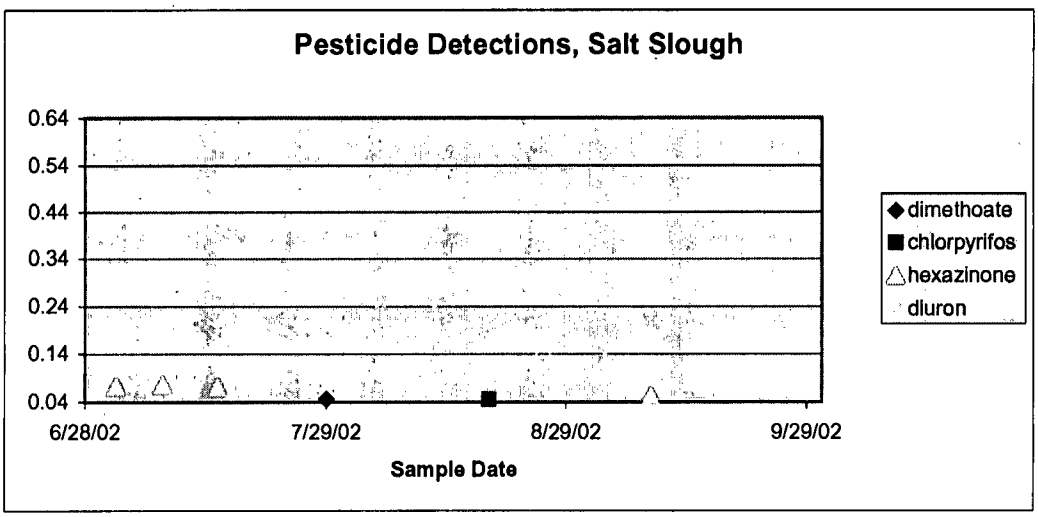
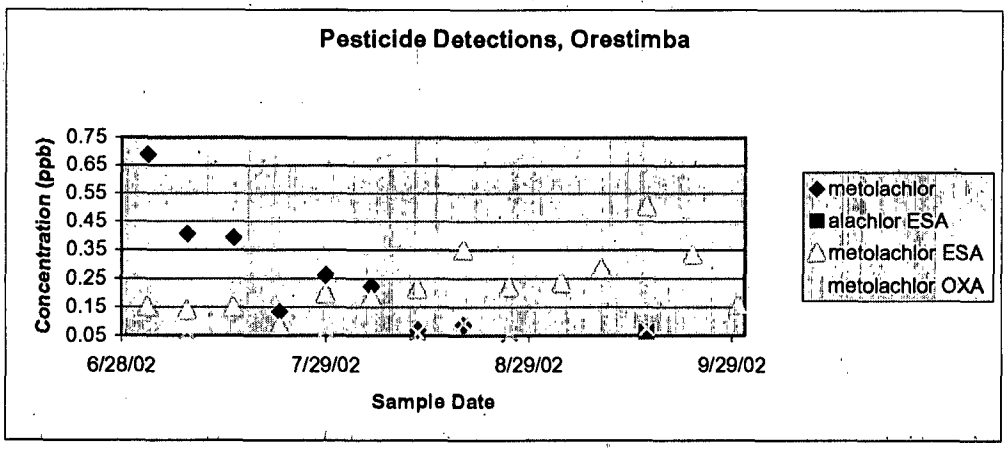
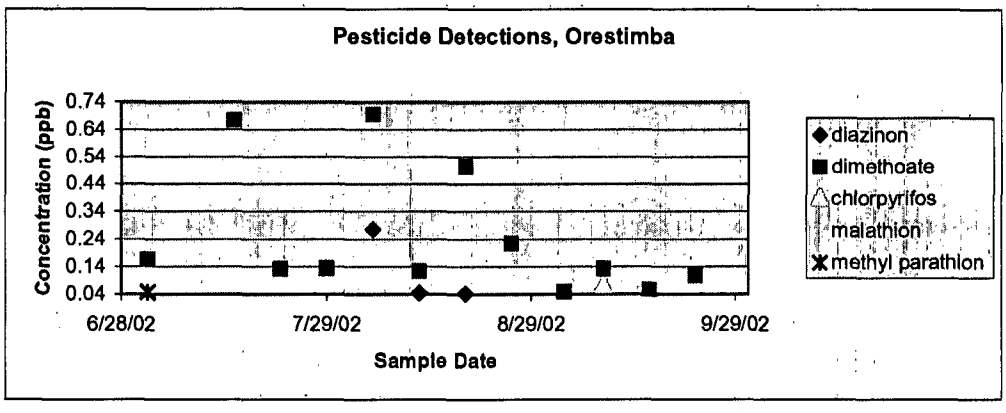


Figure 5. Pesticide detections in surface water samples collected weekly from Orestimba Creek, California.





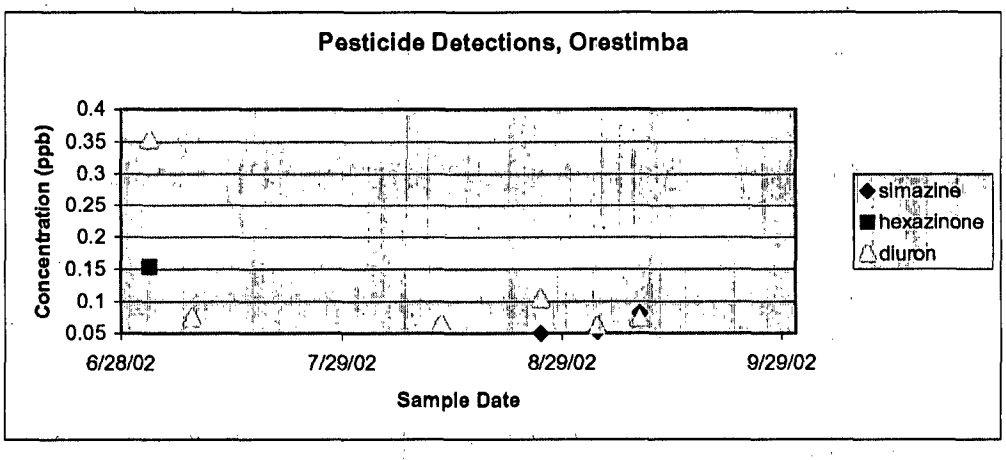


Figure 6. Pesticide detections in surface water samples collected weekly from Tuolumne River at Shiloh, California.

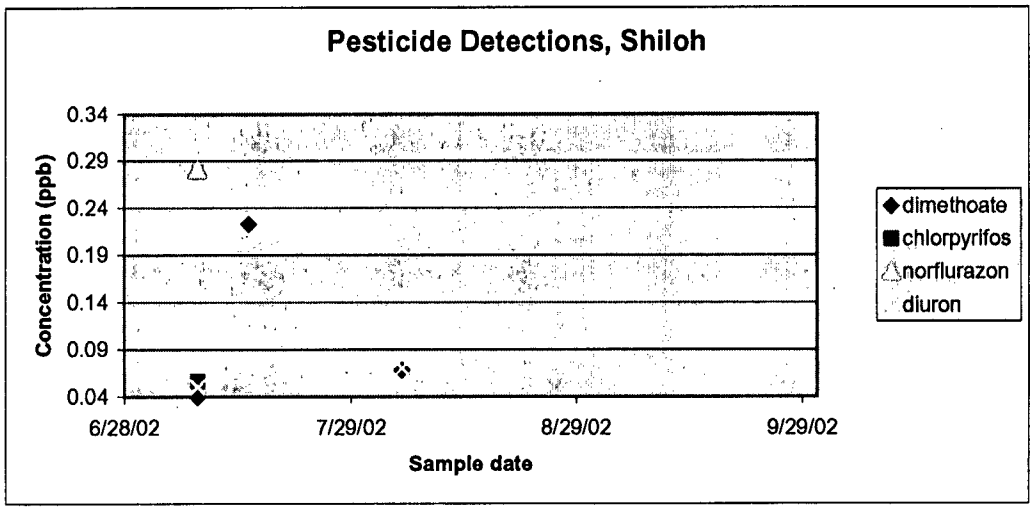


Figure 7. Pesticide detections in surface water samples collected weekly from San Joaquin River at Vernalis, California.

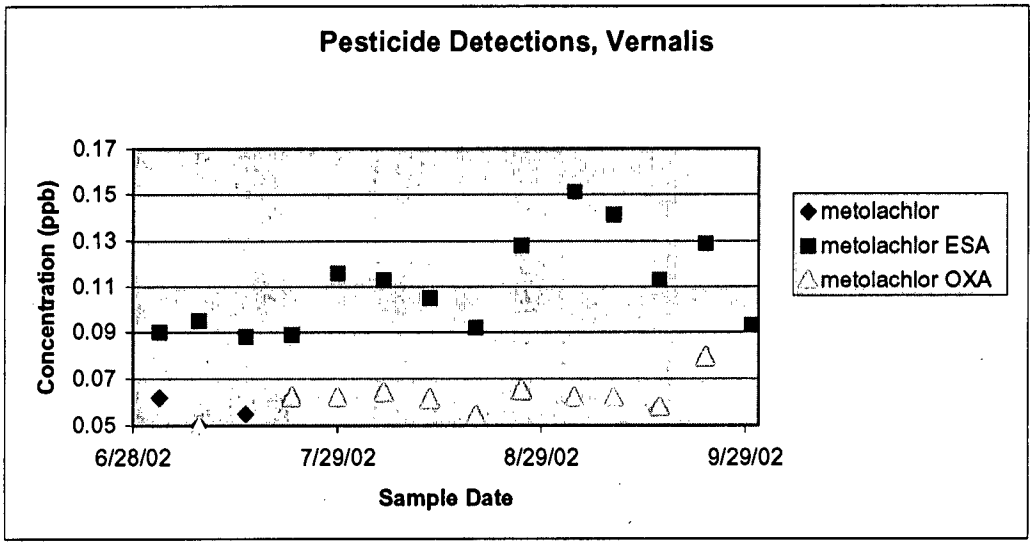
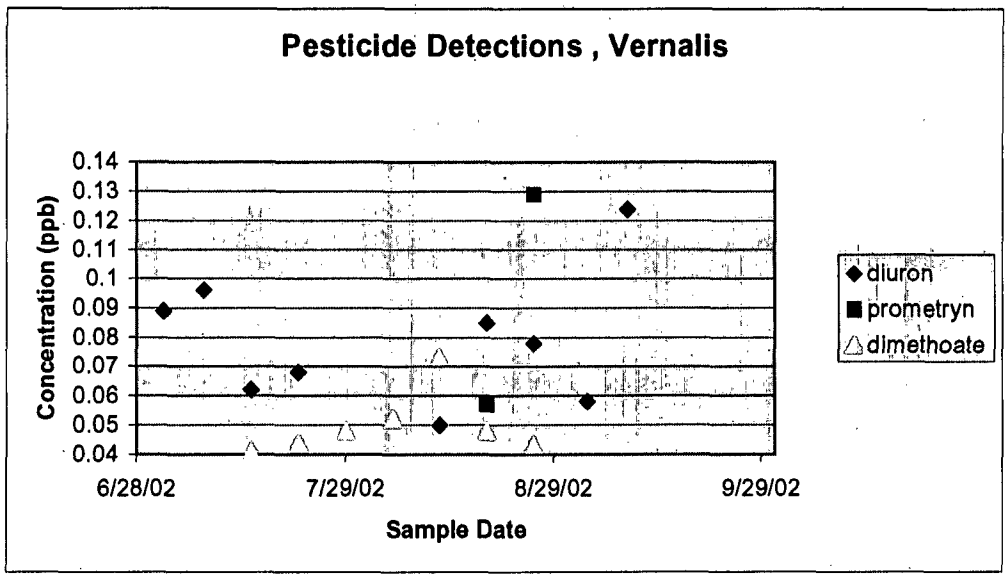


Figure 7 (continued). Pesticide Detections, San Joaquin River at Vernalis



Appendix 1

Analytical Method: Analysis of pyrethroid insecticides by Gas Chromatography.

CALIFORNIA DEPT. OF FOOD & AGRICULTURE.
Center for Analytical Chemistry
Environmental Monitoring Section
3292 Meadowview Road
Sacramento, Ca. 95832
(916) 262-2080,Fax (916) 262-2784

Method #: EM 52.5
Original Date: 09/07/00
Revised Date:

DETERMINATION OF PERMETHRIN AND ESFENVALERATE / FENVALERATE IN SEDIMENT WATER

Scope: This method is for the determination of permethrin (cis and trans), esfenvalerate and its isomer fenvalerate in sediment water. The reporting limits of this method is 0.05 ppb for these compounds using the electron capture detector and 0.1 ppb using the mass selective detector.

Principle: The sediment water was extracted using hexanes. After concentrating the hexanes, the extracted residues were analyzed by gas chromatograph equipped with an electron capture detector (ECD) or by a mass selective detector (MSD). Permethrin was reported as the total of the cis and trans isomers and esfenvalerate was reported as the total of esfenvalerate and its isomer fenvalerate.

Reagents:

1. Permethrin, CAS#52645-53-1, (combination of isomers cis and trans), 1.0 mg/mL in acetone, obtained from CDFA Standard Repository (Center for Analytical Chemistry, California Department of Food and Agriculture)
2. Fenvalerate, CAS#51630-58-1, (combination of isomers fenvalerate and esfenvalerate), 1.0 mg/mL in acetone, obtained from CDFA Standard Repository (Center for Analytical Chemistry, California Department of Food and Agriculture)
3. Hexanes, pesticide residue grade
4. Acetone, pesticide residue grade
5. Sodium sulfate, anhydrous granular (ACS)

Safety:

Most of the reagents used and analyzed for in this method have not been completely characterized. All general laboratory safety rules must be followed.

Equipment:

1. Separatory funnels, 2 L
2. Boiling flasks, flat bottom, 24/40 joints, 500 mL
3. Beakers, 1 L
4. Funnels, glass short stemmed 100 mm diameter
5. Rotary evaporator, Buchi/Brinkmann, R110

Equipment: continued

6. Conical test tubes, graduated, calibrated 15 mL
7. Nitrogen evaporator, Organomation, Model 12

Instruments:

1. GC-ECD: Hewlett-Packard 5890 Gas Chromatograph equipped with an electron capture detector
2. GC/MSD: Hewlett-Packard 6890 Gas Chromatograph equipped with a series 5973 Mass Selective Detector

Interference:

The background had small peaks on the GC-ECD that fell close to the retention times of the compounds of interest but didn't interfere with the quanitation at this time. The MSD has no interferences at this time.

Standard Preparation:

1. The 1mg/mL standards are diluted to 10ug/mL with acetone for spiking purpose.
2. Dilute the mg/mL standards into a series of desired standard sets that will be used for instrument calibration and sample calculation.
3. Keep all prepared standards in the designated refrigerator for storage while not in use.
4. The shelf life of each prepared standard is six months.

Sample Preservation and Storage:

1. Check the temperature of samples upon arrival and record it.
2. Sign the chain of custody and obtain the EMON number.

Procedure:

1. Remove samples from the refrigerator and allow them to come to room temperature before weighing them. Record weight.
2. Transfer water sample to a 2 L separatory funnel leaving as much of the sediment as possible in the bottle.
3. Add 20 mL acetone to the bottle and shake for 10 seconds.
4. Add 100 mL hexanes to the bottle and shake for 30 seconds.
5. Pour acetone, hexanes and sediment to the separatory funnel and shake for 1 min.
5. After phase separation, drain water layer into a 1 L beaker then drain the hexanes layer through glass wool and ~ 45 g sodium sulfate into a 500 mL flask.
6. Pour the sample layer back into the separatory funnel.
7. Repeat the steps 3-6 two more times using 20 mL acetone and 80 mL hexanes.
8. Rinse the sodium sulfate with ~ 20 mL hexanes.
9. Weigh empty bottles and record the weight.
10. Rotoevaporate the extract to ~ 1 mL at 50 ° C under approximately 20 inches of Hg vacuum.
11. Transfer the extract to a 15 mL graduated test tube and rinse the flask twice with approximately 2 mL of hexane and add to the test tube.

Procedure: continued

12. Evaporate the extract to a final volume of 1 mL under a gentle stream of nitrogen in a 50 ° C waterbath. Vortex to mix well.

Preparation of blanks and Spikes

Blank: American River water with 5 grams of sediment added to the bottle. (Prepared by the Department of Pesticide Regulations)

Spike: Spike standard directly into the bottle containing American River water with 5 grams of sediment added. Mix well and let sediment settle before extracting.

Instrument Conditions:

Instrument: HP 5890 Gas Chromatograph equipped with an electron capture detector
Column: HP-1 (Crosslinked methyl silicone gum) 30 m x 0.53 mm x 0.88 μm
Carrier gas: Helium, 5 psi
Injector temperature : 220 °C
Detector temperature: 300 °C
Column oven temperature:
Initial temperature: 150 °C hold for 2 min.
Rate: 40 °C/min.
Final temperature: 280 °C for 20 min.
Injection volume: 1 μL
Retention times: Permethrin (cis & trans): ~ 10.3 & 10.4 minutes
Esfenvalerate (fenvalerate & esfenvalerate):~13.5 & 13.9 minutes

Instrument: HP 6890 Gas Chromatograph equipped with a 5973 Mass Selective Detector
Column: HP-5MS (5% Phenyl Methyl Siloxane), 30m x 0.25 mm x 0.25 μm
Carrier: Helium, 6.4 psi
Column oven temperature:
Initial temperature: 70 °C hold for 1.0 min.
Program Rate 25 °C/ min.
Final temperature: 280 °C hold for 8.00 min.
Injecture temperature: 250 °C
Transfer Line Temperature: 280 °C
Ions Selected for SIM Acquistion: Permethrin cis 163, 165, 183, 184
Permethrin trans 163, 165, 183, 184
Fenvalerate 181, 225, 419
Esfenvalerate 181, 225, 419

Retention times: Permethrin cis ~12.5 minutes
Permethrin trans ~12.6 minutes
Fenvalerate ~15.1 minutes
Esfenvalerate~15.4 minutes

Volume Injected: 2 μL

Instrument Calibration:

1. Load a method, set the desired condition for analysis.
2. Run 0.05, 0.1, 0.25, and 0.5 ηg/uL to check the system linearity

Analysis:

Quality Control:

1. A 4-point calibration curve of 0.05, 0.1, 0.25 and 0.5 ηg/uL for permethrin and esfenvalerate/fenvalerate were obtained at the beginning and the end of each set of samples.
2. Each sample shall be injected two times to insure reliability of the analysis. Results obtained using a calibration curve shall lie within the range of the calibration curve. If results fall outside the calibration curve, the sample must be concentrated/diluted or the calibration curve extended. A sample set is usually comprised of 10 samples, a blank and a spike.

Method Detection Limit (MDL):

Method Detection Limit (MDL) refers to the lowest concentration of analyte that a method can detect reliably in either a sample or a blank. To determine the MDL, spike 7 samples, with 0.1 ppb of permethrin and esfenvalerate/fenvalerate and process through the entire method along with a blank. The standard deviation derived from the 7 spike results was used to calculate the MDL using the following equation:

$$MDL = tS$$

Where: t = the student " t" value for the 99% confidence level with n-1 degrees of freedom (t=3.143 for 6 degrees of freedom). n= the number of replicates.
S = the standard deviation obtained from the 7 replicates analysis

The results for the standard deviations and MDL are in Appendix 1.

Reporting Limit (RL):

RL refers to level above which quantitative results may be obtained. The MDL was used as a guide to determine the RL. The reporting limit is 0.05 ppb for permethrin and esfenvalerate/fenvalerate using the ECD and 0.1ppb for permethrin and esfenvalerate/fenvalerate using the MSD.

Recovery Data:

The analytical method was validated using five sets of spike samples. Each set contained a blank and five levels of spikes. Each set was processed through the entire analytical method. Recoveries of permthrin and esfenvalerate/fenvalerate are shown in Appendix 2.

Calculations:

$$ppb = \frac{\text{(peak ht sample)(response factor, ηg) (sample final volume, mL)(1000 μL/mL)}}{\text{--}}$$

(sample vol. Injected, μL)

Calculations: continued

$$\text{where: response factor}(\eta g) = \frac{[\text{(std. Conc.}_n, \eta g/\mu L)(\text{std. Vol. Injected, } \mu L)/(\text{std. Peak ht..}_n)]}{n}$$

n=number of standards

Acceptance Criteria:

1. The standard curves at the beginning and end of each sample set should not have a percent change greater than 10 % for the ECD and 20% for the MSD. The % change in response was calculated as follows:

   % Change in response = absolute value of [response of (std before - std after)/ std before] x 100

2. The samples were calculated using the response factor average of the curves. If the results between the two injections differ less than 10 % for ECD and 15 % for MSD either result can be reported. A change greater than 10 % for ECD and 15 % for MSD with no known reason requires a third injection.

Discussion: In this project a storage stability study was done. The storage stability study consisted of 0.5 ppb spike level and 3 replicates over a 13 day period. The spiked samples were stored in the refrigerator and then analyzed on days 0, 3, 5, 7, 10, and finally with day 13. It was noticed that by day 3 the esfenvalerate spike had started to transform to its isomer fenvalerate. At the beginning of this project we were just going to analyze for esfenvalerate since that was the analyte being applied in the environment. However, after the transformation of the esfenvalerate to it's isomer fenvalerate it was decided to add the two together and report the total. All the mdl and validation data was recalculated to report the total of fenvalerate and esfenvalerate. A new standard was prepare using fenvalerate which is a ratio of approximately 60% fenvalerate to 40% esfenvalerate, compared to the esfenvalerate standard which was approximately 10% fenvalerate to 90% esfenvalerate. It was also noticed that permethrin over the 13 day storage study showed a little degradation. The results for the storage stability study are shown in appendix 3.

The results for the GC-ECD were calculated using height to minimize any interferences that might be caused by the background. The background had small peaks that fell close to the retention times of the compounds permethrin cis and trans , but didn't interfere with quanitation at this time. The MSD has no interferences.

References:

Determination of Asana Insecticide Residues In Crops, Animal Tissues, Soil And Water: Electron-Capture Gas Chromatographic Method,(MMS-R-581-1) February, 1986, Shell Development Company Biological Sciences Research Center Modesto, California

WRITTEN BY: Jane White

Jane White

TITLE: Agricultural Chemist II

REVIEWED BY: Catherine Cooper

Catherine Cooper

TITLE: Agricultural Chemist III
Supervisor

Appendix: 1

Permethrin and Esfenvalerate/Fenvalerate MDL Results (ppb) for sediment water on GC-ECD

Spike #	Permethrin	Esfenvalerate/Fenvalerate
1	0.0972	0.0938
2	0.0944	0.112
3	0.0945	0.0864
4	0.0952	0.0925
5	0.0969	0.0871
6	0.0937	0.0891
7	0.0930	0.0881
S=	0.00157	0.009
MDL = 3.143 x S	0.00493	0.028

Permethrin and Esfenvalerate/Fenvalerate MDL Results (ppb) for sediment water on MSD

Spike #	Permethrin	Esfenvalerate/Fenvalerate
1	0.117	0.097
2	0.124	0.129
3	0.113	0.128
4	0.099	0.110
5	0.121	0.108
6	0.091	0.113
7	0.105	0.129
S=	0.012	0.013
MDL = 3.143 x S	0.037	0.04

Appendix: 2

Permethrin and Esfenvalerate/Fenvalerate Method Validation Results and Recoveries for sediment water on GC-ECD

	Permethrin (cis & trans)		Esfenvalerate/Fenvalerate	
Spike Level (ppb)	Result (ppb)	Recovery (%)	Result (ppb)	Recovery (%)
0.1	0.0988	98.8	0.089	89
	0.113	113	0.112	112
	0.110	110	0.109	109
	0.106	106	0.109	109
	0.086	86	0.080	80
0.5	0.474	94.8	0.483	96.6
	0.520	104	0.530	106
	0.513	103	0.513	103
	0.483	96.6	0.542	108
	0.495	99	0.520	104
1.0	0.962	96.2	1.00	100
	1.08	108	1.11	111
	1.06	106	1.07	107
	1.11	111	1.18	118
	1.01	101	1.05	105
5.0	4.80	96.0	4.47	89.4
	4.68	93.6	4.73	94.6
	4.30	86.0	3.67	73.4
	3.94	78.8	3.76	75.2
	4.11	82.2	4.77	95.4
10.0	8.43	84.3	10.9	109
	8.87	88.7	9.10	91.0
	8.23	82.3	8.90	89.0
	9.98	99.8	11.0	110
	8.25	82.5	8.69	86.9

Appendix 2: continued

Permethrin and Esfenvalerate/Fenvalerate Method Validation Results and Recoveries for sediment water on MSD

	Permethrin		Esfenvalerate/Fenvalerate	
Spike Level (ppb)	Result (ppb)	Recovery (%)	Result (ppb)	Recovery (%)
0.1	0.0827	82.7	0.0860	86.0
	0.103	103	0.110	110
	0.0975	97.5	0.0944	94.4
	0.100	100	0.0973	97.3
	0.0820	82.8	0.0736	73.6
0.5	0.469	93.8	0.586	117
	0.536	107	0.612	122
	0.441	88.2	0.408	81.7
	0.477	95.4	0.504	100.8
	0.455	91.0	0.403	80.6
1.0	0.963	96.3	0.993	99.3
	1.04	104	1.05	105
	0.907	90.7	0.993	99.3
	1.05	105	1.06	106
	0.821	82.1	0.757	75.7
5.0	4.47	89.4	4.08	81.6
	4.73	94.6	5.05	101
	3.67	73.4	3.58	71.6
	3.76	75.2	3.95	79.0
	4.77	95.4	4.74	94.7
10.0	8.57	85.7	7.61	76.1
	9.10	91.0	8.95	98.5
	9.00	90.0	8.18	81.8
	10.1	101	10.1	101
	7.05	70.5	6.58	65.8

Appendix 3

Permethrin and Esfenvalerate/Fenvalerate Storage Study Results and Recoveries for sediment water on GC-ECD

	Permethrin		Esfenvalerate/Fenvalerate	
Spike Level (ppb)	Result (ppb)	Recovery (%)	Result (ppb)	Recovery (%)
Day 0				
0.1 ppb	0.120	120	0.112	112
spk 1 0.5 ppb	0.483	96.6	0.480	96.0
spk 2 0.5 ppb	0.549	110	0.560	112
spk 3 0.5 ppb	0.571	114	0.582	116
Day 3				
0.1 ppb	0.101	101	0.100	100
spk 1 0.5 ppb	0.382	76.4	0.481	96.2
spk 2 0.5 ppb	0.461	92.2	0.514	103
spk 3 0.5 ppb	0.471	94.2	0.528	106
Day 5				
0.1 ppb	0.099	99	0.088	88
spk 1 0.5 ppb	0.321	64.2	0.456	91.2
spk 2 0.5 ppb	0.387	77.4	0.468	93.6
spk 3 0.5 ppb	0.355	71.0	0.424	84.8
Day 7				
0.1 ppb	0.104	104	0.102	102
spk 1 0.5 ppb	0.289	57.8	0.419	83.8
spk 2 0.5 ppb	0.353	70.6	0.447	89.4
spk 3 0.5 ppb	0.399	79.8	0.459	91.8
Day 10				
0.1 ppb	0.114	114	0.103	103
spk 1 0.5 ppb	0.372	74.4	0.466	93.2
spk 2 0.5 ppb	0.370	74.0	0.468	93.6
spk 3 0.5 ppb	0.372	74.4	0.459	91.8
Day 13				
0.1 ppb	0.103	103	0.0938	93.8
spk 1 0.5 ppb	0.192	38.4	0.466	93.2
spk 2 0.5 ppb	0.345	69.0	0.517	103
spk 3 0.5 ppb	0.331	66.0	0.493	98.6

Spike # 1 for days 0-13 used sediment water that had been stored for sometime, this might have something to do with the lower recoveries.

Appendix 2

Analytical Method: Analysis of metolachlor and degradates by Liquid Chromatography/Mass Spectrometry.

CALIFORNIA DEPT. OF FOOD AND AGRICULTURE
Center for Analytical Chemistry
Environmental Monitoring Section
3292 Meadowview Road
Sacramento, CA. 95832
(916) 262-2080 Fax (916) 262-1572

Method #: EM 38.0
Original Date: 7/1/01
Revised: 10/07/02

Determination of Residues of Alachlor and Metolachlor and Selected Metabolites in Surface Water by Liquid Chromatography-Mass Spectrometry

Scope: This method is for the determination of the residues of Alachlor and Metolachlor and selected metabolites in surface water. These metabolites are ((2-ethyl-6-methylphenyl) (2-methoxy-1-methylethyl)amino) oxo-acetic acid, ((2-ethyl-6-methylphenyl) (2-methoxy-1-methylethyl)amino) 2-oxo-ethanesulfonic acid, ((2,6 diethylphenyl) (methoxymethy)amino) oxo-acetic acid, and ((2,6-diethyl phenyl) (methoxymethyl)amino) 2-oxo-ethanesulfonic acid. These six compounds are analyzed by liquid chromatography with a C-8 reverse phase column with ion trap mass spectrometry in MS/MS mode The reporting limit is 0.05 µg/L for all compounds. The lowest validated spiking level is 0.1 µg/L for all compounds in surface water. The lowest amount standard injected is 0.5 ng, 50 µL of 0.01 ng/µL, for all compounds.

Principle: A 150 mL aliquot of filtered surface water is passed through a C-18 solid phase extraction columns (1 g). The analytes and the adsorbed water are eluted with methanol. The methanol is evaporated at 45 °C with a gentle stream of nitrogen to just below 0.4 mL. A 0.1 mL acetonitrile is added and the final extract volume is adjusted to 0.5 mL with water. The extract is analyzed by LC/MS/MS using a C-8 column and acidified mobile phase. All metabolites are analyzed using ESI negative ion mode. The residues of Alachlor and Metolachlor are analyzed using APCI positive ion mode.

Definitions not in Glossary:

Reagents:

Use residue grade solvents for sample extraction and ultra pure grade solvents (Burdick & Jackson or equivalent) and reagents for HPLC elution and Mass Spectrometry detection.

1. Alachlor, CAS # 015972-60-8, 1.0 mg/mL in methanol, provided by the Standards Repository, Center for Analytical Chemistry, California Department of Food and Agriculture.
2. Metolachlor, CAS #051218-45-2 , 1.0 mg/mL in methanol, provided by the Standards Repository, Center for Analytical Chemistry, California Department of Food and Agriculture

3. Metolachlor OXA, CAS #152019-73-3, 1.0 mg/mL in water, provided by the Standards Repository, Center for Analytical Chemistry, California Department of Food and Agriculture, its chemical name is ((2-ethyl-6-methylphenyl) (2-methoxy-1-methylethyl)amino) oxo-acetic acid.
4. Metolachlor ESA, CAS # not known, 1.0 mg/mL in water, provided by the Standards Repository, Center for Analytical Chemistry, California Department of Food and Agriculture, its chemical name is ((2-ethyl-6-methylphenyl) (2-methoxy-1-methylethyl)amino) 2-oxo-ethanesulfonic acid
5. Alachlor ESA, CAS # not known, 1.0 mg/mL in water, provided by the Standards Repository, Center for Analytical Chemistry, California Department of Food and Agriculture, its chemical name is ((2,6-diethyl phenyl) (methoxymethyl)amino) 2-oxo-ethanesulfonic acid
6. Alachlor OXA, CAS # not known, 1.0 mg/mL in water, provided by the Standards Repository, Center for Analytical Chemistry, California Department of Food and Agriculture its chemical name is (2,6 diethylphenyl) (methoxymethy)amino) oxo-acetic acid
7. Methanol, ultra pure grade from Burdick & Jackson, Cat #230-4 or equivalent
8. Acetonitrile, ultra pure grade from Burdick & Jackson, Cat #o18-04 or equivalent
9. Water, ultra pure grade, Burdick & Jackson, Cat #365-4 or equivalent
10. Acetic acid, HPLC grade Fisher Cat #A35-500 or equivalent
11. Acrodisc® 0.2 µm, Gelman Laboratory, Cat # 09730191.
12. C-18 Solid phase extraction cartridge (1g), Waters Sep-Pak Vac 6 cc, Part #36905 or equivalent
13. Glass fiber filter, Gilman, 47 mm, capable retain particles larger than 1 micron

Safety:

No known carcinogens are used in this method. All general laboratory safety procedures must be followed (e.g. wear safety glasses, gloves, use ventilation hood, etc...)

Equipment:

1. Vacuum manifold, in-house system with multi-channels, a 1 liter glass filtration device attached to each channel.
2. Vacuum manifold, Supelco 24 port model, Cat # 913-0445
3. Larger Volume Sampler, Supelco, Cat #57275
4. Vacuum pump or in-house vacuum, at least 25 inches vacuum
5. Balance, analytical
6. Graduated cylinders
7. Nylon Acrodisc, 0.2 um, Gelman, Part #4436
8. Graduated conical test tube, 15 mL, calibrated for 0.5 mL
9. Nitrogen evaporator, Organomation, Model 112
10. Vortex mixer, Fisher Scientific, Model Vortex-Genie 2
11. Autosampler vial, Waters total recovery vial, 12X32mm and cap with preslit PTFE/Silicon septa, Part #186000385

Instrument: (see detail in operating parameters)

1. HPLC with autosampler and column oven
2. Mass spectrometer

3. Computer

Interference:

The MS/MS detection of all these analytes is specific. Multiple factors are used to eliminate possible interferences. The factors are parent mass $(M-H)^-$, or $(M+H)^+$ and specific daughter ions:

	Parent mass m/z	Parent ion	Daughter ions m/z
Alachlor OXA	264	(M-H)-	192, 160
Alachlor ESA	314	(M-H)-	121
Metolachlor OXA	278	(M-H)-	206
Metolachlor ESA	328	(M-H)-	121, 192
Alachlor	270	$(M+H)^+$	238
Metolachlor	284	$(M+H)^+$	252

Standard Preparation:

The individual stock standards of 1.0 mg/mL are obtained from the Standards Repository, CAC, CDFA. They obtained the neat standards from either the manufactures or from commericial supplers of standards. The individual stock solution of alachlor and metolachlor are prepared in methanol. The individual stock solutions of the four metabolites are prepared in water. They are sealed in ampules and are stored in a refrigerator (less than 5 °C). The working standards of the four metabolites and the two parent compounds are combined and prepared by mixing equal amount of stock solutions, then diluted with a mixtutre of water and acetonitrile (80/20) to the following concentrations: 0.5, 0.2, 0.1, 0.05, 0.02 and 0.01 ng/μL The lowest standard required for the standard curve is 0.017 ng/uL. This concentration equals to the reporting limit of 0.05 ppb.

Sample Preservation and storage:

Check and record sample temperature upon arrival. Store all samples in a locked designated area in the walk-in refrigerator (less than 5 °C). Return samples to the refrigerator immediately after subsample is taken.

Sample Extraction:

1. Measure 200±0.1 gram surface water into a 500 mL beaker. Do sample spike at this step, if required (such as for MDL, method validation, and continuing QC).
2. Set up a multi-channel vacuum manifold with one liter glass filtration device attached to each channel. Use 47 mm Gelman type A/E glass fiber filter for filtration.
3. Filter the 200 mL sample through the glass fiber filter.
4. Measure 150±0.1 gram of the filtered subsample.
5. Set up a Supelco 24 channels manifold extraction device.

6. Connect a C-18 SPE columns (1 gram) to each channel. Turn off the unused channels of the manifold. Pre-condition the SPE columns by passing 10 mL of methanol followed by 20 mL of D.I. water. Do not allow the columns to go dry.
7. Apply the sample at the rate of 5-10 mL per minute by adjusting the vacuum. The typical operating pressure is about 10-15 inch Hg. Maintain at least 1 cm water level in the column until all sample has passed through the cartridge.
8. As soon as the sample has passed through the column, rinse the beaker with 10 mL of D.I. water and continue the extraction until all the rinsate has passed through the columns. Make sure all the columns are properly labeled before disconnecting them.
9. Remove the sampling tube. Apply a 25 inches vacuum for 5 minutes to allow excess water to be removed.
10. Elute the columns with 10 mL methanol and collecte into a 15 mL graduated conical centrifuge tube. Filter the solution through a 0.2 micron Acrodisc and rinse the tube with 2 mL methanol. Pass the rinsate through the same Acrodisc filter and combine the filtrates
11. Evaporate the eluant in a water bath at 45 °C with a gentle stream of nitrogen. Continue the evaporation to just 0.4 mL. Further evaporation will result in a significant low recovery of Alachlor.
12. Add 0.1 mL of acetonitrile and vortex for 20 seconds. Add water to a final volume of 0.50 mL and vortex for 15 seconds.
13. Transfer the entire content to a Waters total recovery autosampler vial.

Equipment Conditions:

1. HPLC System and Operating Parameters

Instrument: Waters Model 2690 HPLC, gradient pump, autosampler, column heater with remote control through the Finnigan Xcalibur system
Detector: Finnigan LCQ Deca Mass spectrometer
Column: Zorbax SB-C8 4.6 x 150mm 3.5 Micron (part number: Agilent 863953-906)
Precolumn: Phenomenex C-18 4 mm L x 2.0 mm ID cartridge (part number: AJO-4286)
Column Temperature: 40 °C
Solvent: Isocratic: 65% solvent A and 35 % solvent B,
Solvent A: 0.1% acetic acid in methanol (Burdick & Jackson or equivalent)
Solvent B: 0.1% acetic acid in ultra pure water (Burdick & Jackson or equivalent)
Note: A gradient mobile phase profile with the same column and the same mobile phase also works, and the retention times change accordingly, although the separations are not significantly improved. However, the retention time consistency is improved. The parameters of the modification are listed in the table 7 and the verification spike/recovery data of the modified method is listed in the table 8.
Flow rate: 0.6 mL/ min
Injection volume: 50 µL
Retention time:

Alachlor OXA:	8.5 min
Alachlor ESA:	8.8 min
Metolachlor OXA:	9.6 min
Metolachlor ESA:	9.23 min

Alachlor	11.50 min
Metolachlor	12.50 min

Note: An alternative C-8 column or other reversed phase column will probably work. The retention times may be different.
The retention times listed above are for reference only. The retention times of alachlor and metolachlor are consistent. But the retention times of the metabolites are not very consistent. It probably due to the high polarity of the metabolites and the large volume injection.

2. Mass Spectrometry System and Operating Parameters:

Instrumentation:

Finnigan LCQ Deca, ion trap mass spectrometer with ESI ion in negative ion mode for the analysis of metabolites and with APCI ion source in positive ion mode for the analysis of Alachlor and Metolachlor.
Instrument control and data handling: Gateway computer model E-4200 with 10 MB hard disk.
Software: Xcalibur Version 1 SR1.

Tune Methods:
Table 3 for ESI tune methods
Table 5 for APCI tune method

Instrument Method:
Table 4 for ESI instrument methods
Table 6 for APCI instrument method

MS Detector Settings : ESI ion source and negative mode for the analysis of the metabolites. APCI ion source and positive mode for the analysis of the parent compounds.

Instrument Calibration:

A 6 level standard curve is run before and after each sample set. The concentration of working standards are 0.01, 0.02, 0.05, 0.1, 0.2 and 0.5 ng/μL and the injection volume is 50 μL.

Analysis:

Build a sequence table and inject the first standard at least twice to condition the instrument. Input the correct dilution factors. The typical sequence order is standards, blank, spikes, 10 samples and standards, then repeat the order for the second injection .

Calculations:

Calculate the concentration of chemical(s) of a sample as follows:

$$\mu g/L = \frac{\text{(peak area. sample) (std. conc.) (std. vol. injected) (final vol. sample, mL)}}{\text{(peak area. std.) (sample vol. injected) (sample vol., mL)}} \times \text{dilution Factor}$$

The LCQuan software in Xcalibur is used for calculations.
In general, std vol. injected = sample vol. injected.
final volume =0.50 mL
sample vol.= 150 mL
The ions used for calculation are listed in the following table

Analytes	Ions used for calculation
Alachlor	238
Metolachlor	252
Alachlor OXA	192,160
Alachlor ESA	121,160
Metolachlor OXA	206
MetolachlorESA	121,192

Method Performance:

Method Detection Limit:

Method Detection Limit (MDL) refers to the lowest concentration of analytes that a method can detect reliably in either a sample or blank. To determine the MDL, each of the 7 samples containing 200 mL of background American River water supplied by DPR (matrix blank) were spiked separately with 0.1 µg/L (15 ng) of Alachlor OXA, Alachlor ESA, Metolachlor OXA and Metolachlor ESA, Alachlor and Metolachlor. These spiked samples along with a blank were analyzed using the described method. The standard deviation derived from the analytical results of the 7 spiked samples was used to calculate the MDL using the following equation:

$$MDL = t\,S$$

where:

t is the Student 't' value for the 99% confidence level with n-1 degrees of freedom (n-1, 1 - α = 0.99). n represents the number of replicates.

S denotes the standard deviation obtained from replicate analyses.

Reporting Limit:

Report Limit (RL) refers to the level above which quantitative results may be obtained usually 1-5 times the MDL. In this case, the reporting limit is 0.05 µg/L for all six compounds.

Spiking solution and spiking volume:

MDL, method validation and QC spikes are made by spiking 200.0 mL of background surface water obtained for this study , which is from the American River.

The concentration of mixed standard for spiking is 1.0 ng/µL and 30.0 ng/µL for all six compounds. The volumes spiked are as in the following table.

	Sample Size (mL)	Volume Added (µL)		Analyte Spiked (ng)	Equivalent to (µg/L)
Spiking Solution		1.0 ng/µL	30 ng/µL		
MDL	200	20		20	0.1
Validation level 1	200	20		20	0.1
Validation level 2	200	40		40	0.2
Validation level 3	200	100		100	0.5
Validation level 4	200		6.66	200	1.0
Validation level 5	200		13.3	400	2.0
Set QC	200	60		60	0.3

MDL Data:

Table 1

Method Validation Data:

Table 2

Acceptance Criteria:

1. The standard curves at the beginning and end of each sample set should not have a percent change greater than 20%. The % change in response is calculated as follows:
   % Change in response = absolute value of [slope of (STD curve before - STD curve after)/ STD curve before] x 10
2. The sample results are calculated based on the average of two adjacent calibration curves using Xcalibur software.
3. The R^2 of each calibration shall be larger than 0.990
4. The recoveries of the spike recovery shall be within the control limit
5. When the above criteria meet, the chemist may report the average of the two injections.

Discussion:

In the beginning, we developed the parameters of analysis for these metabolites with a used C-18 column. As we changed to an identical new column to run the analysis, the method did not work. The reason is unknown. A renewed effort to use a C-8 column and an isocratic mobile phase, as described in this method, provide us with acceptable results.

We presented two instrument methods for determination of the metabolites. One method does not always meet the acceptance criteria for all analytes. When this happens we run the second method.

It was a difficult task to develop a method to analyze these highly water soluble acidic compounds. In order to get an acceptable chromatogram, addition of acid into the mobile phase is necessary, but too much acid reduces the negative ion ionization. We found that 0.1 % acetic acid in mobile phase gives good chromatograms and the required sensitivity.

The evaporation step, in the sample preparation section (step 9), to reduce the volume to 0.4 mL is critical. We experienced a significant low recovery of Alachlor and slightly low recovery of Metolachlor, if the evaporation continues.

We chose to use isocratic elution in the HPLC operation, which provides us a wide, but symmetrical bell shape peak and stable response. It also provides us more data points across each peak and reproducible results. Later, we found the retention time shift significantly between standards and samples. In order to reduce the retention shifting problem, I tried to use gradient with large amount aqueous in the beginning of sample introduction and return to isocratic in 4 minutes. The change has been verified. (See Tables 7 and 8)

In order to achieve sensitivity and stable response, we have to analyze Alachlor and Metolachlor with APCI ion source and their metabolites with ESI ion source.

This method provides acceptable results, as measured by the average recovery at all spiking level for all six analytes. No residues or interferences are found in background water

Reference:

1. Method of Analysis by the U.S. Geological Survey Organic Geochemistry Research Group-Update and Additions to the Determination of Chloroacetanilide Herbicide Degradation Compounds in Water Using High-Performance Liquid Chromatography/Mass Spectrometry. By E.A. Lee, J.L. Kish, L.R. Zimmerman, and E.M. Thurman
   U.S. Department of the Interior, U.S. Geological Survey.
   Open-File report 01-10
2. Determination of Metolachlor (CGA-24705)and CGA-77102, and their Degradates CGA-50212, CGA-354743, CGA-380168, CGA-37735, CGA-67125, and CGA-41638 in Water by High Performance Liquid Chromatography with Mass Spectrometric Detection Including Validation Data.

Determination of Residues of Alachlor and Metolachlor and Selected Metabolites in Surface water by Liquid Chromatography-Mass Spectrometry

Method Number: AG-682 of Novartis Crop Protection, Inc. Enviromental Safety Department, Enviromental Residue Studies.

Written By: Paul Lee

Paul Lee

Title: Agricultural Chemist III

Approved By: Catherine Cooper

Catherine Cooper

Title: Agricultural Chemist III
Supervisor

Table 1 data derived for MDL determination

Replicates	Spiked Amount (ppb)	Alachlor	Metolachlor	Alachlor OXA	Alachlor ESA	Metolachlor OXA	Metolachlor ESA
1	0.1	0.070	0.077	0.073	0.074	0.061	0.076
2	0.1	0.074	0.089	0.081	0.087	0.076	0.102
3	0.1	0.078	0.093	0.084	0.101	0.069	0.091
4	0.1	0.074	0.089	0.077	0.084	0.065	0.108
5	0.1	0.074	0.093	0.076	0.094	0.071	0.098
6	0.1	0.062	0.079	0.084	0.092	0.066	0.069
7	0.1	0.077	0.093	0.081	0.102	0.079	0.081
Average		0.071	0.093	0.079	0.098	0.075	0.090
STDEV		0.0054	0.0066	0.0034	0.0105	0.0075	0.0138
MDL		0.0169	0.0207	0.0108	0.0331	0.0235	0.0434
RL		0.05	0.05	0.05	0.05	0.05	0.05

Table 2. Surface Water Spike Recovery Data

Spiked (0.1ppb)	Alachlor		Metolachlor		Alachlor OXA		Alachlor ESA	
	Found (ppb)	Recovery	Found (ppb)	Recovery	Found (ppb)	Recovery	Found (ppb)	Recovery
0.10	0.074	74.0%	0.087	87.0%	0.089	89.0%	0.096	96.0%
	0.085	85.0%	0.088	88.0%	0.087	87.0%	0.097	97.0%
	0.074	74.0%	0.082	82.0%	0.090	90.0%	0.092	92.0%
	0.087	87.0%	0.099	99.0%	0.079	79.0%	0.088	88.0%
	0.084	84.0%	0.111	111%	0.078	78%	0.097	97%
0.20	0.175	87.5%	0.199	99.5%	0.181	90.5%	0.201	100.5%
	0.152	76.0%	0.179	89.5%	0.179	89.5%	0.202	101.0%
	0.149	74.5%	0.162	81.0%	0.161	80.5%	0.183	91.5%
	0.160	80.0%	0.184	92.0%	0.160	80.0%	0.184	92.0%
	0.152	76.0%	0.186	93.0%	0.171	85.5%	0.181	90.5%
0.50	0.513	102.6%	0.545	109.00%	0.54	108.00%	0.555	111.00%
	0.45	90.0%	0.502	100.40%	0.531	106.20%	0.557	111.40%
	0.455	91.0%	0.472	94.40%	0.518	103.60%	0.554	110.80%
	0.496	99.2%	0.524	104.80%	0.469	93.80%	0.465	93.00%
	0.503	100.6%	0.524	104.80%	0.466	93.20%	0.503	100.60%
1.00	0.832	83.2%	0.866	86.6%	1.004	100.4%	1.046	104.6%
	0.874	87.4%	0.941	94.1%	0.989	98.9%	1.051	105.1%
	0.902	90.2%	0.920	92.0%	1.000	100.0%	0.938	93.8%
	1.013	101%	1.062	106.2%	0.971	97.1%	0.854	85.4%
	0.943	94.3%	1.091	109.1%	1.003	100.3%	1.018	101.8%
2.0	1.621	81.1%	1.708	85.4%	1.826	91.3%	1.881	94.1%
	1.655	82.8%	1.839	92.0%	1.797	89.9%	1.890	94.5%
	1.720	86.0%	1.751	87.6%	1.896	94.8%	1.818	90.9%
	1.961	98.1%	2.052	102.6%	1.912	95.6%	1.906	95.3%
	1.780	89.0%	1.894	94.7%	1.786	89.3%	1.872	93.6%
Average		87.0%		95.4%		92.5%		97.3%
STDEV		8.8%		8.8%		8.2%		7.1%
Control Range		60.5%-113.4%		69.1%-121.7%		67.7%-117.2%		75.9%-118.6%
Warning Range		69.4%-104.6%		77.9%-113%		76%-108.9%		83.0%-113.5%

Table 2 Continued

Spiked (0.1ppb)	Metolachlor OXA		Metolachlor ESA	
	Found (ppb)	Recovery	Found (ppb)	Recovery
0.10	0.081	81.0%	0.115	115.0%
	0.086	86.0%	0.119	119.0%
	0.076	76.0%	0.108	108.0%
	0.074	74.0%	0.089	89.0%
	0.069	69%	0.065	65%
0.20	0.118	59.0%	0.199	99.5%
	0.126	63.0%	0.206	103.0%
	0.148	74.0%	0.167	83.5%
	0.144	72.0%	0.165	82.5%
	0.139	69.5%	0.189	94.5%
0.50	0.507	101.40%	0.55	110.00%
	0.539	107.80%	0.469	93.80%
	0.499	99.80%	0.461	92.20%
	0.408	81.60%	0.498	99.60%
	0.432	86.40%	0.497	99.40%
1.00	0.904	90.4%	1.031	103.1%
	0.961	96.1%	1.067	106.7%
	0.818	81.8%	0.920	92.0%
	0.899	89.9%	1.049	104.9%
	0.887	88.7%	1.052	105.2%
2.0	1.780	89.0%	2.003	100.2%
	1.892	94.6%	2.072	103.6%
	1.662	83.1%	1.870	93.5%
	1.725	86.3%	1.636	81.8%
	1.668	83.4%	1.882	94.1%
Average		83.4%		97.6%
STDEV		12.0%		11.6%
Control Range		47.5%-119.2%		65.6%-132.5%
Warning Range		59.4%-107.3%		74.3%-120.9%

Determination of Residues of Alachlor and Metolachlor and Selected Metabolites in Surface water by Liquid Chromatography-Mass Spectrometry

Table 3 Tune methods

	Tune method 1	Tune method 2
Capillary Temp (C):	275	225
APCI Vaporizer Temp	0	0
Ion Time (ms):	5	5
Sheath Gas Flow ():	75	29
Aux Gas Flow ():	26	54
Source Type:	ESI	ESI
Injection Waveforms:	Type 1	Type 2
AGC:	On	On
POSITIVE POLARITY		
Source Voltage (kV):	5	4.5
Source Current (uA):	80	80
Capillary Voltage (V):	10	11.5
Tube Lens Offset (V):	-5	93
Octapole RF Amplifie	735	735
Octapole 1 Offset (V)	-6.5	-7.6
Octapole 2 Offset (V)	-8.5	-9.5
Entrance Lens (V):	-20	-12
InterOctapole Lens V	-64	-38
Trap DC Offset Voltag	-10	-10
Zoom Micro Scans:	5	5
Zoom AGC Target:	10000000	10000000
Zoom Max Ion Time (	50	50
Full Micro Scans:	3	3
Full AGC Target:	50000000	50000000
Full Max Ion Time (m	50	50
SIM Micro Scans:	5	5
SIM AGC Target:	20000000	20000000
SIM Max Ion Time (m	200	200
MSn Micro Scans:	2	2
MSn AGC Target:	20000000	20000000
MSn Max Ion Time (r	400	400
NEGATIVE POLARITY		
Source Voltage (kV):	5	6
Source Current (uA):	4.5	4.5
Capillary Voltage (V):	-7	-7
Tube Lens Offset (V):	-60	-60
Octapole RF Amplifie	370	370
Octapole 1 Offset (V)	7.75	7.75
Octapole 2 Offset (V)	10.5	12.5
InterOctapole Lens V	20	34
Entrance Lens (V):	40	36
Trap DC Offset Voltag	10	10
Zoom Micro Scans:	5	5
Zoom AGC Target:	10000000	10000000
Zoom Max Ion Time (	0	0
Full Micro Scans:	3	3
Full AGC Target:	20000000	20000000
Full Max Ion Time (m	50	50
SIM Micro Scans:	5	5
SIM AGC Target:	20000000	20000000
SIM Max Ion Time (m	200	200
MSn Micro Scans:	2	2
MSn AGC Target:	20000000	20000000
MSn Max Ion Time (r	400	400

Determination of Residues of Alachlor and Metolachlor and Selected Metabolites in Surface water by Liquid Chromatography-Mass Spectrometry

Table 4. Instrument Methods

Instrument Method 1		Instrument Method 2	
Instrument Method:	D:\A P LEE\1 year2001\Ala&Meto\8-20-01 try out.meth	Instrument Method:	D:\A P LEE\1 year2001\Ala&Meto\metabolites0-1%acid2-22-01-65-35.meth
MS Run Time (min): 13.50		MS Run Time (min): 15.00	
Divert Valve: in use during run		Divert Valve: in use during run	
Valve State		Valve State	
0	To Waste	0	To Waste
8.07	To Source	7.85	To Source
13.41	To Waste	14.77	To Waste
Contact Closure: not used during run		Contact Closure: not used during run	
MS Detector Settings:		MS Detector Settings:	
Acquisition Start Delay (min): 7.50		Acquisition Start Delay (min): 8.00	
Real-time modifications to method disabled		Real-time modifications to method disabled	
Segment 1 Information		Segment 1 Information	
Duration (min): 13.50		Duration (min): 15.00	
Number of Scan Events: 4		Number of Scan Events: 4	
Tune Method: ESI 8-20-01		Tune Method:	ESI negative high flow tune10-10-00acidwaveform2
Scan Event Details:		Scan Event Details:	
1: Neg (278.0)->o(75.0-350.0)		1: Neg (278.0)->o(75.0-350.0)	
MS/MS: CE 34.0% IsoW 2.0		MS/MS: CE 20.0% IsoW 2.0	
2: Neg (328.0)->o(90.0-350.0)		2: Neg (328.0)->o(90.0-350.0)	
MS/MS: CE 44.0% IsoW 2.0		MS/MS: CE 35.0% IsoW 2.0	
3: Neg (264.0)->o(70.0-350.0)		3: Neg (264.0)->o(70.0-350.0)	
MS/MS: CE 32.0% IsoW 2.0		MS/MS: CE 31.0% IsoW 2.0	
4: Neg (314.0)->o(85.0-350.0)		4: Neg (314.0)->o(85.0-350.0)	
MS/MS: CE 33.0% IsoW 2.0		MS/MS: CE 35.0% IsoW 2.0	
Custom Dependent Data Settings:		Custom Dependent Data Settings:	
Not enabled		Not enabled	

Determination of Residues of Alachlor and Metolachlor and Selected Metabolites in Surface water by Liquid Chromatography-Mass Spectrometry

Table 5. APCI Tune Method	
Capillary Temp (C):	150
APCI Vaporizer Temp (C):	500
Ion Time (ms):	5
Sheath Gas Flow ():	89
Aux Gas Flow ():	3
Source Type:	APCI
Injection Waveforms:	Off
AGC:	On
POSITIVE POLARITY	
Source Voltage (kV):	6
Source Current (uA):	5
Capillary Voltage (V):	44
Tube Lens Offset (V):	55
Octapole RF Amplifier (Vp-p):	400
Octapole 1 Offset (V):	-4.75
Octapole 2 Offset (V):	-8
Entrance Lens (V):	-16
InterOctapole Lens Voltage (V)	-52
Trap DC Offset Voltage (V):	-10
Zoom Micro Scans:	5
Zoom AGC Target:	20000000
Zoom Max Ion Time (ms):	50
Full Micro Scans:	1
Full AGC Target:	50000000
Full Max Ion Time (ms):	300
SIM Micro Scans:	3
SIM AGC Target:	20000000
SIM Max Ion Time (ms):	100
MSn Micro Scans:	1
MSn AGC Target:	20000000
MSn Max Ion Time (ms):	1000
NEGATIVE POLARITY	
Source Voltage (kV):	5
Source Current (uA):	80
Capillary Voltage (V):	-47
Tube Lens Offset (V):	-35
Octapole RF Amplifier (Vp-p):	120
Octapole 1 Offset (V):	6.25
Octapole 2 Offset (V):	12
InterOctapole Lens Voltage (V)	68
Entrance Lens (V):	52
Trap DC Offset Voltage (V):	10
Zoom Micro Scans:	5
Zoom AGC Target:	20000000
Zoom Max Ion Time (ms):	0
Full Micro Scans:	3
Full AGC Target:	50000000
Full Max Ion Time (ms):	150
SIM Micro Scans:	5
SIM AGC Target:	20000000
SIM Max Ion Time (ms):	200
MSn Micro Scans:	2
MSn AGC Target:	20000000
MSn Max Ion Time (ms):	800

Tabl 6 APCI Instrument Method				
Instrument Method:	D:\A P LEE\1 year2001\Ala&Meto\parent apci 4-15-01.meth			
MS Run Time (min): 15.00				
Divert Valve: in use during run	Valve State			
Divert Time (min)				
0	To Waste			
5	To Source			
Contact Closure: not used during run				
MS Detector Settings:				
Acquisition Start Delay (min): 8.00				
Real-time modifications to method disabled				
Segment 1 Information				
Duration (min): 15.00				
Number of Scan Events: 2				
Tune Method: apci high flow 238 tune				
Scan Event Details:				
1: Pos (284.0)->o(75.0-290.0)				
MS/MS: CE 25.0% IsoW 3.0				
2: Pos (270.0)->o(150.0-290.0)				
MS/MS: CE 25.0% IsoW 3.0				
Custom Dependent Data Settings:				
Not enabled				

Table 7 Method Modification Table

		Original method	Modified method
HPLC	Mode	Isocratic 65% solution A and 35% solution B	Gradient 0 min 10%A 90%B 2 min 10%A 90%B 4 min 65%A 35%B 16 min 65%A 35%B 18 min 10%A 90%B 20 min 10%A 90%B
	Injection volume	50 µL	Unchanged
MS	Parameters		Unchanged

Determination of Residues of Alachlor and Metolachlor and Selected Metabolites in Surface water by Liquid Chromatography-Mass Spectrometry

Table 8 Method Modification Verification Spike/recovery Data

Verification #1

Date: 9-13-2002

		Alachlor OXA				Alachlor ESA			
	injection #	Calibrateded by linear and Forced 0		Calibrateded by linear and included 0		Calibrateded by linear and Forced 0		Calibrateded by linear and included 0	
Spiked (ppb)		Found (ppb)	Recovery (%)	Found (ppb)	Recovery (%)	Found (ppb)	Recovery (%)	Found (ppb)	Recovery (%)
0.1	1	0.083	83.0%	0.088	88.0%	0.075	75.0%	0.086	86.0%
	2	0.088	88.0%	0.101	101.0%	0.071	71.0%	0.084	84.0%
0.2	1	0.149	74.5%	0.158	79.0%	0.150	75.0%	0.160	80.0%
	2	0.171	85.5%	0.183	91.5%	0.157	78.5%	0.168	84.0%
0.5	1	0.458	91.6%	0.466	93.2%	0.475	95.0%	0.481	96.2%
	2	0.502	100%	0.511	102%	0.438	87.6%	0.447	89.4%
1	1	0.805	80.5%	0.796	79.6%	0.965	96.5%	0.978	97.8%
	2	0.916	91.6%	0.932	93.2%	0.92	92.0%	0.937	93.7%
2	1	1.667	83.4%	1.674	83.7%	1.776	88.8%	1.804	90.2%
	2	1.786	89.3%	1.819	91.0%	1.765	88.3%	1.799	90.0%

		Metolachlor OXA				Metolachlor ESA			
	injection #	Calibrateded by linear and Forced 0		Calibrateded by linear and included 0		Calibrateded by linear and Forced 0		Calibrateded by linear and included 0	
Spiked (ppb)		Found (ppb)	Recovery (%)	Found (ppb)	Recovery (%)	Found (ppb)	Recovery (%)	Found (ppb)	Recovery (%)
0.1	1	0.078	78.0%	0.084	84.0%	0.070	70.0%	0.093	93.0%
	2	0.086	86.0%	0.094	94.0%	0.060	60.0%	0.102	102%
0.2	1	0.163	81.5%	0.168	84.0%	0.154	77.0%	0.176	88.0%
	2	0.16	80.0%	0.168	84.0%	0.165	82.5%	0.202	101%
0.5	1	0.427	85.4%	0.43	86.0%	0.453	90.6%	0.468	93.6%
	2	0.438	87.6%	0.443	88.6%	0.421	84.2%	0.448	89.6%
1	1	0.8	80.0%	0.808	80.8%	0.955	95.5%	0.983	98.3%
	2	0.869	86.9%	0.88	88.0%	0.915	91.5%	0.968	96.8%
2	1	1.598	79.9%	1.611	80.6%	1.912	95.6%	1.969	98.5%
	2	1.825	91.3%	1.839	92.0%	1.797	89.9%	1.904	95.2%

Verification #2

Date 9-18-2002

		Alachlor OXA				Alachlor ESA			
	injection #	Calibrateded by linear and Forced 0		Calibrateded by linear and included 0		Calibrateded by linear and Forced 0		Calibrateded by linear and included 0	
Spiked (ppb)		Found (ppb)	Recovery (%)	Found (ppb)	Recovery (%)	Found (ppb)	Recovery (%)	Found (ppb)	Recovery (%)
0.1	1	0.086	86.0%	0.107	107.0%	0.068	68.0%	0.086	86.0%
	2	0.077	77.0%	0.099	99.0%	0.071	71.0%	0.088	88.0%
0.2	1	0.171	85.5%	0.19	95.0%	0.172	86.0%	0.188	94.0%
	2	0.158	79.0%	0.178	89.0%	0.157	78.5%	0.173	86.5%
0.5	1	0.454	90.8%	0.467	93.4%	0.405	81.0%	0.417	83.4%
	2	0.391	78.2%	0.406	81.2%	0.397	79.4%	0.409	81.8%
1	1	0.788	78.8%	0.818	81.8%	0.859	85.9%	0.882	88.2%
	2	0.805	80.5%	0.834	83.4%	0.832	83.2%	0.856	85.6%
2	1	1.486	74.3%	1.547	77.4%	1.74	87.0%	1.786	89.3%
	2	1.619	81.0%	1.678	83.9%	1.788	89.4%	1.834	91.7%

		Metolachlor OXA				Metolachlor ESA			
	injection #	Calibrateded by linear and Forced 0		Calibrateded by linear and included 0		Calibrateded by linear and Forced 0		Calibrateded by linear and included 0	
Spiked (ppb)		Found (ppb)	Recovery (%)	Found (ppb)	Recovery (%)	Found (ppb)	Recovery (%)	Found (ppb)	Recovery (%)
0.1	1	0.092	92.0%	0.094	94.0%	0.067	67.0%	0.081	81.0%
	2	0.078	78.0%	0.081	81.0%	0.064	64.0%	0.078	78.0%
0.2	1	0.175	87.5%	0.177	88.5%	0.153	76.5%	0.166	83.0%
	2	0.171	85.5%	0.174	87.0%	0.151	75.5%	0.164	82.0%
0.5	1	0.401	80.2%	0.403	80.6%	0.408	81.6%	0.417	83.4%
	2	0.381	76.2%	0.383	76.6%	0.397	79.4%	0.406	81.2%
1	1	0.835	83.5%	0.839	83.9%	0.889	88.9%	0.907	90.7%
	2	0.839	83.9%	0.843	84.3%	0.837	83.7%	0.855	85.5%
2	1	1.739	87.0%	1.747	87.4%	1.888	94.4%	1.922	96.1%
	2	1.857	92.9%	1.864	93.2%	1.805	90.3%	1.841	92.1%

Appendix 3

Analytical Method: Analysis of OP Pesticides by Gas Chromatography.

California Department of Food and Agriculture
Center for Analytical Chemistry
Environmental Monitoring Section
3292 Meadowview Road
Sacramento, CA 95832

EMON-SM-46.0
Revision:
Revision Date:
Original Date: 10/10/2002

Title: Determination of Organophosphate Pesticides in Surface water using Gas Chromatography

1. Scope:

   This section method (SM) documents the selected organophosphate pesticides analysis in surface water by all authorized section personnel.

2. Principle:

   The surface water sample is extracted with methylene chloride. The extract is passed through sodium sulfate to remove residual water. The anhydrous extract is evaporated to almost dryness on a rotary evaporator and diluted to a final volume of 1.0 mL with acetone. The extract is then analyzed by a gas chromatograph equipped with flame photometric detector (FPD) and any positive result is confirmed by mass selective detector (MSD).

3. Safety:

   3.1 All general laboratory safety rules for sample preparation and analysis shall be followed.

   3.2 Methylene chloride is a regulated and controlled carcinogenic hazardous substance. It must be stored and handled in accordance with California Code of Regulations, Title 8, Subchapter 7, Group 16, Article 110, Section 5202.

   3.3 All solvents should be handled with care in a ventilated area.

4. Interferences:

   There are matrix interferences that cause quantitative problems. Therefore the calibration standards will be made up in appropriate matrix.

5. Apparatus and Equipment:

   5.1 Rotary evaporator (Büchi/Brinkman or equivalent)
   5.2 Nitrogen evaporator (Meyer N-EVAP Organomation Model # 112 or equivalent)
   5.3 Vortex-vibrating mixer
   5.4 Balance (Mettler PC 4400) or equivalent

5.5 Gas Chromatograph equipped with a flame photometric detector (FPD) in phosphorus mode
5.6 Gas Chromatograph equipped with mass selective detector(MSD)

6. Reagents and Supplies

6.1 Methylene Chloride, nanograde or equivalent pesticide grade
6.2 Acetone, nanograde or equivalent pesticide grade
6.3 Anhydrous Sodium Sulfate, granular
6.4 Ethoprophos CAS# 13194-48-4
6.5 Diazinon CAS# 333-41-5
6.6 Disulfoton CAS# 298-04-4
6.7 Chlorpyrifos CAS# 2921-88-2
6.8 Malathion CAS# 121-75-5
6.9 Methidation CAS# 950-37-8
6.10 Fenamiphos CAS# 22224-92-6
6.11 Azinphos Methyl CAS# 86-50-0
6.12 Dichlorvos CAS# 62-73-7
6.13 Phorate CAS# 298-02-2
6.14 Fonofos CAS# 66767-39-3
6.15 Dimethoate CAS# 60-51-5
6.16 Parathion methyl CAS# 298-00-0
6.17 Tribufos (DEF) CAS# 13071-79-9
6.18 Profenofos CAS# 41198-08-7
6.19 Conical tube with glass stopper, 15-mL graduated, 0.1 mL subdivision
6.20 Separatory funnel, 2 L
6.21 Boiling flask, 500 mL
6.22 Whatman filter paper, #4, 15 cm
6.23 Funnel, long stem, 10 mm diameter
6.24 Disposable Pasteur pipettes, and other laboratory ware as needed
6.25 Recommended analytical columns:

For FPD – Restek's Rtx® - OPPesticides (fused silica column), 30 m x 0.25 mm x 0.4 µm film thickness or 30 m x 0.32 mm x 0.5 µm film thickness, and Rtx® - OPPesticides2 (fused silica column), 30 m x 0.25 mm x 0.25 µm film thickness or 30 m x 0.32 mm x 0.32 µm film thickness.

For MSD - 5% phenyl Methylsilicone (HP-5ms or equivalent) fused silica column, 30 m x 0.25 mm x 0.25 µm film thickness.

7. Standards Preparation:

   7.1 Dilute the 1 mg/mL Organophosphate standards obtained from the CDFA/CAC Standards Repository with acetone to make up a series of mixed working standards(see 10.2). These standards shall be prepared to cover the linear range from 0.025 ηg/μL to 0.5 ηg/μL.

   7.2 The calibration standards are added to matrix blank extracts (9.1.2.1) to correct for matrix background interference.

   7.3 Keep all standards in designated refrigerator for storage.

   7.4 The expiration date of each mixed working standard is six months from the preparation date.

8. Sample Preservation and Storage:

   All water samples and sample extracts shall be stored in the refrigerator (32-40 ° F).

9. Test Sample Preparation:

   9.1 Sample Preparation

      9.1.1 Remove samples from refrigerator and allow samples to come to room temperature before extraction.

      9.1.2 Preparation of matrix blank and matrix spike:

         The Department of Pesticide Regulations (DPR) provide the background water for matrix blank and spikes.

         9.1.2.1 Matrix blank: Weigh out 1000 g of background water and follow the test sample extraction procedure.

         9.1.2.2 Matrix spike: Weigh out 1000 g of background water. Spike a client requested amount of organophosphate pesticides into the background water and let it stand for 1 minute. Follow the test sample extraction procedure.

9.2 Test Sample Extraction

9.2.1 Record the weight of water by subtracting the weight of the sample container before and after water has been transferred into a separatory funnel.

9.2.2 Shake with 100 mL of methylene chloride for 2 minutes. Vent frequently to relieve pressure.

9.2.3 After phases have separated, drain lower methylene chloride layer through 20 g of anhydrous sodium sulfate, into a 500 mL boiling flask.

9.2.4 Repeat steps 9.2.2 & 9.2.3 two more times using 80 mL of methylene chloride each time. Combine the extracts in the same boiling flask.

9.2.5 After draining the final extraction, rinse the sodium sulfate with 25 mL of methylene chloride.

9.2.6 Evaporate the sample extract to ~ 3 mL on a rotary evaporator using a water bath at ~ 35 °C and ~ 15 - 20 inch Hg vacuum. Add ~ 3 mL of acetone and rotoevaporate to 1 - 2 mL. Transfer the extract to a calibrated 15 mL graduated test tube.

9.2.7 Rinse flask 3 more times with 3 mL of acetone and transfer each rinse to the same test tube.

9.2.8 Evaporate the extract to a volume slightly less than 1 mL in a water bath at 25 to 35 ° C under a gentle stream of nitrogen. Then bring to a final volume of 1 mL with acetone, mix well and transfer into two autosampler vials.

9.2.9 Submit extract for GC analysis.

10. Instrument Calibration:

10.1 The calibration standards are added to a matrix blank extract to correct for matrix background interference.

10.2 A calibration standard curve consists of minimum of three levels. The concentration of 0.025, 0.05, 0.1, 0.25, 0.5 or 1.0 ηg/μL standards are recommended. Calibration is obtained using a linear or quadratic regression with the correlation coefficient (r) equal to or greater than 0.995.

10.3 Suggested composition of calibration mixed standards are as follow.

OP-1 Mixed Standard	OP-2 Mixed Standard
Ethoprophos	Dichlorvos
Diazinon	Phorate
Disulfoton	Fonofos
Chlorpyifos	Dimethoate
Malathion	Parthion-methyl
Methidathion	DEF
Fenamiphos	Profenofos
Azinphos-methyl	

11. Analysis:

11.1 Injection Scheme

Follow the sequence of Solvent, Calibration standards, Solvent, Matrix Bank, Matrix Spike, Test Samples (maximum of 10-12 samples) and Calibration standards. Inject an old sample or matrix blank before the sequence analysis to condition the instrument is recommended.

11.2 GC Instrumentation

11.2.1 Analyze OP pesticides by a gas chromatograph equipped with two flame photometric detectors and two different columns.

11.2.2 Recommended instrument (GC/FPD) parameters: Injector 250 °C; detector 250 °C; oven temperature 80 °C (hold 2 min.) to 180 °C @ 20 °C/min. to 280 °C @ 6 °C/min. (hold 6 min.); injection volume 4 µL.

11.2.3 Confirm OP pesticides by a gas chromatograph equipped with mass selective detector.

11.2.4 Recommended instrument (GC/MSD) parameters: Injector 250 °C; MSD transfer line heater 280 °C; oven temperature 70 °C (hold 1 min.) to 190 °C @ 15 °C/min.(hold 2 min.) to 250 °C@ 15 °C/min. (hold 6 min.); injection volume 4 µL.

12. Quality Control:

12.1 Each set of samples shall have a matrix blank and minimum of one matrix spike sample.

12.2 The matrix blank shall be free of target compounds.

12.3 The recoveries of the matrix spike should be within the control limits.

12.4 The retention time shall be within ± 2 per cent of that of the standard.

12.5 The sample must be diluted if results fall outside the linear range of the standard curve.

12.6 Bracketing standard curves should have a percent change less than 15 % for most of organophosphate compounds, and 20 – 25 % for late eluted OP compounds.

12.7 Method Detection Limits (MDL)

The method detection limit refers to the lowest concentration of analyte that a method can detect reliably. To determine the MDL, 7 replicate water samples are spiked at 0.05 ppb. The standard deviation from the spiked sample recoveries are used to calculate the MDL for each analyte using the follow equation:

$$MDL = tS$$

Where t is the Student t test value for the 99% confidence level with n-1 degrees of freedom and S denotes the standard deviation obtained from n replicate analyses. For the n=7 replicate used to determine the MDL, t=3.143.

12.8 Reporting limit (RL):

The reporting limit (RL) refers to the level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. Agreed upon per client agreement, the RL is chosen in a range 1-5 times the MDL.

MDL data and the RL are tabulated in Appendix I.

12.9 Method Validation Recovery Data and Control Limits:

12.9.1 The method validation consisted of five samples sets. Each set included seven levels of fortification (0.05, 0.1, 0.25, 0.5, 1.0, 2.0, and 5.0 ppb) and a method blank. All spikes and method blank samples were processed through the entire analytical method.

12.9.2 Upper and lower warning and control limits are set at ± 2 and 3 standard deviations of the average % recovery, respectively.

Method validation results and control limits are tabulated in Appendix II.

13. Calculations:

Quantitation is based on external standard (ESTD) calculation using either the peak area or height. The software uses a linear or quadratic curve fit, with all levels weighted equally. Alternatively, at chemist discretion, concentrations may be calculated using the response factor for the standard whose value is closest to the level in the sample.

$$\text{ppb} = \frac{\text{(sample peak ht. or area) (std. conc.) (std. vol. injected) (sample final vol., (mL))(1000 µL/mL)}}{\text{(std. peak ht. or area) (sample vol. injected) (sample wt., g)}}$$

14. Reporting Procedure:

14.1 Identification of Analyte

For responses within calibration range, compare the retention time of the peaks with the retention time of standards. For positive results retention times shall not vary from the standards more than 2 percent.

14.2 The Restek's Rtx® - OPPesticides column is used as the primary analytical column, the 2nd column, Rtx® - OPPesticides2 column and GC/MSD used as confirmation.

Sample results and the data reported in the Appendix I and II were calculated from the Rtx® - OPPesticides column.

14.3 Sample results are reported out according to the client's analytical laboratory specification sheet.

15. Discussion and References:

15.1 Sample response and quantitation vary depending on matrix background in the samples. The calibration standards were added to a matrix blank extract to correct for matrix background interference.

15.2 Two different sizes of analytical column (ID of 0.25 and 0.32 mm) were used in this method. The column with larger ID (0.32 mm) seems to give more reproducible results, since 4 µL sample extract was injected.

The retention times for OP pesticides are tabulated in Appendix III.

15.3 Some of the late eluting compounds were observed to suffer gradual losses in sensitivity. We recommend changing the injector liner and trimming the column when this occurs.

16. References:

16.1 *EPA Method 507, Pesticides, Capillary Column.* EPA Test Method for Drinking Water and Raw Source Water, 1987.

16.2 Hsu, J. and Hernandez J. *Determination of Organophosphate Pesticides in Surface Water using Gas Chromatography,* 1997, Environmental Monitoring Method, Center for Analytical Chemistry, CDFA.

APPENDIX I

The determination of Method Detection Limit (MDL) data and Reporting Limit (RL)

Spk \ Analyte	Ethoprophos	Diazinon	Disulfoton	Chlorpyrofos	Malathion
0.05 ppb spk1	0.0503	0.0580	0.0528	0.0573	0.0602
0.05 ppb spk2	0.0500	0.0561	0.0513	0.0552	0.0581
0.05 ppb spk3	0.0482	0.0524	0.0490	0.0534	0.0555
0.05 ppb spk4	0.0538	0.0582	0.0525	0.0616	0.0657
0.05 ppb spk5	0.0498	0.0548	0.0514	0.0574	0.0600
0.05 ppb spk6	0.0559	0.0593	0.0569	0.0617	0.0630
0.05 ppb spk7	0.0469	0.0496	0.0477	0.0534	0.0558
SD	0.00313	0.00349	0.00296	0.00348	0.00371
MDL	0.0098	0.0110	0.0093	0.0109	0.0117
RL	0.050	0.040	0.040	0.040	0.050

Spk \ Analyte	Methidathion	Fenamiphos	Dichlorvos	Phorate	Fonofos
0.05 ppb spk1	0.0576	0.0610	0.0417	0.0458	0.0476
0.05 ppb spk2	0.0574	0.0585	0.0476	0.0468	0.0486
0.05 ppb spk3	0.0540	0.0587	0.0461	0.0474	0.0493
0.05 ppb spk4	0.0643	0.0683	0.0393	0.0404	0.0430
0.05 ppb spk5	0.0613	0.0638	0.0398	0.0459	0.0485
0.05 ppb spk6	0.0628	0.0674	0.0422	0.0429	0.0451
0.05 ppb spk7	0.0599	0.0608	0.0416	0.0476	0.0503
SD	0.00355	0.00397	0.00311	0.00266	0.00256
MDL	0.0111	0.0125	0.0098	0.0083	0.0080
RL	0.050	0.050	0.050	0.050	0.040

Spk \ Analyte	Dimethoate	Propenofos	DEF	Parathion Methyl	Azinophos Methyl
0.05 ppb spk1	0.0502	0.0538	0.0558	0.0495	0.0612
0.05 ppb spk2	0.0502	0.0541	0.0555	0.0503	0.0606
0.05 ppb spk3	0.0495	0.0526	0.0544	0.0501	0.0621
0.05 ppb spk4	0.0468	0.0519	0.0520	0.0464	0.0678
0.05 ppb spk5	0.0472	0.0535	0.0576	0.0499	0.0631
0.05 ppb spk6	0.0431	0.0440	0.0448	0.0440	0.0671
0.05 ppb spk7	0.0486	0.0545	0.0579	0.0509	0.0598
SD	0.00253	0.00371	0.00452	0.00254	0.00316
MDL	0.0079	0.0114	0.0142	0.0080	0.0099
RL	0.050	0.050	0.050	0.030	0.050

All concentrations are expressed in ppb.

APPENDIX II

Method Validation Data and Control Limit

Analyte	Spike ppb	Recovery (%) Set 1	Set 2	Set 3	Set 4	Set 5	%
Ethoprop	0.05	95.6	64.2	100.0	79.0	91.8	Mean: 91.6
	0.10	88.0	76.1	100.5	94.6	88.4	SD: 10.48
	0.25	84.8	90.8	86.0	90.0	82.0	
	0.50	91.2	88.0	100.6	84.0	84.8	UCL: 123.0
	1.0	83.7	82.6	87.9	76.2	96.7	UWL: 112.6
	2.0	107.2	103.9	95.6	91.6	90.8	LWL: 70.7
	5.0	113.1	108.9	97.2	107.6	103.2	LCL: 60.2
Diazinon	0.05	100.8	69.2	104.0	85.2	96.2	Mean: 96.6
	0.10	173.0	80.0	102.3	95.3	90.7	SD: 16.83
	0.25	90.0	94.0	88.0	91.2	84.0	
	0.50	93.4	89.8	100.8	88.6	87.2	UCL: 147.0
	1.0	85.4	87.2	88.1	79.9	97.9	UWL: 130.2
	2.0	106.5	104.4	96.7	92.1	92.6	LWL: 62.9
	5.0	109.4	123.5	98.3	113.6	100.1	LCL: 46.1
Disulfoton	0.05	95.2	58.8	92.4	80.2	83.0	Mean: 88.3
	0.10	88.0	70.5	96.7	92.3	82.2	SD: 10.09
	0.25	87.2	87.2	84.0	76.4	84.7	
	0.50	91.6	82.6	98.0	78.8	80.0	UCL: 118.6
	1.0	83.9	82.5	83.6	75.3	92.0	UWL: 108.5
	2.0	100.1	100.7	94.3	87.6	90.0	LWL: 68.1
	5.0	103.8	103.7	96.2	106.8	96.4	LCL: 58.0
Chlorpurifos	0.05	95.6	69.0	102.0	90.2	94.2	Mean: 94.5
	0.10	92.5	83.1	101.5	97.1	91.1	SD: 8.84
	0.25	92.4	95.2	88.4	90.0	116.4	
	0.50	95.0	89.4	99.6	91.6	86.4	UCL: 121.1
	1.0	86.0	91.9	87.6	81.7	97.7	UWL: 112.2
	2.0	102.8	101.2	96.3	90.1	91.2	LWL: 76.9
	5.0	105.8	107.5	98.1	111.4	98.7	LCL: 68.0

APPENDIX II (Continued)

Method Validation Data and Control Limit

Analyte	Spike ppb	Recovery (%) Set 1	Set 2	Set 3	Set 4	Set 5	%
Malathion	0.05	97.4	66.4	102.2	88.2	95.2	Mean: 95.7
	0.10	91.1	86.4	100.6	94.4	91.8	SD: 10.01
	0.25	92.8	97.6	90.0	86.8	84.0	
	0.50	95.4	91.0	1002	95.4	88.6	UCL: 125.7
	1.0	85.8	91.5	86.8	87.7	96.3	UWL: 115.7
	2.0	109.4	110.5	101.0	96.1	96.3	LWL: 75.7
	5.0	114.	112.6	102.5	117.8	105.0	LCL: 65.7
Methidathion	0.05	101.0	66.2	103.6	89.0	93.4	Mean: 95.9
	0.10	91.8	84.3	101.3	94.4	93.0	SD: 10.65
	0.25	92.0	89.6	88.8	84.0	84.8	
	0.50	93.0	89.4	99.6	95.0	89.8	UCL: 127.8
	1.0	84.9	93.0	86.0	93.3	96.7	UWL: 117.2
	2.0	111.1	111.3	102.0	97.3	96.8	LWL: 74.6
	5.0	116.4	113.7	106.0	118.6	104.4	LCL: 63.9
Fenamiphos	0.05	99.4	67.8	104.0	93.6	90.4	Mean: 96.2
	0.10	90.8	90.3	104.2	98.2	94.4	SD: 9.43
	0.25	92.8	97.2	90.0	90.0	84.4	
	0.50	95.4	90.4	100.0	95.6	88.4	UCL: 124.5
	1.0	85.8	94.6	88.2	86.3	97.5	UWL: 115.1
	2.0	108.9	106.3	101.7	94.6	97.2	LWL: 77.3
	5.0	110.3	113.0	103.4	117.8	104.0	LCL: 67.9
Azinphos Methyl	0.05	85.4	59.0	98.6	71.2	92.8	Mean: 93.2
	0.10	79.6	4.2	96.0	107.4	95.2	SD: 14.58
	0.25	83.2	86.8	84.0	84.8	89.6	
	0.50	82.6	80.0	99.4	83.4	91.6	UCL: 136.9
	1.0	77.1	90.2	83.7	113.1	90.0	UWL: 122.3
	2.0	108.3	113.5	101.1	96.6	92.2	LWL: 64.0
	5.0	124.9	113.6	112.5	118.8	101.2	LCL: 49.4

APPENDIX II (Continued)

Method Validation Data and Control Limit

Analyte	Spike ppb	Recovery (%) Set 1	Set 2	Set 3	Set 4	Set 5	%
Dichlorvos	0.05	72.6	95.6	95.2	72.6	82.6	Mean: 82.6
	0.10	92.3	91.5	91.1	82.3	81.1	SD: 7.80
	0.25	87.2	78.0	77.6	87.2	77.2	
	0.50	83.0	79.0	85.0	83.0	55.6	UCL: 106.0
	1.0	82.9	82.3	79.1	82.9	77.2	UWL: 98.2
	2.0	82.1	82.5	92.2	80.7	78.7	LWL: 67.0
	5.0	83.5	99.0	81.6	90.0	76.2	LCL: 59.2
Phorate	0.05	83.4	89.0	95.6	83.4	86.8	Mean: 87.9
	0.10	82.8	90.5	97.6	82.8	85.3	SD: 7.21
	0.25	90.4	86.0	83.2	90.4	80.8	
	0.50	85.2	83.4	94.2	852	75.6	UCL: 109.5
	1.0	80.7	79.5	87.5	80.7	78.7	UWL: 102.3
	2.0	92.1	86.1	100.3	91.3	84.1	LWL: 73.5
	5.0	100.6	106.2	90.9	102.5	84.0	LCL: 66.3
Fonofos	0.05	88.2	92.0	101.4	88.2	89.4	Mean: 90.3
	0.10	85.9	92.2	100.4	85.9	87.3	SD: 7.40
	0.25	91.6	86.8	86.0	91.6	82.8	
	0.50	86.0	83.4	97.2	86.0	79.2	UCL: 112.5
	1.0	81.6	78.2	91.1	81.6	81.6	UWL: 105.1
	2.0	94.7	88.9	105.1	95.1	88.1	LWL: 75.5
	5.0	97.9	107.3	95.4	104.7	88.1	LCL: 68.1
Dimethoate	0.05	96.2	96.6	88.4	96.2	84.6	Mean: 90.5
	0.10	82.7	95.4	95.8	82.7	86.5	SD: 8.67
	0.25	93.2	82.4	82.8	93.2	78.8	
	0.50	91.8	76.0	97.8	91.8	79.2	UCL: 116.6
	1.0	104.2	68.2	97.7	104.2	83.2	UWL: 107.9
	2.0	88.5	89.7	103.6	93.6	90.8	LWL: 73.2
	5.0	92.6	101.0	86.4	106.2	87.0	LCL: 64.5

APPENDIX II (Continued)

Method Validation Data and Control Limit

Analyte	Spike ppb	Recovery (%) Set 1	Set 2	Set 3	Set 4	Set 5	%
Parathion Methyl	0.05	93.2	99.0	97.2	93.2	91.4	Mean: 93.7
	0.10	86.1	98.6	101.4	86.1	88.1	SD: 8.55
	0.25	97.2	87.2	92.8	97.2	82.4	
	0.50	91.4	81.2	105.2	91.4	79.8	UCL: 119.3
	1.0	98.9	73.4	110.8	98.9	84.2	UWL: 110.8
	2.0	91.9	90.3	105.9	98.6	91.6	LWL: 76.6
	5.0	97.2	105.1	90.2	111.5	90.5	LCL: 68.0
DEF	0.05	96.6	97.2	102.4	96.6	92.6	Mean: 95.3
	0.10	91.6	98.3	106.7	91.6	90.3	SD: 10.2
	0.25	94.0	88.0	96.0	94.0	84.8	
	0.50	92.2	77.6	112.0	92.2	83.4	UCL: 126.0
	1.0	84.3	69.4	108.7	84.3	84.9	UWL: 115.8
	2.0	99.7	94.4	115.1	103.2	93.8	LWL: 74.9
	5.0	103.5	99.7	104.2	118.1	95.9	LCL: 64.7
Profenofos	0.05	96.8	105.2	104.0	97.8	85.4	Mean: 94.3
	0.10	88.0	100.4	104.3	88.0	87.0	SD: 10.06
	0.25	102.0	84.0	94.8	102.0	83.2	
	0.50	95.6	73.0	107.0	95.6	79.8	UCL: 124.5
	1.0	98.5	63.5	105.8	98.5	87.9	UWL: 114.5
	2.0	93.6	91.5	106.5	99.	91.6	LWL: 74.2
	5.0	96.8	96.4	93.5	112.3	92.1	LCL: 64.1

APPENDIX III

Retention Time for OP Pesticides:

RT(min.) / Op Pesticides	Rtx®-OPPesticides column		Rtx®-OPPesticides2 column	
	30m x 0.25mm x 0.4µm	30m x 0.32mm x 0.5µm	30m x 0.25mm x 0.25µm	30m x 0.25mm x 0.32µm
Ethoprophos	11.7	9.7	11.7	9.6
Diazinon	12.5	10.4	13.6	11.2
Disulfoton	13.1	10.9	13.9	11.5
Chlorpyrifos	15.2	12.8	16.5	13.8
Malathion	16.3	13.8	16.2	13.5
Methidation	18.2	15.5	18.7	15.8
Fenamiphos	18.9	16.3	18.9	16.1
Azinphos methyl	23.9	21.0	25.1	21.8
Dichlorvos	8.4	7.0	7.8	6.3
Phorate	11.8	9.8	12.5	10.2
Fonofos	13.0	10.8	13.8	11.3
Dimethoate	14.4	12.0	13.6	11.1
Parathion methyl	16.4	13.8	15.5	12.8
Tribufos (DEF)	17.5	15.0	19.1	16.1
Profenofos	18.3	15.7	19.3	16.3

Author:

Jean Hsu
Agricultural Chemist II

1/14/03
Date

Author:

Hsiao Feng
Agricultural Chemist II

1/14/03
Date

Approved By:

Catherine Cooper
Section Supervisor

1/14/03
Date

Reviewed By:

Terry Jackson
Quality Assurance Officer

1/16/03
Date

Approved By:

Lilia Rivera
Program Supervisor

1/15/03
Date

Revision Log:

Date	What was Revised? Why?

Appendix 4

Analytical Method: Analysis of herbicides by Liquid Chromatography/Mass Spectrometry.

CALIFORNIA DEPT. OF FOOD & AGRICULTURE
Center for Analytical Chemistry
Environmental Monitoring Section
3292 Meadowview Road
Sacramento, CA 95832
(916) 262-2080 Fax (916) 262-1572

Method #: 62.9
Original Date: 7/21/1999
Revised:

Determination of Atrazine, Bromacil, Cyanazine, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), and Diamino Chlorotriazine (DACT) in Well Water By Liquid Chromatography-Atmospheric Pressure Chemical Ionization Mass Spectrometry

Scope: This method is applicable to analysis of Atrazine, Bromacil, Cyanazine, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), and Diamino Chlorotriazine (DACT) in well water using two different HPLC columns. Data obtained from these two columns are presented in this method. The reporting limit for all chemicals is 0.05 µg/g with APCI/LCMS/MS instrument.

Principle: Two conditioned Waters Oasis®MCX Cartridges connected in tandem are used to retain the analytes from well water samples. The cartridges are placed under vacuum to eliminate any remaining water. The chemicals are eluted with 5% ammonium hydroxide in methanol. The eluant is then filtered, concentrated, reconstituted in 75/25 water / methanol and analyzed by APCI/LC/MS/MS. Two different HPLC columns have been validated to provide flexibility to the analyst, and to provide a means of confirmation for samples that have matrix interferences which are not present in the reference well water used for the validations.

Reagents, Equipment and Instruments:

Reagents:

1. Methanol, LCQ grade. Burdick & Jackson 230-4.
2. Distilled water, LCQ grade. Burdick & Jackson 365-4. Burdick & Jackson solvents are available from VWR and other suppliers.
3. Formic acid.
4. Ammonium formate.
5. Ammonium hydroxide.
6. Elution reagent: 5% ammonium hydroxide in methanol.
7. Reconstitution reagent: 75/25 water / methanol.
8. Mobil phase A: 95/5 (10 mM ammonium formate/methanol), 0.1% formic acid. For 500 mL, mix 470 ± 2 mL Burdick & Jackson water, 25 ± 0.5 mL Burdick & Jackson methanol, 4.50 ± 0.25 mL 1 M ammonium formate, and 0.5 ± 0.05 mL formic acid. Double these quantities to prepare 1L.
9. Mobil phase B: 90/10 (methanol/0.1 M ammonium formate), 0.1% formic acid
   For 500 mL, mix 450 ± 2 mL Burdick & Jackson methanol and 45 ± 0.5 mL Burdick & Jackson water with 4.5 ± 0.25 mL of 1 M ammonium formate and 0.5 ± 0.05 mL of formic acid. Double these quantities to prepare 1L.
10. Working standards in 75/25 water / methanol (diluted from stock standards).
    Note: The highest available purity reagents (1,2,3,4,5) should be specified when ordering.

Reagents: (cont.)

Chemicals	*CAS Registry Numbers*
Diamino Chlorotriazine (DACT)	3397-62-4
Deisopropyl Atrazine (ACET)	11007-28-9
Deethyl Atrazine (DEA)	6190-65-4
Metribuzin	21087-64-9
Bromacil	314-40-9
Atrazine	1912-24-9
Norflurazon	27314-13-2
Cyanazine	21725-46-2
Simazine	122-34-9
Hexazinone	51235-04-2
Diuron	330-54-1
Prometon	1610-18-0
Prometryn	7287-19-6
Propazine	139-40-2
Trietazine	1912-26-1

Equipment:

1. In-house vacuum manifold.
2. Solid phase extraction cartridges: Waters Oasis® MCX 6 cc (150 mg), 60-micron particle size cartridge, Waters Division of Millipore Corporation.
3. Nylon Acrodisc®, 0.2 micron, Gelman Sciences.
4. Vac-Elut SPS 24, Varian Analytical.
5. N-EVAP, Meyers Organomation Associates Incorporated-Model 112.
6. Vibrating or vortex mixer.
7. Syringe and plunger for filtration, 10 mL.
8. Graduated test tube, 15 mL (calibrated at 0.5 mL with methanol).

Instruments:

System A:

1. LCQ™LC/MS^n System. ThermoQuest/Finnigan Corporation
2. ThermoQuest/ThermoSeparation Products HPLC system, consisting of the SPC 1000 membrane degasser solvent module, the P4000 quaternary pump module, and the AS3000 autosampler.

System B:

1. LCQ™DECA LC/MS^n System. ThermoQuest/Finnigan Corporation
2. Waters 2690 HPLC system with autosampler.

System B is provided as a back up system in case of the unavailability of system A. This analytical method was validated using system A.

Analysis:

Sample Extraction:

1. Allow each sample to come to room temperature. Pour the sample from 1 L amber glass bottle into a 1000 mL beaker. Record the sample weight in grams (g) by weighing the bottle before and after transfer. Sample weight should be close to 500.0 g. Adjust pH to ~3 with 6N HCL. Add 0.1 µg propazine (100 µL of 1ng/µL spiking solution in methanol) as a surrogate to the sample. Note: The volume of methanol in spiking solution added to the sample should be 0.1% or less of the sample volume.
2. Two MCX cartridges are connected together in tandem and connected to the house vacuum using the manifold as shown in Diagram # 1.
3. Condition the cartridges at a flow rate of about 10 mL/minute with about 15 mL of methanol followed by about 15 mL of purified water by applying vacuum. ***Do not let the cartridges go to dryness***. Turn off the vacuum when the purified water has just passed through the cartridges. Detach the cartridges from the vacuum line and fill up the cartridges with purified water.

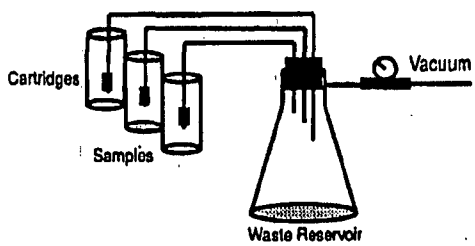


Diagram # 1

4. Reattach the conditioned cartridges to the vacuum line and transfer to the 1000 mL beaker containing the water sample. Allow the sample to pass through the conditioned cartridges by applying vacuum. Adjust the flow rate to about 10 mL/minute to 15 mL/minute.
5. After all of the water sample has passed through the cartridges, remove the cartridges and insert them into the inlets of the Vac-Elut SPS 24 at the "waste position". Turn the vacuum on (~5 psi) for 2 minutes to dry the cartridges. Turn the vacuum off and reverse the order of the cartridge positions. Add 5 mL of elution reagent to each cartridge. Switch the Vac-Elut SPS 24 to the "collect position" and turn the vacuum on. Elute all chemicals with ~5 mL of 5 % ammonium hydroxide in methanol at a flow rate of about 5 mL/minute. Collect the eluant into a 15 mL graduated test tube.
6. Filter the eluant through a 0.2 µm Acrodisc into a 15 mL graduated test tube which has been calibrated at 0.5 mL using methanol with a 500 µL syringe. Concentrate the eluant to ~0.2 mL in a 40 °C waterbath under a stream of nitrogen. Add 0.1 µg trietazine (100 µL of 1 ng/µL spiking solution) to the eluant as an internal standard. Bring to a final volume of 0.5 mL with reconstitution reagent (75/25 water / methanol). Vortex for 30 seconds. Transfer the eluant into three autosampler vials with inserts. Analyze by APCI/LC/MS/MS.

Instrument Conditions:

Tuning and Calibration of the LCQ/DECA Ion Trap LC/MS:

SOP # EM 501.4 describes the procedures to be followed for tuning and calibration of the LCQ Ion Trap LC/MS. After a retune or recalibration according to these procedures, the tune should be optimized for the triazine screen by tuning on the 253 $(M+H)^+$ pseudomolecular ion of hexazinone. With the APCI source installed, a 10 ng/µL solution of hexazinone standard in methanol is infused at 5 µL/minute into an HPLC column flow of 75:25 mobile Phase A: mobile Phase B. The manual tuning procedures outlined in SOP # EM 501.5 are used to optimize each of the source parameters by maximizing the signal at m/z 253. The optimized tune should be saved as a new tune file, with the starting tune file and the tune procedure recorded in the audit trail. All retuning and recalibration must be recorded in the LCQ instrument log book.

Data File Handling:

All applicable procedures specified in SOP # EM 501.5 "LCQ Ion Trap LC/MS Data File Handling", must be followed. Data files will not be stored properly if there is insufficient disk space on the destination drive (C: or D:). Before beginning a data acquisition sequence, the free disk space on the destination drive must be checked. If less than 1.2 Gbytes is available, files should be moved to the alternate drive or CD Rom or ZIP media and deleted from the destination drive before proceeding. Data acquisition sequences must be recorded in the LCQ Injection Log notebook, noting the project, column, and approximate number of standard, blank and sample solutions injected.

Convectron and ion vacuum gauge readings taken after equilibration of the source at the method operating conditions should also be recorded in the back of the Injection Log notebook.

Following a successful data acquisition sequence, all files (tune, method, sample list, data, LCQuan and Excel) should be archived on CD Rom or ZIP media dedicated to the specific project. Each instrument operator should maintain a separate notebook documenting LCQ method development, and sample preparation and analysis.

Instrument Settings and Parameters:

All specified instrument settings and parameters for both the LCQ and the liquid chromatograph are those used for method validation. It is the responsibility of the analyst to evaluate the method performance for a mixture of standards or other system suitability check solution. Over time, conditions may change due to a variety of effects including reagent batch, ambient temperature or system contamination. The analyst has the discretion to modify the tune or method files as required to fine tune the method performance. Note that a complete copy of the method as run, along with continuous status checks of all parameters and settings are stored with the data file, so that modifications are self-documenting. A summary of any modifications should also be recorded in the appropriate project notebook.

Instrument Conditions: *(con't)*

APCI Source Settings:

Vaporizer Temp (°C):	450
Sheath Gas Flow Rate (arb):	90
Aux Gas Flow Rate (arb):	10
Discharge Current (µA):	5
Discharge Voltage (kV):	5
Capillary Temp (°C):	200
Capillary Voltage (V):	36
Tube Lens Off Set (V):	30
Total Microscans:	3

Note: The listed values are typical for the specified parameters. Values will vary somewhat (Discharge Voltage, Tube Lens Off Set) when the instrument is tuned. The values saved in the method tune file should not be changed unless the LCQ is retuned (see above for LCQ tuning and calibration).

HPLC Settings for Waters SymmetryShield™C18:

Analytical column: Waters SymmetryShield™ 150 mm x 3.9 mm x 5 µm.
Guard column: RP-18, C18 7 µm x 15 mm x 3.2 mm.
Injection volume: 50 µL.
Pump program steps:

Time (min.)	*Flow rate (mL/min.)*	*%A*	*%B*
0.00	0.75	15	85
4.00	0.75	15	85
15.00	0.75	100	00
20.00	0.75	100	00
20.50	0.75	15	85
25.00	0.75	15	85

Mobil phase A: 95/5 (10 mM ammonium formate/methanol), 0.1% formic acid.
Mobil phase B: 90/10 (methanol/0.1 M ammonium formate), 0.1% formic acid.
Note: Method performance for a given analyte can be affected by LC column aging, system contamination, and especially matrix interferences in a given sample. The analyst has the discretion to modify the data acquisition parameters to fine tune method performance based on the data observed.

LCQMS Detector Settings for Waters SymmetryShield™C18: These MS detector settings (*alpha method*) are for the analyses of Diamino Chlorotriazine (DACT), Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), Propazine, Trietazine, Hexazinone, Cyanazine, Prometon, Atrazine, Diuron, and Prometryn.

MS run time (min.): 18.0
Divert valve (min.): 0.00 to waste.
1.50 to source.
17.25 to waste.

LCQMS Detector Settings for Waters SymmetryShield™C18: (con't)

Segment: 1
Duration time (min.): 5.00
Number of scan events: 1
Tune method: 3 mm apci hexaz 1-2000 06-03-99
Scan event details:
1. Pos [146]⇒ [50-160] for DACT
   Ms/Ms: Amp: 31% Q: 0.400 Time (msec.): 30 IsoW: 1.5

Segment: 2
Duration time (min.): 5.80
Number of scan events: 3
Tune method: 3 mm apci hexaz 2-750 06-03-99
Scan event details:
1. Pos [175]⇒ [50-190] for ACET
   Ms/Ms: Amp: 32% Q: 0.300 Time (msec.): 30 IsoW: 4.0
2. Pos [189]⇒ [50-200] for DEA
   Ms/Ms: Amp: 30% Q: 0.300 Time (msec.): 30 IsoW: 4.0
3. Pos [253]⇒ [70-275] for Hexazinone
   Ms/Ms: Amp: 25% Q: 0.250 Time (msec.): 30 IsoW: 1.5

Segment: 3
Duration time (min.): 2.00
Number of scan events: 3
Tune method: 3 mm apci hexaz 2-750 06-03-99
Scan event details:
1. Pos [242]⇒ [65-240] for Cyanazine
   Ms/Ms: Amp: 30% Q: 0.300 Time (msec.): 30 IsoW: 4.0
2. Pos [189]⇒ [50-200] for DEA
   Ms/Ms: Amp: 30% Q: 0.300 Time (msec.): 30 IsoW: 4.0
3. Pos [253]⇒ [70-275] for Hexazinone
   Ms/Ms: Amp: 25% Q: 0.250 Time (msec.): 30 IsoW: 1.5

Segment: 4
Duration time (min.): 1.20
Number of scan events: 3
Tune method: 3 mm apci hexaz 2-500 06-03-99
Scan event details:
1. Pos [253]⇒ [70-275] for Hexazinone
   Ms/Ms: Amp: 25% Q: 0.250 Time (msec.): 30 IsoW: 1.5
2. Pos [242]⇒ [65-260] for Cyanazine
   Ms/Ms: Amp: 30% Q: 0.300 Time (msec.): 30 IsoW: 4.0
3. Pos [226]⇒ [60-240] for Prometon
   Ms/Ms: Amp: 32.5% Q: 0.300 Time (msec.): 30 IsoW: 1.5

LCQMS Detector Settings for Waters SymmetryShield™C18 (alpha method): (con't)

Segment: 5
Duration time (min.): 0.500
Number of scan events: 3
Tune method: 3 mm apci hexaz 2-500 06-03-99
Scan event details:
1. Pos [226]⇒ [60-240] for Prometon
   Ms/Ms: Amp: 32.5% Q: 0.300 Time (msec.): 30 IsoW: 1.5
2. Pos [217]⇒ [60-230] for Atrazine
   Ms/Ms: Amp: 33% Q: 0.300 Time (msec.): 30 IsoW: 4.0
3. Pos [231]⇒ [60-250] for Propazine
   Ms/Ms: Amp: 34% Q: 0.300 Time (msec.): 30 IsoW: 4.0

Segment: 6
Duration time (min.): 0.500
Number of scan events: 3
Tune method: 3 mm apci hexaz 2-500 06-03-99
Scan event details:
1. Pos [217]⇒ [60-230] for Atrazine
   Ms/Ms: Amp: 33% Q: 0.300 Time (msec.): 30 IsoW: 4.0
2. Pos [231]⇒ [60-250] for Propazine
   Ms/Ms: Amp: 34% Q: 0.300 Time (msec.): 30 IsoW: 4.0
3. Pos [235]⇒ [65-250] for Diuron
   Ms/Ms: Amp: 30% Q: 0.230 Time (msec.): 30 IsoW: 6.0

Segment: 7
Duration time (min.): 0.900
Number of scan events: 4
Tune method: 3 mm apci hexaz 2-500 06-03-99
Scan event details:
1. Pos [242]⇒ [65-260] for Prometryn
   Ms/Ms: Amp: 32.5% Q: 0.300 Time (msec.): 30 IsoW: 1.5
2. Pos [231]⇒ [60-250] for Propazine
   Ms/Ms: Amp: 34% Q: 0.300 Time (msec.): 30 IsoW: 4.0
3. Pos [235]⇒ [65-250] for Diuron
   Ms/Ms: Amp: 30% Q: 0.230 Time (msec.): 30 IsoW: 6.0
4. Pos [231]⇒ [60-250] for Trietazine
   Ms/Ms: Amp: 39% Q: 0.250 Time (msec.): 30 IsoW: 4.0

Segment: 8
Duration time (min.): 2.10
Number of scan events: 3
Tune method: 3 mm apci hexaz 2-500 06-03-99
Scan event details:
1. Pos [231]⇒ [60-250] for Trietazine
   Ms/Ms: Amp: 39% Q: 0.250 Time (msec.): 30 IsoW: 4.0
2. Pos [242]⇒ [65-260] for Prometryn
   Ms/Ms: Amp: 32.5% Q: 0.300 Time (msec.): 30 IsoW: 1.5

LCQMS Detector Settings for Waters SymmetryShield™C18 (alpha method): (con't)

3. Pos [231]⇒ [60-250] for Propazine
   Ms/Ms: Amp: 34% Q: 0.300 Time (msec.): 30 IsoW: 4.0

LCQMS Detector Settings for Waters SymmetryShield™C18: These MS detector settings (*beta method*) are for the analyses of Diamino Chlorotriazine (DACT), Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), Propazine, Trietazine, Metribuzin, Bromacil, Simazine, and Norflurazon.

MS run time (min.): 18.0
Divert valve (min.): 0.00 to waste
1.50 to source
17.25 to waste

Segment: 1
Duration time (min.): 5.00
Number of scan events: 1
Tune method: 3 mm apci hexaz 1-2000 06-03-99
Scan event details:

1. Pos [146]⇒ [50-160] for DACT
   Ms/Ms: Amp: 31% Q: 0.400 Time (msec.): 30 IsoW: 1.5

Segment: 2
Duration time (min.): 7.20
Number of scan events: 2
Tune method: 3 mm apci hexaz 2-750 06-03-99
Scan event details:

1. Pos [175]⇒ [50-190] for ACET
   Ms/Ms: Amp: 32% Q: 0.300 Time (msec.): 30 IsoW: 4.0
2. Pos [189]⇒ [50-200] for DEA
   Ms/Ms: Amp: 30% Q: 0.300 Time (msec.): 30 IsoW: 4.0

Segment: 3
Duration time (min.): 2.10
Number of scan events: 3
Tune method: 3 mm apci hexaz 2-500 06-03-99
Scan event details:

1. Pos [215]⇒ [60-240] for Metribuzine
   Ms/Ms: Amp: 30% Q: 0.300 Time (msec.): 30 IsoW: 1.5
2. Pos [203]⇒ [55-220] for Simazine
   Ms/Ms: Amp: 33% Q: 0.300 Time (msec.): 30 IsoW: 4.0
3. Pos [262]⇒ [70-275] for Bromacil
   Ms/Ms: Amp: 20.5% Q: 0.230 Time (msec.): 30 IsoW: 6.0

LCQMS Detector Settings for Waters SymmetryShield™C18 (beta method): (con't)

Segment: 4

Duration time (min.): 3.70
Number of scan events: 3
Tune method: 3 mm apci hexaz 2-500 06-03-99
Scan event details:

1. Pos [231]⇒ [60-250] for Propazine
   Ms/Ms: Amp: 34% Q: 0.300 Time (msec.): 30 IsoW: 4.0
2. Pos [231]⇒ [60-260] for Trietazine
   Ms/Ms: Amp: 39% Q: 0.300 Time (msec.): 30 IsoW: 4.0
3. Pos [305]⇒ [85-350] for Norflurazon
   Ms/Ms: Amp: 39% Q: 0.300 Time (msec.): 30 IsoW: 4.0

LCQHPLC Settings for Phenyl-hexyl column:

Analytical column: Phenyl-hexyl 5 cm x 3.00 mm x 3 µm
Guard column: RP-18, Phenyl-hexyl 1.5 mm x 3.2 mm x 7µm
Injection volume: 50 µL
Pump program steps:

Time (min.)	*Flow rate (mL/min.)*	*%A*	*%B*
0.00	0.40	0.00	100
2.50	0.40	0.00	100
3.00	0.40	50.0	50.0
15.00	0.40	60.0	40.0
20.00	0.40	60.0	40.0
21.00	0.40	100	0.00
25.00	0.40	100	0.00
26.00	0.40	0.00	100
31.00	0.40	0.00	100

Mobile phase A: 95/5 (10 mM ammonium formate/methanol), 0.1% formic acid
Mobile phase B: 90/10 (methanol/0.1 M ammonium formate), 0.1% formic acid

LCQMS Detector Settings for Phenyl-hexyl column: These MS detector settings are for the analyses of Diamino Chlorotriazine (DACT), Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), Propazine, Trietazine, Hexazinone, Cyanazine, Prometon, Atrazine, Diuron, Metribuzin, Bromacil, Simazine, Norflurazon, and Prometryn.

MS run time (min.): 18.00
Divert valve (min.): 0.00 to waste
0.75 to source
20.75 to waste

Segment: 1

Duration time (min.): 4.75
Number of scan events: 1
Tune method: 3 mm apci hexaz 1-2000 06-03-99
Scan event details:

1. Pos [146]⇒ [50-160] for DACT
   Ms/Ms: Amp: 31% Q: 0.400 Time (msec.): 30 IsoW: 1.5

LCQMS Detector Settings for Phenyl-hexyl column: (con't)

Segment: 2
Duration time (min.): 3.25
Number of scan events: 2
Tune method: 3 mm apci hexaz 2-750 06-03-99
Scan event details:
1. Pos [175]⇒ [50-190] for ACET
Ms/Ms: Amp: 34.% Q: 0.300 Time (msec.): 30 IsoW: 4.0
2. Pos [189]⇒ [50-200] for DEA
Ms/Ms: Amp: 32% Q: 0.300 Time (msec.): 30 IsoW: 4.0

Segment: 3
Duration time (min.): 1.10
Number of scan events: 2
Tune method: 3 mm apci hexaz 2-250 06-03-99
Scan event details:
1. Pos [203]⇒ [55-220] for Simazine
Ms/Ms: Amp: 33% Q: 0.300 Time (msec.): 30 IsoW: 4.0
2. Pos [242]⇒ [65-260] for Cyanazine
Ms/Ms: Amp: 30% Q: 0.300 Time (msec.): 30 IsoW: 4.0
3. Pos [253]⇒ [70-275] for Hexazinone
Ms/Ms: Amp: 25% Q: 0.250 Time (msec.): 30 IsoW: 1.5

Segment: 4
Duration time (min.): 0.500
Number of scan events: 4
Tune method: 3 mm apci hexaz 2-500 06-03-99
Scan event details:
1. Pos [215]⇒ [70-275] for Metribuzine
Ms/Ms: Amp: 29% Q: 0.300 Time (msec.): 30 IsoW: 1.5
2. Pos [262]⇒ [70-275] for Bromacil
Ms/Ms: Amp: 20.5% Q: 0.230 Time (msec.): 30 IsoW: 6.0
3. Pos [203]⇒ [55-220] for Simazine
Ms/Ms: Amp: 33% Q: 0.300 Time (msec.): 30 IsoW: 4.0
4. Pos [242]⇒ [65-260] for Cyanazine
Ms/Ms: Amp: 30% Q: 0.300 Time (msec.): 30 IsoW: 4.0

Segment: 5
Duration time (min.): 0.400
Number of scan events: 3
Tune method: 3 mm apci hexaz 2-500 06-03-99
Scan event details:
1. Pos [226]⇒ [60-240] for Prometon
Ms/Ms: Amp: 32.5% Q: 0.300 Time (msec.): 30 IsoW: 1.5
2. Pos [215]⇒ [60-240] for Metribuzine
Ms/Ms: Amp: 29% Q: 0.300 Time (msec.): 30 IsoW: 1.5
3. Pos [262]⇒ [70-275] for Bromacil
Ms/Ms: Amp: 20.5% Q: 0.230 Time (msec.): 30 IsoW: 6.0

LCQMS Detector Settings for Phenyl-hexyl column: (con't)

Segment: 6
Duration time (min.): 0.500
Number of scan events: 4
Tune method: 3 mm apci hexaz 2-500 06-03-99
Scan event details:
1. Pos [253]⇒ [70-275] for Hexazinone
   Ms/Ms: Amp: 24% Q: 0.300 Time (msec.): 30 IsoW: 1.5
2. Pos [226]⇒ [60-240] for Prometon
   Ms/Ms: Amp: 32.5% Q: 0.300 Time (msec.): 30 IsoW: 1.5
3. Pos [215]⇒ [65-240] for Metribuzine
   Ms/Ms: Amp: 29% Q: 0.230 Time (msec.): 30 IsoW: 6.0
4. Pos [262]⇒ [70-275] for Bromacil
   Ms/Ms: Amp: 20.5% Q: 0.230 Time (msec.): 30 IsoW: 6.0

Segment: 7
Duration time (min.): 1.60
Number of scan events: 3
Tune method: 3 mm apci hexaz 2-500 06-03-99
Scan event details:
1. Pos [226]⇒ [60-240] for Prometon
   Ms/Ms: Amp: 32.5% Q: 0.300 Time (msec.): 30 IsoW: 1.5
2. Pos [253]⇒ [70-275] for Hexazinone
   Ms/Ms: Amp: 24% Q: 0.300 Time (msec.): 30 IsoW: 1.5
3. Pos [217]⇒ [60-230] for Atrazine
   Ms/Ms: Amp: 33% Q: 0.300 Time (msec.): 30 IsoW: 4.0

Segment: 8
Duration time (min.): 2.50
Number of scan events: 2
Tune method: 3 mm apci hexaz 2-750 06-03-99
Scan event details:
1. Pos [231]⇒ [60-250] for Propazine
   Ms/Ms: Amp: 29% Q: 0.300 Time (msec.): 30 IsoW: 4.0
2. Pos [235]⇒ [65-250] for Diuron
   Ms/Ms: Amp: 27% Q: 0.230 Time (msec.): 30 IsoW: 1.5

Segment: 9
Duration time (min.): 0.700
Number of scan events: 3
Tune method: 3 mm apci hexaz 2-500 06-03-99
Scan event details:
1. Pos [305]⇒ [85-350] for Norflurazon
   Ms/Ms: Amp: 39% Q: 0.300 Time (msec.): 30 IsoW: 4.0
2. Pos [242]⇒ [65-265] for Prometryn
   Ms/Ms: Amp: 32.5% Q: 0.300 Time (msec.): 30 IsoW: 1.5
3. Pos [231]⇒ [60-250] for Propazine
   Ms/Ms: Amp: 29% Q: 0.300 Time (msec.): 30 IsoW: 4.0

LCQMS Detector Settings for Phenyl-hexyl column: (con't)

Segment: 10
Duration time (min.): 2.40
Number of scan events: 2
Tune method: 3 mm apci hexaz 2-500 06-03-99
Scan event details:
1. Pos [305]⇒ [85-350] for Norflurazon
   Ms/Ms: Amp: 39% Q: 0.300 Time (msec.): 30 IsoW: 4.0
2. Pos [242]⇒ [65-265] for Prometryn
   Ms/Ms: Amp: 32.5% Q: 0.300 Time (msec.): 30 IsoW: 1.5

Segment: 11
Duration time (min.): 3.30
Number of scan events: 1
Tune method: 3 mm apci hexaz 2-500 06-03-99
Scan event details:
1. Pos [231]⇒ [60-260] for Tritazine
   Ms/Ms: Amp: 34% Q: 0.300 Time (msec.): 30 IsoW: 4.0

LCQDECA HPLC Settings for Waters SymmetryShield™C18 column (for system B as a back up method) :

Analytical column: Waters SymmetryShield™ C18 150 mm x 3.9 mm x 5 µm
Guard column: RP-18, C18 15 mm x 3.2 mm x 7µm
Injection volume: 50 µL
Pump program steps:

Time (min.)	*Flow rate (mL/min.)*	%A	%B
0.00	0.75	15	85
4.00	0.75	15	85
30.00	0.75	100	00
32.00	0.75	100	00
34.00	0.75	15	85
36.00	0.75	15	85

Mobile phase A: 95/5 (10 mM ammonium formate/methanol), 0.1% formic acid
Mobile phase B: 90/10 (methanol/0.1 M ammonium formate), 0.1% formic acid

LCQDECA MS Detector Settings for Waters SymmetryShield™C18 column(for system B as a back up method) : These MS detector settings are for the analyses of Diamino Chlorotriazine (DACT), Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), Propazine, Trietazine, Hexazinone, Cyanazine, Prometon, Atrazine, Diuron, Metribuzin, Bromacil, Simazine, Norflurazon, and Prometryn.

MS run time (min.): 22.00
Divert valve (min.): 0.00 to waste
1.50 to source

LCQDECA MS Detector Settings for Waters SymmetryShield™C18 column) :(con't)

Segment: 1
Duration time (min.): 5.00
Number of scan events: 1
Tune method: DECADACT
Scan event details:
1. Pos [146]⇒ [60-160] for DACT
   Ms/Ms: Amp: 31% Q: 0.400 Time (msec.): 30 IsoW: 1.5

Segment: 2
Duration time (min.): 8.50
Number of scan events: 3
Tune method: HEXAZIAPCIDECA
Scan event details:
1. Pos [175]⇒ [55-190] for ACET
   Ms/Ms: Amp: 32% Q: 0.300 Time (msec.): 30 IsoW: 4.0
2. Pos [189]⇒ [60-200] for DEA
   Ms/Ms: Amp: 30% Q: 0.300 Time (msec.): 30 IsoW: 4.0
3. Pos [226]⇒ [70-250] for Prometon
   Ms/Ms: Amp: 32.5% Q: 0.300 Time (msec.): 30 IsoW: 1.5

Segment: 3
Duration time (min.): 3.00
Number of scan events: 5
Tune method: HEXAZIAPCIDECA
Scan event details:
1. Pos [253]⇒ [80-350] for Hexazinone
   Ms/Ms: Amp: 25% Q: 0.300 Time (msec.): 30 IsoW: 4.0
2. Pos [242]⇒ [75-280] for Cyanazine
   Ms/Ms: Amp: 30% Q: 0.300 Time (msec.): 30 IsoW: 4.0
3. Pos [215]⇒ [70-250] for Metribuzine
   Ms/Ms: Amp: 30% Q: 0.300 Time (msec.): 30 IsoW: 1.5
4. Pos [203]⇒ [65-250] for Simazine
   Ms/Ms: Amp: 33% Q: 0.300 Time (msec.): 30 IsoW: 4.0
5. Pos [262]⇒ [65-280] for Bromacil
   Ms/Ms: Amp: 20.5% Q: 0.230 Time (msec.): 30 IsoW: 1.5

Segment: 4
Duration time (min.): 3.20
Number of scan events: 5
Tune method: HEXAZIAPCIDECA
Scan event details:
1. Pos [217]⇒ [70-250] for Atrazine
   Ms/Ms: Amp: 33% Q: 0.300 Time (msec.): 30 IsoW: 4.0
2. Pos [242]⇒ [75-250] for Prometryn
   Ms/Ms: Amp: 32.5% Q: 0.300 Time (msec.): 30 IsoW: 1.5
3. Pos [231]⇒ [75-250] for Propazine
   Ms/Ms: Amp: 39% Q: 0.300 Time (msec.): 30 IsoW: 4.0

LCQDECA MS Detector Settings for Waters SymmetryShield™C18 column) :(con't)

4. Pos [235]⇒ [60-280] for Diuron
   Ms/Ms: Amp: 30% Q: 0.250 Time (msec.): 30 IsoW: 6.0
5. Pos [305]⇒ [100-350] for Norflurazon
   Ms/Ms: Amp: 39% Q: 0.300 Time (msec.): 30 IsoW: 4.0

Segment: 5
Duration time (min.): 2.30
Number of scan events: 1
Tune method: HEXAZIAPCIDECA
Scan event details:

1. Pos [231]⇒ [75-280] for Trietazine
   Ms/Ms: Amp: 34% Q: 0.300 Time (msec.): 30 IsoW: 4.0

LCQDECA HPLC Settings for Phenyl-hexyl column:

Analytical column: Phenyl-hexyl 5 cm x 3.00 mm x 3 µm
Guard column: RP-18, Phenyl-hexyl 1.5 mm x 3.2 mm x 7µm
Injection volume: 50 µL
Pump program steps:

Time (min.)	*Flow rate (mL/min.)*	*%A*	*%B*
0.00	0.40	0.00	100
2.50	0.40	0.00	100
5.00	0.40	30.0	70.0
25.00	0.40	60.0	40.0
26.00	0.40	60.0	40.0
27.00	0.40	100	0.00
30.00	0.40	100	0.00
32.00	0.40	0.00	100
35.00	0.40	0.00	100

Mobile phase A: 95/5 (10 mM ammonium formate/methanol), 0.1% formic acid
Mobile phase B: 90/10 (methanol/0.1 M ammonium formate), 0.1% formic acid

LCQDECA MS Detector Settings for Phenyl hexyl column: These MS detector settings are for the analyses of Diamino Chlorotriazine (DACT), Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), Propazine, Trietazine, Hexazinone, Cyanazine, Prometon, Atrazine, Diuron, Metribuzin, Bromacil, Simazine, Norflurazon, and Prometryn.

MS run time (min.): 26.00
Divert valve (min.): 0.00 to waste
1.00 to source

Segment: 1
Duration time (min.): 5.00
Number of scan events: 1
Tune method: DECADACT
Scan event details:

1. Pos [146]⇒ [108-112] for DACT
   Ms/Ms: Amp: 34% Q: 0.400 Time (msec.): 30 IsoW: 1.5

LCQDECA MS Detector Settings for Phenyl hexyl column: :(con't)

Segment: 2
Duration time (min.): 6.00
Number of scan events: 2
Tune method: HEXAZIAPCIDECA
Scan event details:
1. Pos [175]⇒ [80-200] for ACET
   Ms/Ms: Amp: 34% Q: 0.300 Time (msec.): 30 IsoW: 4.0
2. Pos [189]⇒ [60-200] for DEA
   Ms/Ms: Amp: 32% Q: 0.300 Time (msec.): 30 IsoW: 4.0

Segment: 3
Duration time (min.): 3.50
Number of scan events: 5
Tune method: HEXAZIAPCIDECA
Scan event details:
1. Pos [242]⇒ [75-250] for Cyanazine
   Ms/Ms: Amp: 30% Q: 0.300 Time (msec.): 30 IsoW: 4.0
2. Pos [203]⇒ [65-250] for Simazine
   Ms/Ms: Amp: 33% Q: 0.300 Time (msec.): 30 IsoW: 4.0
3. Pos [226]⇒ [70-250] for Prometon
   Ms/Ms: Amp: 32.5% Q: 0.300 Time (msec.): 30 IsoW: 1.5
4. Pos [215]⇒ [70-250] for Metribuzine
   Ms/Ms: Amp: 30% Q: 0.300 Time (msec.): 30 IsoW: 4.0
5. Pos [262]⇒ [85-270] for Bromacil
   Ms/Ms: Amp: 20.5% Q: 0.300 Time (msec.): 30 IsoW: 6.0

Segment: 4
Duration time (min.): 2.50
Number of scan events: 4
Tune method: HEXAZIAPCIDECA
Scan event details:
1. Pos [253]⇒ [80-270] for Hexazinone
   Ms/Ms: Amp: 24% Q: 0.300 Time (msec.): 30 IsoW: 1.5
2. Pos [217]⇒ [70-250] for Atrazine
   Ms/Ms: Amp: 33% Q: 0.300 Time (msec.): 30 IsoW: 4.0
3. Pos [215]⇒ [70-250] for Metribuzine
   Ms/Ms: Amp: 30% Q: 0.300 Time (msec.): 30 IsoW: 1.5
4. Pos [262]⇒ [85-270] for Bromacil
   Ms/Ms: Amp: 20.5% Q: 0.300 Time (msec.): 30 IsoW: 6.0

Segment: 5
Duration time (min.): 5.00
Number of scan events: 5
Tune method: HEXAZIAPCIDECA
Scan event details:
1. Pos [235]⇒ [55-270] for Diuron
   Ms/Ms: Amp: 27% Q: 0.230 Time (msec.): 30 IsoW: 1.5

LCQDECA MS Detector Settings for Phenyl hexyl column: :(con't)

2. Pos [242]⇒ [75-275] for Prometryn
   Ms/Ms: Amp: 32.5% Q: 0.300 Time (msec.): 30 IsoW: 1.5
3. Pos [231]⇒ [75-250] for Diuron
   Ms/Ms: Amp: 39.5% Q: 0.300 Time (msec.): 30 IsoW: 4.0
4. Pos [305]⇒ [100-350] for Norflurazon
   Ms/Ms: Amp: 39% Q: 0.300 Time (msec.): 30 IsoW: 4.0
5. Pos [217]⇒ [70-250] for Atrazine
   Ms/Ms: Amp: 33% Q: 0.300 Time (msec.): 30 IsoW: 4.0

Segment: 6
Duration time (min.): 4.00
Number of scan events: 1
Tune method: HEXAZIAPCIDECA
Scan event details:

1. Pos [231]⇒ [75-350] forTrietazine
   Ms/Ms: Amp: 39.5% Q: 0.300 Time (msec.): 30 IsoW: 4.0

Calculations:

The results are reported in µg/L :

$$\mu g/L = \frac{\mu g/mL \text{ (from standard curve)} \times \text{final volume (mL)} \times 1000 \text{ g/L}}{\text{Sample weight (g)}}$$

Method Performance:

Quality Control:

1. Sample storage: All field samples shall be kept refrigerated at 4 °C ± 2 until extracted.
2. Sample extraction: All extracts shall be kept refrigerated at 4 °C ± 2 until analyzed.
3. For each set of samples, at least one matrix blank and one matrix spike shall be included. Each set of samples shall not contain more than twelve samples.

Recovery data:

This analytical method was validated by preparing five sets of samples using the provided background well water. Each set contained four different levels of spike and a matrix blank. Each set was processed through the entire analytical method on a different day. Each sample was injected twice on each column. The results were averaged and are shown in Appendices I and II.

Method detection limit (MDL):

Method Detection Limit (MDL) refers to the lowest concentration of analytes that a method can detect reliably. To determine the MDL, 7 replicate background samples were spiked at 0.100 µg. The standard deviation from the spiked samples was used to calculate the MDL using the following equation:

$$MDL = tS$$

Method detection limit (MDL): :(con't)

where:

t is the Student t value for the 99% confidence level with n-1 degrees of freedom and S denotes the standard deviation obtained from n replicate analyses. For the n=7 replicates used to determine the MDL, t=3.143. See Appendix IV for recovery data from the determination of the Method Detection Limits.

The Reporting Limit (RL) refers to the level at which quantitative results may be obtained. By convention, the RL is chosen in a range 1-5 times the MDL. The Reporting Limit for this method is 0.05 µg/L for all analytes.

Discussion:

Propazine is used as a surrogate for the method analytes. 0.1 µg of propazine is added into each sample and processed through the entire analytical method. This allows the extraction steps to be monitored for acceptable recovery. A calculated recovery for propazine of 75 - 125% (acceptable range) of the amount spiked indicates that the recovery of the analytes in that sample is within acceptable range. If the recovery of the analyte is out of the acceptable range, the sample needs to be re-extracted. See Appendix III for recovery data.

Trietazine is used as an internal standard to monitor the injection volume supplied by the autosampler. The internal standard is added to each sample at the end of the evaporation of excess methanol from sample and matrix extracts. 0.1 µg of trietazine is added to the eluant when it is evaporated just below 0.2 mL. The volume of the extract is then adjusted to 0.5 mL with 75:25 water : methanol. See Appendix III for recovery data.

The segment durations in mass spectrometer settings determine the retention time windows for each analyte. As the HPLC column performance may change over time because of irreversible contamination, phase stripping, etc., it may be necessary to adjust these windows before beginning a sequence for the observed retention times of the analytes. Installation of a new guard column or analytical column may also necessitate adjustments of window times.

Two instrument methods have been developed on system B (LCQDECA) using Phenyl-hexyl and Waters SymmetryShield™ C18 columns. These methods were not used to validate the analytical method. They should be used only as back-up methods.

A standard curve consisting of five levels was used for every twelve injections. Each sample was injected twice back to back. The external standard technique with the average of all standard levels from the begining of a sequence to the end of a sequence was used to quantify samples. The response of a same level standard before and after samples should not differ by more than 25%. If the results are not in acceptable range, a root analysis should be done to indentify the causes. Diuron and Bromacil sometimes have shown very high recoveries on the phenyl-hexyl column for an unknown reason.

After each sequence is completed, the column should be rinsed with high organic mobile phase solution for few hours and stored in that condition. Before starting a sequence, test standards should be run first to ensure that the column is fully equilibrated. Test standards will not be used in quantitation.

References:

SOP # EM 501.4
SOP # EM 501.5

Acknowledgment:

Thanks to Janice Temple for her help and patience in sample extraction for method validation.

Written By: Duc Tran

Duchan

TITLE: Agricultural Chemist II

Written By: Pamela Fitch

Pamela Fitch

TITLE: Agricultural Chemist III

Approved By: Catherine Cooper

Catherine Cooper

TITLE: Agricultural Supervising Chemist III

Appendix I: Recovery data for method validation by SymmetryShield™ C18 column by alpha(α) and (β) methods

Diamino Chlorotriazine (DACT): (α,β methods)

Spike level (µg/L)	Recovery (µg/L) (α)	Recovery (%)	Recovery (µg/L) (β)	Recovery (%)	Spike level (µg/L)	Recovery (µg/L) (α)	Recovery (%)	Recovery (µg/L) (β)	Recovery (%)
0.1	0.076	76.0	0.083	83.0	2.0	1.918	95.9	1.936	96.8
0.1	0.091	91.0	0.088	88.0	2.0	2.017	101.0	2.068	103.0
0.1	0.102	102.0	0.114	114.0	2.0	1.877	93.9	1.833	91.7
0.1	0.098	98.0	0.099	99.0	2.0	1.747	87.4	1.732	86.6
0.1	0.091	91.0	0.085	85.0	2.0	1.898	94.9	1.939	96.9
0.5	0.392	78.4	0.411	82.2	6.0	3.758	62.6	3.878	64.6
0.5	0.385	77.0	0.410	82.0	6.0	3.905	65.1	4.118	68.6
0.5	0.463	92.6	0.420	84.0	6.0	4.626	77.1	4.540	75.7
0.5	0.425	85.0	0.413	82.6	6.0	5.073	84.5	5.127	85.4
0.5	0.449	89.9	0.415	83.0	6.0	5.846	97.4	5.677	94.6

Atrazine: (α method only)

Spike level (µg/L)	Recovery (µg/L)	Recovery (%)	Spike level (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.118	118	2.0	2.033	102.0
0.1	0.109	109	2.0	2.445	122.0
0.1	0.132	132.0	2.0	2.030	101.5
0.1	0.119	119.0	2.0	1.915	95.7
0.1	0.107	107	2.0	2.198	109.9
0.5	0.476	95.2	6.0	6.050	101.0
0.5	0.433	86.6	6.0	5.547	92.4
0.5	0.538	107.6	6.0	6.036	100.6
0.5	0.503	100.6	6.0	6.325	105.4
0.5	0.492	98.4	6.0	6.075	101.2

Deisopropyl Atrazine (ACET): (α, β method)

Spike level (µg/L)	Recovery (µg/L) (α)	Recovery (%)	Recovery (µg/L) (β)	Recovery (%)	Spike level (µg/L)	Recovery (µg/L) (α)	Recovery (%)	Recovery (µg/L) (β)	Recovery (%)
0.1	0.135	135.0	0.125	125.0	2.0	2.226	111.3	2.294	114.7
0.1	0.119	119.0	0.114	114.0	2.0	2.719	136.0	2.694	134.7
0.1	0.133	133.0	0.124	124.0	2.0	2.538	126.9	2.327	116.3
0.1	0.134	134.0	0.129	129.0	2.0	2.024	101.2	2.012	100.6
0.1	0.120	120.0	0.110	110.0	2.0	2.372	118.6	2.337	116.3
0.5	0.559	111.8	0.578	115.6	6.0	5.985	99.7	6.545	109.0
0.5	0.522	104.4	0.505	101.0	6.0	5.989	99.8	5.874	97.9
0.5	0.607	121.4	0.538	107.6	6.0	6.458	107.6	6.276	104.6
0.5	0.568	113.6	0.556	111.2	6.0	7.477	124.6	6.726	112.1
0.5	0.571	114.2	0.505	101.0	6.0	6.695	111.6	5.969	99.5

Determination of Atrazine, Bromacil, Cyanazine, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), and Diamino Chlorotriazine (DACT) in Well Water By Liquid Chromatography-Atmospheric Pressure Chemical Ionization Mass Spectrometry

Appendix I: Recovery data for method validation by SymmetryShield™ C18 column by alpha(α) and (β) methods

Deethyl Atrazine (DEA):

Spike level (µg/L)	Recovery (µg/L) (α)	Recovery (%)	Recovery (µg/L) (β)	Recovery (%)	Spike level (µg/L)	Recovery (µg/L)	Recovery (%) (α)	Recovery (µg/L)	Recovery (%) (β)
0.1	0.117	117.0	0.125	125.0	2.0	2.346	117.3	2.206	110.3
0.1	0.104	104.0	0.113	113.0	2.0	2.601	130.0	2.686	134.3
0.1	0.124	124.0	0.125	125.0	2.0	2.404	120.2	2.277	113.9
0.1	0.119	119.0	0.118	118.0	2.0	2.108	105.4	2.057	102.9
0.1	0.110	110.0	0.105	105.0	2.0	2.428	121.4	2.350	117.5
0.5	0.561	112.2	0.532	106.4	6.0	6.445	107.0	6.163	103.0
0.5	0.497	99.4	0.496	99.2	6.0	6.327	105.4	6.317	105.2
0.5	0.549	109.8	0.515	103.0	6.0	6.675	111.3	6.569	109.5
0.5	0.541	108.2	0.537	107.4	6.0	6.293	104.9	6.663	111.0
0.5	0.527	105.4	0.513	102.6	6.0	6.866	114.4	6.476	108.0

Bromacil: **(β method only)**

Spike level (µg/L)	Recovery (µg/L)	Recovery (%)	Spike level (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.099	99.0	2.0	1.947	97.4
0.1	0.105	105.0	2.0	2.445	122.2
0.1	0.106	106.0	2.0	2.004	100.2
0.1	0.107	107.0	2.0	1.795	89.7
0.1	0.097	97.0	2.0	2.041	102.1
0.5	0.524	104.8	6.0	6.168	102.8
0.5	0.440	88.0	6.0	5.673	94.5
0.5	0.473	94.6	6.0	6.140	102.3
0.5	0.458	91.6	6.0	5.911	98.5
0.5	0.427	85.4	6.0	5.396	89.9

Cyanazine: **(α method only)**

Spike level (µg/L)	Recovery (µg/L)	Recovery (%)	Spike level (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.102	102.0	2.0	2.088	104.4
0.1	0.107	107.0	2.0	2.327	116.3
0.1	0.102	102.0	2.0	1.999	99.9
0.1	0.098	98.0	2.0	1.648	82.4
0.1	0.087	87.0	2.0	1.926	96.3
0.5	0.547	109.4	6.0	5.574	92.9
0.5	0.420	84.0	6.0	5.873	97.9
0.5	0.495	99.0	6.0	5.695	94.9
0.5	0.445	89.0	6.0	5.862	97.7
0.5	0.441	88.2	6.0	5.861	97.7

Determination of Atrazine, Bromacil, Cyanazine, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), and Diamino Chlorotriazine (DACT) in Well Water By Liquid Chromatography-Atmospheric Pressure Chemical Ionization Mass Spectrometry

Appendix I: Recovery data for method validation by SymmetryShield™ C18 column by alpha(α) and (β) methods

Diuron: (α method only)

Spike level (µg/L)	Recovery (µg/L)	Recovery (%)	Spike level (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.122	122.0	2.0	1.821	91.0
0.1	0.098	98.0	2.0	2.503	125.2
0.1	0.113	113.0	2.0	2.023	101.1
0.1	0.095	95.0	2.0	1.772	88.6
0.1	0.089	89.0	2.0	2.047	102.4
0.5	0.500	100.0	6.0	6.306	105.1
0.5	0.425	85.0	6.0	6.228	103.8
0.5	0.476	95.2	6.0	6.890	114.8
0.5	0.479	95.8	6.0	5.586	93.1
0.5	0.454	90.8	6.0	5.934	98.9

Hexazinone: (α method only)

Spike level (µg/L)	Recovery (µg/L)	Recovery (%)	Spike level (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.080	80.0	2.0	1.887	94.3
0.1	0.088	88.0	2.0	2.312	115.6
0.1	0.097	97.0	2.0	1.935	96.7
0.1	0.088	88.0	2.0	1.590	79.5
0.1	0.076	76.0	2.0	1.913	95.7
0.5	0.448	89.6	6.0	4.876	81.3
0.5	0.412	82.4	6.0	5.644	94.1
0.5	0.466	93.2	6.0	5.657	94.3
0.5	0.424	84.8	6.0	5.605	93.4
0.5	0.417	83.4	6.0	5.339	89.0

Metribuzin: (β method only)

Spike level (µg/L)	Recovery (µg/L)	Recovery (%)	Spike level (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.120	120.0	2.0	2.127	106.3
0.1	0.104	104.0	2.0	2.499	125.0
0.1	0.111	111.0	2.0	2.251	112.5
0.1	0.129	129.0	2.0	2.008	100.4
0.1	0.109	109.0	2.0	2.181	109.1
0.5	0.551	110.2	6.0	5.952	99.2
0.5	0.493	98.6	6.0	5.645	94.1
0.5	0.545	109.0	6.0	6.152	102.5
0.5	0.501	100.2	6.0	6.592	109.9
0.5	0.491	98.2	6.0	6.017	100.3

Determination of Atrazine, Bromacil, Cyanazine, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), and Diamino Chlorotriazine (DACT) in Well Water By Liquid Chromatography-Atmospheric Pressure Chemical Ionization Mass Spectrometry

Appendix I: Recovery data for method validation by SymmetryShield™ C18 column by alpha(α) and (β) methods

Norflurazon: (β method only)

Spike level (µg/L)	Recovery (µg/L)	Recovery (%)	Spike level (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.112	112.0	2.0	2.186	109.3
0.1	0.107	107.0	2.0	2.499	124.9
0.1	0.124	124.0	2.0	2.025	101.3
0.1	0.106	106.0	2.0	1.829	91.4
0.1	0.094	94.0	2.0	2.009	100.5
0.5	0.503	100.6	6.0	6.309	105.1
0.5	0.489	97.8	6.0	6.120	102.0
0.5	0.517	103.4	6.0	5.871	97.8
0.5	0.471	94.2	6.0	6.269	104.5
0.5	0.441	88.2	6.0	6.043	100.7

Prometryn: (α method only)

Spike level (µg/L)	Recovery (µg/L)	Recovery (%)	Spike level (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.111	111.0	2.0	2.124	106.2
0.1	0.108	108.0	2.0	2.509	125.4
0.1	0.121	121.0	2.0	2.164	108.2
0.1	0.114	114.0	2.0	1.741	87.0
0.1	0.089	89.0	2.0	2.114	105.7
0.5	0.542	108.4	6.0	5.988	99.8
0.5	0.545	109.0	6.0	6.234	103.9
0.5	0.578	115.6	6.0	6.141	102.3
0.5	0.509	101.8	6.0	6.138	102.3
0.5	0.431	86.2	6.0	5.833	97.2

Prometon: (α method only)

Spike level (µg/L)	Recovery (µg/L)	Recovery (%)	Spike level (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.093	93.0	2.0	1.917	95.8
0.1	0.098	98.0	2.0	2.168	108.4
0.1	0.109	109.0	2.0	1.957	97.8
0.1	0.098	98.0	2.0	1.715	85.7
0.1	0.089	89.0	2.0	2.072	103.6
0.5	0.422	84.4	6.0	5.385	89.7
0.5	0.419	83.8	6.0	5.574	92.9
0.5	0.491	98.2	6.0	5.851	97.5
0.5	0.456	91.2	6.0	5.957	99.3
0.5	0.441	88.2	6.0	5.797	96.6

Appendix I: Recovery data for method validation by SymmetryShield™ C18 column by alpha(α) and (β) methods

Simazine:

Spike level (µg/L)	Recovery (µg/L)	Recovery (%)	Spike level (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.113	113.0	2.0	1.943	97.1
0.1	0.104	104.0	2.0	2.285	114.3
0.1	0.120	120.0	2.0	2.013	100.7
0.1	0.110	110.0	2.0	1.760	88.0
0.1	0.089	89.0	2.0	2.106	105.3
0.5	0.461	92.2	6.0	6.066	101.1
0.5	0.424	84.8	6.0	5.584	93.1
0.5	0.440	88.0	6.0	6.092	101.5
0.5	0.458	91.6	6.0	6.179	103.0
0.5	0.433	86.6	6.0	5.834	97.2

Appendix II: Recovery data for method validation by Phenyl hexyl column

Diamino Chlorotriazine (DACT):

Spiked levels (μg/L)	Results (μg/L)	Recovery (%)	Spiked levels (μg/L)	Results (μg/L)	Recovery (%)
0.1	0.087	87.0	2.0	2.136	106.8
0.1	0.113	113.0	2.0	2.449	122.5
0.1	0.120	120.0	2.0	1.836	91.8
0.1	0.101	101.0	2.0	1.751	87.6
0.1	0.100	100.0	2.0	1.895	94.8
0.5	0.481	96.2	6.0	3.876	64.6
0.5	0.486	97.2	6.0	4.563	76.0
0.5	0.526	105.2	6.0	4.752	79.2
0.5	0.457	91.4	6.0	5.671	94.5
0.5	0.466	93.2	6.0	4.987	83.1

Atrazine:

Spiked levels (μg/L)	Results (μg/L)	Recovery (%)	Spiked levels (μg/L)	Results (μg/L)	Recovery (%)
0.1	0.118	118.0	2.0	2.148	107.4
0.1	0.131	131.0	2.0	2.676	133.8
0.1	0.139	139.0	2.0	2.235	111.8
0.1	0.121	121.0	2.0	1.948	97.4
0.1	0.109	109.0	2.0	2.274	113.7
0.5	0.494	98.8	6.0	5.804	96.7
0.5	0.502	100.4	6.0	6.676	111.3
0.5	0.545	109.0	6.0	6.238	104.0
0.5	0.526	105.2	6.0	6.570	109.5
0.5	0.515	103.0	6.0	6.293	104.9

Deisopropyl Atrazine (ACET) :

Spiked levels (μg/L)	Results (μg/L)	Recovery (%)	Spiked levels (μg/L)	Results (μg/L)	Recovery (%)
0.1	0.153	153.0	2.0	2.610	130.5
0.1	0.158	158.0	2.0	3.135	156.8
0.1	0.177	177.0	2.0	2.530	126.5
0.1	0.144	144.0	2.0	2.228	111.4
0.1	0.151	151.0	2.0	2.666	133.3
0.5	0.650	130.0	6.0	6.675	111.2
0.5	0.630	126.0	6.0	7.151	119.2
0.5	0.669	133.8	6.0	6.867	114.4
0.5	0.633	126.6	6.0	6.946	115.8
0.5	0.643	128.6	6.0	6.753	112.5

Appendix II: Recovery data for method validation by Phenyl hexyl column

Deethyl Atrazine (DEA) :

Spiked levels (µg/L)	Results (µg/L)	Recovery (%)	Spiked levels (µg/L)	Results (µg/L)	Recovery (%)
0.1	0.134	134.0	2.0	2.484	124.2
0.1	0.142	142.0	2.0	3.242	162.1
0.1	0.145	145.0	2.0	2.599	129.9
0.1	0.131	131.0	2.0	2.261	113.0
0.1	0.137	137.0	2.0	2.695	134.7
0.5	0.616	123.2	6.0	6.784	113.1
0.5	0.605	121.0	6.0	7.327	122.1
0.5	0.668	133.6	6.0	7.051	117.5
0.5	0.643	128.6	6.0	7.725	128.7
0.5	0.615	123.0	6.0	7.153	119.2

Bromacil :

Spiked levels (µg/L)	Results (µg/L)	Recovery (%)	Spiked levels (µg/L)	Results (µg/L)	Recovery (%)
0.1	0.107	107.0	2.0	2.107	105.3
0.1	0.111	111.0	2.0	2.607	130.4
0.1	0.125	125.0	2.0	2.147	107.3
0.1	0.116	116.0	2.0	1.907	95.3
0.1	0.102	102.0	2.0	2.262	113.1
0.5	0.531	106.2	6.0	6.287	104.8
0.5	0.500	100.0	6.0	6.406	106.8
0.5	0.521	104.2	6.0	5.765	96.1
0.5	0.510	102.0	6.0	6.675	111.2
0.5	0.493	98.6	6.0	6.529	108.8

Cyanazine :

Spiked levels (µg/L)	Results (µg/L)	Recovery (%)	Spiked levels (µg/L)	Results (µg/L)	Recovery (%)
0.1	0.107	107.0	2.0	2.127	106.4
0.1	0.110	110.0	2.0	2.500	125.0
0.1	0.123	123.0	2.0	2.074	103.7
0.1	0.095	95.0	2.0	1.767	88.3
0.1	0.104	104.0	2.0	2.076	103.8
0.5	0.549	109.8	6.0	6.103	101.7
0.5	0.503	100.6	6.0	6.220	103.7
0.5	0.539	107.8	6.0	5.697	94.9
0.5	0.475	95.0	6.0	5.949	99.1
0.5	0.474	94.8	6.0	6.035	100.6

Determination of Atrazine, Bromacil, Cyanazine, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), and Diamino Chlorotriazine (DACT) in Well Water By Liquid Chromatography-Atmospheric Pressure Chemical Ionization Mass Spectrometry

Appendix II: Recovery data for method validation by Phenyl hexyl column

Diuron :

Spiked levels (µg/L)	Results (µg/L)	Recovery (%)	Spiked levels (µg/L)	Results (µg/L)	Recovery (%)
0.1	0.102	102.0	2.0	2.148	107.4
0.1	0.120	120.0	2.0	2.600	130.0
0.1	0.131	131.0	2.0	2.187	109.4
0.1	0.106	106.0	2.0	1.835	91.8
0.1	0.093	93.0	2.0	2.039	101.9
0.5	0.552	110.4	6.0	5.937	98.9
0.5	0.530	106.0	6.0	6.376	106.3
0.5	0.522	104.4	6.0	5.865	97.7
0.5	0.507	101.4	6.0	6.781	113.0
0.5	0.488	97.6	6.0	6.464	107.7

Hexazinon :

Spiked levels (µg/L)	Results (µg/L)	Recovery (%)	Spiked levels (µg/L)	Results (µg/L)	Recovery (%)
0.1	0.093	93.0	2.0	1.908	95.4
0.1	0.112	112.0	2.0	2.375	118.8
0.1	0.109	109.0	2.0	1.949	97.5
0.1	0.090	90.0	2.0	1.844	92.2
0.1	0.091	91.0	2.0	1.482	74.1
0.5	0.470	94.0	6.0	5.098	85.0
0.5	0.463	92.6	6.0	6.017	100.3
0.5	0.446	89.2	6.0	4.987	83.1
0.5	0.430	86.0	6.0	5.481	91.3
0.5	0.418	83.6	6.0	5.320	88.7

Metribuzin :

Spiked levels (µg/L)	Results (µg/L)	Recovery (%)	Spiked levels (µg/L)	Results (µg/L)	Recovery (%)
0.1	0.133	133.0	2.0	2.094	104.7
0.1	0.128	128.0	2.0	2.772	138.6
0.1	0.131	131.0	2.0	2.157	107.9
0.1	0.136	136.0	2.0	2.435	121.7
0.1	0.110	110.0	2.0	2.001	100.0
0.5	0.539	107.8	6.0	5.635	93.9
0.5	0.547	109.4	6.0	6.077	101.3
0.5	0.582	116.4	6.0	5.724	95.4
0.5	0.542	108.4	6.0	6.676	111.3
0.5	0.557	111.4	6.0	6.481	108.0

Appendix II: Recovery data for method validation by Phenyl hexyl column

Norflurazon:

Spiked levels (µg/L)	Results (µg/L)	Recovery (%)	Spiked levels (µg/L)	Results (µg/L)	Recovery (%)
0.1	0.123	123.0	2.0	2.342	117.1
0.1	0.131	131.0	2.0	2.785	139.2
0.1	0.142	142.0	2.0	2.230	111.5
0.1	0.104	104.0	2.0	1.895	94.7
0.1	0.115	115.0	2.0	2.236	111.8
0.5	0.629	125.8	6.0	6.657	110.9
0.5	0.563	112.6	6.0	6.757	112.6
0.5	0.590	118.0	6.0	6.100	101.7
0.5	0.523	104.6	6.0	6.282	104.7
0.5	0.548	109.6	6.0	6.377	106.3

Prometryn:

Spiked levels (µg/L)	Results (µg/L)	Recovery (%)	Spiked levels (µg/L)	Results (µg/L)	Recovery (%)
0.1	0.125	125.0	2.0	2.204	110.2
0.1	0.131	131.0	2.0	2.644	132.2
0.1	0.153	153.0	2.0	2.242	112.1
0.1	0.105	105.0	2.0	2.239	111.9
0.1	0.135	135.0	2.0	1.849	92.5
0.5	0.608	121.6	6.0	5.835	97.2
0.5	0.581	116.2	6.0	6.128	102.1
0.5	0.623	124.6	6.0	6.025	100.4
0.5	0.498	99.6	6.0	5.971	99.5
0.5	0.582	116.4	6.0	6.247	104.1

Prometon:

Spiked levels (µg/L)	Results (µg/L)	Recovery (%)	Spiked levels (µg/L)	Results (µg/L)	Recovery (%)
0.1	0.100	100.0	2.0	1.837	91.8
0.1	0.103	103.0	2.0	2.400	120.0
0.1	0.117	117.0	2.0	1.933	96.6
0.1	0.098	98.0	2.0	2.145	107.2
0.1	0.109	109.0	2.0	1.797	89.9
0.5	0.473	94.6	6.0	5.408	90.1
0.5	0.453	90.6	6.0	6.142	102.4
0.5	0.493	98.6	6.0	5.704	95.1
0.5	0.497	99.4	6.0	6.252	104.2
0.5	0.489	97.8	6.0	6.303	105.0

Appendix II: Recovery data for method validation by Phenyl hexyl column

Simazine:

Spiked levels (µg/L)	Results (µg/L)	Recovery (%)	Spiked levels (µg/L)	Results (µg/L)	Recovery (%)
0.1	0.132	132.0	2.0	2.395	119.8
0.1	0.131	131.0	2.0	2.073	103.6
0.1	0.145	145.0	2.0	2.500	125.0
0.1	0.141	141.0	2.0	2.215	110.7
0.1	0.119	119.0	2.0	2.585	129.2
0.5	0.560	112.0	6.0	6.655	110.9
0.5	0.552	110.4	6.0	7.059	117.6
0.5	0.636	127.2	6.0	7.176	119.6
0.5	0.586	117.2	6.0	7.090	118.2
0.5	0.611	122.2	6.0	7.084	118.1

Appendix III: Recovery data for propazine (surrogate) and trietazine (internal standard) by SymmetryShield ™ C18 and Phenyl hexyl columns.

Propazine (as surrogate for SymmetryShield ™ C18 column) recovery data for alfa method:

Spiked levels (µg/L)	Results (µg/L)	Recovery (%)	Spiked levels (µg/L)	Results (µg/L)	Recovery (%)
0.200	0.205	102.5	0.200	0.197	98.5
0.200	0.216	108.0	0.200	0.195	97.5
0.200	0.203	101.5	0.200	0.202	101.0
0.200	0.197	98.5	0.200	0.210	105.0
0.200	0.208	104.0	0.200	0.189	94.5
0.200	0.188	94.0	0.200	0.224	112.0
0.200	0.234	117.0	0.200	0.183	91.5
0.200	0.194	97.0	0.200	0.201	100.5
0.200	0.227	113.5	0.200	0.212	106.0
0.200	0.231	115.5	0.200	0.2147	107.0

Propazine (as surrogate for SymmetryShield ™ C18 column) recovery data for beta method:

Spiked levels (µg/L)	Results (µg/L)	Recovery (%)	Spiked levels (µg/L)	Results (µg/L)	Recovery (%)
0.200	0.209	104.5	0.200	0.198	99.0
0.200	0.220	110.0	0.200	0.203	101.5
0.200	0.211	105.5	0.200	0.203	101.5
0.200	0.198	99.0	0.200	0.207	103.5
0.200	0.206	103.0	0.200	0.184	92.0
0.200	0.203	101.5	0.200	0.219	109.5
0.200	0.248	124.0	0.200	0.183	91.5
0.200	0.206	103.0	0.200	0.197	98.5
0.200	0.233	116.5	0.200	0.191	95.5
0.200	0.211	105.5	0.200	2.147	107.3

Trietazine (internal standard for SymmetryShield ™ C18 column) recovery data for alfa method:

Spiked levels (µg/L)	Results (µg/L)	Recovery (%)	Spiked levels (µg/L)	Results (µg/L)	Recovery (%)
0.2000	0.200	100.0	0.200	0.242	121.0
0.200	0.211	105.5	0.200	0.247	123.5
0.200	0.218	109.0	0.200	0.213	106.5
0.200	0.247	123.5	0.200	0.247	123.5
0.200	0.208	104.0	0.200	0.207	103.5
0.200	0.215	107.5	0.200	0.250	125.0
0.200	0.253	126.5	0.200	0.200	100.0
0.200	0.242	121.0	0.200	0.211	105.5
0.200	0.259	129.5	0.200	0.218	109.0
0.200	0.262	131.0	0.200	0.247	123.5

Determination of Atrazine, Bromacil, Cyanazine, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), and Diamino Chlorotriazine (DACT) in Well Water By Liquid Chromatography-Atmospheric Pressure Chemical Ionization Mass Spectrometry

Appendix III: Recovery data for propazine (surrogate) and trietazine (internal standard) by SymmetryShield ™ C18 and Phenyl hexyl columns.

Trietazine (internal standard for SymmetryShield™ C18 column) recovery data for beta method:

Spiked levels (µg/L)	Results (µg/L)	Recovery (%)	Spiked levels (µg/L)	Results (µg/L)	Recovery (%)
0.200	0.234	117.0	0.200	0.248	124.0
0.200	0.258	129.0	0.200	0.227	113.5
0.200	0.235	118.0	0.200	0.238	119.0
0.200	0.243	121.5	0.200	0.202	101.0
0.200	0.215	107.5	0.200	0.256	128.0
0.200	0.241	120.5	0.200	0.257	128.5
0.200	0.226	113.0	0.200	0.203	101.5
0.200	0.258	129.0	0.200	0.203	101.5
0.200	0.236	118.0	0.200	0.229	114.5
0.200	0.227	113.5	0.200	0.249	124.5

Propazine (as surrogate for Phenyl-hexyl column) recovery data:

Spiked levels (µg/L)	Results (µg/L)	Recovery (%)	Spiked levels (µg/L)	Results (µg/L)	Recovery (%)
0.200	0.244	122.0	0.200	0.215	107.5
0.200	0.256	128.0	0.200	0.215	107.5
0.200	0.238	119.0	0.200	0.191	95.5
0.200	0.215	107.5	0.200	0.230	115.0
0.200	0.254	127.0	0.200	0.223	111.5
0.200	0.248	124.0	0.200	0.223	111.5
0.200	0.283	141.5	0.200	0.216	108.0
0.200	0.235	117.5	0.200	0.229	114.5
0.200	0.252	126.0	0.200	0.194	97.0
0.200	0.269	134.5	0.200	0.240	120.0

Trietazine (internal standard for Phenyl-hexyl column):

Spiked levels (µg/L)	Results (µg/L)	Recovery (%)	Spiked levels (µg/L)	Results (µg/L)	Recovery (%)
0.200	0.268	134.0	0.200	0.254	127.0
0.200	0.315	157.5	0.200	0.2575	128.7
0.200	0.264	132.0	0.200	0.240	120.0
0.200	0.263	131.5	0.200	0.254	127.0
0.200	0.282	141.0	0.200	0.250	125.0
0.200	0.287	143.5	0.200	0.255	127.5
0.200	0.296	148.0	0.200	0.256	128.0
0.200	0.264	132.0	0.200	0.276	138.0
0.200	0.314	157.0	0.200	0.227	113.5
0.200	0.306	153.0	0.200	0.264	132.0

Appendix IV: Recovery data for determination of method detection limits on Phenyl hexyl columns.

Atrazine:

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.087	87.0
0.1	0.094	94.0
0.1	0.099	99.0
0.1	0.100	100.0
0.1	0.096	96.0
0.1	0.091	91.0
0.1	0.103	103.0

Average: 0.096
Std Dev: 0.006
MDL: 0.0188
RL: 0.05

Diamino Chlorotriazine (DACT):

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.077	77.0
0.1	0.070	70.0
0.1	0.078	78.0
0.1	0.109	109.0
0.1	0.097	97.0
0.1	0.092	92.0
0.1	0.094	94.0

Average: 0.088
Std Dev: 0.0146
MDL: 0.0457
RL: 0.05

Deethyl Atrazine (DEA):

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.111	111.0
0.1	0.103	103.0
0.1	0.115	115.0
0.1	0.107	107.0
0.1	0.108	108.0
0.1	0.100	100.0
0.1	0.116	116.0

Average: 0.109
Std Dev: 0.0064
MDL: 0.02007
RL: 0.05

Deisopropyl Atrazine(ACET):

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.120	120.0
0.1	0.115	115.0
0.1	0.135	135.0
0.1	0.120	120.0
0.1	0.113	113.0
0.1	0.116	116.0
0.1	0.133	133.0

Average: 0.122
Std Dev: 0.0093
MDL: 0.02922
RL: 0.05

Cyanazine:

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.078	78.0
0.1	0.088	88.0
0.1	0.097	97.0
0.1	0.085	85.0
0.1	0.088	88.0
0.1	0.083	83.0
0.1	0.095	95.0

Average: 0.088
Std Dev: 0.00717
MDL: 0.02253
RL: 0.05

Diuron:

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.088	88.0
0.1	0.067	67.0
0.1	0.094	94.0
0.1	0.086	86.0
0.1	0.092	92.0
0.1	0.092	92.0
0.1	0.095	95.0

Average: 0.088
Std Dev: 0.0103
MDL: 0.03236
RL: 0.05

Appendix IV: Recovery data for determination of method detection limits on Phenyl hexyl columns.

Hexazinon:

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.074	74.0
0.1	0.084	84.0
0.1	0.086	86.0
0.1	0.093	93.0
0.1	0.084	84.0
0.1	0.081	81.0
0.1	0.080	80.0

Average: 0.083
Std Dev: 0.00619
MDL: 0.01945
RL: 0.05

Metribuzin:

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.085	85.0
0.1	0.099	99.0
0.1	0.088	88.0
0.1	0.089	89.0
0.1	0.096	96.0
0.1	0.094	94.0
0.1	0.114	114.0

Average: 0.095
Std Dev: 0.01056
MDL: 0.03318
RL: 0.05

Norflurazon:

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.086	86.0
0.1	0.099	99.0
0.1	0.110	110.0
0.1	0.097	97.0
0.1	0.094	94.0
0.1	0.089	89.0
0.1	0.097	97.0

Average: 0.096
Std Dev: 0.00815
MDL: 0.02559
RL: 0.05

Prometon:

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.071	71.0
0.1	0.083	83.0
0.1	0.084	84.0
0.1	0.078	78.0
0.1	0.080	80.0
0.1	0.079	79.0
0.1	0.083	93.0

Average: 0.080
Std Dev: 0.00475
MDL: 0.01492
RL: 0.05

Prometryn:

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.089	89.0
0.1	0.096	96.0
0.1	0.105	105.0
0.1	0.095	95.0
0.1	0.091	91.0
0.1	0.100	100.0
0.1	0.098	98.0

Average: 0.096
Std Dev: 0.00605
MDL: 0.019
RL: 0.05

Simazine:

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.096	96.0
0.1	0.107	107.0
0.1	0.103	103.0
0.1	0.102	102.0
0.1	0.098	98.0
0.1	0.094	94.0
0.1	0.100	100.0

Average: 0.100
Std Dev: 0.00469
MDL: 0.01473
RL: 0.05

Appendix IV: Recovery data for determination of method detection limits on Phenyl hexyl columns.

Bromacil:

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.091	91.0
0.1	0.102	102.0
0.1	0..096	96.0
0.1	0.091	91.0
0.1	0.097	97.0
0.1	0.098	98.0
0.1	0.103	103.0

Average: 0.097
Std Dev: 0.00514
MDL: 0.01614
RL: 0.05

Appendix V: Recovery data for determination of method detection limits on SymmetryShield™ C18 column by alpha method.

Atrazine:

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.106	106.0
0.1	0.103	103.0
0.1	0.112	112.0
0.1	0.101	101.0
0.1	0.105	105.0
0.1	0.104	104.0
0.1	0.106	106.0

Average: 0.105
Std Dev: 0.0039
MDL: 0.0123
RL: 0.05

Diamino Chlorotriazine (DACT):

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.105	105.0
0.1	0.107	107.0
0.1	0.096	96.0
0.1	0.109	109.0
0.1	0.104	104.0
0.1	0.096	96.0
0.1	0.085	85.0

Average: 0.100
Std Dev: 0.009
MDL: 0.0283
RL: 0.05

Deethyl Atrazine (DEA):

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.108	108.0
0.1	0.109	109.0
0.1	0.135	135.0
0.1	0.116	116.0
0.1	0.116	116.0
0.1	0.096	96.0
0.1	0.107	107.0

Average: 0.112
Std Dev: 0.0129
MDL: 0.0406
RL: 0.05

Cyanazine:

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.092	92.0
0.1	0.075	75.0
0.1	0.083	83.0
0.1	0.106	106.0
0.1	0.087	87.0
0.1	0.086	86.0
0.1	0.081	81.0

Average: 0.087
Std Dev: 0.0105
MDL: 0.0331
RL: 0.05

Diuron:

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.070	70.0
0.1	0.070	70.0
0.1	0.095	95.0
0.1	0.099	99.0
0.1	0.082	82.0
0.1	0.092	92.0
0.1	0.107	107.0

Average: 0.088
Std Dev: 0.0154
MDL: 0.0484
RL: 0.05

Appendix V: Recovery data for determination of method detection limits on SymmetryShield™ C18 column by alpha method.

Hexazinon:

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.080	80.0
0.1	0.080	80.0
0.1	0.073	73.0
0.1	0.084	84.0
0.1	0.083	83.0
0.1	0.077	77.0
0.1	0.073	73.0

Average: 0.079
Std Dev: 0.0048
MDL: 0.015
RL: 0.05

Prometon:

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.083	83.0
0.1	0.085	85.0
0.1	0.095	95.0
0.1	0.081	81.0
0.1	0.088	88.0
0.1	0.084	84.0
0.1	0.077	77.0

Average: 0.085
Std Dev: 0.0060
MDL: 0.019
RL: 0.05

Prometryn:

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.108	108.0
0.1	0.098	98.0
0.1	0.110	110.0
0.1	0.098	98.0
0.1	0.107	107.0
0.1	0.101	101.0
0.1	0.087	87.0

Average: 0.101
Std Dev: 0.0085
MDL: 0.00267
RL: 0.05

Appendix VI: Recovery data for determination of method detection limits on SymmetryShield™ C18 column by beta method.

Atrazine:

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.092	92.0
0.1	0.099	99.0
0.1	0.101	101.0
0.1	0.114	114.0
0.1	0.099	99.0
0.1	0.095	95.0
0.1	0.088	88.0

Average: 0.098
Std Dev: 0.0088
MDL: 0.0277
RL: 0.05

Deethyl Atrazine (DEA):

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.085	85.0
0.1	0.089	89.0
0.1	0.101	101.0
0.1	0.103	103.0
0.1	0.110	110.0
0.1	0.102	102.0
0.1	0.097	97.0

Average: 0.098
Std Dev: 0.0091
MDL: 0.0287
RL: 0.05

Deisopropyl Atrazine (ACET):

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.091	91.0
0.1	0.085	85.0
0.1	0.097	97.0
0.1	0.107	107.0
0.1	0.113	113.0
0.1	0.113	113.0
0.1	0.104	104.0

Average: 0.101
Std Dev: 0.0118
MDL: 0.037
RL: 0.05

Appendix VI: Recovery data for determination of method detection limits on SymmetryShield™ C18 column by beta method.

Metribuzin:

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.083	83.0
0.1	0.087	87.0
0.1	0.107	107.0
0.1	0.117	117.0
0.1	0.098	98.0
0.1	0.098	98.0
0.1	0.091	91.0

Average: 0.097
Std Dev: 0.0127
MDL: 0.0398
RL: 0.05

Norflurazon:

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.081	81.0
0.1	0.078	78.0
0.1	0.087	87.0
0.1	0.103	103.0
0.1	0.105	105.0
0.1	0.102	102.0
0.1	0.087	87.0

Average: 0.092
Std Dev: 0.0120
MDL: 0.0378
RL: 0.05

Simazine:

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.093	93.0
0.1	0.085	85.0
0.1	0.091	91.0
0.1	0.103	103.0
0.1	0.093	93.0
0.1	0.104	104.0
0.1	0.099	99.0

Average: 0.095
Std Dev: 0.0239
MDL: 0.0239
RL: 0.05

Appendix VI: Recovery data for determination of method detection limits on SymmetryShield™ C18 column by beta method.

Bromacil:

Spiked levels (µg/L)	Recovery (µg/L)	Recovery (%)
0.1	0.081	81.0
0.1	0.109	109.0
0.1	0.105	105.0
0.1	0.109	109.0
0.1	0.092	92.0
0.1	0.096	96.0
0.1	0.098	98.0

Average: 0.099
Std Dev: 0.0109
MDL: 0.0343
RL: 0.05

Appendix 5

Quality Assurance/ Quality Control sample results

Blind Spike Recoveries

Extraction Date	Screen	Pesticide	Spike Level	Recovery	Percent Recovery	Exceed CL[1]
7/30/02	Pyrethroid	Permethrin	0.15	0.164	109	No
7/30/02	Pyrethroid	Esfenvalerate	0.2	0.220	110	No
7/30/02	Organophosphate	Dimethoate	0.20	0.196	98.0	No
7/30/02	Organophosphate	Diazinon	0.15	0.142	94.7	No
7/30/02	Organophosphate	Chlorpyrifos	0.25	0.225	90.0	No
7/31/02	Alachlor/Metolachlor	Metolachlor	0.25	0.244	97.6	No
7/31/02	Alachlor/Metolachlor	Metolachlor ESA	0.10	0.073	73.0	LWL
7/31/02	Alachlor/Metolachlor	Alachlor	0.25	0.185	74.0	No
7/31/02	Alachlor/Metolachlor	Metolachlor	0.3	0.319	106	No
7/30/02	Triazine/Herbicides	Simazine	0.25	0.197	78.8	No
		Bromacil	0.35	0.201	57.4	LCL
7/30/02	Triazine/Herbicides	DEA	0.2	0.223	112	UWL
9/17/02	Pyrethroid	Esfenvalerate	0.15	0.173	115	No
9/17/02	Pyrethroid	Permethrin	0.25	0.259	104	No
9/17/02	Organophosphate	DDVP	0.25	0.201	80.4	No
		M. Parathion	0.35	0.282	80.6	No
9/17/02	Organophosphate	Disulfoton	0.2	0.155	77.5	No
9/25/02	Alachlor/Metolachlor	Alachlor ESA	0.25	0.213	85.2	No
9/25/02	Alachlor/Metolachlor	Alachlor OXA	0.3	0.219	73.0	No
		Metolachlor ESA	0.20	0.129	64.5	LWL
9/25/02	Alachlor/Metolachlor	Metolachlor OXA	0.15	0.101	67.3	No
10/2/02	Organophosphate	Diuron	0.30	0.309	103.0	No
10/2/02	Organophosphate	ACET	0.20	0.168	84.0	No
	Organophosphate	DACT	0.25	0.172	68.8	LWL
10/2/02	Triazine/Herbicides	Norflurazon	0.25	0.225	90.0	No

(1) UCL/LCL =Upper/Lower Control Limit; UWL/LWL = Upper/Lower Warning Limit.

Continuing Quality Control, Pyrethroid Insecticides

Extraction Date	Percent Recovery	
	Permethrin	Esfenvalerate
7/3/02	103	110
7/9/02	114	120
7/13/02	107	115
7/16/02	97.0	106
7/30/02	98.0	107
8/6/02	96.0	107
8/13/02	93.0	111
8/20/02	89.0	114
8/27/02	103	108
9/4/02	96.0	103
9/10/02	109	121
9/17/02	109	124
9/24/02	96.0	105
10/1/02	109	119
Average Recovery	**101**	**112**
Standard Deviation	**7.40**	**6.72**
CV	**7.30**	**6.00**
Upper Control Limit	**127**	**131**
Upper Warning Limit	**117**	**121**
Lower Warning Limit	**76.0**	**80.2**
Lower Control Limit	**65.9**	**70.0**

Continuing Quality Control, Alachlor, Metolachlor and degradates.

Extraction Date	Percent Recovery					
	Alachlor	Alachlor ESA	Alachlor OXA	Metolachlor	Metolachlor ESA	Metolachlor OXA
	101	87	85.0	102	78.0	87.0
7/10/2002	96.0	83.0	81.0	93.0	75.0	88.0
7/24/02	79.0	73.0	87.0	89.0	68.0	83.0
	91.0	83.0	94.0	100	79.0	96.0
7/31/02	73.0	83.0	94.0	100	79.0	98.0
	73.0	83.0	94.0	103	80.0	99.0
8/14/02	88.0	94.0	80.0	96.0	91.0	86.0
	82.0	91.0	89.0	95.0	87.0	98.0
8/28/02	75.0	79.0	89.0	89.0	74.0	91.0
	87.0	81.0	93.0	99.0	81.0	92.0
9/11/02	91.0	82.0	84.0	91.0	85.0	85.0
	99.0	89.0	92.0	100	89.0	97.0
9/25/02	94.0	84.0	89.0	99.0	74.0	71.0
	92.0	81.0	86.0	97.0	72.0	82.0
9/25/02	95.0	81.0	91.0	104.0	67.0	84.0
	90.0	75.0	76.0	97.0	65.0	86.0
10/2/02	92.0	84.0	92.0	96.0	77.0	82.0
Average Recovery	**87.6**	**83.1**	**88.7**	**96.3**	**77.7**	**88.3**
Standard Deviation	**8.83**	**5.0**	**5.9**	**5.38**	**7.28**	**7.38**
CV	**10.09**	**6.1**	**6.7**	**5.58**	**9.38**	**8.36**
Upper Control Limit	**113**	**115**	**117**	**122**	**133**	**119**
Upper Warning Limit	**105**	**108**	**109**	**113**	**121**	**107**
Lower Warning Limit	**69.4**	**79.4**	**76**	**77.9**	**74.3**	**59.5**
Lower Control Limit	**60.6**	**72.3**	**67.8**	**69.1**	**62.7**	**47.5**

Continuing Quality Control, Organophosphate Insecticides

Extract	Percent Recovery														
Date	Etho-prop	Diaz-inon	Di-sulfoton	Chlor-pyrifos	Mal-athion	Meth-idathion	Fen-amiphos	Azinphos-methyl	DDVP	Thimet (Phorate)	Fono-phos	Di-methoate	Methyl Parathion	Tribufos (DEF)	Pro-fenofos
7/3/02	113	115	110	112	116	109	106	109	98.6	112	118	124	125	127	130
7/9/02	101	105	98.2	100	103	96.3	91.3	96.6	120	115	121	118	120	120	122
7/16/02	91	90.9	88.2	92	88.6	86	87	74.4	93.8	91.6	94.9	89.1	93.5	70	99.5
7/23/02	110	112	107	109	111	104	101	76	96.8	94.6	97.1	88.7	99.2	95.3	91.6
7/30/02	101	101	96.8	103	99.9	103	105	115	98.4	96.1	98.7	98	104	106	107
8/6/02	100	105	100	104	106	113	108	118	92.8	90.9	91.3	89.1	95	100	102
8/13/02	85.1	86.8	84.3	87.3	87	83.8	86.1	83.7	77.5	84.2	88.3	86.7	84.4	84	85
8/20/02	90.1	93.2	89.7	93.4	93.5	93.7	90.1	87.9	89.5	91.9	91.1	96.9	101	103	104
8/27/02	77.6	86.6	78.1	90.4	90.3	89	88.7	88	69	80.6	85.4	90	88.4	97	97
9/4/02	93.7	94.7	90.3	100	100	103	103	103	83.9	86.7	87	85.9	86.9	92.5	93.4
9/10/02	89.5	87.2	88.2	78.1	90	86.4	84.3	80.3	64.6	73.3	77.6	76	77.8	84.5	82.9
9/17/02	75.1	80.8	78.2	79.2	87.6	75.6	70.9	71.7	70.5	75.5	76.7	77.2	77.4	82	72.7
9/24/02	76.7	81.4	78.5	77.1	79.9	78.1	79.3	76.9	79	80.2	83.7	87.7	88.5	90.8	90.2
10/1/02	73.3	78.1	73.3	76.7	83.3	78.9	82	73.3	70.9	75.4	78.2	90.1	88.2	91.3	94
Ave Recovery	91.2	94.1	90.1	93.0	95.4	92.8	91.6	89.6	86.1	89.1	92.1	92.7	95.0	96.0	98.0
Standard Deviation	11.1	10.1	9.6	10.8	9.0	11.2	10.5	15.0	14.9	10.9	11.3	10.0	11.1	12.0	11.8
CV	12.21	10.78	10.70	11.63	9.41	12.04	11.49	16.80	17.28	12.19	12.27	10.78	11.72	12.53	12.05
Upper Control Limit	123	147	119	121	126	128	125	137	106	110	113	117	119	126	125
Upper Warning Limit	113	130	109	112	116	117	115	122	98	102	105	108	111	116	115
Lower Warning Limit	71	63	68	77	76	75	77	64	67	74	76	73	77	75	74
Lower Control Limit	60	46	58	68	66	64	68	49	59	66	68	65	68	65	64

Highlighted fields are percent recoveries exceeding control limits

Continuing Quality Control, Herbicide Screen

Extraction Date	Percent Recovery Atrazine	Sim-azine	Diuron	Prom-eton	Brom-acil	Hex-azinone	Metri-buzin	Pro-metryn	DEA	ACET (Deiso)	DACT	Nor-flurazon	Prop-azine (Surr)
7/10/02	84.0	91.5	87.5	84.0	102	90.5	80.5	71.0	83.0	79.0	65.0	93.0	81.5
	88.5	92.0	102	89.0	96.0	95.5	85.0	86.0	89.0	81.0	71.0	101	89.0
7/23/02	82.5	87.5	102	84.5	89.0	89.5	82.5	76.5	82.5	73.5	94.5	84.0	81.0
	77.5	86.5	65.0	76.0	80.5	87.5	76.5	62.0	81.5	78.0	75.5	79.0	71.5
Re-extract* 7/26/02								97.0					119
								99.5					99.5
7/30/02	94.5	105	95.0	86.5	120	96.0	94.5	60.0	105	118	106	103	83.0
	101	107	102	89.0	111	88.5	89.5	60.5	104	114	83	102	84.5
Re-extract*								107					129
								110					139
8/13/02	107	109	111	87.5	108	104	95.0	122	115	100	106	109	110
	117	114	101	85.5	104	107	104	88.0	120	105	95.5	121	116
8/22 - 8/27/02	105	104	95.0	95.5	95.0	102	99.0	93.5	105	102	90.0	105	100
	106	105	107	101	105	104	101	111	108	114	96.0	111	110
9/12/02	87.0	80.5	94.5	75.5	79.0	102	73.0	94.0	82.5	72.0	92.0	104	70.5
	90.5	84.5	87.0	73.0	83.5	103	75.0	78.5	86.0	69.5	96.5	103	68.5
10/2/02	69.0	77.0	99.5	74.5	100	77.5	71.5	70.5	85.5	88.5	69.5	92.5	63.5
	77.5	86.0	70.0	72.5	84.5	70.0	75.5	73.5	88.0	96.0	65.5	81.5	74.5
10/7/02	100	110	89.5	84.0	101	106	109	71.5	105	118	92.5	104	90
	85.5	99.0	80.0	79.0	87.0	90.0	83.5	86.5	96.0	102	95.5	87.5	84.0
Average Recovery	91.9	96.1	92.9	83.6	96.5	94	87.2	85.9	95.9	94.3	87.0	98.7	93.1
Standard Deviation	12.93	11.7	12.7	8.14	11.79	10.51	11.89	18.13	12.72	17.05	13.62	11.45	21.21
CV	14.07	12.2	13.7	9.74	12.21	11.13	13.64	21.10	13.26	18.08	15.65	11.60	22.77
Upper Control Limit	105	108	118	106	117	121	110	111	116	140	101	113	115
Upper Warning Limit	98.2	101	109	99.2	111	113	103	105	109	128	95.7	107	107
Lower Warning Limit	72.2	73.2	73.4	73.8	84.9	76.9	75.0	78.9	79.1	78.3	73.7	84.8	72.4
Lower Control Limit	65.8	66.3	64.4	67.4	78.4	68.1	68.0	72.4	71.7	66.0	68.2	79.2	63.8

Highlighted fields are percent recoveries exceeding control limits