#26

Old letter
Sent 6/10/04

More Data in MAR/2004 303(d) list/DATA/TISSUE/SMW-3 ORG_WET_1987-2000_by RWQCB (27)

CITY OF
SANTA ROSA

OFFICE OF THE CITY MANAGER
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June 10, 2004

Craig J. Wilson
Division of Water Quality
State Water Resources Control Board
P.O. Box 100
Sacramento, CA 95812-0100

SUBJECT: 2004 Clean Water Act Section 303(d) List Solicitation of Data--Laguna de Santa Rosa Phosphorus

Dear Mr. Wilson:

Thank you for the opportunity to provide input to the 2004 303(d) list update. Attached to this letter are the City's detailed technical comments and data to support the City's contention that the Laguna de Santa Rosa should be de-listed for phosphorus and, instead, further studies be conducted to determine the causes of low dissolved. We appreciate your careful consideration of the data and issues supporting the de-listing of the Laguna for phosphorus.

Despite the State's well-founded decision to place the Laguna on the 2002 303(d) monitoring list for phosphorus, the U.S. EPA overruled the State's decision and placed the Laguna on the 2002 303(d) list as impaired for phosphorus, which the U.S. EPA believes has led to the Laguna's impairment for dissolved oxygen. EPA believes phosphorus promotes algal growth in the Laguna and that algae are responsible for dissolved oxygen depletion. However, the link between algae and dissolved oxygen depletion in the Laguna has never been substantiated. Even if algae were controlling oxygen in the Laguna, phosphorus is not the algal-growth limiting nutrient in the Laguna. The data we provide here indicate that nitrogen, rather than phosphorus, is the limiting nutrient in the Laguna. No evidence exists that reducing phosphorus concentrations would improve dissolved oxygen concentrations or reduce the abundance of the nuisance weed, *Ludwigia*. The U.S. EPA's decision to list the Laguna as impaired was based on inappropriate criteria for phosphorus in the Laguna. No criterion for phosphorus has been developed for the Laguna.

The City of Santa Rosa remains strongly committed to do its part to protect water quality in our region, and in the Laguna specifically. We urge the SWRCB reassess the listing of the Laguna de Santa Rosa as impaired for phosphorus. De-listing will enable the City and the Regional Board to move forward with a more focused study of the Laguna to determine the specific limiting pollutants, rather than divert resources to development of a phosphorus TMDL, which the available data indicate will not improve water quality conditions in the Laguna.

Thank you for consideration of our concerns.

Sincerely,

GREG SCOLES
Deputy City Manager

GDS:rca
Attachments
c: Catherine Kuhlman, NCRWQCB
David W. Smith, Ph.D., Merritt Smith Consulting
Craig Johns, California Resource Strategies
Roberta Larson, Somach, Simmons & Dunn

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MERRITT SMITH
CONSULTING
ENVIRONMENTAL SCIENCE AND COMMUNICATION

MEMORANDUM

TO: Greg Scoles, City of Santa Rosa
Dan Carlson, City of Santa Rosa

FROM: Marcie Commins, Ph.D.
James Roth, Ph.D.
Dave Smith, Ph.D.

COPIES: Craig S.J. Johns, California Resource Strategies
Bobbi Larson, Somach, Simmons & Dunn

DATE: 2 June 2004

SUBJECT: Information for State's 2004 303(d) list

This memorandum is in response to the State Water Resources Control Board's (SWRCB) request for information and data regarding water quality conditions in surface waters of California. Specifically it addresses data and information pertaining to the decision by the U.S. EPA (EPA) to include the Laguna de Santa Rosa on the 2002 303(d) list as impaired for phosphorus despite the SWRCB's decision to place the Laguna on the monitoring list for further study. We recommend that the City of Santa Rosa (City) request reassessment of the listing of the Laguna as impaired for phosphorus for the reasons listed below.

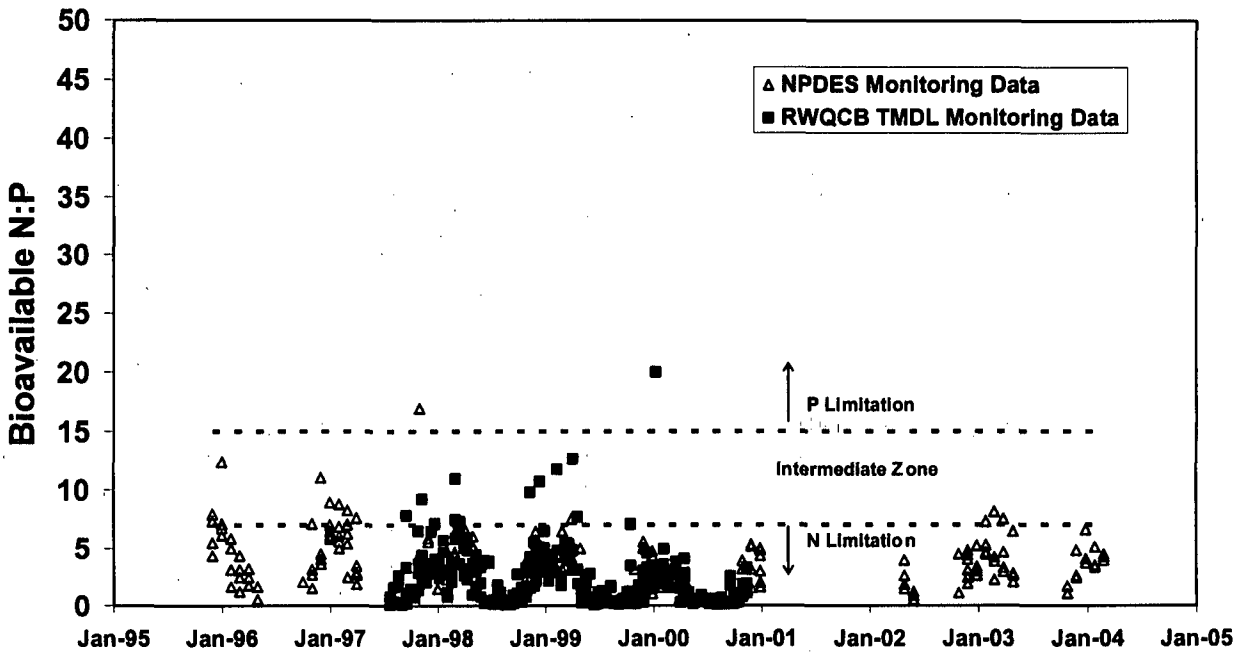
- The decision to list the Laguna as impaired for both phosphorus and nitrogen came about because the Regional Water Quality Control Board (Regional Board) is concerned about dissolved oxygen levels in the Laguna. Nutrients can affect oxygen through stimulation of algae, which deplete oxygen at night when not photosynthesizing, and upon their death and decomposition. However, the link between algae and dissolved oxygen depletion in the Laguna has never been substantiated. Chlorophyll *a* data in the Laguna are limited in number and spatial extent. In fact, according to the Regional Board, "the cause of the low dissolved oxygen levels is not certain." (North Coast Regional Water Quality Control Board November 16, 2001 303(d) List Update Recommendations (Staff Recommendations)). Other factors may be causing the low dissolved oxygen. For example organic loading contributes to the oxygen deficit, but organic loading, like algal biomass, has not been adequately studied.

- Even if algae were controlling oxygen in the Laguna, phosphorus is not the algal-growth limiting nutrient in the Laguna. The Staff Recommendations point out that data show that *nitrogen* - - and not phosphorus - - is the limiting nutrient in the Laguna. The ratio of bioavailable N to P is an indication of which nutrient is limiting in an aquatic system. Figure 1 shows the ratio of N to P in the Laguna

for data collected by the Regional Board as part of its nitrogen TMDL monitoring that is the basis for the Regional Board staff's conclusion that nitrogen is the likely limiting nutrient in the Laguna. These data were collected in the Laguna at Stony Point, Occidental, Guerneville, and Trenton Healdsburg roads and are presented in Appendix A. Since the TMDL monitoring program is no longer active, no samples have been collected since November 2000. However, the City collects nitrogen and phosphorus data as part of its NPDES discharge permit compliance monitoring. Nutrient data collected during the discharge season between December 1995 and March 2004 are available and are also shown in Figure 1. These data are monthly averages of samples collected weekly during the discharge season and are presented in Appendix B. The NPDES data are summarized for all Laguna stations where measurements were made and were collected between the Laguna at Llano Road and the confluence of the Laguna and Santa Rosa Creek. Lee et al. (1980) found that for a wide variety of aquatic habitats, a good estimate of the bioavailable phosphorus is given by the sum of the dissolved orthophosphate and 0.2 x the particulate phosphorus in a water sample. For both the Regional Board data set and the NPDES data set, total phosphorus was measured, but dissolved P was not. However, based on 82 pairs of total and dissolved P in water samples collected at Laguna stations in 1993-1999, the dissolved orthophosphate averaged 76% of total P. Assuming 76% of P is dissolved, bioavailable P is estimated as 0.8 x total P (see Roth 2001). The ratio of bioavailable N:P from the two data sets are calculated as TIN÷0.8 TP. These results are shown in Figure 1, which shows that the ratio of bioavailable N:P is usually less than 7, which indicates that nitrogen, not phosphorus, is the nutrient limiting algal growth in the Laguna de Santa Rosa.

Since the NPDES N:P ratios shown in Figure 1 are derived from monthly averages, an evaluation was conducted to determine N:P ratios determined from monthly averaged nitrogen and phosphorus data are representative of N:P ratios from individual measurements. The individual sample data for 2003 (N= 101 samples) were used to calculate individual N:P ratios for comparison to the monthly average values. These data are provided in Appendix C. The average of these individual N:P ratios was 4.4 with a 99 percent confidence interval of ±0.8 compared to the average of the monthly average N:P ratios for the same period of 3.9. No statistically significant difference exists between the monthly and the daily data (Mann Whitney Rank Sum test $p = 0.683$). In addition, the NPDES average data track quite well the TMDL data which are not averages. Therefore, the N:P ratios based on monthly average values are representative of nutrient conditions in the Laguna.

Figure 1. Ratio of Bioavailable N:P
Laguna de Santa Rosa Stations 1995-2004



- In recent years, *Ludwigia* has increased in abundance in the Laguna. This is problematic due to the difficulty of controlling mosquito larvae in areas where *Ludwigia* is particularly abundant. Nutrients also potentially limit growth of plants such as *Ludwigia* that obtain nutrients from the water column and the sediment. According to Lars Anderson (USDA ARS Exotic and Invasive Weed Research, Weed Science Program), nitrogen is the most important factor to control *Ludwigia* "He [Lars Anderson] also said eliminating as many of the nitrogen pollution sources as possible was crucial. ..."the $10 answer would be, nitrogen, nitrogen, nitrogen," said Anderson." " (Sonoma West January 20, 2003). Other factors such as low flow in the Laguna in recent years due to

drought conditions also may be controlling or contributing to the control of *Ludwigia* abundance. ** I am working on better substantiating nutrient limitation in *Ludwigia*.

- More study is needed to determine whether elevated phosphorus in the Laguna is the cause of the low dissolved oxygen and increased *Ludwigia* abundance and whether reducing phosphorus will result in improving dissolved oxygen and controlling *Ludwigia* in the Laguna. Without these additional studies, placing the Laguna on the 2002 303(d) List for phosphorus could result in significant economic impacts to the ratepayers of Santa Rosa with no known or reasonably expected environmental benefits. The SWRCB recognized the merit of these arguments, and decided to place the Laguna on the 2002 Monitoring List for phosphorus. These studies are a necessary first step to determine whether phosphorus reduction is necessary.

- Despite the State's well-founded decision to place the Laguna on the 2002 303(d) monitoring list for phosphorus, the EPA overruled the State's decision and placed the Laguna on the 2002 303(d) list as impaired for phosphorus. The EPA's review of California's 2002 Section 303(d) List presented the EPA's rationale for listing the Laguna for nutrients. We have reviewed the analysis, and disagree with the U.S. EPA's analysis for the following reasons:

  1. The EPA review concludes that "the nitrogen and phosphorus levels found in the Laguna far exceed the levels associated with excessive aquatic growths that can adversely affect beneficial uses, and that the Basin Plan narrative water quality standard for biostimulatory substances is violated." While this statement may be true in the abstract, to our knowledge, little or no information about the levels of aquatic growths in the Laguna is available. There is no information presented in the EPA review to substantiate this statement.

  2. EPA's decision to overrule the State Board was based on EPA's erroneous application of nitrogen and phosphorus criteria (1 mg/L and 0.1 mg/L, respectively) that EPA claimed is required to protect the Laguna. These criteria are inappropriate for the following reasons:

     - EPA justifies the use of the 1 mg/L criterion for nitrogen by reference to the nitrogen objective (1 mg/L) included in the San Diego Regional Basin Plan. However, this objective was developed by taking a 1970's recommendation for phosphorus of 0.1 mg/L and applying a 10:1 N:P ratio, resulting in the N objective of 1 mg/L. The P recommendation is presumably the EPA's "Red Book" recommendation and is outdated and

not based on region-specific, let alone waterbody-specific, information. Similarly, EPA's application of a 10:1 N:P ratio to derive a standard does not take into account region-specific information. We have taken site-specific information into account when application of the N:P ratio, and site-specific information indicates that phosphorus is not limiting algal growth (see above).

- EPA's decision to overrule the State Board also relies upon the nitrogen and phosphorus targets in the Malibu Creek TMDL document (U.S.EPA 2003).

  - The Malibu Creek TMDL document states that various nutrient standards, including the San Diego Regional Board standard, "have little predictive power in explaining the patterns in algal abundance or biomass within the Malibu Creek watershed". The Malibu Creek TMDL document also indicates "uncertainty as to what factors control algal abundances in the Malibu Creek watershed. ... Therefore, when establishing a numeric target to control algal biomass and chlorophyll *a* concentrations, it is important to consider the factors limiting algal growth. No single study element was identified as the factor most likely limiting algal growth. ... However, it is anticipated that the limiting condition will be determined prior to full implementation of these TMDLs. ... After these determinations, the Regional Board may need to revise these TMDLs." Therefore, EPA (in the Malibu Creek TMDL document) acknowledged the criteria (which were also applied by the EPA to list the Laguna) were applied despite a lack of information to assess whether they were correct, and that the TMDL targets may need to be revised based upon site-specific information.

- The EPA review also cites as support for the reasonableness of both the nitrogen and phosphorus criteria Dodds and Welch (2000).

  - Dodds and Welch (2000) state " ...so many factors are related to DO depletion rates, existing data for most streams are insufficient to develop nutrient criteria for avoiding DO deficits. . . . As more data become available, it will be possible to directly link frequency and severity of low DO events with nutrient loading."

  - The various standards Dodds and Welch (2000) provides for controlling benthic chlorophyll *a* were derived from data collected from temperate streams throughout the world and thus may not be applicable to streams in semiarid regions such as the Laguna. In

temperate climates, rain falls for much of the year and is rarely torrential, resulting in more continuous vegetative ground cover and in little natural soil erosion. Regions with semiarid climates have fewer, often larger storms and less continuous ground cover. The main natural source of nitrogen in all watersheds is rainfall, and the main natural source of phosphorus is soil erosion. Thus rivers in semiarid climates tend to have excess phosphate and to be nitrogen-limited, while those in temperate climates have excess nitrate and tend to be phosphorus-limited. (Horne and Goldman, 1994. *Limnology*)

- Additionally, Dodds and Welch (2000) state "[m]oreover, a large amount of the variance in benthic chlorophyll levels in streams is not related to nutrient levels." They also conclude that "a significant amount of monitoring data are necessary to refine recommendations for nutrient criteria," including seasonal means and maxima for benthic and planktonic chlorophyll *a*, associated water column nutrients and diurnal DO concentrations. These are the sorts of data would likely be collected in the study on the Laguna that the City of Santa Rosa has proposed to conduct.

The draft Water Quality Control Policy For Developing California's Clean Water Act Section 303(d) List (303(d) Policy) provides the following factors for placement or removal of water segments on the list:

1. Numeric Water Quality Objectives and Criteria for Toxicants in Water
2. Numeric Water Quality Objectives for Conventional or Other Pollutants in Water
3. Numerical Water Quality Objectives or Standards for Bacteria Where Recreational Uses Apply
4. Health Advisories
5. Bioaccumulation of Pollutants in Aquatic Life Tissue
6. Water/Sediment Toxicity
7. Nuisance
8. Adverse Biological Response

9. Degradation of Biological Populations and Communities

EPA invoked factors 2 (Numeric Water Quality Objectives for Conventional or Other Pollutants in Water) and factor 7 (Nuisance from excessive plant growth) in its decision to place the Laguna on the 303(d) list. The draft 303(d) policy states that, for excessive algae growth, a water segment should be placed on the list if acceptable nutrient-related numeric criteria are exceeded. As discussed above, no numeric criterion yet exists for phosphorus in the Laguna. Therefore, under the proposed policy, the Laguna could not be listed as impaired for phosphorus. Since no evidence exists to indicate lowering phosphorus concentrations will improve water quality conditions in the Laguna, the Laguna should be de-listed for phosphorus.

SUPPLEMENTAL DATA NECESSARY TO ENABLE THE SWRCB TO CONDUCT A COMPLETE REASSESSMENT

The supplemental information provided here are for the NPDES data collected by the City since the State presumably has information for the RWQCB data.

Name of the person or organization providing the information:

City of Santa Rosa
PO Box 1678
Santa Rosa, CA 95402

Mailing address, phone number, and email address of a contact responsible for answering questions about the information submitted:

Dave Smith
Merritt Smith Consulting
3620 Happy Valley Road Suite 103
Lafayette, CA 94549
925-284-6490
davesmith@merritt-smith.com

Bibliographic citations for all published information provided

Dodds and Welch. 2000. *Establishing Nutrient Criteria in Streams.* J. North. Am. Benthol. Soc. 19(1): 186-196.

Horne and Goldman, 1994. *Limnology.* McGraw Hill, Inc.

Lee, G.F., R.A. Jones, and W. Rast. 1980. Availability of phosphorus to phytoplankton and its implications for phosphorus management strategies. P. 259-308, *In*:

"Phosphorus Management Strategies for Lakes," Ann Arbor Science Publishers, Inc.

Roth, J.C. 2001. Comments on Proposed 303(d) listing for Laguna de Santa Rosa. Letter dated 10/5/2001 submitted to the NCRWQCB (reference #118 in North Coast Region Water Quality Control Board 303(d) List Update Recommendations November 16, 2001).

EPA. 2003. Total Maximum Daily Loads for Nutrients: Malibu Creek. EPA Region 9.

To the extent possible, all information should be submitted in electronic format:

Data provided in the Appendices will also be provided electronically.

Detailed quality assurance and quality control information about sampling and analysis of all numeric data:

The quality assurance manual for the Laguna Environmental Laboratory who collected and analyzed the samples is found in Appendix D.

Water body name and California water body identification number.

Laguna de Santa Rosa, California Watershed number 11421020

Geographic extent of the potential water quality limited segment:

The entire Laguna from the headwaters to the confluence with the Russian River is on the 303(d) list.

Pollutant(s) of concern:

phosphorus

Applicable water quality objective or criterion:

Biostimulatory substances – waters shall not contain biostimulatory substances in concentrations that promote aquatic growths to the extent that such growths cause a nuisance or adversely affect beneficial uses.

Comparison of results against applicable water quality objective or criterion:

N/A

Designated beneficial use(s) that may be impacted by pollutant(s):

Phosphate does not directly impact any beneficial uses. However, if the phosphate results in a substantial increase in aquatic plant biomass, the resulting low dissolved oxygen and filter clogging can impact the following beneficial uses: agricultural supply, industrial service supply, contact water recreation, non-contact water recreation, commercial and sport fishing, cold freshwater habitat, wildlife habitat,

Complete background information (metadata) for field data (i.e., when and where measurements were taken, number of samples, detection limits, etc.):

See Appendices A, B and C.

Full identification of any citizen volunteer water quality monitoring efforts:

N/A

Data quality assurance assessment(s):

The Laguna Environmental Laboratory is an ELAPHE certified laboratory. No reason exists to think the data would not be of high quality.

Spatial representation:

Data come from a variety of locations in the Laguna from the Laguna at Stony Point Road to the Laguna at Trenton Healdsburg Road.

Temporal representation:

TMDL data were collected throughout the year. NPDES data were collected during the discharge season (October 1 through May 14)

Age(s) of the data:

Data were collected December 1995 through March 2004.

Effects of seasonality:

The data in Figure 1 indicate that the N:P ratio tends to be lower in the summer.

Effects of any events that might influence data evaluation (e.g., storm events, flow conditions, laboratory data qualifiers, etc.):

No laboratory qualifiers are known that might influence the data evaluation. Although environmental events such as storms can influence data, a large data set such as that provided with the NPDES data will cover most environmental conditions and not be

skewed by a single type of environmental condition. The exception to this is that, as noted above, the NPDES data were collected only during the discharge season.

The total number of samples:

The TMDL data consist of 318 N:P ratios, the NPDES data consist of 217 N:P ratios.

The number of samples exceeding standards:

No standards exist for N:P ratios. However, only two of the ratios (out of 535) fall within the phosphorus limitation range.

The source or reference for samples:

The TMDL samples were collected by the North Coast RWQCB. The NPDES samples were collected and analyzed by the City of Santa Rosa's Laguna Environmental Laboratory.

The potential sources of pollutants

Internal nutrient cycling, point and nonpoint sources such as wastewater discharge, agricultural and urban runoff.

Any program that might address the water quality problem in lieu of a TMDL.

More study is needed to determine whether elevated phosphorus in the Laguna is the cause of the low dissolved oxygen and *Ludwigia* growth and whether reducing phosphorus will result in improving dissolved oxygen in the Laguna and reducing *Ludwigia*. Without these additional studies, having the Laguna on the 303(d) List for phosphorous could result in massive economic impacts to the ratepayers of Santa Rosa with no known or reasonably expected environmental benefits. Santa Rose has a long history of taking responsibility when necessary to address actual or suspected water quality problems. Should the Board remove phosphorus from the 303(d) list and place it on the monitoring list, the City is prepared to fund and perform a study necessary to help evaluate if phosphorus is adversely affecting water quality and thus should be moved from the monitoring list to the 303(d) list.

Appendix A

utrient Data from RWQCB TMDL Monitoring Program
LGR=Laguna at Gumville Road
LOR=Laguna at Occidental Road
LSP=Laguna at Stony Point Road
LTH=Laguna at Trenton-Healdsburg Road
BU= agr, ind,rec1, rec2, comm, wild, aqua

STATION	DATE	TIME	SOURCE	AMMONIA NITROGEN	No Objective	NITRATE	MUNI 45 ppm	NITRITE	MUNI 1 ppm	TOTAL PHOS		TIN	80% of TP	TIN:80%TP
LGR	7/23/97	845	RB	0.0695	No Objective	0.025	No			0.15	No Obj	0.09	0.12	0.79
LOR	7/23/97	920	RB	0.025	No Objective	0.025	No		No	1.79	No Obj	0.05	1.43	0.03
LSP	7/23/97	1130	RB	0.025	No Objective	0.0531	No		No	0.234	No Obj	0.08	0.19	0.42
LTH	7/23/97	815	RB	0.025	No Objective	0.0965	No		No	0.224	No Obj	0.12	0.18	0.68
LGR	8/5/97	1030	RB	0.025	No Objective	0.025	No	0.025	No	0.22	No Obj	0.08	0.18	0.43
LOR	8/5/97	1125	RB	2.38	No Objective	0.025	No	0.025	No	1.87	No Obj	2.43	1.50	1.62
LSP	8/5/97	1150	RB	0.025	No Objective	0.025	No	0.025	No	0.349	No Obj	0.08	0.28	0.27
LTH	8/5/97	910	RB	0.025	No Objective	0.025	No	0.025	No	0.294	No Obj	0.08	0.24	0.32
LGR	8/21/97	930	RB	0.025	No Objective	0.396	No		No	0.307	No Obj	0.42	0.25	1.71
LOR	8/21/97	955	RB	0.025	No Objective	0.095	No		No	0.832	No Obj	0.12	0.67	0.18
LSP	8/21/97	1035	RB	0.025	No Objective	0.0927	No		No	0.665	No Obj	0.12	0.53	0.22
LTH	8/21/97	905	RB	0.025	No Objective	0.432	No		No	0.216	No Obj	0.46	0.17	2.64
LGR	9/2/97	940	RB	0.025	No Objective	0.0654	No	0.025	No	0.462	No Obj	0.12	0.37	0.31
LOR	9/2/97	1020	RB	0.025	No Objective	0.0593	No	0.025	No	1.37	No Obj	0.11	1.10	0.10
LSP	9/2/97	1105	RB	0.025	No Objective	0.0536	No	0.025	No	0.626	No Obj	0.10	0.50	0.21
LTH	9/2/97	915	RB	0.025	No Objective	0.0953	No	0.025	No	0.652	No Obj	0.15	0.52	0.28
LGR	9/17/97	900	RB	1.3	No Objective	0.025	No		No	0.493	No Obj	1.33	0.39	3.36
LOR	9/17/97	930	RB	0.105	No Objective	0.025	No		No	0.847	No Obj	0.13	0.68	0.19
LSP	9/17/97	1030	RB	3.24	No Objective	0.025	No		No	0.523	No Obj	3.27	0.42	7.80
LTH	9/17/97	830	RB	0.117	No Objective	0.0761	No		No	0.211	No Obj	0.19	0.17	1.14
LGR	10/1/97	1105	RB	0.182	No Objective	0.025	No	0.025	No	0.262	No Obj	0.23	0.21	1.11
LOR	10/1/97	1145	RB	0.84	No Objective	0.025	No	0.025	No	0.739	No Obj	0.89	0.59	1.51
LSP	10/1/97	1220	RB	0.156	No Objective	0.025	No	0.025	No	0.366	No Obj	0.21	0.29	0.70
LTH	10/1/97	1010	RB	0.135	No Objective	0.0561	No	0.025	No	0.342	No Obj	0.22	0.27	0.79
LGR	10/15/97	920	RB	0.275	No Objective	0.025	No		No	0.494	No Obj	0.30	0.40	0.76
LOR	10/15/97	1025	RB	0.6	No Objective	0.108	No		No	0.612	No Obj	0.71	0.49	1.45
LSP	10/15/97	1220	RB	0.119	No Objective	0.025	No		No	0.27	No Obj	0.14	0.22	0.67
LTH	10/15/97	850	RB	0.269	No Objective	0.0526	No		No	0.359	No Obj	0.32	0.29	1.12
LGR	10/28/97	945	RB	0.534	No Objective	0.025	No	0.025	No	0.252	No Obj	0.58	0.20	2.90
LOR	10/28/97	1030	RB	0.528	No Objective	0.025	No	0.025	No	0.525	No Obj	0.58	0.42	1.38
LSP	10/28/97	1120	RB	0.919	No Objective	0.025	No	0.025	No	0.186	No Obj	0.97	0.15	6.51
LTH	10/28/97	845	RB	0.678	No Objective	0.0615	No	0.025	No	0.259	No Obj	0.76	0.21	3.69
LGR	11/10/97	1005	RB	0.55	No Objective	0.602	No	0.025	No	0.331	No Obj	1.18	0.26	4.44
LOR	11/10/97	1100	RB	1.13	No Objective	0.025	No	0.025	No	0.611	No Obj	1.18	0.49	2.41
LSP	11/10/97	1200	RB	1.28	No Objective	0.523	No	0.025	No	0.248	No Obj	1.83	0.20	9.21
LTH	11/10/97	935	RB	0.587	No Objective	0.0907	No	0.025	No	0.25	No Obj	0.70	0.20	3.51
LOR	11/24/97	1040	RB	0.025	No Objective	2.7	No		No	1.49	No Obj	2.73	1.19	2.29
LSP	11/24/97	1130	RB	1.05	No Objective	0.508	No		No	0.751	No Obj	1.56	0.60	2.59
LTH	11/24/97	925	RB	0.786	No Objective	0.66	No		No	0.87	No Obj	1.45	0.70	2.08
LOR	12/10/97	1000	RB	0.338	No Objective	3.02	No		No	1.13	No Obj	3.36	0.90	3.71
LSP	12/10/97	1120	RB	0.025	No Objective	2.84	No		No	0.554	No Obj	2.87	0.44	6.46
LTH	12/10/97	850	RB	0.174	No Objective	2.11	No		No	0.993	No Obj	2.28	0.79	2.88
LOR	12/23/97	1020	RB	0.025	No Objective	2.32	No	0.025	No	0.874	No Obj	2.37	0.70	3.39
LSP	12/23/97	1110	RB	0.025	No Objective	2.25	No	0.025	No	0.404	No Obj	2.30	0.32	7.12
LTH	12/23/97	930	RB	0.025	No Objective	1.79	No	0.025	No	0.559	No Obj	1.84	0.45	4.11
LOR	1/7/98	905	RB	0.0893	No Objective	1.58	No		No	0.852	No Obj	1.67	0.68	2.45
LSP	1/7/98	1000	RB	0.792	No Objective	1.26	No		No	0.656	No Obj	2.05	0.52	3.91
LTH	1/7/98	825	RB	0.025	No Objective	1.34	No		No	0.43	No Obj	1.37	0.34	3.97
LOR	1/21/98	1000	RB	0.496	No Objective	2.74	No	0.025	No	0.872	No Obj	3.26	0.70	4.67
LSP	1/21/98	1100	RB	0.385	No Objective	1.82	No	0.025	No	0.487	No Obj	2.23	0.39	5.72
LTH	1/21/98	905	RB	0.354	No Objective	1.18	No	0.025	No	0.614	No Obj	1.56	0.49	3.17
LOR	2/3/98	1035	RB	0.233	No Objective	0.11	No	0.23	No	0.927	No Obj	0.57	0.74	0.77
LSP	2/3/98	1115	RB	0.227	No Objective	0.025	No	0.28	No	0.679	No Obj	0.53	0.54	0.98
LTH	2/3/98	930	RB	0.0723	No Objective	0.256	No	0.11	No	0.456	No Obj	0.44	0.36	1.20
LOR	2/18/98	1000	RB	0.544	No Objective	1.03	No	0.0776	No	0.976	No Obj	1.65	0.78	2.12
LSP	2/18/98	1120	RB	0.165	No Objective	0.949	No	0.0545	No	0.518	No Obj	1.17	0.41	2.82
LTH	2/18/98	845	RB	0.238	No Objective	1.45	No	0.0619	No	0.573	No Obj	1.75	0.46	3.82
LOR	3/4/98	930	RB	0.206	No Objective	5.22	No		No	0.911	No Obj	5.43	0.73	7.45
LSP	3/4/98	1015	RB	0.0833	No Objective	1.95	No		No	0.232	No Obj	2.03	0.19	10.96
LTH	3/4/98	830	RB	0.263	No Objective	2.14	No		No	0.506	No Obj	2.40	0.40	5.94
LOR	3/18/98	945	RB	0.025	No Objective	2.55	No	0.0706	No	0.894	No Obj	2.65	0.72	3.70
LSP	3/18/98	1115	RB	0.025	No Objective	0.609	No	0.025	No	0.113	No Obj	0.66	0.09	7.29
LTH	3/18/98	840	RB	0.0509	No Objective	1.53	No	0.025	No	0.32	No Obj	1.61	0.26	6.27
LOR	4/1/98	940	RB	0.106	No Objective	3.98	No		No	1	No Obj	4.09	0.80	5.11
LSP	4/1/98	1015	RB	0.446	No Objective	0.476	No		No	0.428	No Obj	0.92	0.34	2.69
LTH	4/1/98	855	RB	0.239	No Objective	0.426	No		No	0.259	No Obj	0.67	0.21	3.21
LOR	4/13/98	935	RB	0.329	No Objective	2.93	No	0.0881	No	0.863	No Obj	3.35	0.69	4.85
LSP	4/13/98	1000	RB	0.424	No Objective	0.519	No	0.0912	No	0.556	No Obj	1.03	0.44	2.33
LTH	4/13/98	845	RB	0.229	No Objective	0.422	No	0.025	No	0.142	No Obj	0.68	0.11	5.95
LOR	4/30/98	930	RB	0.15	No Objective	3.05	No		No	1.07	No Obj	3.20	0.86	3.74
LSP	4/30/98	1000	RB	0.202	No Objective	0.568	No		No	0.297	No Obj	0.77	0.24	3.24
LTH	4/30/98	845	RB	0.0686	No Objective	0.373	No		No	0.571	No Obj	0.44	0.46	0.97
LOR	5/11/98	1020	RB	0.025	No Objective	1.84	No	0.11	No	0.817	No Obj	1.98	0.65	3.02

STATION	DATE	TIME	SOURCE	AMMONIA NITROGEN	No Objective	NITRATE	MUNI 45 ppm	NITRITE	MUNI 1 ppm	TOTAL PHOS		TIN	80% of TP	TIN:80%TP
LSP	5/11/98	1115	RB	0.0854	No Objective	0.624	No	0.0649	No	0.216	No Obj	0.77	0.17	4.48
LTH	5/11/98	850	RB	0.0531	No Objective	0.335	No	0.057	No	0.318	No Obj	0.45	0.25	1.75
LOR	5/28/98	935	RB	0.296	No Objective	0.124	No		No	0.668	No Obj	0.42	0.53	0.79
LSP	5/28/98	1010	RB	0.112	No Objective	0.453	No		No	0.208	No Obj	0.57	0.17	3.40
LTH	5/28/98	845	RB	0.0574	No Objective	0.24	No		No	0.184	No Obj	0.30	0.15	2.02
LOR	6/9/98	1000	RB	0.0667	No Objective	0.0748	No	0.025	No	1.03	No Obj	0.17	0.82	0.20
LSP	6/9/98	1100	RB	0.0944	No Objective	0.421	No	0.025	No	0.17	No Obj	0.54	0.14	3.97
LTH	6/9/98	850	RB	0.025	No Objective	0.059	No	0.025	No	0.294	No Obj	0.11	0.24	0.46
LGR	6/25/98	940	RB	0.05	No Objective	0.025	No		No	0.025	No Obj	0.08	0.02	3.75
LOR	6/25/98	1015	RB	0.18	No Objective	0.025	No		No	0.73	No Obj	0.21	0.58	0.35
LSP	6/25/98	1050	RB	0.28	No Objective	0.41	No		No	0.22	No Obj	0.69	0.18	3.92
LTH	6/25/98	905	RB	0.06	No Objective	0.025	No		No	0.34	No Obj	0.09	0.27	0.31
LGR	7/9/98	945	RB	0.1	No Objective	0.05	No	0.05	No	0.46	No Obj	0.20	0.37	0.54
LOR	7/9/98	1000	RB	0.1	No Objective	0.05	No	0.05	No	2	No Obj	0.20	1.60	0.13
LSP	7/9/98	1045	RB	0.1	No Objective	0.05	No	0.05	No	0.46	No Obj	0.20	0.37	0.54
LTH	7/9/98	845	RB	0.1	No Objective	0.05	No	0.05	No	0.47	No Obj	0.20	0.38	0.53
LGR	7/24/98	930	RB	0.186	No Objective	0.025	No		No	0.218	No Obj	0.21	0.17	1.21
LOR	7/24/98	1000	RB	0.127	No Objective	0.025	No		No	0.651	No Obj	0.15	0.52	0.29
LSP	7/24/98	1100	RB	0.633	No Objective	0.025	No		No	0.518	No Obj	0.66	0.41	1.59
LTH	7/24/98	900	RB	0.352	No Objective	0.153	No		No	0.343	No Obj	0.51	0.27	1.84
LGR	8/4/98	915	RB	0.134	No Objective	0.025	No	0.025	No	0.264	No Obj	0.18	0.21	0.87
LOR	8/4/98	1000	RB	0.025	No Objective	0.025	No	0.025	No	0.478	No Obj	0.08	0.38	0.20
LSP	8/4/98	1045	RB	0.124	No Objective	0.025	No	0.025	No	0.381	No Obj	0.17	0.30	0.57
LTH	8/4/98	845	RB	0.165	No Objective	0.132	No	0.025	No	0.341	No Obj	0.32	0.27	1.18
LGR	8/19/98	925	RB	0.119	No Objective	0.025	No		No	0.461	No Obj	0.14	0.37	0.39
LOR	8/19/98	1015	RB	0.025	No Objective	0.025	No		No	0.888	No Obj	0.05	0.71	0.07
LSP	8/19/98	1130	RB	0.025	No Objective	0.025	No		No	1.06	No Obj	0.05	0.85	0.06
LTH	8/19/98	900	RB	0.225	No Objective	0.17	No		No	0.914	No Obj	0.40	0.73	0.54
LGR	9/4/98	905	RB	0.025	No Objective	0.079	No	0.025	No	0.351	No Obj	0.13	0.28	0.46
LOR	9/4/98	935	RB	0.025	No Objective	0.025	No	0.025	No	1.66	No Obj	0.08	1.33	0.06
LSP	9/4/98	1030	RB	0.05	No Objective	0.025	No	0.025	No	0.668	No Obj	0.10	0.53	0.19
LTH	9/4/98	840	RB	0.025	No Objective	0.116	No	0.025	No	0.626	No Obj	0.17	0.50	0.33
LGR	9/14/98	930	RB	0.0605	No Objective	0.025	No		No	0.181	No Obj	0.09	0.14	0.59
LOR	9/14/98	1010	RB	0.16	No Objective	0.025	No		No	1.15	No Obj	0.19	0.92	0.20
LSP	9/14/98	1100	RB	0.025	No Objective	0.025	No		No	0.29	No Obj	0.05	0.23	0.22
LTH	9/14/98	900	RB	0.0878	No Objective	0.141	No		No	0.301	No Obj	0.23	0.24	0.95
LGR	9/29/98	915	RB	0.0854	No Objective	0.066	No	0.025	No	0.19	No Obj	0.18	0.15	1.16
LOR	9/29/98	945	RB	1.95	No Objective	0.122	No	0.025	No	0.951	No Obj	2.10	0.76	2.76
LSP	9/29/98	1050	RB	0.072	No Objective	0.025	No	0.025	No	0.257	No Obj	0.12	0.21	0.59
LTH	9/29/98	840	RB	0.103	No Objective	0.14	No	0.025	No	0.387	No Obj	0.27	0.31	0.87
LGR	10/14/98	920	RB	0.025	No Objective	0.129	No		No	0.23	No Obj	0.15	0.18	0.84
LOR	10/14/98	950	RB	0.549	No Objective	0.447	No		No	0.755	No Obj	1.00	0.60	1.65
LSP	10/14/98	1020	RB	0.025	No Objective	0.025	No		No	0.189	No Obj	0.05	0.15	0.33
LTH	10/14/98	900	RB	0.0683	No Objective	0.161	No		No	0.327	No Obj	0.23	0.26	0.88
LGR	10/29/98	900	RB	0.254	No Objective	2.28	No	0.0904	No	0.988	No Obj	2.62	0.79	3.32
LOR	10/29/98	955	RB	0.208	No Objective	0.788	No	0.062	No	0.795	No Obj	1.06	0.64	1.66
LSP	10/29/98	1025	RB	0.025	No Objective	0.317	No	0.025	No	0.608	No Obj	0.37	0.49	0.75
LTH	10/29/98	845	RB	0.153	No Objective	1.18	No	0.069	No	0.606	No Obj	1.40	0.48	2.89
LGR	11/12/98	950	RB	0.245	No Objective	3.19	No		No	1.33	No Obj	3.44	1.06	3.23
LOR	11/12/98	1040	RB	0.206	No Objective	1.41	No		No	0.206	No Obj	1.62	0.16	9.81
LSP	11/12/98	1115	RB	0.102	No Objective	0.372	No		No	0.384	No Obj	0.47	0.31	1.54
LTH	11/12/98	920	RB	0.124	No Objective	2.62	No		No	0.803	No Obj	2.74	0.64	4.27
LOR	11/25/98	945	RB	0.235	No Objective	1.31	No	0.0919	No	1.18	No Obj	1.64	0.94	1.73
LSP	11/25/98	1140	RB	0.28	No Objective	1.35	No	0.113	No	0.533	No Obj	1.74	0.43	4.09
LTH	11/25/98	840	RB	0.215	No Objective	1.59	No	0.0673	No	0.422	No Obj	1.87	0.34	5.55
LOR	12/3/98	1000	RB	0.526	No Objective	2.97	No		No	1.63	No Obj	3.50	1.30	2.68
LSP	12/3/98	1120	RB	0.672	No Objective	2.92	No		No	0.847	No Obj	3.59	0.68	5.30
LTH	12/3/98	915	RB	0.233	No Objective	1.24	No		No	0.776	No Obj	1.47	0.62	2.37
LOR	12/15/98	1050	RB	0.565	No Objective	4.46	No	0.025	No	1.23	No Obj	5.05	0.98	5.13
LSP	12/15/98	1100	RB	1.08	No Objective	2.83	No	0.0871	No	0.466	No Obj	4.00	0.37	10.72
LTH	12/15/98	925	RB	0.159	No Objective	1.7	No	0.025	No	0.663	No Obj	1.88	0.53	3.55
LOR	12/30/98	1000	RB	0.36	No Objective	2.93	No		No	0.815	No Obj	3.29	0.65	5.05
LSP	12/30/98	1035	RB	0.0593	No Objective	0.964	No		No	0.196	No Obj	1.02	0.16	6.53
LTH	12/30/98	915	RB	0.12	No Objective	0.47	No		No	0.167	No Obj	0.59	0.13	4.42
LOR	1/14/99	1000	RB	0.215	No Objective	3.06	No	0.025	No	1.06	No Obj	3.30	0.85	3.89
LSP	1/14/99	1040	RB	0.025	No Objective	0.145	No	0.025	No	0.111	No Obj	0.20	0.09	2.20
LTH	1/14/99	900	RB	0.192	No Objective	1.53	No	0.025	No	0.859	No Obj	1.75	0.69	2.54
LOR	1/27/99	1050	RB	0.173	No Objective	4.69	No		No	1.46	No Obj	4.86	1.17	4.16
LSP	1/27/99	1200	RB	0.23	No Objective	1.15	No		No	0.383	No Obj	1.38	0.31	4.50
LTH	1/27/99	940	RB	0.213	No Objective	1.74	No		No	0.8	No Obj	1.95	0.64	3.05
LOR	2/12/99	1007	RB	0.34	No Objective	2.63	No	0.1	No	0.792	No Obj	3.07	0.63	4.85
LSP	2/12/99	1035	RB	0.191	No Objective	2.07	No	0.025	No	0.243	No Obj	2.29	0.19	11.76
LTH	2/12/99	928	RB	0.138	No Objective	0.859	No	0.075	No	0.457	No Obj	1.07	0.37	2.93
LOR	2/25/99	955	RB	0.29	No Objective	1.5	No		No	0.858	No Obj	1.79	0.69	2.61
LSP	2/25/99	1120	RB	0.125	No Objective	0.611	No		No	0.518	No Obj	0.74	0.41	1.78
LTH	2/25/99	850	RB	0.128	No Objective	0.509	No		No	0.391	No Obj	0.64	0.31	2.04
LOR	3/11/99	950	RB	0.216	No Objective	2.04	No	0.0625	No	0.674	No Obj	2.32	0.54	4.30
LSP	3/11/99	1255	RB	0.025	No Objective	1.25	No	0.025	No	0.297	No Obj	1.30	0.24	5.47
LTH	3/11/99	855	RB	0.102	No Objective	1.18	No		No	0.351	No Obj	1.28	0.28	4.57

STATION	DATE	TIME	SOURCE	AMMONIA NITROGEN	No Objective	NITRATE	MUNI 45 ppm	NITRITE	MUNI 1 ppm	TOTAL PHOS		TIN	80% of TP	TIN:80%TP
LOR	3/23/99	1010	RB	0.0881	No Objective	2.3	No		No	0.617	No Obj	2.39	0.49	4.84
LSP	3/23/99	1140	RB	0.0691	No Objective	0.927	No		No	0.231	No Obj	1.00	0.18	5.39
LTH	3/23/99	910	RB	0.0518	No Objective	0.495	No		No	0.174	No Obj	0.55	0.14	3.93
LOR	4/5/99	945	RB	0.025	No Objective	1.63	No	0.025	No	0.431	No Obj	1.68	0.34	4.87
LSP	4/5/99	1145	RB	0.181	No Objective	1.04	No	0.025	No	0.123	No Obj	1.25	0.10	12.66
LTH	4/5/99	855	RB	0.104	No Objective	0.575	No	0.025	No	0.28	No Obj	0.70	0.22	3.14
LOR	4/22/99	1000	RB	0.235	No Objective	1.97	No	0.0845	No	0.897	No Obj	2.29	0.72	3.19
LSP	4/22/99	1110	RB	0.159	No Objective	0.552	No	0.025	No	0.12	No Obj	0.74	0.10	7.67
LTH	4/22/99	900	RB	0.0519	No Objective	0.347	No	0.025	No	0.272	No Obj	0.42	0.22	1.95
LOR	5/5/99	1010	RB	0.025	No Objective	0.576	No	0.025	No	0.566	No Obj	0.63	0.45	1.38
LSP	5/5/99	1200	RB	0.161	No Objective	0.414	No	0.025	No	2.98	No Obj	0.60	2.38	0.25
LTH	5/5/99	920	RB	0.025	No Objective	0.098	No	0.025	No	0.253	No Obj	0.15	0.20	0.73
LOR	5/20/99	920	RB	0.0527	No Objective	0.063	No	0.025	No	0.694	No Obj	0.14	0.56	0.25
LSP	5/20/99	1010	RB	0.141	No Objective	0.159	No	0.058	No	0.205	No Obj	0.36	0.16	2.18
LTH	5/20/99	820	RB	0.107	No Objective	0.153	No	0.025	No	0.237	No Obj	0.29	0.19	1.50
LGR	6/3/99	930	RB		No Objective	0.056	No		No	0.025	No Obj	0.06	0.02	2.80
LOR	6/3/99	1015	RB	0.14	No Objective	0.057	No		No	0.599	No Obj	0.20	0.48	0.41
LSP	6/3/99	1045	RB		No Objective	0.088	No		No	0.143	No Obj	0.09	0.11	0.77
LTH	6/3/99	850	RB		No Objective	0.141	No		No	0.23	No Obj	0.14	0.18	0.77
LGR	6/17/99	1020	RB	0.025	No Objective	0.025	No		No	0.298	No Obj	0.05	0.24	0.21
LOR	6/17/99	1130	RB	0.025	No Objective	0.025	No		No	0.926	No Obj	0.05	0.74	0.07
LSP	6/17/99	1210	RB	0.025	No Objective	0.025	No		No	0.508	No Obj	0.05	0.41	0.12
LTH	6/17/99	945	RB	0.0616	No Objective	0.076	No		No	0.327	No Obj	0.14	0.26	0.53
LGR	6/29/99	850	RB	0.0892	No Objective	0.153	No	0.025	No	0.27	No Obj	0.27	0.22	1.24
LOR	6/29/99	930	RB	0.025	No Objective	0.093	No	0.025	No	0.274	No Obj	0.14	0.22	0.65
LSP	6/29/99	1005	RB	0.025	No Objective	0.025	No	0.025	No	0.626	No Obj	0.08	0.50	0.15
LTH	6/29/99	825	RB	0.0956	No Objective	0.141	No	0.025	No	0.371	No Obj	0.26	0.30	0.88
LGR	7/14/99	915	RB	0.025	No Objective	0.0863	No	0.025	No	0.144	No Obj	0.14	0.12	1.18
LOR	7/14/99	1000	RB	0.025	No Objective	0.118	No		No	0.623	No Obj	0.14	0.50	0.29
LSP	7/14/99	1050	RB	0.025	No Objective	0.0899	No	0.025	No	0.71	No Obj	0.14	0.57	0.25
LTH	7/14/99	855	RB	0.0672	No Objective	0.183	No	0.025	No	0.263	No Obj	0.28	0.21	1.31
LGR	7/27/99	945	RB	0.111	No Objective	0.05	No	0.025	No	0.209	No Obj	0.19	0.17	1.11
LOR	7/27/99	1100	RB	0.025	No Objective	0.166	No	0.025	No	0.64	No Obj	0.22	0.51	0.42
LSP	7/27/99	1130	RB	0.025	No Objective	0.132	No	0.025	No	0.553	No Obj	0.18	0.44	0.41
LTH	7/27/99	905	RB	0.025	No Objective	0.221	No	0.025	No	0.278	No Obj	0.27	0.22	1.22
LGR	8/12/99	950	RB	0.155	No Objective	0.098	No	0.025	No	0.2	No Obj	0.28	0.16	1.74
LOR	8/12/99	1020	RB	0.0942	No Objective	0.025	No	0.025	No	0.429	No Obj	0.14	0.34	0.42
LSP	8/12/99	1050	RB	0.063	No Objective	0.025	No	0.025	No	0.514	No Obj	0.11	0.41	0.27
LTH	8/12/99	910	RB	0.148	No Objective	0.147	No	0.025	No	0.248	No Obj	0.32	0.20	1.61
LGR	8/24/99	910	RB	0.025	No Objective	0.025	No	0.025	No	0.201	No Obj	0.08	0.16	0.47
LOR	8/24/99	945	RB	0.025	No Objective	0.025	No	0.025	No	0.495	No Obj	0.08	0.40	0.19
LSP	8/24/99	1015	RB	0.025	No Objective	0.025	No	0.025	No	0.629	No Obj	0.08	0.50	0.15
LTH	8/24/99	845	RB	0.025	No Objective	0.025	No	0.025	No	0.265	No Obj	0.08	0.21	0.35
LGR	9/9/99	955	RB	0.025	No Objective	0.025	No		No	0.186	No Obj	0.05	0.15	0.34
LOR	9/9/99	1035	RB	0.025	No Objective	0.025	No		No	0.476	No Obj	0.05	0.38	0.13
LSP	9/9/99	1200	RB	0.025	No Objective	0.025	No		No	0.461	No Obj	0.05	0.37	0.14
LTH	9/9/99	935	RB	0.025	No Objective	0.025	No		No	0.223	No Obj	0.05	0.18	0.28
LGR	9/21/99	1045	RB	0.025	No Objective	0.025	No	0.025	No	0.149	No Obj	0.08	0.12	0.63
LOR	9/21/99	1135	RB	0.025	No Objective	0.025	No	0.025	No	0.337	No Obj	0.08	0.27	0.28
LSP	9/21/99	1215	RB	0.025	No Objective	0.025	No	0.025	No	0.395	No Obj	0.08	0.32	0.24
LTH	9/21/99	1010	RB	0.025	No Objective	0.054	No		No	0.195	No Obj	0.08	0.16	0.51
LGR	10/7/99	1015	RB	0.0714	No Objective	0.062	No		No	0.136	No Obj	0.13	0.11	1.23
LOR	10/7/99	1100	RB	0.025	No Objective	0.025	No		No	0.338	No Obj	0.05	0.27	0.18
LSP	10/7/99	1145	RB	0.0502	No Objective	0.025	No		No	0.315	No Obj	0.08	0.25	0.30
LTH	10/7/99	940	RB	0.0572	No Objective	0.054	No		No	0.178	No Obj	0.11	0.14	0.78
LGR	10/19/99	1040	RB	0.624	No Objective	0.167	No	0.025	No	0.144	No Obj	0.82	0.12	7.08
LOR	10/19/99	1130	RB	0.131	No Objective	0.025	No	0.025	No	0.43	No Obj	0.18	0.34	0.53
LSP	10/19/99	1245	RB	0.621	No Objective	0.025	No	0.025	No	0.239	No Obj	0.67	0.19	3.51
LTH	10/19/99	1000	RB	0.0548	No Objective	0.135	No	0.025	No	0.209	No Obj	0.21	0.17	1.28
LGR	11/3/99	950	RB	0.257	No Objective	0.22	No		No	0.581	No Obj	0.48	0.46	1.03
LOR	11/3/99	1040	RB	0.0851	No Objective	0.346	No		No	0.545	No Obj	0.43	0.44	0.99
LSP	11/3/99	1125	RB	0.0534	No Objective	0.025	No		No	0.648	No Obj	0.08	0.52	0.15
LTH	11/3/99	850	RB	0.0899	No Objective	0.202	No		No	0.396	No Obj	0.29	0.32	0.92
LGR	11/16/99	945	RB	0.257	No Objective	0.168	No	0.025	No	0.854	No Obj	0.45	0.68	0.66
LOR	11/16/99	1020	RB	0.482	No Objective	0.39	No	0.081	No	0.76	No Obj	0.95	0.61	1.57
LSP	11/16/99	1100	RB	0.025	No Objective	0.066	No	0.025	No	0.407	No Obj	0.12	0.33	0.36
LTH	11/16/99	920	RB	0.025	No Objective	0.352	No	0.025	No	0.276	No Obj	0.40	0.22	1.82
LGR	12/1/99	1100	RB	0.025	No Objective	0.493	No	0.025	No	0.218	No Obj	0.54	0.17	3.11
LOR	12/1/99	1150	RB	0.285	No Objective	1.19	No	0.08	No	0.766	No Obj	1.56	0.61	2.54
LSP	12/1/99	1220	RB	0.055	No Objective	0.328	No	0.025	No	0.526	No Obj	0.41	0.42	0.97
LTH	12/1/99	1015	RB	0.025	No Objective	0.025	No	0.025	No	0.297	No Obj	0.08	0.24	0.32
LGR	12/14/99	1050	RB	0.134	No Objective	1.64	No	0.05	No	0.699	No Obj	1.82	0.56	3.26
LOR	12/14/99	1200	RB	0.178	No Objective	3.5	No	0.025	No	0.997	No Obj	3.70	0.80	4.64
LSP	12/14/99	1245	RB	0.0651	No Objective	0.14	No	0.025	No	0.196	No Obj	0.23	0.16	1.47
LTH	12/14/99	1010	RB	0.0693	No Objective	1.41	No	0.025	No	0.558	No Obj	1.50	0.45	3.37
LGR	12/29/99	1020	RB	0.232	No Objective	2.34	No	0.025	No	1.6	No Obj	2.60	1.28	2.03
LOR	12/29/99	1115	RB	0.18	No Objective	4.18	No	0.025	No	1.77	No Obj	4.39	1.42	3.10
LSP	12/29/99	1145	RB	0.142	No Objective	0.082	No	0.025	No	0.207	No Obj	0.25	0.17	1.50
LTH	12/29/99	1000	RB	0.025	No Objective	1.96	No	0.025	No	0.73	No Obj	2.01	0.58	3.44

Appendix A

STATION	DATE	TIME	SOURCE	AMMONIA NITROGEN		NITRATE	MUNI 45 ppm	NITRITE	MUNI 1 ppm	TOTAL PHOS		TIN	80% of TP	TIN:80%TP
LGR	1/12/00	1020	RB	4.08	No Objective	0.324	No	0.064	No	0.279	No Obj	4.47	0.22	20.02
LOR	1/12/00	1110	RB	0.351	No Objective	3.66	No	0.05	No	1.64	No Obj	4.06	1.31	3.10
LSP	1/12/00	1150	RB	0.068	No Objective	0.485	No	0.052	No	0.302	No Obj	0.61	0.24	2.50
LTH	1/12/00	940	RB	0.0631	No Objective	0.374	No	0.064	No	0.217	No Obj	0.50	0.17	2.89
LGR	1/24/00	1000	RB	0.117	No Objective	0.799	No	0.1	No	0.356	No Obj	1.02	0.28	3.57
LOR	1/24/00	1050	RB	0.267	No Objective	2.77	No	0.1	No	1.14	No Obj	3.14	0.91	3.44
LSP	1/24/00	1120	RB	0.379	No Objective	0.841	No	0.1	No	0.627	No Obj	1.32	0.50	2.63
LTH	1/24/00	925	RB	0.025	No Objective	0.787	No	0.1	No	0.371	No Obj	0.91	0.30	3.07
LGR	2/9/00	1050	RB	0.225	No Objective	1.76	No	0.025	No	0.817	No Obj	2.01	0.65	3.08
LOR	2/9/00	1140	RB	0.0898	No Objective	3.81	No	0.025	No	0.989	No Obj	3.92	0.79	4.96
LSP	2/9/00	1230	RB	0.0678	No Objective	0.944	No	0.025	No	0.356	No Obj	1.04	0.28	3.64
LTH	2/9/00	1010	RB	0.213	No Objective	1.35	No	0.025	No	0.611	No Obj	1.59	0.49	3.25
LOR	2/23/00	1315	RB	0.398	No Objective	0.655	No	0.106	No	0.861	No Obj	1.16	0.69	1.68
LSP	2/23/00	1230	RB	0.195	No Objective	0.814	No	0.064	No	0.55	No Obj	1.07	0.44	2.44
LTH	2/23/00	940	RB	0.117	No Objective	0.278	No	0.087	No	0.289	No Obj	0.48	0.23	2.08
LOR	3/8/00	1000	RB	0.212	No Objective	2.2	No	0.025	No	1.01	No Obj	2.44	0.81	3.02
LSP	3/8/00	1100	RB	0.23	No Objective	0.415	No	0.076	No	0.568	No Obj	0.72	0.45	1.59
LTH	3/8/00	915	RB	0.214	No Objective	0.546	No	0.025	No	0.312	No Obj	0.79	0.25	3.15
LOR	3/21/00	1000	RB	0.025	No Objective	2.64	No	0.025	No	0.888	No Obj	2.69	0.71	3.79
LSP	3/21/00	1040	RB	0.0797	No Objective	0.608	No	0.025	No	0.23	No Obj	0.71	0.18	3.87
LTH	3/21/00	910	RB	0.0554	No Objective	0.571	No	0.025	No	0.299	No Obj	0.65	0.24	2.72
LGR	4/5/00	1020	RB	0.025	No Objective	0.025	No	0.025	No	0.352	No Obj	0.08	0.28	0.27
LOR	4/5/00	1115	RB	0.0525	No Objective	1.02	No	0.025	No	0.756	No Obj	1.10	0.60	1.81
LSP	4/5/00	1150	RB	0.0826	No Objective	0.35	No	0.025	No	0.258	No Obj	0.46	0.21	2.22
LTH	4/5/00	940	RB	0.025	No Objective	0.025	No	0.025	No	0.295	No Obj	0.08	0.24	0.32
LGR	4/18/00	1020	RB	0.0619	No Objective	0.154	No		No	0.285	No Obj	0.22	0.23	0.95
LOR	4/18/00	1115	RB	0.297	No Objective	0.86	No	0.072	No	0.615	No Obj	1.23	0.49	2.50
LSP	4/18/00	1150	RB	0.214	No Objective	0.942	No	0.08	No	0.375	No Obj	1.24	0.30	4.12
LTH	4/18/00	940	RB	0.0914	No Objective	0.564	No	0.051	No	0.306	No Obj	0.71	0.24	2.89
LGR	5/3/00	1030	RB	0.0853	No Objective	0.025	No	0.025	No	0.461	No Obj	0.14	0.37	0.37
LOR	5/3/00	1120	RB	0.0975	No Objective	0.745	No	0.025	No	0.891	No Obj	0.87	0.71	1.22
LSP	5/3/00	1200	RB	0.025	No Objective	0.025	No	0.025	No	0.249	No Obj	0.08	0.20	0.38
LTH	5/3/00	1000	RB	0.101	No Objective	0.062	No	0.025	No	0.419	No Obj	0.19	0.34	0.56
LGR	5/17/00	1000	RB	0.025	No Objective	0.025	No	0.025	No	0.486	No Obj	0.08	0.39	0.19
LOR	5/17/00	1040	RB	0.0515	No Objective	0.145	No	0.108	No	0.638	No Obj	0.30	0.51	0.60
LSP	5/17/00	1110	RB	0.0978	No Objective	0.025	No	0.025	No	0.295	No Obj	0.15	0.24	0.63
LTH	5/17/00	935	RB	0.0607	No Objective	0.081	No	0.025	No	0.385	No Obj	0.17	0.31	0.54
LGR	6/15/00	1020	RB	0.218	No Objective	0.025	No		No	0.4	No Obj	0.24	0.32	0.76
LOR	6/15/00	1100	RB	0.0752	No Objective	0.025	No		No	0.394	No Obj	0.10	0.32	0.32
LSP	6/15/00	1130	RB	0.0524	No Objective	0.025	No		No	0.249	No Obj	0.08	0.20	0.39
LTH	6/15/00	1000	RB	0.249	No Objective	0.12	No		No	0.486	No Obj	0.37	0.39	0.95
LGR	6/27/00	1030	RB	0.0528	No Objective	0.025	No	0.025	No	0.212	No Obj	0.10	0.17	0.61
LOR	6/27/00	1140	RB	0.025	No Objective	0.0547	No	0.025	No	0.383	No Obj	0.10	0.31	0.34
LSP	6/27/00	1215	RB	0.025	No Objective	0.025	No	0.025	No	0.18	No Obj	0.08	0.14	0.52
LTH	6/27/00	1010	RB	0.025	No Objective	0.0718	No	0.025	No	0.272	No Obj	0.12	0.22	0.56
LGR	7/12/00	1030	RB	0.025	No Objective	0.025	No		No	0.162	No Obj	0.05	0.13	0.39
LOR	7/12/00	1110	RB	0.025	No Objective	0.025	No		No	0.429	No Obj	0.05	0.34	0.15
LSP	7/12/00	1140	RB	0.025	No Objective	0.025	No		No	0.21	No Obj	0.05	0.17	0.30
LTH	7/12/00	1000	RB	0.025	No Objective	0.025	No		No	0.235	No Obj	0.05	0.19	0.27
LGR	7/27/00	950	RB	0.025	No Objective	0.025	No	0.025	No	0.153	No Obj	0.08	0.12	0.61
LOR	7/27/00	1040	RB	0.025	No Objective	0.025	No	0.025	No	0.473	No Obj	0.08	0.38	0.20
LSP	7/27/00	1115	RB	0.025	No Objective	0.025	No	0.025	No	0.206	No Obj	0.08	0.16	0.46
LTH	7/27/00	925	RB	0.025	No Objective	0.025	No	0.025	No	0.326	No Obj	0.08	0.26	0.29
LGR	8/8/00	940	RB	0.025	No Objective	0.025	No		No	0.163	No Obj	0.05	0.13	0.38
LOR	8/8/00	1030	RB	0.025	No Objective	0.025	No		No	0.56	No Obj	0.05	0.45	0.11
LSP	8/8/00	1130	RB	0.025	No Objective	0.0747	No		No	0.326	No Obj	0.10	0.26	0.38
LTH	8/8/00	900	RB	0.025	No Objective	0.063	No		No	0.294	No Obj	0.09	0.24	0.37
LGR	8/24/00	950	RB	0.025	No Objective	0.025	No	0.025	No	0.131	No Obj	0.08	0.10	0.72
LOR	8/24/00	1015	RB	0.025	No Objective	0.025	No	0.025	No	0.727	No Obj	0.08	0.58	0.13
LSP	8/24/00	1110	RB	0.025	No Objective	0.025	No	0.025	No	0.346	No Obj	0.08	0.28	0.27
LTH	8/24/00	920	RB	0.025	No Objective	0.025	No	0.025	No	0.278	No Obj	0.08	0.22	0.34
LGR	9/7/00	1015	RB		No Objective	0.025	No	0.025	No	0.254	No Obj	0.05	0.20	0.25
LOR	9/7/00	1100	RB		No Objective	0.025	No	0.025	No	0.429	No Obj	0.05	0.34	0.15
LOR2	9/7/00	1230	RB		No Objective	0.025	No	0.025	No	0.419	No Obj	0.05	0.34	0.15
LSP	9/7/00	1130	RB		No Objective	0.025	No	0.025	No	0.465	No Obj	0.05	0.37	0.13
LTH	9/7/00	940	RB		No Objective	0.025	No	0.025	No	0.262	No Obj	0.05	0.21	0.24
LGR	9/21/00	1030	RB	0.025	No Objective	0.0669	No	0.025	No	0.711	No Obj	0.12	0.57	0.21
LOR	9/21/00	1115	RB	0.126	No Objective	0.025	No	0.025	No	0.622	No Obj	0.18	0.50	0.35
LSP	9/21/00	1200	RB	0.184	No Objective	0.0634	No	0.025	No	0.195	No Obj	0.27	0.16	1.75
LTH	9/21/00	1005	RB	0.532	No Objective	0.0548	No	0.025	No	0.298	No Obj	0.61	0.24	2.57
LGR	10/3/00	945	RB	0.025	No Objective	0.0599	No	0.025	No	0.137	No Obj	0.11	0.11	1.00
LOR	10/3/00	1040	RB	0.025	No Objective	0.025	No	0.025	No	0.519	No Obj	0.08	0.42	0.18
LSP	10/3/00	1110	RB	0.025	No Objective	0.025	No	0.025	No	0.201	No Obj	0.08	0.16	0.47
LTH	10/3/00	910	RB	0.025	No Objective	0.0639	No	0.025	No	0.227	No Obj	0.11	0.18	0.63
LGR	10/19/00	1045	RB	0.06	No Objective	0.132	No	0.025	No	0.502	No Obj	0.22	0.40	0.54
LOR	10/19/00	1200	RB	0.025	No Objective	0.375	No	0.025	No	0.817	No Obj	0.43	0.65	0.65
LRR	10/19/00	1015	RB	0.025	No Objective	0.094	No	0.025	No	0.157	No Obj	0.14	0.13	1.15
LSP	10/19/00	1230	RB	0.025	No Objective	0.025	No	0.025	No	0.304	No Obj	0.08	0.24	0.31
LTH	10/19/00	950	RB	0.025	No Objective	0.083	No	0.025	No	0.157	No Obj	0.13	0.13	1.06

STATION	DATE	TIME	SOURCE	AMMONIA NITROGEN	No Objective	NITRATE	MUNI 45 ppm	NITRITE	MUNI 1 ppm	TOTAL PHOS		TIN	80% of TP	TIN:80%TP
LGR	11/1/00	1055	RB	0.0651	No Objective	0.209	No	0.025	No	0.475	No Obj	0.30	0.38	0.79
LOR	11/1/00	1130	RB	0.229	No Objective	0.682	No	0.0586	No	0.841	No Obj	0.97	0.67	1.44
LSP	11/1/00	1200	RB	0.107	No Objective	0.325	No	0.025	No	0.296	No Obj	0.46	0.24	1.93
LTH	11/1/00	1010	RB	0.0772	No Objective	0.258	No	0.025	No	0.338	No Obj	0.36	0.27	1.33
LGR	11/16/00	1015	RB	0.116	No Objective	0.136	No	0.025	No	0.272	No Obj	0.28	0.22	1.27
LOR	11/16/00	1105	RB	0.557	No Objective	0.487	No	0.0513	No	0.686	No Obj	1.10	0.55	2.00
LSP	11/16/00	1215	RB	0.0937	No Objective	0.268	No	0.0523	No	0.155	No Obj	0.41	0.12	3.34
LTH	11/16/00	930	RB	0.121	No Objective	0.174	No	0.025	No	0.358	No Obj	0.32	0.29	1.12

Appendix B

Source of data: Santa Rosa NPDES receiving water monitoring
All Laguna de Santa Rosa stations shown
Data shown are monthly averages of weekly observations
Detection limits not given in this spreadsheet

Date	Location	Ammonia Nitrogen (mg/L) Avg	Nitrate Nitrogen (mg/L) Avg	Total Phosphorus (mg/L) Avg	Total Inorganic Nitrogen (TIN)	Bioavailable N:P Ratio (TIN/.8 TP)
Dec-95	Laguna at Llano Road	0.5	2.3	0.8	2.8	4.4
Dec-95	Laguna at Todd Road	1	6.6	1.2	7.6	7.9
Dec-95	Laguna at Hwy 12	0.6	6	1.5	6.6	5.5
Dec-95	Laguna at Occidental Bridge	0.8	5.1	1	5.9	7.4
Jan-96	Laguna at Llano Road	6.8	5.1	1.2	11.9	12.4
Jan-96	Laguna at Todd Road	1.2	5.7	1.4	6.9	6.2
Jan-96	Laguna at Hwy 12	0.6	6.8	1.3	7.4	7.1
Jan-96	Laguna at Occidental Bridge	0.5	6	1.2	6.5	6.8
Feb-96	Laguna at Llano Road	0.4	1.2	1.2	1.6	1.7
Feb-96	Laguna at Todd Road	0.9	3.8	1	4.7	5.9
Feb-96	Laguna at Hwy 12	0.4	3.9	1.7	4.3	3.2
Feb-96	Laguna at Occidental Bridge	0.5	3.5	1	4	5.0
Mar-96	Laguna at Llano Road	0.1	0.9	0.5	1	2.5
Mar-96	Laguna at Todd Road	0.7	2.1	0.8	2.8	4.4
Mar-96	Laguna at Hwy 12	0.3	2	0.9	2.3	3.2
Mar-96	Laguna @ Confluence S.R. Creek	0.2	1	1.2	1.2	1.3
Mar-96	Laguna at Occidental Bridge	0.3	1.7	1	2	2.5
Apr-96	Laguna at Llano Road	0.2	1.1	0.5	1.3	3.3
Apr-96	Laguna at Todd Road	0.4	1	0.7	1.4	2.5
Apr-96	Laguna at Hwy 12	0.2	0.8	0.7	1	1.8
Apr-96	Laguna at Occidental Bridge	0.7	0.9	0.8	1.6	2.5
May-96	Laguna at Hwy 12	0.2	0.2	0.3	0.4	1.7
May-96	Laguna at Occidental Bridge	0.1	0.3	0.9	0.4	0.6
Oct-96	Laguna at Llano Road	0	0.5	0.3	0.5	2.1
Nov-96	Laguna at Llano Road	0.9	0.2	0.9	1.1	1.5
Nov-96	Laguna at Todd Road	1.3	6.1	1.3	7.4	7.1
Nov-96	Laguna at Hwy 12	0.4	2.4	1.1	2.8	3.2
Nov-96	Laguna at Occidental Bridge	0.7	1.7	1.1	2.4	2.7
Dec-96	Laguna at Llano Road	1.5	1.1	0.8	2.6	4.1
Dec-96	Laguna at Todd Road	1	4.8	1.6	5.8	4.5
Dec-96	Laguna at Hwy 12	0.4	3.4	1.3	3.8	3.7
Dec-96	Laguna @ Confluence S.R. Creek	0.1	5.2	0.6	5.3	11.0
Jan-97	Laguna at Llano Road	0.8	1.8	0.5	2.6	6.5
Jan-97	Laguna at Todd Road	1.5	4.2	0.8	5.7	8.9
Jan-97	Laguna at Hwy 12	0.8	3.6	0.9	4.4	6.1
Jan-97	Laguna @ Confluence S.R. Creek	0.5	1.9	0.5	2.4	6.0
Jan-97	Upstream Laguna @ Arlington	0.3	2.5	0.5	2.8	7.0
Jan-97	Laguna at Occidental Bridge	0.8	3.4	0.9	4.2	5.8
Feb-97	Laguna at Llano Road	0.6	1.6	0.4	2.2	6.9
Feb-97	Laguna at Todd Road	1.4	4.2	0.8	5.6	8.8
Feb-97	Laguna at Hwy 12	0.2	2.5	0.6	2.7	5.6
Feb-97	Laguna @ Confluence S.R. Creek	0.4	1.6	0.5	2	5.0
Feb-97	Laguna at Occidental Bridge	0.4	3	0.7	3.4	6.1
Mar-97	Laguna at Llano Road	0.4	0.9	0.3	1.3	5.4
Mar-97	Laguna at Todd Road	0.7	7.2	1.2	7.9	8.2
Mar-97	Laguna at Hwy 12	0.3	2.7	0.6	3	6.3
Mar-97	Laguna @ Confluence S.R. Creek	0.2	0.4	0.3	0.6	2.5
Mar-97	Laguna at Occidental Bridge	0.3	3.1	0.6	3.4	7.1
Apr-97	Laguna at Llano Road	0.1	0.5	0.4	0.6	1.9
Apr-97	Laguna at Todd Road	0.5	8	1.4	8.5	7.6
Apr-97	Laguna at Hwy 12	0.3	2.5	1	2.8	3.5
Apr-97	Laguna @ Confluence S.R. Creek	0.1	1.2	0.6	1.3	2.7
Apr-97	Laguna at Occidental Bridge	0.1	2	0.9	2.1	2.9
Nov-97	Laguna at Todd Road	1	6.9	2.2	7.9	4.5
Nov-97	Laguna 100' Upstream of D-Pond Incline Pump	0.2	1.1	0.5	1.3	3.3
Nov-97	Laguna 150' Downstream of D-Pond Incline Pump	0.3	11.9	0.9	12.2	16.9
Dec-97	Laguna at Todd Road	1.2	6.4	1.7	7.6	5.6
Dec-97	Laguna at La Franchi	0.4	3.8	1.5	4.2	3.5
Dec-97	Upstream Laguna @ Delta	0.8	2.9	1.4	3.7	3.3
Dec-97	Laguna 100' Upstream of D-Pond Incline Pump	1.2	2.1	0.7	3.3	5.9
Dec-97	Laguna 150' Downstream of D-Pond Incline Pump	1.3	5.3	1.4	6.6	5.9
Jan-98	Laguna at Todd Road	0.6	2.7	1	3.3	4.1
Jan-98	Laguna at Hwy 12	0.4	2.6	0.9	3	4.2
Jan-98	Laguna at La Franchi	0.2	1.2	0.5	1.4	3.5
Jan-98	Laguna 100' Upstream of D-Pond Incline Pump	0.1	1.1	1	1.2	1.5
Jan-98	Laguna 150' Downstream of D-Pond Incline Pump	0.3	2.4	0.9	2.7	3.8
Feb-98	Laguna at Todd Road	0.9	2.2	0.8	3.1	4.8
Feb-98	Laguna at Hwy 12	1.3	1.8	0.9	3.1	4.3
Feb-98	Laguna at La Franchi	0.3	1.2	0.6	1.5	3.1
Feb-98	Laguna 100' Upstream of D-Pond Incline Pump	0.4	0.9	0.7	1.3	2.3

Date	Location	Ammonia Nitrogen (mg/L) Avg	Nitrate Nitrogen (mg/L) Avg	Total Phosphorus (mg/L) Avg	Total Inorganic Nitrogen (TIN)	Bioavailable N:P Ratio (TIN/.8 TP)
Feb-98	Laguna 150' Downstream of D-Pond Incline Pump	0.5	1.4	0.7	1.9	3.4
Mar-98	Laguna at Todd Road	0.6	5.5	1.2	6.1	6.4
Mar-98	Laguna 100' Upstream of D-Pond Incline Pump	0.1	1.3	0.4	1.4	4.4
Mar-98	Laguna 150' Downstream of D-Pond Incline Pump	0.4	4.3	1	4.7	5.9
Mar-98	Laguna Upstream of D-Pond 36"	0.5	4.4	1.3	4.9	4.7
Apr-98	Laguna at Todd Road	2	4	1.1	6	6.8
Apr-98	Laguna at Hwy 12	0.4	2.2	1.1	2.6	3.0
Apr-98	Laguna 100' Upstream of D-Pond Incline Pump	0.4	0.9	0.5	1.3	3.3
Apr-98	Laguna 150' Downstream of D-Pond Incline Pump	0.5	5.1	1.3	5.6	5.4
May-98	Laguna at Todd Road	0.2	6.1	1.3	6.3	6.1
May-98	Laguna 100' Upstream of D-Pond Incline Pump	0.4	0.6	0.4	1	3.1
May-98	Laguna 150' Downstream of D-Pond Incline Pump	0.4	4.2	1.1	4.6	5.2
May-98	Laguna Upstream of D-Pond 36"	0.2	5	1.3	5.2	5.0
Nov-98	Laguna at Todd Road	0.5	2.4	1.8	2.9	2.0
Nov-98	Laguna 100' Upstream of D-Pond Incline Pump	0.4	2.1	1.2	2.5	2.6
Nov-98	Laguna Upstream of D-Pond 36"	0.2	1.5	1.2	1.7	1.8
Nov-98	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.4	4.8	1.6	5.2	4.1
Dec-98	Laguna at Todd Road	0.8	4.6	1.5	5.4	4.5
Dec-98	Laguna at Hwy 12	0.5	3.6	1.4	4.1	3.7
Dec-98	Laguna at La Franchi	0.4	1.7	1.2	2.1	2.2
Dec-98	Upstream Laguna @ Delta	0.7	2.3	1.5	3	2.5
Dec-98	Laguna 100' Upstream of D-Pond Incline Pump	0.5	4.1	1	4.6	5.8
Dec-98	Laguna Upstream of D-Pond 36"	0.5	3.8	1.1	4.3	4.9
Dec-98	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.5	2.6	0.6	3.1	6.5
Jan-99	Laguna at Todd Road	0.8	4.7	1.6	5.5	4.3
Jan-99	Laguna at Hwy 12	0.5	3.9	1.5	4.4	3.7
Jan-99	Laguna at La Franchi	0.4	1.5	0.8	1.9	3.0
Jan-99	Upstream Laguna @ Delta	0.6	2.2	1	2.8	3.5
Jan-99	Laguna Upstream of D-Pond Incline	0.7	2.8	1.3	3.5	3.4
Jan-99	Laguna Upstream of D-Pond 36"	0.6	3.1	1.3	3.7	3.6
Jan-99	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.5	1.1	0.6	1.6	3.3
Feb-99	Laguna at Todd Road	0.9	2.5	1	3.4	4.3
Feb-99	Laguna Upstream of D-Pond Incline	0.5	1.6	0.7	2.1	3.8
Feb-99	Laguna Upstream of D-Pond 36"	0.4	1.5	0.7	1.9	3.4
Feb-99	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.4	1.4	0.6	1.8	3.8
Mar-99	Laguna at Todd Road	0.7	1.9	0.5	2.6	6.5
Mar-99	Laguna Upstream of D-Pond Incline	0.3	1.4	0.5	1.7	4.3
Mar-99	Laguna Upstream of D-Pond 36"	0.3	1.4	0.5	1.7	4.3
Mar-99	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.3	1	0.5	1.3	3.3
Apr-99	Laguna at Todd Road	0.6	3	0.6	3.6	7.5
Apr-99	Laguna Upstream of D-Pond Incline	0.6	1.7	0.6	2.3	4.8
Apr-99	Laguna Upstream of D-Pond 36"	0.7	1.5	0.5	2.2	5.5
Apr-99	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.3	0.7	0.3	1	4.2
May-99	Laguna Upstream of D-Pond Incline	0.2	1.8	0.5	2	5.0
May-99	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.1	0.4	0.2	0.5	3.1
Nov-99	Laguna Upstream of D-Pond Incline	0.3	2	0.9	2.3	3.2
Nov-99	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.1	0.1	0.5	0.2	0.5
Dec-99	Laguna at Todd Road	0.2	5	1.3	5.2	5.0
Dec-99	Laguna at Hwy 12	0.1	6	1.5	6.1	5.1
Dec-99	Laguna Upstream of D-Pond Incline	0.1	5.7	1.3	5.8	5.6
Dec-99	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.1	0.2	0.3	0.3	1.3
Jan-00	Laguna at Todd Road	0.3	2.5	0.8	2.8	4.4
Jan-00	Laguna at Hwy 12	0	3.3	3.9	3.3	1.1
Jan-00	Laguna at La Franchi	0.2	1.1	0.8	1.3	2.0
Jan-00	Upstream Laguna @ Delta	0.1	1.6	1.2	1.7	1.8
Jan-00	Laguna Upstream of D-Pond Incline Pump	0.5	3.7	1.1	4.2	4.8
Jan-00	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.1	0.8	0.7	0.9	1.6
Feb-00	Laguna at Todd Road	0.7	1.4	1	2.1	2.6
Feb-00	Laguna at Hwy 12	0.4	2.7	1.2	3.1	3.2
Feb-00	Laguna at La Franchi	0	1.3	1	1.3	1.6
Feb-00	Upstream Laguna @ Delta	0.2	2	1.1	2.2	2.5

Date	Location	Ammonia Nitrogen (mg/L) Avg	Nitrate Nitrogen (mg/L) Avg	Total Phosphorus (mg/L) Avg	Total Inorganic Nitrogen (TIN)	Bioavailable N:P Ratio (TIN/.8 TP)
Feb-00	Laguna Upstream of D-Pond Incline Pump	0.5	1.3	0.9	1.8	2.5
Feb-00	Laguna Upstream of D-Pond 36"	0.4	0.8	0.8	1.2	1.9
Feb-00	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.5	1	0.9	1.5	2.1
Mar-00	Laguna at Todd Road	0.5	1.2	0.7	1.7	3.0
Mar-00	Laguna at Hwy 12	0.2	2.4	1.1	2.6	3.0
Mar-00	Laguna Upstream of D-Pond Incline Pump	0.3	1.1	0.6	1.4	2.9
Mar-00	Laguna Upstream of D-Pond 36"	0.6	0.8	0.8	1.4	2.2
Mar-00	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.2	0.5	0.5	0.7	1.8
Apr-00	Laguna at Todd Road	0.1	1	0.7	1.1	2.0
Apr-00	Laguna at Hwy 12	0.1	1.4	1.2	1.5	1.6
Apr-00	Laguna Upstream of D-Pond Incline Pump	0.1	1.1	0.7	1.2	2.1
Apr-00	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.1	0.1	0.4	0.2	0.6
May-00	Laguna at Todd Road	0.2	0.7	0.7	0.9	1.6
May-00	Laguna at Hwy 12	0	1.4	1.5	1.4	1.2
May-00	Laguna Upstream of D-Pond Incline Pump	0.2	0.9	0.9	1.1	1.5
May-00	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.2	0.1	0.4	0.3	0.9
Nov-00	Laguna at Todd Road	0.1	1.7	0.7	1.8	3.2
Nov-00	Laguna at Hwy 12	0.1	1.3	1.1	1.4	1.6
Nov-00	Laguna Upstream of D-Pond Incline Pump	0.2	3.9	1.3	4.1	3.9
Nov-00	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.1	0.2	0.4	0.3	0.9
Dec-00	Laguna at Todd Road	0.2	4.5	1.1	4.7	5.3
Dec-00	Laguna at Hwy 12	0.2	4.4	1.8	4.6	3.2
Dec-00	Laguna Upstream of D-Pond Incline Pump	0.3	5.1	1.3	5.4	5.2
Dec-00	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.1	0.4	0.4	0.5	1.6
Jan-01	Laguna at Todd Road	0.5	3.1	0.9	3.6	5.0
Jan-01	Laguna at Hwy 12	0.2	4.7	1.4	4.9	4.4
Jan-01	Laguna at La Franchi	0.1	1.6	0.7	1.7	3.0
Jan-01	Upstream Laguna @ Delta	0.1	1.7	1.1	1.8	2.0
Jan-01	Laguna Upstream of D-Pond Incline Pump	0.1	3.8	1	3.9	4.9
Jan-01	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.4	0.9	1	1.3	1.6
Feb-01	Laguna at Todd Road	0.6	2.6	1.3	3.2	3.1
Feb-01	Laguna at Hwy 12	0.4	4.3	1.6	4.7	3.7
Feb-01	Russian River At Wohler Bridge	0.3	0.5	0.25	0.8	4.0
Feb-01	Russian River at Mirabel	0.3	0.8	0.3	1.1	4.6
Feb-01	Upstream Roseland Cr. @ Llano Rd	0.3	1.3	0.3	1.6	6.7
Feb-01	Downstream Roseland Cr. @ Summer Crossing/South of Alpha Bldg.	0.7	6.6	2.2	7.3	4.1
Feb-01	Upstream Kelly-Downstream Confl of Duer Cr. & Kelly Farm Drainage	0.3	0.7	0.6	1	2.1
Feb-01	Downstream Duer Creek at Kelly	0.3	6.2	2.1	6.5	3.9
Feb-01	Laguna Upstream of D-Pond Incline Pump	0.3	2.4	1	2.7	3.4
Feb-01	Laguna Downstream of D-Pond Incline Pump	0.4	2.6	1	3	3.8
Feb-01	Colgan Creek Upstream Confluence with Laguna	2	1.2	1.5	3.2	2.7
Feb-01	Laguna Upstream of D-Pond 36" Discha	0.8	1.2	1	2	2.5
Feb-01	Laguna Approx. 100Ft Upstream of Llan	0.3	1.2	0.6	1.5	3.1
Mar-01	Laguna at Todd Road	0.3	5	1.2	5.3	5.5
Mar-01	Laguna at Hwy 12	0.1	4.8	1.5	4.9	4.1
Mar-01	Russian River At Wohler Bridge	0.2	0.6	0.2	0.8	5.0
Mar-01	Russian River at Mirabel	0.2	0.6	0.2	0.8	5.0
Mar-01	Upstream Roseland Cr. @ Llano Rd	0.2	1.4	0.2	1.6	10.0
Mar-01	Downstream Roseland Cr. @ Summer Crossing/South of Alpha Bldg.	0.4	9.7	2	10.1	6.3
Mar-01	Upstream Kelly-Downstream Confl of Duer Cr. & Kelly Farm Drainage	0.3	0.4	0.4	0.7	2.2
Mar-01	Downstream Duer Creek at Kelly	0.3	6.7	2	7	4.4
Mar-01	Laguna Upstream of D-Pond Incline Pump	0.2	1.9	0.7	2.1	3.8
Mar-01	Laguna Downstream of D-Pond Incline Pump	0.2	3.8	1	4	5.0
Mar-01	Colgan Creek Upstream Confluence with Laguna	1	2.4	0.9	3.4	4.7
Mar-01	Laguna Upstream of D-Pond 36" Discha	0.2	2.8	0.9	3	4.2
Mar-01	Laguna Approx. 100Ft Upstream of Llan	0.2	1.4	0.6	1.6	3.3

Date	Location	Ammonia Nitrogen (mg/L) Avg	Nitrate Nitrogen (mg/L) Avg	Total Phosphorus (mg/L) Avg	Total Inorganic Nitrogen (TIN)	Bioavailable N:P Ratio (TIN/.8 TP)
Apr-01	Russian River at Wohler Br	0.2	0.4	0.1	0.6	7.5
Apr-01	Russian River at Mirabel	0.2	0.4	0.1	0.6	7.5
Apr-01	Upstream Roseland Cr. @ Llano Rd	0.2	0.8	0.2	1	6.3
Apr-01	Downstream Roseland Cr. @ Summer Crossing/South of Alpha Bldg.	0.4	5.2	1.8	5.6	3.9
Apr-01	Upstream Kelly-Downstream Confl of Duer Cr. & Kelly Farm Drainage	0.2	0.4	0.4	0.6	1.9
Apr-01	Downstream Duer Creek at Kelly	0.3	8.7	3.1	9	3.6
Apr-01	Laguna Upstream of D-Pond Incline Pump	0.4	4.5	1.8	4.9	3.4
Apr-01	Laguna Approx. 100Ft Upstream of Llan	0.3	0.4	0.5	0.7	1.8
May-01	Laguna at Todd Road	0.1	1.5	1.2	1.6	1.7
May-01	Laguna at Hwy 12	0.1	0.4	1.6	0.5	0.4
May-01	Russian River at Wohler Br	0.1	0.4	0.1	0.5	6.3
May-01	Russian River at Mirabel	0.1	0.4	0.1	0.5	6.3
May-01	Upstream Kelly-Downstream confl of Duer Creek & Kelly Farm Drainage	0.1	1.3	0.9	1.4	1.9
May-01	Downstream Duer Creek at Kelly	0.1	6.2	3.3	6.3	2.4
May-01	Laguna Upstream of D-Pond Incline Pur	0.1	6.7	2.1	6.8	4.0
May-01	Laguna Approx. 100Ft Upstream of Llan	0.1	0.4	0.6	0.5	1.0
May-01	Laguna at Kelly/Dei Crossing	0.1	0.4	1.8	0.5	0.3
May-01	Laguna at Inlet of Occidental Pond	0.1	0.4	1.2	0.5	0.5
Nov-01	Laguna at Todd Road	0.3	3.7	1.4	4	3.6
Nov-01	Russian River at Wohler Br	0.2	0.7	0.2	0.9	5.6
Nov-01	Russian River at Mirabel	0.2	0.7	0.3	0.9	3.8
Nov-01	Upstream Kelly-Downstream confl of Duer Creek & Kelly Farm Drainage	0.3	0.5	1	0.8	1.0
Nov-01	Downstream Duer Creek at Kelly	0.4	1.9	2	2.3	1.4
Nov-01	Laguna Upstream of D-Pond Incline Pur	0.5	1.8	1	2.3	2.9
Nov-01	Colgan Creek Upstream Confluence witl	0.6	1.3	1.2	1.9	2.0
Nov-01	Laguna Upstream of D-Pond 36" Discha	0.5	1.1	1	1.6	2.0
Nov-01	Laguna Approx. 100Ft Upstream of Llan	0.4	0.6	0.8	1	1.6
Dec-01	Laguna at Todd Road	0.3	4.3	1.1	4.6	5.2
Dec-01	Laguna at Hwy 12	0.4	4.2	1.4	4.6	4.1
Dec-01	Laguna at La Franchi	0.7	1.4	1.1	2.1	2.4
Dec-01	Russian River at Wohler Br	0.2	0.6	0.2	0.8	5.0
Dec-01	Russian River at Mirabel	0.7	0.9	0.4	1.6	5.0
Dec-01	Downstream Santa Rosa Cr @ Delta	0.3	1.6	0.2	1.9	11.9
Dec-01	Upstream Laguna @ Delta	0.7	1.2	1.1	1.9	2.2
Dec-01	Upstream Kelly-Downstream confl of Duer Creek & Kelly Farm Drainage	0.3	0.6	0.8	0.9	1.4
Dec-01	Downstream Duer Creek at Kelly	0.3	4.1	1.4	4.4	3.9
Dec-01	Laguna Upstream of D-Pond Incline Pur	0.4	2.3	0.8	2.7	4.2
Dec-01	Colgan Creek Upstream Confluence witl	0.5	2.1	1	2.6	3.3
Dec-01	Laguna Upstream of D-Pond 36" Discha	0.3	2	0.8	2.3	3.6
Dec-01	Laguna Approx. 100Ft Upstream of Llan	0.3	1.7	0.6	2	4.2
Jan-02	Laguna at Todd Road	0.4	5.1	1.2	5.5	5.7
Jan-02	Laguna at Hwy 12	0.4	3.2	1.1	3.6	4.1
Jan-02	Russian River at Wohler Br	0.2	0.7	0.1	0.9	11.3
Jan-02	Russian River at Mirabel	0.2	0.8	0.1	1	12.5
Jan-02	Laguna at Occidental Rd Bridge	0.3	0.9	0.9	1.2	1.7
Jan-02	Upstream Roseland Cr. @ Llano Rd	0.6	2	0.9	2.6	3.6
Jan-02	Downstream Roseland Cr. @ Summer Crossing/South of Alpha Bldg.	0.4	4.6	1.8	5	3.5
Jan-02	Upstream Kelly-Downstream confl of Duer Creek & Kelly Farm Drainage	0.3	0.5	0.6	0.8	1.7
Jan-02	Downstream Duer Creek at Kelly	0.3	4.7	1.6	5	3.9
Jan-02	Laguna Upstream of D-Pond Incline Pur	0.5	2	1	2.5	3.1
Jan-02	Laguna Downstream of D-Pond Incline Pump	0.6	2.5	0.8	3.1	4.8
Jan-02	Colgan Creek Upstream Confluence witl	0.5	2.5	0.7	3	5.4
Jan-02	Laguna Upstream of D-Pond 36" Discha	0.4	2.2	0.8	2.6	4.1
Jan-02	Laguna Approx. 100Ft Upstream of Llan	0.3	1.6	0.7	1.9	3.4
Feb-02	Laguna at Todd Road	0.4	6.6	1.6	7	5.5
Feb-02	Laguna at La Franchi	0.1	0.9	0.8	1	1.6
Feb-02	Russian River at Wohler Br	0.2	0.6	0.1	0.8	10.0
Feb-02	Russian River at Mirabel	0.2	0.6	0.1	0.8	10.0
Feb-02	Downstream Santa Rosa Cr @ Delta	0.1	0.4	0.1	0.5	6.3
Feb-02	Upstream Laguna @ Delta	0.2	1.5	1.2	1.7	1.8
Feb-02	Upstream Kelly-Downstream confl of Duer Creek & Kelly Farm Drainage	0.2	0.4	0.4	0.6	1.9
Feb-02	Downstream Duer Creek at Kelly	0.2	7.8	2.2	8	4.5
Feb-02	Laguna Upstream of D-Pond Incline Pur	0.4	2	1.1	2.4	2.7
Feb-02	Colgan Creek Upstream Confluence witl	0.2	2.6	0.5	2.8	7.0
Feb-02	Laguna Upstream of D-Pond 36" Discha	0.3	1.7	0.8	2	3.1
Feb-02	Laguna Approx. 100Ft Upstream of Llan	0.2	4.6	0.9	4.8	6.7
Mar-02	Laguna at Todd Road	0.2	4.8	1.4	5	4.5
Mar-02	Laguna at La Franchi	0.2	2.2	1.1	2.4	2.7
Mar-02	Russian River at Wohler Br	0.1	0.5	0.1	0.6	7.5
Mar-02	Russian River at Mirabel	0.1	0.7	0.2	0.8	5.0

Date	Location	Ammonia Nitrogen (mg/L) Avg	Nitrate Nitrogen (mg/L) Avg	Total Phosphorus (mg/L) Avg	Total Inorganic Nitrogen (TIN)	Bioavailable N:P Ratio (TIN/.8 TP)
Mar-02	Downstream Santa Rosa Cr @ Delta	0.1	0.5	0.1	0.6	7.5
Mar-02	Upstream Laguna @ Delta	0.2	3.8	1.3	4	3.8
Mar-02	Upstream Kelly-Downstream confl of Duer Creek & Kelly Farm Drainage	0.1	0.4	0.3	0.5	2.1
Mar-02	Downstream Duer Creek at Kelly	0.1	5.2	1.8	5.3	3.7
Mar-02	Laguna Upstream of D-Pond Incline Pur	0.4	1.2	0.6	1.6	3.3
Mar-02	Colgan Creek Upstream Confluence witl	0.2	2.1	0.3	2.3	9.6
Mar-02	Laguna Upstream of D-Pond 36" Discha	0.3	1.2	0.7	1.5	2.7
Mar-02	Laguna Approx. 100Ft Upstream of Llan	0.2	0.7	0.5	0.9	2.3
Apr-02	Laguna at Todd Road	0.2	2.5	1	2.7	3.4
Apr-02	Laguna at Hwy 12	0.2	1.5	1	1.7	2.1
Apr-02	Russian River at Wohler Br	0.2	0.4	0.1	0.6	7.5
Apr-02	Russian River at Mirabel	0.2	0.4	0.1	0.6	7.5
Apr-02	Upstream Kelly-Downstream confl of Duer Creek & Kelly Farm Drainage	0.2	0.4	0.4	0.6	1.9
Apr-02	Downstream Duer Creek at Kelly	0.2	5.9	2.1	6.1	3.6
Apr-02	Laguna Upstream of D-Pond Incline Pur	0.3	1.7	0.9	2	2.8
Apr-02	Colgan Creek Upstream Confluence witl	0.3	1.2	0.3	1.5	6.3
Apr-02	Laguna Upstream of D-Pond 36" Discha	0.3	1	1	1.3	1.6
Apr-02	Laguna Approx. 100Ft Upstream of Llan	0.3	0.4	0.5	0.7	1.8
May-02	Laguna at Todd Road	0.2	1.5	0.8	1.7	2.7
May-02	Laguna Upstream of D-Pond Incline Pur	0.3	2.9	1	3.2	4.0
May-02	Laguna Upstream of D-Pond 36" Discha	0.2	1	0.8	1.2	1.9
May-02	Laguna Approx. 100Ft Upstream of Llan	0.2	0.4	0.5	0.6	1.5
Jun-02	Laguna at Todd Road	0.2	0.4	1.5	0.6	0.5
Jun-02	Laguna Upstream of D-Pond Incline Pur	0.2	0.4	0.6	0.6	1.3
Jun-02	Laguna Upstream of D-Pond 36" Discha	0.3	0.4	1	0.7	0.9
Jun-02	Laguna Approx. 100Ft Upstream of Llan	0.6	0.4	2.3	1	0.5
Nov-02	Laguna Upstream of D-Pond Incline Pur	0.6	5.2	1.6	5.8	4.5
Nov-02	Laguna Approx. 100Ft Upstream of Llan	0.6	0.4	1.1	1	1.1
Dec-02	Laguna at Todd Road	0.7	2.5	0.9	3.2	4.4
Dec-02	Laguna at La Franchi	0.5	1.3	0.9	1.8	2.5
Dec-02	Upstream Laguna @ Delta	0.6	1.1	1.1	1.7	1.9
Dec-02	Laguna Upstream of D-Pond Incline Pur	0.6	2	0.8	2.6	4.1
Dec-02	Laguna Upstream of D-Pond 36" Discha	0.6	2.5	0.8	3.1	4.8
Dec-02	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.6	0.9	0.6	1.5	3.1
Jan-03	Laguna at Todd Road	0.6	3.6	1	4.2	5.3
Jan-03	Laguna at La Franchi	0.6	1.3	0.9	1.9	2.6
Jan-03	Upstream Laguna @ Delta	0.6	1.6	1	2.2	2.8
Jan-03	Laguna Upstream of D-Pond Incline Pur	0.7	1.5	0.8	2.2	3.4
Jan-03	Laguna Upstream of D-Pond 36" Discha	0.6	1.5	0.8	2.1	3.3
Jan-03	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.7	1	0.7	1.7	3.0
Feb-03	Laguna at Todd Road	0.4	6.6	1.2	7	7.3
Feb-03	Laguna Upstream of D-Pond Incline Pur	0.6	2.8	0.8	3.4	5.3
Feb-03	Laguna Upstream of D-Pond 36" Discha	0.5	2.4	0.8	2.9	4.5
Feb-03	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.6	0.9	0.4	1.5	4.7
Mar-03	Laguna at Todd Road	0.6	7.2	1.2	7.8	8.1
Mar-03	Laguna Upstream of D-Pond Incline Pur	0.5	2.9	1	3.4	4.3
Mar-03	Laguna Upstream of D-Pond 36" Discha	0.6	2.2	0.9	2.8	3.9
Mar-03	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.6	0.5	0.6	1.1	2.3
Apr-03	Laguna at Todd Road	0.5	5.5	1	6	7.5
Apr-03	Laguna Upstream of D-Pond Incline Pur	0.6	2.4	0.8	3	4.7
Apr-03	Laguna Upstream of D-Pond 36" Discha	0.6	1.8	0.9	2.4	3.3
Apr-03	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.6	0.6	0.5	1.2	3.0
May-03	Laguna at Todd Road	0.3	5.9	1.2	6.2	6.5
May-03	Laguna Upstream of D-Pond Incline Pur	0.4	1.1	0.7	1.5	2.7
May-03	Laguna Upstream of D-Pond 36" Discha	0.5	1.3	0.8	1.8	2.8
May-03	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.5	0.5	0.6	1	2.1
Nov-03	Laguna Upstream of D-Pond Incline Pur	0.3	0.8	0.8	1.1	1.7
Nov-03	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.2	0.4	0.7	0.6	1.1
Dec-03	Laguna at Todd Road	0.4	3.1	0.9	3.5	4.9
Dec-03	Laguna Upstream of D-Pond Incline Pur	0.4	1.2	0.8	1.6	2.5
Dec-03	Laguna Upstream of D-Pond 36" Discha	0.5	1.2	0.8	1.7	2.7
Dec-03	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.4	1	0.7	1.4	2.5
Jan-04	Laguna at Todd Road	0.3	5	1	5.3	6.6
Jan-04	Laguna Upstream of D-Pond Incline Pur	0.6	1.7	0.7	2.3	4.1
Jan-04	Laguna Upstream of D-Pond 36" Discha	0.5	1.8	0.7	2.3	4.1
Jan-04	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.5	1.3	0.6	1.8	3.8
Feb-04	Laguna at Todd Road	0.4	3.3	0.9	3.7	5.1
Feb-04	Laguna Upstream of D-Pond Incline Pur	0.6	1.3	0.7	1.9	3.4
Feb-04	Laguna Upstream of D-Pond 36" Discha	0.4	1.3	0.6	1.7	3.5
Feb-04	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.6	1.1	0.6	1.7	3.5

Date	Location	Ammonia Nitrogen (mg/L) Avg	Nitrate Nitrogen (mg/L) Avg	Total Phosphorus (mg/L) Avg	Total Inorganic Nitrogen (TIN)	Bioavailable N:P Ratio (TIN/.8 TP)
Mar-04	Laguna at Todd Road	0.4	2	0.7	2.4	4.3
Mar-04	Laguna Upstream of D-Pond Incline Pur	0.6	1.2	0.5	1.8	4.5
Mar-04	Laguna Upstream of D-Pond 36" Discha	0.5	1.1	0.5	1.6	4.0
Mar-04	Laguna-Approx 100' Upstream of Llano Rd Bridge	0.6	1.1	0.5	1.7	4.3

Appendix C NPDES

Monthly average NAP data

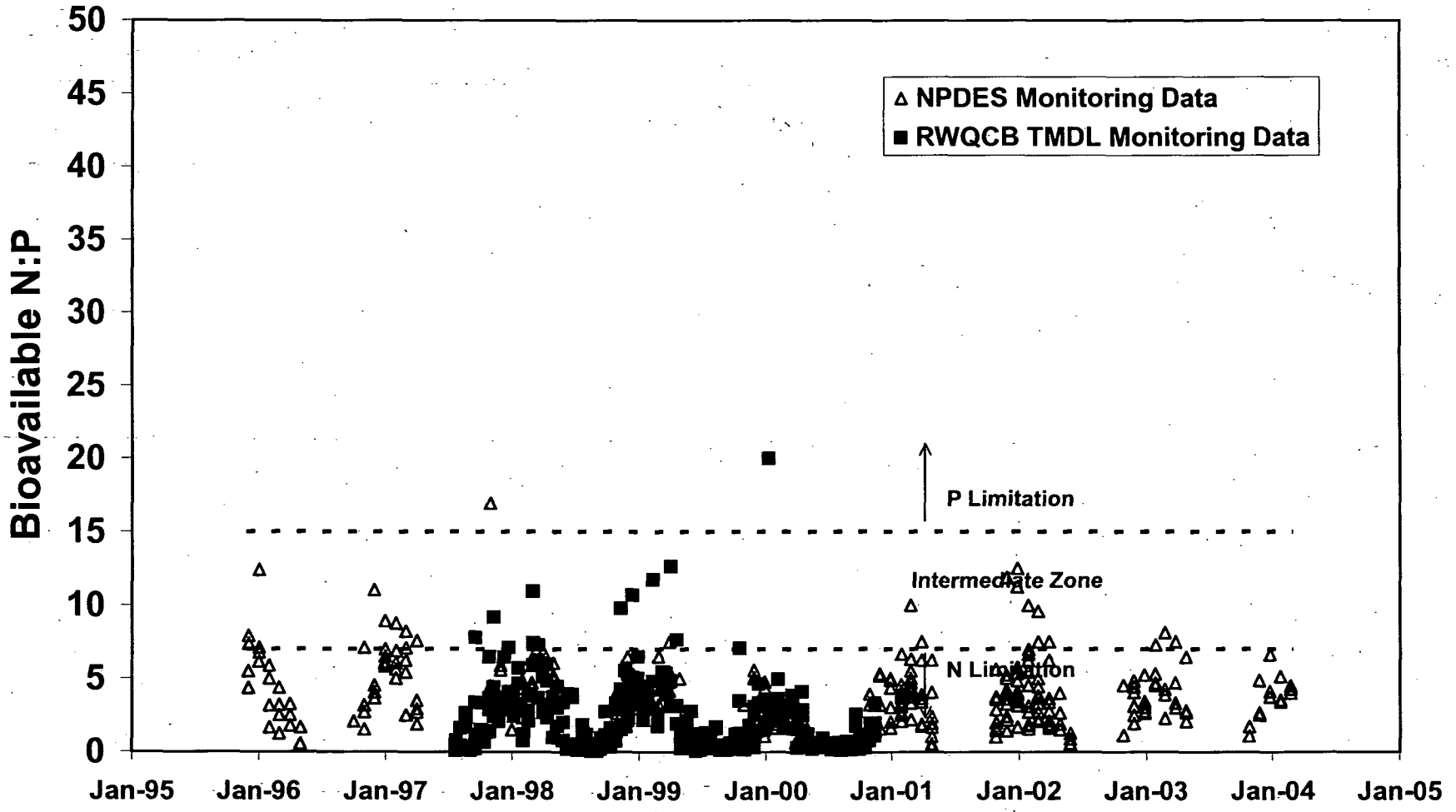
25 events 2-4 sites

Date	Location	Ammonia Nitrogen (mg/L)	Nitrate Nitrogen (mg/L)	Organic Nitrogen (mg/L)	Total Phosphorus (mg/L)	TIN:TP
1/8/03	Laguna at Todd Road	0.6	5.7	0.5	0.8	9.84375
1/8/03	Upstream Laguna at Delta	0.6	1.7	1.4	1	2.875
1/8/03	Laguna Upstream of D-Pond Incline Pump	0.5	1.8	1.1	0.6	4.7916667
1/8/03	Laguna Upstream of D-Pond 36" Discharge	0.5	1.9	0.9	0.6	5
1/8/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.5	1.3	0.9	0.5	4.5
1/15/03	Laguna at Todd Road	0.6	3.3	0.5	0.9	5.4166667
1/15/03	Upstream Laguna at Delta	0.4	1.1	1.1	1.1	1.7045455
1/15/03	Laguna Upstream of D-Pond Incline Pump	0.8	0.9	1.1	0.8	2.65625
1/15/03	Laguna Upstream of D-Pond 36" Discharge	0.7	0.9	1	0.8	2.5
1/15/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.7	0.8	0.7	0.7	2.6785714
1/22/03	Laguna at Todd Road	0.6	3.1	1	1	4.625
1/22/03	Upstream Laguna at Delta	0.7	1.9	0.7	1	3.25
1/22/03	Laguna Upstream of D-Pond Incline Pump	1	1.4	0.9	0.8	3.75
1/22/03	Laguna Upstream of D-Pond 36" Discharge	0.5	1.4	0.9	0.8	2.96875
1/22/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.9	1.1	0.9	0.8	3.125
1/29/03	Laguna at Todd Road	0.4	2.4	0.7	1.2	2.9166667
1/29/03	Laguna Upstream of D-Pond Incline Pump	0.5	1.8	0.2 *	0.8	3.59375
1/29/03	Laguna Upstream of D-Pond 36" Discharge	0.7	1.7	0.6	0.8	3.75
1/29/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.6	0.9	0.2 *	0.8	2.34375
2/5/03	Laguna at Todd Road	0.3	5.5	1	1	7.25
2/5/03	Laguna Upstream of D-Pond Incline Pump	0.4	2.7	0.7	0.7	5.5357143
2/5/03	Laguna Upstream of D-Pond 36" Discharge	0.3	2.4	0.8	0.7	4.8214286
2/5/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.4	1	0.6	0.4	4.375
2/12/03	Laguna at Todd Road	0.3	5.8	1.1	1	7.625
2/12/03	Laguna Upstream of D-Pond Incline Pump	0.4	3.9	0.7	0.7	7.6785714
2/12/03	Laguna Upstream of D-Pond 36" Discharge	0.3	3.2	0.6	0.7	6.25
2/12/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.4	1	0.3	0.3	5.8333333
2/19/03	Laguna at Todd Road	0.7	8.9	1.2	1.6	7.5
2/19/03	Laguna Upstream of D-Pond Incline Pump	0.9	1.8	0.8	0.8	4.21875
2/19/03	Laguna Upstream of D-Pond 36" Discharge	1.1	1.5	1.2	0.8	4.0625
2/19/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.9	0.8	0.7	0.6	3.5416667
2/26/03	Laguna at Todd Road	0.2 *	6.2	1.5	1.2	6.6666667
2/26/03	Laguna Upstream of D-Pond Incline Pump	0.5	2.9	0.5	0.8	5.3125
2/26/03	Laguna Upstream of D-Pond 36" Discharge	0.4	2.4	0.5	0.8	4.375
2/26/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.5	0.9	0.2 *	0.4	4.375
3/5/03	Laguna at Todd Road	0.6	4.6	2	1.1	5.9090909
3/5/03	Laguna Upstream of D-Pond Incline Pump	0.8	3.1	0.6	1	4.875
3/5/03	Laguna Upstream of D-Pond 36" Discharge	0.8	2.4	0.5	0.9	4.4444444
3/5/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.7	0.6	0.3	0.4	4.0625
3/12/03	Laguna at Todd Road	0.7	8.2	2.3	1.6	6.953125
3/12/03	Laguna Upstream of D-Pond Incline Pump	0.5	3.5	0.5	1.1	4.5454545
3/12/03	Laguna Upstream of D-Pond 36" Discharge	0.4	2.7	0.9	1	3.875
3/12/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.4	0.5	0.7	0.5	2.25
3/19/03	Laguna at Todd Road	0.5	9.2	1	1.6	7.578125
3/19/03	Laguna Upstream of D-Pond Incline Pump	0.6	2	1.1	1	3.25
3/19/03	Laguna Upstream of D-Pond 36" Discharge	0.6	1.6	0.2 *	0.9	3.0555556
3/19/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.8	0.5	0.2 *	0.8	2.03125
3/26/03	Laguna at Todd Road	0.4	6.6	1.4	0.3	29.166667
3/26/03	Laguna Upstream of D-Pond Incline Pump	0.2	2.8	1.6	1	3.75
3/26/03	Laguna Upstream of D-Pond 36" Discharge	0.4	2	0.2	0.9	3.3333333
3/26/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.3	0.5	0.3	0.6	1.6666667
4/2/03	Laguna at Todd Road	0.2 *	7.6	1.3	0.8	12.1875
4/2/03	Laguna Upstream of D-Pond Incline Pump	0.2 *	3.8	1	0.7	7.1428571
4/2/03	Laguna Upstream of D-Pond 36" Discharge	0.2 *	2.5	1.1	1.2	2.8125
4/2/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.2 *	0.6	0.2 *	0.2	5
4/9/03	Laguna at Todd Road	0.2	3.2	0.7	0.7	6.0714286
4/9/03	Laguna Upstream of D-Pond Incline Pump	0.2 *	3.3	0.8	0.6	7.2916667
4/9/03	Laguna Upstream of D-Pond 36" Discharge	0.5	2.2	0.2 *	0.7	4.8214286
4/9/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.2 *	0.6	0.2 *	0.4	2.5
4/16/03	Laguna at Todd Road	0.8	7	0.8	0.9	10.833333
4/16/03	Laguna Upstream of D-Pond Incline Pump	0.9	1.7	0.2	0.7	4.6428571
4/16/03	Laguna Upstream of D-Pond 36" Discharge	0.8	1.3	0.2 *	0.7	3.75
4/16/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.9	0.6	0.2 *	0.6	3.125
4/23/03	Laguna at Todd Road	0.2 *	5.6	2.1	1.4	5.1785714
4/23/03	Laguna Upstream of D-Pond Incline Pump	0.6	2.4	0.9	0.9	4.1666667
4/23/03	Laguna Upstream of D-Pond 36" Discharge	0.6	2.1	1.3	0.9	3.75
4/23/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.5	0.5	0.6	0.5	2.5
4/30/03	Laguna at Todd Road	1.1	4.3	1.7	1.3	5.1923077
4/30/03	Laguna Upstream of D-Pond Incline Pump	1.1	0.7	0.2	1.1	2.0454545
4/30/03	Laguna Upstream of D-Pond 36" Discharge	1	0.7	0.9	1	2.125
4/30/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	1	0.5	0.2 *	1	1.875
5/7/03	Laguna at Todd Road	0.2 *	6.4	1.8	1.4	5.8928571
5/7/03	Laguna Upstream of D-Pond Incline Pump	0.6	1.2	1	0.8	2.8125
5/7/03	Laguna Upstream of D-Pond 36" Discharge	0.5	1.1	1.5	0.8	2.5
5/7/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.6	0.5	0.2	0.7	1.9642857
5/14/03	Laguna at Todd Road	0.3	5.3	1.5	1	7
5/14/03	Laguna Upstream of D-Pond Incline Pump	0.2	1	1.1	0.6	2.5

5/14/03	Laguna Upstream of D-Pond 36" Discharge	0.4	1.4	0.8	0.7	3.2142857
5/14/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.3	0.4 *	0.6	0.5	1.75
11/25/03	Laguna Upstream of D-Pond Incline Pump	0.3	0.8	0.6	0.8	1.71875
11/25/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.2 *	0.4 *	0.7	0.7	1.0714286
12/3/03	Laguna at Todd Road	0.2 *	0.7	0.7	0.4	2.8125
12/3/03	Laguna Upstream of D-Pond Incline Pump	0.2 *	0.8	0.5	0.5	2.5
12/3/03	Laguna Upstream of D-Pond 36" Discharge	0.2 *	0.7	0.6	0.4	2.8125
12/3/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.2 *	0.3	0.6	0.4	1.5625
12/10/03	Laguna at Todd Road	0.3	1	1.6	1	1.625
12/10/03	Laguna Upstream of D-Pond Incline Pump	0.2 *	0.7	1.2	0.8	1.40625
12/10/03	Laguna Upstream of D-Pond 36" Discharge	0.4	0.7	1	0.9	1.5277778
12/10/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.2 *	0.7	1.1	0.8	1.40625
12/17/03	Laguna at Todd Road	0.3	7.9	1.5	1.1	9.3181818
12/17/03	Laguna Upstream of D-Pond Incline Pump	0.5	1.2	0.7	0.9	2.3611111
12/17/03	Laguna Upstream of D-Pond 36" Discharge	0.5	1	0.6	0.9	2.0833333
12/17/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.2 *	0.5	1.4	0.8	1.09375
12/22/03	Laguna at Todd Road	0.6	3.9	1.6	1	5.625
12/22/03	Laguna Upstream of D-Pond Incline Pump	0.5	1.7	1.6	0.9	3.0555556
12/22/03	Laguna Upstream of D-Pond 36" Discharge	0.8	1.8	0.4	1	3.25
12/22/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.8	1.6	0.9	0.8	3.75
12/30/03	Laguna at Todd Road	0.8	2.1	2.1	1	3.625
12/30/03	Laguna Upstream of D-Pond Incline Pump	0.7	1.7	1.7	0.8	3.75
12/30/03	Laguna Upstream of D-Pond 36" Discharge	0.8	1.7	2.1	0.9	3.4722222
12/30/03	Laguna Aprox 100ft Upstream of Llano Rd. Bridge	0.8	1.7	1.8	0.8	3.90625
average						4.3647086
stdev						3.281621
N						101
99% confidence interval						0.8410952

Figure 1. Ratio of Bioavailable N:P

Laguna de Santa Rosa Stations 1995-2004



Quality Assurance Manual

City of Santa Rosa

Laguna Environmental Laboratory

County: Sonoma

Certificate number: 1126

2004

Table of Contents

Section 1: Organization and Responsibility

ORGANIZATIONAL CHART

TITLE	INCUMBENT
Laboratory Director	Scott Stinebaugh
Utilities Laboratory Superintendent	Lynn Small
Principal Laboratory Analysts	Kenneth Bowens Kathryn McClellan Lisa Seale
Laboratory Analysts	Cynthia Larkin Raul Regalado Terence Sotelo Melanie White-Lam
Laboratory Aide	Renae Bertacco

A. QUALIFICATIONS of STAFF

NAME	DEGREE	CHEM UNITS	BIOLOGY UNITS	LAB CERTIFICATE	YEARS LAB EXPERIENCE
Lisa Seale	BA Microbiology	30	60	CWEA III	23
Kenneth Bowens	BA BioChemistry	50	45	CWEA IV	18
Melanie White-Lam	BA Biology	16	60	CWEA II	14
Kathryn McClellan	MS Agric. & Environ. Chemistry	65	25		12
Terence Sotelo	BS Microbiology	47	62	CWEA IV AWWA III	13
Raul Regalado	BS Microbiology	35	45	CWEA IV	19
Cynthia Larkin	BS Natural Resources Sciences	20	60	CWEA I	7

B. RESPONSIBILITIES of STAFF

(1) **Laboratory Superintendent:** Under general direction of the director, the Superintendent supervises all activities of the laboratory. The laboratory supervisor has immediate responsibility for quality assurance, sample control, and chemical hygiene; prepares budget requests, and approves routine requisitions; performs evaluations of the laboratory staff; communicates with the operations staff on process monitoring; and reports to the director on all issues relating to the conduct of the laboratory.

(2) **Principal Laboratory Analyst:** Under supervision by the Superintendent, the Principal Laboratory Analyst is the operator at the skilled level of the gas chromatograph/mass spectrometry, atomic absorption and inductively-coupled plasma spectroscopy, and inductively-coupled plasma/mass spectrometry. The Principal Laboratory Analyst will check compliance with standard analytical procedures, review the comparison of QC data with acceptance limits, verify computations, date and initial all QC documentation upon review, and submit a report to the supervisor on all QC problems. The Principal Laboratory Analyst assists the superintendent in conducting certification correspondence and communication with the Environmental Laboratory Accreditation Program, coordinating Performance Evaluation studies and responses, maintaining the Quality Assurance document, keeping service contract records, and evaluating responses to Requests for Proposals. The Principal Laboratory Analyst reviews and approves laboratory test reports for release.

(3) **Laboratory Analyst:** Under supervision by the Superintendent, the Laboratory Analyst performs routine testing on water, wastewater, and gas samples; prepares standard reagents; calibrates and maintains instrumentation; and prepares reports on all laboratory activities. The Laboratory Analyst maintains QC documentation and control charts, verifies computations, and reports QC violations immediately to the supervisor.

(4) **Laboratory Aide:** Under supervision by the superintendent, the laboratory aide performs the tasks of sample login, glassware preparation and purchasing. The laboratory aid also provides assistance to the analysts when necessary.

Section 2: QA Objectives for Measurement Data

FoT E101 and FoT E107: Microbiology of Drinking Water and Wastewater

E 101.060: Total coliforms and E. Coli by MMO-MUG technique: Conduct a quality control check on every Colilert lot. Check Colilert media with positive/negative cultures of E.coli-yellow and florescent (ATCC #25922, 11775 or equivalent), Klebsiella pneumoniae - yellow and no fluorescence (ATCC #9997 or equivalent), Pseudomonas aeruginosa - no color or fluorescence, (ATCC #10145, 27853 or equivalent) and a control blank each time a batch is received. Document date media lots are received, put into service, and emptied. Call Access Analytical Systems (1-800-321-0207) if the quality control check fails 2 times. Document results. Pre-sterilized Idexx bottles are checked with Tryptic Soy Broth (any turbidity within 24 hours indicates an un-sterile bottle). The MMO-MUG (Colilert) system is approved for use only for potable water total coliform analysis (September 25, 1995). A parallel study with multiple tube fermentation was run in Dec. of 1992 and Jan. of 1993. Contact ELAP (510.540-2800) for information about approved parallel procedure. Document the lot number of the color comparator and the date it expires. Document set up and read times of samples. Read samples twenty-four (24) hours after set up time. Samples read after twenty-eight (28) hours are valid if samples are negative. If samples are read after 28 hours and are positive, they are invalid and must be resampled. Heterotrophic bacteria can overgrow inhibitors in the media and cause a positive test.

E 101.010 & E 107.010: Heterotrophic Plate Count: Monthly, set up the media preparation water in duplicate for heterotrophic plate count. Counts must be less than 1000 CFU/mL. Occasionally check #1 water faucets, and drinking fountain in the reception area for contamination, especially during times of construction.

E 107.020: Total Coliforms in Wastewater by Multiple Tube Fermentation: Check media with positive/negative cultures of E. coli (gas formation) and S. aureus (no gas formation). Do not use if media does not give expected result. Use pre-sterilized Idexx bottles that have been checked for QC according to Section 2, E 101.060. Annually, check glassware for inhibitory residue from dishwashing soap. Perform a completed test on 10% of positive confirmed tubes using MacConkey Agar (or equivalent). Double confirm by inoculating into BGB broth.

Check the quality of purified water used in media preparation by:

(1) Checking that the pH is between 5.5 and 7.5 with each use. Document in media prep log.
(2) Measuring the resistivity at each use and documenting on media prep log.
(3) Checking for the absence of chlorine and documenting on media prep log.
(4) Performing a monthly heterotrophic plate count.
(5) Measuring the concentration of metals (lead, cadmium, chromium, copper, nickel, and zinc) annually.
(6) Monthly, check for the absence of TOL, NH_3 and TKN.
(7) Annually, run a water suitability analysis.

All samples are autoclaved for 30 minutes before disposal. Autoclaving of samples and spent media is documented in "Autoclave Log" with date, initials of preparer, item sterilized, time in, time out, total time in autoclave, sterile run time at pressure and temperature, and sterility indicator results. All media autoclave information (same as above) is documented in the media prep log.

Media preparation is documented in "Media Preparation" log with date, initials of preparer, media type, media lot number, media expiration date, strength of media solution to be prepared, grams of dry media weighed, mLs of deionized water used, pH before and after sterilization, and the results of a pipettor delivery check in mLs to the first decimal place. Document time of preparation and of sterilization. Use sterile indicating tape and Baccillus microbiological indicators. Media preparations are reviewed for compliance with the following requirements:

SUBJECT FOR COMPLIANCE	LIMITATIONS
Dry media storage	6 months from date opened, 1 year from date received.
Agar in closed screw-cap tubes	4° C for 3 months
Media strength	To equal value calculated from grams weighed and mLs of deionized water used.
pH range of lauryl tryptose	6.6 to 7.0
pH range brilliant green bile	7.0 to 7.4
Maximum pipettor error	2.5 %
Maximum allowable time until sterilization	2 hours

Check glassware used in the preparation of media for inhibitory residues left by the washing procedure (Standard Methods, 18th edition, Section 9020B; 3 – 2a pg. 9 – 5). Check balances monthly with certified weights.

E 107.040: Fecal Coliforms in Wastewater by Multiple Tube Fermentation: Check media with positive (E. coli) and negative (S. aureus) cultures before use. Immerse samples in water bath at 44.5 ∀ 0.2E C for 24 hours. Read samples 24 ∀ 2 hours from setup time.

FoT E102: Inorganic Chemistry and Physical Properties of Drinking Water excluding Toxic Chemical Elements

E 102.030: Chloride, E 102.030: Fluoride, E 102.030: nitrate, E 102.030: sulfate by ion chromatography: Before every analysis, demonstrate the ability to generate acceptable accuracy and precision with a laboratory performance standard, and check for interferences with a reagent blank. Verify that standards have been prepared correctly with a reference check standard prepared from an independent source. The check standard result must be within 10% of the true value. With each sample batch, or for a minimum of 10% of all samples, analyze a fortified blank containing each analyte. Evaluate the accuracy as percent recovery.

E 102.100: Alkalinity: Duplicate analyses are to be performed on a minimum of 5% of all samples and at least once a day/batch. The relative percent difference (%R.P.D.) is calculated as the difference divided by the mean, multiplied by 100. %R.P.D. values are documented on the Q.C. Chart for this test daily. Follow laboratory procedures for Q.C. auditing and retest if unacceptable.

Corrosivity: Corrosivity is calculated using a software called **Water Indices! Pro:** by **ChemSW**. It is based on a calculation from the EPA document a Corrosion Manual for Internal Corrosion of Water Distribution Systems EPA 570/9-84-01.

E 102.120: Total Hardness by Calculation from Ca/Mg (SM18th 2340B): Perform by calculation of Calcium and Magnesium analysis by ICP per 200.7. The calculation is as follows: Analyze calcium and magnesium as per method. Multiply calcium result in mg/L by 2.5 and magnesium result in mg/L by 4.12, add together for total hardness result as CaCO3 in mg/L. Samples with turbidities of 1.0 NTU or less do not have to be digested

Hardness = Ca (mg/L) 2.5 + Mg (mg/L) 4.12

E 102.140 & E 102.130: Total Filterable Residue and Conductivity: See E 108.441 and E 108.430.

E 102.190: Cyanide by Automated Color: The initial demonstration of performance is used to characterize instrument performance (determination of LCR's and analysis of QCS) and laboratory performance (determination of MDL's prior to performing analyses by this method.

Method Detection Limit (MDL) -- MDL's must be established for all analytes, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit. To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = t\ S$$

Where, t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates, t = 2.528 for twenty one replicates]. S = standard deviation of the replicate analyses.

MDL's should be determined every year, when a new operator begins work, or whenever there is a significant change in the background or instrument response.

Where reference materials are available, they should be analyzed to provide additional performance data. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably.

E 102.500: Sodium by flame atomic absorption spectroscopy:

E 102.500: Potassium by flame atomic absorption spectroscopy: Evaluate precision as relative standard deviation and accuracy as percent recovery. Verify reporting limits, **blank and matrix spikes** with 80 to 120 % recovery. **Verify precision at less than 20% RSD. Calibration is verified with a secondary source midpoint check standard every 10 samples.** Calibration verification standard results must be within 10% of true value, **if not re-analyze.** A sample blank, blank spike, matrix spike and matrix spike duplicate will be analyzed every 10 samples or with each batch.

FoT E 103: <u>Analysis of Toxic Chemical Elements in Drinking Water</u>

For all drinking water samples, pH and Turbidity will be included on Chain of Custody as an analysis.

E 103.160: Mercury Analysis (245.1): <u>Blanks</u> - Three types of blanks are required for the analysis. The Calibration blank is used in establishing the analytical curve, the Laboratory Reagent Blank (LRB) is used to assess possible contamination from the sample preparation procedure, and the Laboratory Fortified Blank (LFB) is used to assess routine laboratory performance. The calibration blank must contain all reagents in the same concentrations and in the same volume as used in preparing the calibration solutions. The LRB is prepared in the manner as the calibration blank except the LRB must be carried through the entire sample preparation scheme. The laboratory must analyze at least one LRB with each batch of 20 or fewer samples of the same matrix. The LFB is prepared by fortifying a sample size volume of laboratory reagent blank solution with mercury. The LFB must be carried through the entire sample scheme. The LFB must be analyzed with each batch of samples and must meet the required control limits of 85 - 115%.

<u>**Instrument Performance Check (IPC) or Instrument Calibration Verification (ICV)**</u> - This solution is used to periodically verify instrument performance during analysis. It must contain all reagents in the same concentration as the calibration solutions and mercury at an appropriate concentration to approximate the midpoint of the calibration curve. For all determinations the laboratory must analyze the IPC solution and a calibration blank immediately following each calibration, after every tenth sample, and at the end of the sample run.

Analysis of the IPC solution immediately following calibration must verify that the instrument is within ∀ 5% of calibration. Subsequent analyses of the IPC solution must be within ∀ 10% of calibration. If the calibration cannot be verified within the specified limits, analysis must be discontinued, the cause determined and/or in the case of drift, and instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed. The analysis data of the calibration blank and IPC solution must be kept on file with the sample analyses data.

Quality Control Sample (QCS) or External Standard (Ext Std) - For initial and periodic verification of calibration standards and instrument performance, analysis of a QCS is required. The QCS must be obtained from an outside source different from the standard stock solution, but prepared in the same manner as the calibration solutions. To verify the calibration standards, the determined concentration of the QCS must be within ∀ 10% of the stated value.

Method Detection Limits (MDL's) – MDL's are determined by analyzing seven replicates of Laboratory fortified blanks. MDL's must be determined annually.

Laboratory Fortified Matrix (LFM) - The laboratory must add a known amount of mercury to a minimum of 10% samples or one sample per sample set. In each case the LFM aliquot must be a duplicate of the aliquot used for sample analysis. The values of the control limits to the designated LFM must be in the recovery range of 70 - 130%.

Matrix Spike/Matrix Spike Duplicate - A known amount of each analyte is added to a minimum of 10% of the routine samples or one sample per sample set, whichever is greater. The percent recovery is calculated in units appropriate to the matrix (mg/L), using the following equation:

$$R = \frac{C_3 - C}{S} \times 100$$

where,

R = percent recovery

C_3 = fortified sample concentration
C = sample background concentration
s = concentration equivalent of analyte added to sample

If recovery of any analyte falls outside the designated range, the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The data user should be informed that the result for that analyte in the unfortified sample is suspect due to matrix effects and analysis by method of standard addition is considered.

The matrix spike duplicate is analyzed for each analyte on every 10% of the routine samples or on one sample per sample set, whichever is greater. The Percent Relative Standard Deviation (%RSD) is calculated in units appropriate to the matrix (mg/L), using the following equation:

$$\%RSD - \frac{SD}{MEAN} \times 100$$

where, %RSD = percent relative standard deviation
SD = standard deviation of matrix spike and the matrix spike duplicate
MEAN = mean result of matrix spike and the matrix spike duplicate

If the relative standard deviation of any analyte falls outside the designated range, the sample needs to be redigested and run again.

E 103.130: ICP Analysis (200.7):

Blanks - ***Four types of blanks*** are required for the analysis. The **Calibration blank** is used in establishing the analytical curve, the **Laboratory Reagent Blank (LRB)** is used to assess possible contamination from the sample preparation procedure. The **Laboratory Fortified Blank (LFB)** is used

to assess routine laboratory performance. The **Rinse Blank** is used to flush the instrument uptake system and nebulizer between standards, check solutions, and samples to reduce memory interferences. The calibration blank must contain all reagents in the same concentrations and in the same volume as used in preparing the calibration solutions. The LRB is prepared in the manner as the calibration blank except the LRB must be carried through the entire sample preparation scheme. The laboratory must analyze at least one LRB with each batch of 20 or fewer samples of the same matrix. The LFB is prepared by fortifying a sample size volume of laboratory reagent blank solution with all analytes to a suitable concentration. The LFB must be carried through the entire sample scheme. The LFB must be analyzed with each batch of samples. If the recovery of any analyte falls outside the required control limits of 85 - 115%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses. The rinse blank is prepared by acidifying reagent water to the same concentrations of acids as used in the calibration blank and stored in a convenient manner.

Instrument Performance Check (IPC) or Instrument Calibration Verification (ICV) - This solution is used to periodically verify instrument performance during analysis. It must contain all reagents in the same concentration as the calibration solutions and mercury at an appropriate concentration to approximate the midpoint of the calibration curve. For all determinations the laboratory must analyze the IPC solution and a calibration blank immediately following each calibration, after every tenth sample and at the end of the sample run.

Analysis of the IPC solution immediately following calibration must verify that the instrument is within ∀ 5% of calibration. Subsequent analyses of the IPC solution must be within ∀ 10% of calibration. If the calibration cannot be verified within the specified limits, analysis must be discontinued, the cause determined and/or, in the case of drift, the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed. The analysis data of the calibration blank and IPC solution must be kept on file with the sample analyses data.

Quality Control Sample (QCS) or External Standard (Ext Std) - For initial and periodic verification of calibration standards and instrument performance, analysis of a QCS is required. The QCS must be obtained from an outside source different from the standard stock solution, but prepared in the same manner as the calibration solutions. To verify the calibration standards, the determined concentration of the QCS must be within ∀ 10% of the stated value.

Laboratory Fortified Matrix - The laboratory must add a known amount of each analyte to a minimum of 10% of samples or one sample per sample set. In each case the LFM must be a duplicate of the aliquot used for sample analysis. The values of the control limits to the designated LFM must be in the recovery range of 70 - 130%.

Spectral Interference Check (SIC) or Interference Check Standard - When interelement corrections are applied, SIC solutions are needed containing concentrations of the interfering elements at levels that will provide an adequate test of the correction factors. The correction factors tested on a daily basis are found to be within a10% criteria for 5 consecutive days, the required verification frequency of those factors in compliance may be extended to a weekly basis.

Matrix Spike/Matrix Spike Duplicate - A known amount of each analyte is added to a minimum of 10% of the routine samples or one sample per sample set, whichever is greater. The percent recovery is calculated in units appropriate to the matrix (mg/L), using the following equation:

$$R = \frac{C_3 - C}{S} \times 100$$

where,
R = percent recovery
C_3 = fortified sample concentration
C = sample background concentration
s = concentration equivalent of analyte added to sample

If recovery of any analyte falls outside the designated range, the recovery problem encountered with the

fortified sample is judged to be matrix related, not system related. The data user should be informed that the result for that analyte in the unfortified sample is suspect due to matrix effects and analysis by method of standard addition is considered.

The matrix spike duplicate is analyzed for each analyte on every 10% of the routine samples or on one sample per sample set, whichever is greater. The Relative Percent Difference is calculated in units appropriate to the matrix (mg/L), using the following equation:

$$RPD - \frac{Diff}{MEAN} \times 100$$

where, RPD = relative percent difference
Diff = The Difference of the matrix spike and the matrix spike duplicate
MEAN = mean result of matrix spike and the matrix spike duplicate

If the relative of percent difference any analyte falls outside the designated range, the sample needs to be redigested and run again.

E 103.140: ICP/MS Analysis (200.8):

Blanks - Four types of blanks are required for the analysis. The **Calibration blank** is used in establishing the analytical curve. The **Laboratory Reagent Blank (LRB)** is used to assess possible contamination from the sample preparation procedure. The **Laboratory Fortified Blank (LFB)** is used to assess routine laboratory performance. The **Rinse Blank** is used to flush the instrument uptake system and nebulizer between standards, check solutions, and samples to reduce memory interferences. The calibration blank must contain all reagents in the same concentrations and in the same volume as used in preparing the calibration solutions. The LRB is prepared in the manner as the calibration blank except the LRB must be carried through the entire sample preparation scheme. The laboratory must analyze at least one LRB with each batch of 20 or fewer samples of the same matrix. The LFB is prepared by fortifying a sample size volume of laboratory reagent blank solution with all analytes to a suitable concentration. The LFB must be carried through the entire sample scheme. The LFB must be analyzed with each batch of samples. If the recovery of any analyte falls outside the required control limits of 85 - 1105%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses. The rinse blank is prepared by acidifying reagent water to the same concentrations of acids as used in the calibration blank and stored in a convenient manner.

Instrument Performance Check (IPC) or Instrument Calibration Verification (ICV) - This solution is used to periodically verify instrument performance during analysis. It must contain all reagents in the same concentration as the calibration solutions and mercury at an appropriate concentration to approximate the midpoint of the calibration curve. For all determinations the laboratory must analyze the IPC solution and a calibration blank immediately following each calibration, after every tenth sample and at the end of the sample run.

Analysis of the IPC solution immediately following calibration must verify that the instrument is within ∀ 5% of calibration. Subsequent analyses of the IPC solution must be within ∀ 10% of calibration. If the calibration cannot be verified within the specified limits, analysis must be discontinued, the cause determined and/or, in the case of drift, the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed. The analysis data of the calibration blank and IPC solution must be kept on file with the sample analyses data.

Quality Control Sample (QCS) or External Standard (Ext Std) - For initial and periodic verification of calibration standards and instrument performance, analysis of a QCS is required. The QCS must be obtained from an outside source different from the standard stock solution, but prepared in the same manner as the calibration solutions. To verify the calibration standards, the determined concentration of the QCS must be within ∀ 10% of the stated value.

Laboratory Fortified Matrix - The laboratory must add a known amount of each analyte to a minimum

of 10% of samples or one sample per sample set. In each case the LFM must be a duplicate of the aliquot used for sample analysis. The values of the control limits to the designated LFM must be in the recovery range of 70 - 130%.

Interference - Isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z) cause isobaric elemental interferences in ICP-MS. The HP-4500 ChemStation data system is be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Isobaric molecular and doubly charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences, which could affect ICP-MS determinations, have been identified. Examples include $ArCl^+$ ions on the As signal and MoO^+ ions on the cadmium isotopes. The approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotopic abundance=s from the literature. The most precise coefficients for an instrument must be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting statistics. Because the ^{35}Cl natural abundance of 75.77 percent is 3.13 times the ^{37}Cl abundance of 24.23 percent, the chloride correction for arsenic can be calculated (approximately) as follows (where the $^{38}Ar^{37}Cl^+$ contribution at m/z 75 is a negligible 0.06 percent of the $^{40}Ar\ ^{35}Cl^+$ signal): corrected arsenic signal (using natural isotopes abundance=s for coefficient approximation=s) = (m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal), where the final term adjusts for any selenium contribution at 77 m/z).

NOTE: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}Se^+$, (e.g. , $^{81}BrH^+$ from bromine wastes [6] or ^{82}Kr from krypton contamination in the Ar). Similarly, corrected cadmium signal (using natural isotopes abundances for coefficient approximations) = (m/z 114 signal) - (0.027)(m/z 118 signal) - (1.63)(m/z 108 signal), (where last 2 terms adjust for any tin or MoO^+ contributions at m/z 114).

NOTE: Cadmium values will be biased low by this type of equation, $^{92}ZrO^+$ ions contribute at m/z 108, but use of m/z 111 for Cd is even subject to direct ($^{92}ZrOH^+$) ions and indirect ($^{90}ZrO^+$) additive interferences when Zr is present.

NOTE: As for the arsenic equation above, the coefficients in the Cd equation are **ONLY** illustrative. The most appropriate coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<l percent) counting precision.

The accuracy of these types of equations is based upon the constancy of the OBSERVED isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the Aparent@ ion have not been found to be reliable, e.g., oxide levels can vary. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferent. This type of correction has been reported for oxide-ion corrections using ThO^+/Th^+ for the determination of rare earth elements. The use of aerosol desolvation and/or mixed plasmas have been shown to greatly reduce molecular interferences. These techniques can be used provided that method detection limit, accuracy, and precision requirements for analysis of the samples can be met.

Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity.

Changes in matrix composition can cause significant signal suppression or enhancement. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) have been currently recommended to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes. When the intensity level of an internal standard is less than 30 percent or greater than 120 percent of the intensity of the first standard used during calibration, the sample must be reanalyzed after a fivefold (1+4) or greater dilution has been performed.

Memory interferences can occur when there are large concentration differences between samples or standards, which are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences, which are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

Interference Equations

The following interference equations are used to correct for isobaric elemental and polyatomic interferences. All equations must be specified in the ChemStation method before any other data acquisition or data analysis parameters are set.

C[a]	(1.000)(44C)-(0.0271)(88C)
V	(1.000)(51C)-(3.127)(53C)+(0.353)(52C)
As	(1.000)(75C)-(3.127)(77C)+(2.736)(82C)-(2.760)(83C)
Mo	(1.000)(98C)-(0.146)(99C)
Cd	(1.000)(111C)-(1.073)(108C)+(0.764)(106C)
In	(1.000)(115C)-(0.016)(118C)
Pb	(1.000)(208C)+(1.000)(207C)+(1.000)(206C)

Recommended Elemental Interference Equations

Matrix Spike/Matrix Spike Duplicate - A known amount of each analyte is added to a minimum of 10% of the routine samples or one sample per sample set, whichever is greater. The percent recovery is calculated in units appropriate to the matrix (mg/L), using the following equation:

$$R = \frac{C_3 - C}{s} \times 100$$

where, R = percent recovery

C_3 = fortified sample concentration

C = sample background concentration

s = concentration equivalent of analyte added to sample

If recovery of any analyte falls outside the designated range, the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The data user should be informed that the result for that analyte in the unfortified sample is suspect due to matrix effects and analysis by method of standard addition is considered.

The matrix spike duplicate is analyzed for each analyte on every 10% of the routine samples or on one sample per sample set, whichever is greater. The Relative Percent Difference is calculated in units appropriate to the matrix (mg/L), using the following equation:

$$RPD = \frac{Diff}{MEAN} \times 100$$

where, RPD = Relative Percent Difference

Diff = Diff of the Matrix Spike and the Matrix Spike Duplicate

MEAN = mean result of matrix spike and the matrix spike duplicate

If the Relative Percent Difference of any analyte falls outside the designated range, the sample needs to be redigested and run again.

FoT E 104: Organic Chemistry of Drinking Water (measurement by GC/MS combination)

E 104.040, E 104.045, E 104.050: EPA Method 524.2: BFB tuning criteria and GC/MS calibration verification criteria must be met every 8 hours before analyzing samples. Purge 25 ng of 4-bromofluorobenzene (BFB) by the method to be used. The BFB mass spectra must meet all criteria as follows.

Mass	Intensity Required (relative abundance)
50	15 to 40% of mass 95
75	30 to 80% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

Perform a continuing calibration check by purging a medium CAL solution (10 ppb). The absolute response areas of the quantitation ions of the internal standard and the surrogates must not have decreased by more than 30% since the most recent continuing calibration check, or by more than 50% since the initial calibration. The response factor for each analyte and surrogate must be within 30% of the mean value measured in the initial calibration.

Before analyzing samples, demonstrate that a laboratory reagent blank is free of contaminants that would interfer with the determination of any target analyte. With each set of field samples a field reagent blank should be analyzed.

With each batch of samples analyze a laboratory fortified blank (LFB) at the level used in initial demonstration of accuracy and precision (1 ppb). For each analyte and surrogate, the mean accuracy, expressed as a percentage of the true value, should be 80-120% and the RSD should be <20%. Use control charts to plot the accuracy and precision of the LFB as a function of time.

FoT E 108: Wastewater Inorganic Chemistry, Nutrients and Demand

E 108.050: pH by Electrometric Method: Check the procedure on standard buffer solutions. Calibrate pH meter daily using buffers that bracket the expected pH values. A duplicate sample is run daily. An R.P.D. is generated and plotted on a control chart. Control charts are generated every 30 points and new control values are established.

E 108.090: Residue, Volatile: A duplicate sample is run weekly on plant samples and every incidence when a sample or a group of samples from another source are to be tested. An R.P.D. is generated and plotted on a control chart. After 30 points, a new control chart is generated and new control values are established.

E 108.120: Chloride, E 108.120: Fluoride, E 108.120: Nitrate, E 108.120: Sulfate by IC: Before every analysis, demonstrate the ability to generate acceptable accuracy and precision with a laboratory performance standard, and check for interferences with a reagent blank. Verify that standards have been prepared correctly with a reference check standard prepared from an independent source. The check standard result must be within 10% of the true value. With each sample batch, or for a minimum of 20% of all samples, analyze a fortified blank containing each analyte. Evaluate the accuracy as percent recovery.

E 108.171: Chlorine Residual by Iodometric Back-titration: By pre-standardized 0.00564 N PAO. Check normality of 0.0282 N iodine weekly by blank titration with PAO. For chlorine concentrations of 10 mg/L chlorine or less, titrate 200 mls sample. For greater chlorine concentrations, use proportionately less sample. Use sample of such size that not more than 10 ml PAO solution is required. Titrate to the

first appearance of blue color that persists after complete mixing.

E 108.262: Phosphate (ortho), E 108.263 Phosphorous (total): One replicate is done with every batch, or with every 20 samples. Relative Percent Difference is calculated and documented on the control chart. Percent recoveries are calculated on both the matrix spike and the blank spike. The matrix spike is documented on the control chart. If the R.P.D and/or percent recoveries are outside control limits, reanalyze and troubleshoot. Do not use sample results until QC results are in control.

E 108.390: Turbidity: Hach On-line turbidity analyzers are checked against Hach 2100N turbidimeters. Initially, and as necessary (at least every quarter), calibrate both on-line turbidimeters and bench top models with formazin standards. Set values on secondary standards. Weekly check calibration of 2100N with secondary gel standards; if values vary by 5% or more from set values at calibration, recalibrate with formazin standards. Monthly, clean sample cells and discard scratched cells with blank NTUs above 0.1.

E 108.421: Total Hardness: (same as FoT 102.120

E 108.430: Specific Conductance: Calibrate meter with an air blank and a 1413 µmhos certified standard with each use. Check performance with ERA Mineral Reference Standards occasionally.

E 108.440: Residue, Total: Choose a sample volume that will yield a residue between 10 and 200 mg. Pipet a volume of well-mixed sample to a pre-weighed evaporating dish and evaporate on a steam bath to dryness. Dry dish in a 103-105 C oven for at least an hour, or until a constant weight is achieved, less than 4% change from previous weighing. An R.P.D. is generated daily by running a duplicate sample. R.P.D. values are plotted on a control chart. Control charts are generated every 30 points and new control values are established.

E 108.441: Residue, Filterable (TDS): Mix sample well and filter through a standard glass fiber filter. Measure filtered sample into a pre-weighed evaporating dish. Evaporate samples to dryness on a steam bath. Dry TDS samples for at least an hour at 180 ∀ 2EC. Repeat drying cycle until a constant weight is obtained or weight change is less than 4% of previous weight. A blank is run to assure the integrity of the evaporating dishes. Duplicate samples are run and an R.P.D. is generated and plotted on a control chart. After 30 points, a new control chart is generated and new control values are established.

E 108.442: Suspended Solids: Wash glass fiber filters with 3 successive portions of DI water, dry in the muffle furnace for 1 hour. Store filters in a dessicator until use. Weigh filter and aluminum dish, put filter on filtration apparatus, filter a pre-measured volume of sample through the filter and rinse with 3 successive portions of DI water. Dry filter in 103 - 105EC oven for at least one hour, and to a constant weight. Check precision by sample duplication. Calculate the relative percent difference (R.P.D.) of duplicates. Establish a control chart using the mean and standard deviation (SD) from 30 sets of duplicate values.

E 108.443: Settleable Solids: Periodically run ERA Settleable Solids Standard.

E 108.464: Chlorine Residual by DPD-FAS Titrimetric Method: For chlorine concentrations of up to 5 mg/L, use 100 ml of sample. If the chlorine concentration is greater than 5 mg/L, use smaller sample size and dilute up to 100 ml. DPD indicator in solution B stored in amber glass and discarded when discolored. FAS titrant is good for one month and can be checked with potassium dichromate. Titrate until red color is discharged / disappears.

E 108.472: Total Cyanide by Distillation and Automated Color Reference: E 102.190 above

E 108.490: pH by Electrometric Method: Check the procedure on standard buffer solutions. Calibrate pH meter daily using buffers that bracket the expected pH values. A duplicate sample is run daily. An R.P.D. is generated and plotted on a control chart. Control charts are generated every 30 points and new control values are established.

E 108.506: Ammonia by Ion-selective Electrode (SM 18th, 4500 – NH_3G): Check electrode performance daily, or with each analytical batch, by monitoring the slope as the change in potential for a tenfold change in concentration. The optimum value is -59 mV, and the allowable range is -54 to -60 mV per decade when the solution temperature is 20 to 25 degrees C. Check instrument performance daily, or with each analytical batch, with an internal check standard (blank spike) prepared in a concentration about midway in the expected concentration range. Calculate the percent recovery (PR) by dividing the test result by the standard value, and multiplying by 100. Blank Spike results must be between 90 - 110 %. Check precision by performing a duplicate analysis with each batch. Calculate the relative percent difference (R.P.D). Calculate the mean and standard deviation (SD) of 30 consecutive RPDs. Establish a warning limit at the mean plus 2 SDs, and an acceptance limit at the mean plus 3 SDs.

Check accuracy daily by spiking at least one sample with a volume of standard solution calculated to approximately double the concentration. Calculate the percent recovery (PR) by subtracting the sample result from the spiked sample result, dividing by the spike added, and multiplying by 100. Calculate the mean and standard deviation (SD) of 30 consecutive PRs. Establish a warning limit at the mean plus or minus 2 SDs, and an acceptance limit at the mean plus or minus 3 SDs.

E 108.510: Nitrite: A duplicate and spike are run with every 20 samples, or each batch. A 0.20 ppm laboratory control standard is run with each batch, and recoveries must be between 90-110% for analysis to continue. If it is not, stop analysis and troubleshoot. Rerun standard curve if necessary. With each batch run a fortified blank containing the analyte. Control charts are prepared for duplicates and spikes, control limits are recalculated every 30 samples and a new chart generated. Relative percent difference and % Recovery are used for control limit calculations. If results are not within control limits, do not use test results, but reanalyze and/or troubleshoot.

E 108.531: Dissolved Oxygen by Membrane Electrode: Monthly check DO meter against a Winkler titration. Do maintenance as necessary. Document maintenance in Maintenance log book.

E 108.580: Sulfide: Perform replicate analyses and calculate the Relative Percent Difference. Record and graph on control chart.

E 108.590: Biochemical Oxygen Demand (SM 18th, 5210B): The dissolved oxygen uptake of the BOD dilution water over 5 days at 20 degrees C should not be more than 0.2 mg/L. The dissolved oxygen uptake of the seeded dilution water should be between 0.6 and 1.0 mg/L. Check for dilution water quality, seed effectiveness, and analytical technique with a glucose-glutamic acid check (SM 5-3 4.c.). The 5 day 20 degree C BOD of the check must be in the range 167 to 229 mg/L. Check precision by sample duplication. Calculate the relative percent difference (R.P.D.) of duplicates from the mean value. Establish a control chart using the mean and standard deviation (SD) from 30 sets of duplicate values. Use two SDs above the mean as a warning limit, and three SDs above the mean as an acceptance limit. With each batch set two blanks, seeded dilution water, duplicate Hach glucose-glutamic acid standard, and a duplicate sample.

E 108.610: Organic Carbon: Replicate analyses are to be performed on a minimum of 10% of all samples and at least once a day/batch. The % R.P.D. is calculated and recorded on a control chart. % Standard Recovery is calculated from a known amount of standard added to the sample. This value is also obtained for 10% of all samples and at least once per day/batch. % Std. Recovery values are documented daily on the Q.C. chart for this test. If the % R.P.D. or the % Std. Recovery fall out of the acceptable control ranges, troubleshoot and repeat the analysis.

E 108.660: Chemical Oxygen Demand: Reference standard is to be run with each digestion. Check standards must be 90 - 110% recovery. Also, replicate analyses are to be performed on a minimum of 20% of all samples. The relative percent difference is calculated and plotted on a control chart. If the % R.P.D. falls out of the acceptable control range, repeat the analysis.

FoT E 109: Toxic Chemical Elements in Wastewater

E 109.190: Mercury (245.1) - refer to 103.160.

E 109.010: ICP (200.7) - Refer to 103.130

E 109.020: ICP/MS (200.8) - Refer to 103.140

FoT E 110: Organic Chemistry of Wastewater (measurements by GC/MS combination)

E 110.040: EPA Method 624: BFB tuning criteria and GC/MS calibration verification criteria must be met every 24 hours before analyzing samples. Purge 50 ng of 4-bromofluorobenzene (BFB) by the method to be used. The BFB mass spectra must meet all criteria as follows.

Mass	Intensity Required (relative abundance)
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

Once every 24 hours, or every 20 samples, verify the initial calibration by analyzing a check standard of Calibration Check Compounds (CCCs). The response factors (RFs) of the CCCs relative to the initial calibration may be obtained as a Continuing Calibration Report. The minimum relative standard deviation for the CCCs must be less than 35% before sample analysis begins. See SOP for special considerations.

Internal standard responses and retention times must be evaluated. The retention time must not vary more than 30 seconds since the last calibration check. The response must not vary more than a factor of two (-50% to +100%) since the last calibration check.

A blank analysis must be free of interferences. Matrix spike and matrix spike duplicates, spiked with a second source, should show a recovery in the range 71 to 138%, or as listed in table 5 of Method 624. Control charts are kept to document actual recoveries. The relative percent difference between spike and spike duplicate must be less than 30%.

FoT E 113.010: Aquatic Toxicity Bioassays

E 113.003A: Wastewater Testing According to EPA/600/4-90/027F using rainbow trout (Onchorinchus mykiss): Quality Assurance Manual attached under separate cover.

FoT E 114: Inorganic Chemistry and Toxic Chemical Elements of Hazardous Waste

E 114.140 & E 114.141: Mercury Analysis: 7471 A/7470A
Blanks - Refer to Field of Testing E 103.160 Mercury.

Instrument Performance Check (IPC) or Instrument Calibration Verification (ICV) - Refer to Field of Testing E 103.160 Mercury.

Quality Control Sample (QCS) or External Standard (Ext Std) - Refer to Field of Testing E 103.160 Mercury.

Fortified Matrix - Refer to Field of Testing E 103.160 Mercury.

E 114.010: ICP Analysis (6010B)
Blanks - Three types of blanks are required for the analysis. The Calibration blank is used in establishing the analytical curve, the Laboratory Reagent Blank (LRB) is used to assess possible contamination from the sample preparation procedure, and the Laboratory Fortified Blank (LFB) is used to assess routine laboratory performance.

Calibration blank - Refer to Field of Testing E 103.130 ICP Analysis.

LRB - Refer to Field of Testing E 103.130 ICP Analysis.

LFB - Refer to Field of Testing E 103.130 ICP Analysis.

Instrument Performance Check (IPC) - Refer to Field of Testing E 103.130 ICP Analysis.

Quality Control Sample (QCS) or External Standard (Ext Std) - Refer to Field of Testing E 103.130 ICP Analysis.
Laboratory Fortified Matrix - The laboratory must add a known amount of each analyte to a minimum of 5% of samples or one sample per sample set. In each case the LFM aliquot must be a duplicate of the aliquot used for sample analysis. The values of the control limits to the designated LFM must be in the recovery range of 80 - 120%.
Spectral Interference Check (SIC) or Interference Check Standard - When inter-element corrections are applied, SIC solutions are needed containing concentrations of the interfering elements at levels that will provide an adequate test of the correction factors. The correction factors are tested on a daily basis at the beginning and end of an analytical run and are to be found within a 20% recovery range.

E 114.221: Cyanide by Distillation and Automated Color –
Refer to E 109.020

FoT E 115: Extraction Tests of Hazardous Waste

E 115.030: California Waste Extraction Test (WET)(Title 22, CCR, 66261.100, Appendix II.

FoT E 116: Organic Chemistry of Hazardous Waste (measurements by GC/combination)

E 116.080 EPA Method 8260B: BFB tuning criteria and GC/MS calibration verification criteria must be met every 12 hours before analyzing samples. Purge 50 ng of 4-bromofluorobenzene (BFB) by the method to be used. The BFB mass spectra must meet all criteria as follows.

Mass	Intensity Required (relative abundance)
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

Once every 12 hours verify the initial calibration by analyzing a second source check standard of System Performance Check Compounds (SPCCs) and Calibration Check Compounds (CCCs). The response factors (RFs) of the SPCCs relative to the initial calibration may be obtained as a Continuing Calibration Report. The minimum relative response factors for the SPCCs are:

Chloromethane	0.10

1,1-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

The percent drift for each CCC must be shown to be less than 20% before sample analysis begins. The CCCs are: 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene, and vinyl chloride.

Internal standard responses and retention times must be evaluated. The retention time must not vary more than 30 seconds since the last calibration check. The response must not vary more than a factor of two (-50% to +100%) since the last calibration check.

A blank analysis must be free of interferences. Matrix spike and matrix spike duplicates must show a recovery in the range 75 to 125%. The relative percent difference between spike and spike duplicate must be less than 30%. The matrix spike compounds are 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene.

Section 3: Sampling Procedures

TEST	VOLUME NEEDED mLs	CONTAINER P=plastic G=glass	PRESERVATIVE USED	MAXIMUM HOLDING TIME
Coliform	125	P,G	Sodium Thiosulfate to dechlor.; 4 EC	6 hrs refrigerated
Colilert	100	P,G	Thiosulfate to dechlor.; Cool 4 NC.	24 hrs refrigerated
Alkalinity	200	P,G	Cool 4 NC.	14 days
Ammonia	500	P,G	Cool 4 NC; H2SO4 to pH<2	28 days
BOD	1000	P,G	Cool 4 NC.	48 hrs.
Chloride	100	P,G	Cool 4 NC.	28 days
Chlorine Residual	500	P,G	None	Analyze immediately
Conductivity	500	P,G	Cool to 4 C	28 days
Dissolved Oxygen	300	glass BOD bottle & stopper	None required	Analyze immediately
Fluoride	100	Plastic	4° C	28 days
Hardness	100	P,G	HNO_3 to pH<2	6 months

TEST	VOLUME NEEDED mLs	CONTAINER P=plastic G=glass	PRESERVATIVE USED	MAXIMUM HOLDING TIME
Hexavalent Chromium	500	P,G	Cool to 4 C	24 hours
Nitrates	200	P,G	Cool to 4 C	48 hours
Nitrites	100	P,G	Cool to 4 C	48 hrs.
Organic Carbon	100	G	Cool to 4 C HCl to pH<2	Analyze Immediately or preserve for 7 days
pH	100	P,G	None required	Analyze immediately
Phosphate-P, total	50	P,G	Cool to 4 C; H2SO4 to pH <2	28 days
Phosphate-P, ortho	50	P,G	Cool to 4 C.	48 hours
Residue, total & volatile	1000	P,G	Cool to 4 C	7 days
Sulfate	100	P.G.	None	28 days
Sulfide	500	P.G.	Cool to 4 C Add 4 drops 2N Zinc Acetate per 100 mL, add NaOH to pH>9	7 days
Suspended Solids	1000	P, G	Cool 4 NC.	7 days
Settleable Solids	1000	P, G	Cool 4 NC.	24 hrs.
TDS	500	P, G	Cool 4 C	7 days
Temperature	1000	P, G	None	Immediate
Turbidity	100	P, G	Cool 4NC.	48 hrs.
EPA 524.2 Purgeable Organics	40 mL	Amber glass VOA vials, protect from light	Ascorbic acid to dechlor; HCl to < 2; cool to 4EC	14 days

TEST	VOLUME NEEDED mLs	CONTAINER P=plastic G=glass	PRESERVATIVE USED	MAXIMUM HOLDING TIME
THMs only by EPA 524.2	40 mL	Amber glass VOA vials, protect from light	SodiumThiosulfate to dechlor.; Cool 4NC.	14 days
EPA 624 Purgeable Organics	40 mL	Amber glass VOA vials, protect from light	Cool to 4EC	7 days
			HCl to <2	14 days
EPA 608 Pesticides & PCBs	1000 mL	Amber glass 1 Liter	Thiosulfate to dechlor; Cool to 4 NC.	7 days
EPA 8260B: Purgeable Organics	40 mL	Amber glass VOA vials, protect from light	Thiosulfate to dechlor.; Cool 4 NC.	7 days
			HCl to < 2	14 days
EPA 625: base/neutral & acids	1000 mL	Amber glass 1 Liter	Thiosulfate to dechlor.; Cool to 4 NC.	7 days
Mercury, total or dissolved	500	P, G	HNO3 to pH <2	28 days
Metals, dissolved	500	P, G	no preservative	filter 0.45u ASAP then HNO3 to pH <2
Metals, total	1000	P, G	HNO3 to pH <2	6 mos.

Fot E 101: <u>Microbiology of Drinking Water and Wastewater</u>

E 101.060: Disinfect the outside of the distribution-system tap with bleach solution, allowing a five minute contact time, or flame with a propane torch. Open fully and let run for 2 or 3 minutes. Reduce flow to fill a sterile bottle without splashing. Leave air space at the top.

E 107.020: Total Coliforms in Wastewater by Multiple Tube Fermentation: Sampling is documented in a Sample Log with date, initials of the sampler, type of sample, sampling location, time of collection, time of receipt in the laboratory, time inoculated, chlorine residual (if appropriate), and the results of analysis.

FoT E 102: <u>Inorganic Chemistry and Physical Properties of Drinking Water excluding Toxic Chemical Elements</u>.

E 102.030 Chloride, 28-days; E 102.030 Fluoride, 28-days; E 102.030 nitrate, 48-hours; E 102.030 sulfate, 28-days: Collect 500 mLs in plastic or glass (fluoride in plastic only).

E 102.190: Cyanide by Automated Color: Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water volume collected should be sufficient to insure a representative sample, allow for replicate analysis (if required), and minimize waste disposal.

If the sample contains chlorine or hydrogen sulfide, they must be preserved with sodium hydroxide pH>12 and cooled to 4°C at the time of collection. Holding Time is 14 days.

Oxidizing agents, such as chlorine, decompose most cyanide. Test by placing a drop of sample on a strip of potassium iodide (KI)-starch paper previously moistened with acetate buffer solution, pH 4. If a bluish discoloration is noted, add 0. 1 g sodium arsenite cyanide (NaAs02)/L sample and retest. Repeat addition if necessary. Sodium thiosulfate also may be used, but avoid an excess greater than 0.1 gm Na2S203/L. Manganese dioxide, nitrosyl chloride, etc., if present, also may cause discoloration of the test paper. If possible, carry out this procedure before preserving sample as described above. If the following test indicates presence of sulfide, oxidizing compounds would not be expected.

Oxidized products of sulfide convert CN- to SCN- rapidly, especially at high pH. Test for S2- by placing a drop of sample on lead acetate test paper previously moistened with acetic acid buffer solution, pH 4. Darkening of the paper indicates presence of S2-. Add lead acetate, or if the S2- concentration is too high, add powdered lead carbonate [Pb(C03)21 to avoid significantly reducing pH. Repeat test until a drop of treated sample no longer darkens the acidified lead acetate paper. Filter sample before raising pH for stabilization. When particulate, metal cyanide complexes are suspected filter solution before removing S2-. Reconstitute sample by returning filtered particulates to the sample bottle after S2- removal. Homogenize particulates before analyses.

Aldehydes convert cyanide to cyanohydrins. Longer contact times between cyanide and the aldehyde and the higher ratios of aldehyde to cyanide both result in increasing losses of cyanide that are not reversible during analysis. If the presence of Aldehydes is suspected, stabilize with NaOH at time of collection and add 2 mL 3.5% ethylene -diamine solution per 100 mL of sample.

E 102.500 Sodium by flame atomic absorption spectroscopy: *Use precleaned plastic 100 ML* containers. Acidify with 1:1 redistilled nitric acid to a pH of less than 2 at the time of collection.

E 102.520 Calcium, E 102.520 Magnesium, by ICP EPA 200.7.

FoT E 104: <u>Organic Chemistry of Drinking Water (measurement by GC/MS combination)</u>

E 104.040, E 104.045, E 104.050 EPA Method 524.2: Collect all samples in duplicate 40 mL glass screw-cap VOA vials with Teflon lined silicone septa. Samples are poured into vials without introducing air bubbles, and are completely filled, so that when the cap is replaced, and the vial inverted, no headspace is visible. If samples contain residual chlorine, add about 25 mg of ascorbic acid to the sample bottle before filling. Fill sample bottle to overflowing, but take care not to flush out rapidly dissolving ascorbic acid. Adjust the pH of the samples to <2 by carefully adding two drops of 1:1 HCl. *Seal the sample bottle, PFTE-face down, and shake for 1 minute.*

When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (about 10 minutes). Adjust the flow to about 500 mL/min and collect duplicate samples. When sampling from an open body of water, fill a 1-quart wide-mouth bottle or 1-liter beaker with sample, and then fill duplicate sample bottles.

If samples foam vigorously when acid is added, discard the sample. Collect a fresh sample with ascorbic acid to dechlor, do not add HCl. Samples must be analyzed within 24 hours.

Chill samples to 4 degrees C on day of collection and maintain at that temperature until analysis. Analyze all samples within 14 days of collection.

Duplicate field reagent blanks must be handled along with each sample set. Fill field blank sample bottles in the laboratory with reagent water, seal, and ship along with empty sample bottles and back to the laboratory with filled sample bottles. Prepare field reagent blanks as sample bottles.

If analyzing for Trihalomethanes only, dechlor with 3 mg sodium thiosulfate per 40 mL. Store at 4OC and analyze within 14 days.

FoT E 108: Wastewater Inorganic Chemistry, Nutrients and Demand

E 108.410 Alkalinity: Collect at least 200 mLs in plastic or glass. Fill completely and cap tightly.

E 108.472: Total Cyanide by Distillation and Automated Color
Reference: E 102.190 above.

E 108.510 Chloride, 28-days; E 102.030 Fluoride, 28-days; E 102.030 nitrate, 48-hours; E 102.030 sulfate, 28-days: Collect 500 mLs in plastic or glass (fluoride in plastic only).

FoT E 109: Toxic Chemical Elements in Wastewater

E 109.020: ICP-MS (200.8) Reference: 103.140

FoT E 110: Organic Chemistry of Wastewater (measurement by GC/MS combination)

E 110.040 EPA Method 624: Standard 40 mL glass screw-cap VOA vials with Teflon lined silicone septa are used for liquid samples. Liquid samples are poured into vials without introducing air bubbles, and are completely filled, so that when the cap is replaced, and the vial inverted, no headspace is visible.

Samples are iced or refrigerated at 4EC from time of collection until extraction. Vials for collection of wastewater samples with residual chlorine are prepared by adding sodium thiosulfate at a dose of 10 mg per 40 mL vial for each 5 ppm of chlorine. Vials of wastewater samples to be analyzed for benzene, ethyl benzene, or toluene are preserved with two drops of 1:1 HCl. Non-preserved samples have a 7 day hold time; preserved sample a 14 day hold time.

Samples are submitted with a Chain-of-Custody (CoC) documenting date and time, sampler, description, and preservative. A unique sample number is assigned during log-in for use on the sample container and documentation. Sample refrigerator temperatures are verified and documented daily. VOA vials are checked at each stage of handling for air bubbles.

FoT E 114: Inorganic Chemistry and Toxic Chemical Elements of Hazardous Waste

E 114.221 Cyanide by Distilled Automated Color – Refer: E102.190.

FoT E 116: Organic Chemistry of Hazardous Waste (measurement by GC/MS combination)

E 116.080 EPA Method 8260B: Standard 40 mL glass screw-cap VOA vials with Teflon lined silicone septa are used for both liquid and solid matrices. Liquid samples are poured into vials without introducing air bubbles, and are completely filled, so that when the cap is replaced, and the vial inverted, no headspace is visible. Solid samples are collected by filling vials with soil or sludge as full as possible, tapping and packing to exclude air spaces.

Samples are iced or refrigerated at 4 C from time of collection until extraction. Vials for collection of wastewater samples with residual chlorine are prepared by adding sodium thiosulfate at a dose of 10 mg per 40 mL vial for each 5 ppm of chlorine. Vials of wastewater samples without chlorine residual are preserved with two drops of 1:1 HCl. Non-preserved samples have a 7 day hold time; preserved sample a 14 day hold time. Solid samples have a 14 day hold time.

Samples are submitted with a Chain-of-Custody (CoC) documenting date and time, sampler, description, and preservative. A unique sample number is picked up during log-in for use on the sample container and documentation. Sample refrigerator temperatures are verified and documented daily. VOA vials are checked at each stage of handling for air bubbles.

Section 4: Sample Custody

Sample Log-in for Process Control and Permit Self-monitoring: Daily samples are logged into a Sample Log by entering the sampling time, the sample date, a source ID label, a unique sample control number, the name of the sampler, the receiving time into the lab, and the name of the sample recipient. Sample labels record the control number, the sample date, and the source ID. Document the condition of all samples upon receipt.

Field Sample Tracking Form for Discharge and Receiving Water Monitoring: Weekly samples and field test results are logged on to a field tracking form prepared with a control number and an ID label for each permit discharge point and each receiving water sampling station. Field samplers enter the date, the name(s) of the sampler(s), the time of each sample, and data collected on temperature, pH, dissolved oxygen, and chlorine residual. Document the condition of all samples upon receipt.

Sample Chain of Custody with Outside Analytical Services: Permit-regulated analyses for toxic elements and organic compounds are performed by a contract laboratory. Samples are submitted through a chain-of-custody protocol which documents the company name, the name of the sampler, a sample ID number, the date and time of sample collection, the number of items, preservatives used, the analyses requested, and a signature track of samples relinquished and received.

Each sample submitted to the laboratory is assigned a unique sample identifier by logging the sample into the sample log next to a sequential five digit Laboratory Log Number. The assigned log number is recorded on the sample container label and on all documentation, including Chain of Custody, analytical worksheet and final report.

The LIMS software is currently being implemented in the laboratory. The LIMS automatically assigns log numbers using two letters and five digits, i.e., LL00316. The number is distinct and non-alterable.

FoT E 101 and E 107: Microbiology of Drinking Water and Wastewater

E 101.060 and E 107.020 Sample holding times and temperatures are reviewed for compliance with the following requirements: (1) maximum travel time at greater than 10 C is 1 hour, (2) maximum travel time at less than 10 C is 6 hours, (3) maximum holding time in the laboratory at less 10 C is 2 hours, and (4) no holding time is allowed at greater than 10 C. Incubator temperature is documented in vol. 2 "Incubator Temperature Log" with the date, initials of the analyst, and temperature by NIST traceable glass thermometer. Temperatures are reviewed for compliance as follows:

MIN. TEMP IN DEGREES C	MAX. TEMP IN DEGREES C
34.5	35.5

E 101.060: Drinking water samples are submitted with a sample log-in sheet recording sample source, date sample taken, initials of sampler, time sample taken, time sample received in lab, initials of analyst receiving sample, chlorine residual, type designation number, and sample log number. Type designation identifies each sample as Routine (1), Repeat (1R) (following a total coliform-positive sample), Special (2), Repeat for positive special (2R), and Replacement (3) (resubmitted for invalidated samples).

FoT E 102: Inorganic Chemistry and Physical Properties of Drinking Water excluding Toxic Chemical Elements

E 102.030: Chloride, E 102.030: Fluoride, E 102.030: Sulfate; Store at 4E C and analyze within 28 days.

E 102.030: nitrate, E 102.220 nitrite: Store at 4C and analyze within 48 hours

E 102.100: Alkalinity: Store at 4 C and analyze within 14-days.

E 102.500: Sodium and E 102.500 Potassium by flame atomic absorption spectroscopy: Check pH of samples to verify <2. Initial COC.

FoT E 108: Wastewater Inorganic Chemistry, Nutrients and Demand

E 108.120: Chloride, E 108.120: Fluoride, E 108.120: Sulfate; Store at 4E C and analyze within 28 days.

E 108.120: nitrate: Store at 4C and analyze within 48 hours

E 108.100: Alkalinity: Store at 4 C and analyze within 14-days.

E 108.472: Total Cyanide by Distillation and Automated Color
Reference: E 102.190 above

E 108.500: Sodium and E 108.500 Potassium by flame atomic absorption spectroscopy: Check pH of samples to verify <2. Initial COC.

E 108.510 nitrite: Store at 4C and analyze within 48 hours

FoT E 109: Toxic Elements of Wastewater: Check pH to ensure <2.

FoT E 114: Toxic Elements of Hazardous Waste: Check pH to ensure <2.

Section 5: Calibration Procedure and Frequency

FoT E 101: Microbiology of Drinking Water and Wastewater

Incubator temperature is checked twice daily (at least 4 hours apart) with NIST traceable glass thermometer. Check balances weekly with certified weights.

FoT E 102: Inorganic Chemistry and Physical Properties of Drinking Water excluding Toxic Chemical Elements

E 102.030: Chloride, E 102.030: Fluoride, E 102.030: nitrate, E 102.030: sulfate: Prepare calibration standards at a minimum of three concentration levels and a blank. Place in the autosampler in the order they were entered into the schedule. Verify the calibration curve daily, or whenever eluent is changed, and after every 10 samples

E 102.100 Alkalinity: None

E 102.140 & 102.130: Conductivity meter with an air blank and a 1413 µs certified standard with each use.

E 102.190: Cyanide by Automated Color

Prepare a series of 5 standards, by diluting suitable volumes of standard solution, covering the desired range, (0.200, 0.100, 0.050, 0.010 and 0.003 mg/L) and a blank.
Prepare standard curve by plotting instrument response against concentration values.

A calibration curve may be fitted to the calibration solution concentration/response data using the computer. For the best analytical results, a new curve must be generated for each new analytical run. All working calibration standards **must** be made daily.
Acceptance or control limits should be established using the difference between the measured value of the calibration solution and the "true value" concentration.

After the calibration has been established, it must be verified by the analysis of a suitable quality control sample (QCS). If measurements exceed +/-10% of the established QCS value, the analysis should be terminated and the instrument recalibrated. The new calibration must be verified before continuing analysis.

E 102.500 Sodium, E 102.500 Potassium by atomic absorption spectroscopy:

Sodium Standard Calibration	Sodium Curve Calibration Verification	Potassium Standard Calibration	Potassium Curve Calibration Verification
1.0 mg/L	3.0 mg/L	0.1 mg/L	0.5 mg/L
2.0 mg/L		0.3 mg/L	
3.0 mg/L		0.5 mg/L	
5.0 mg/L		1.0 mg/L	

Calibration is performed with each analysis. Curves must be 0.995 or better. Calibration standards are prepared from 1000 mg/L single element standards every 6 months. Calibration verification standards are made from a custom ERA standard and must be within 10% of true value for analysis to continue. 1,000 mg/L Cesium added as an ionization suppressant to all samples and standards with 0.1 % nitric acid matrix.

E 102.520: Total Hardness: None

FoT E 103: Analysis of Toxic Chemical Elements in Drinking Water

E 103.130: ICP Analysis (200.7): All standards are recorded in the ICP Standard Prep book and documented by element, supplier, Lot #, date prepared, technician who prepared the standard, the initial volume of standard, the initial concentration of standard, the final volume of standard, and the final concentration of standard. The water used for standard preparation is, Barnstead ultra pure water. There are three combination calibration solutions utilized to calibrate the instrument, these are per EPA method 200.7and 200.15. The instrument performs an internal calibration wavelength check. Calibration is performed utilizing a calibration blank, prepared by diluting a mixture of 20 ml of Conc. nitric acid and 100 ml of Conc. hydrochloric acid to 1000 ml with ASTM type 1 water, and the calibration standards listed are analyzed.

The calibration is checked by using an outside reference, which has an initial 95%to105% recovery. After every ten samples are run, a calibration check is employed to determine if stability exists. If the calibration check does not give a 90% to 110% recovery then recalibration is required.

E 103.140: ICP/MS Analysis (200.8): All standards are recorded in the ICP Standard Prep book and documented by element, supplier, Lot #, date prepared, technician who prepared the standard, the initial

volume of standard, the initial concentration of standard, the final volume of standard, and the final concentration of standard. The water used for standard preparation is, Barnstead ultra pure water.

Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required periodically throughout sample analysis as dictated by results of continuing calibration checks. After initial calibration is successful, a calibration check is required at the beginning and end of each period during which analyses are performed, and at requisite intervals. Calibration must include a calibration blank and at least 1 additional calibration point for each element, which brackets the expected sample analyte concentration range.

It is recommended that at least one calibration point for each detector mode (pulse or analog) be included for those elements, which are calibrated over a range, which might include analog acquisition mode.

Initial calibration accuracy must be evaluated before any samples are analyzed through the analysis of a Quality Control Sample (QCS), which includes all analytes of interest. The QCS should be at or near the midpoint of the calibration range and must quantitate within 10% of the expected value.

Calibration drift is monitored through the analysis of a Continuing Calibration Verification standard (CCV) at the beginning of the sample block, after every 10 samples and again at the end of samples. It must quantitate within 10% of expected value. If the calibration check does not give a 90% to 110% recovery then the system must be recalibrated and the last 10 samples reanalyzed. The calibration is checked by using an outside reference, which has an initial 95% to 105% recovery. After every ten samples are run, a calibration check is employed to determine if stability exists

Method Detection Limits (MDL's). MDL's are determined by analyzing seven replicates of Laboratory fortified blanks. MDL's must be determined annually.

E 103.160: Mercury (245.1): Refer to Section 2

FoT E 104: <u>Organic Chemistry of Drinking Water (measurement by GC/MS combination)</u>

E 104.040, E 104.045, E 104.050 EPA Method 524.2: Purge and analyze calibration (CAL) solutions prepared at 0.5, 1.0, 5.0, 10, 20, 40 and 60 ug/L for a seven point calibration curve. Purge and analyze CAL solutions of freon 113 in the range 0.5 to 60 ug/L. Check calibration linearity by generating a Response Factor Report and examine the percent relative standard deviation (%RSD) of response factors at all levels. The RSD should be less than 20% for each compound. As an alternative to calculating mean response factors and applying the RSD test, use the data system software to generate a regression calibration curve. The correlation coefficient factor of the regression curve should be greater than 0.995. Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed. A continuing calibration check is required at the beginning of each 8 hour period during which analyses are performed.

FoT E 108: <u>Wastewater Inorganic Chemistry, Nutrients and Demand</u>

E 108.050: pH: Store electrodes in saturated KCL when not in use. Rinse and blot dry before use. Calibrate daily at a minimum of two points that bracket the expected pH of the sample and are approximately three pH units or more apart.

E 108.120: Chloride, E 108.120: Fluoride, E 108.120: Nitrate, E 108.120: Sulfate by IC: Before every analysis, demonstrate the ability to generate acceptable accuracy and precision with a laboratory performance standard, and check for interferences with a reagent blank. Verify that standards have been prepared correctly with a reference check standard prepared from an independent source. The check standard result must be within 10% of the true value. With each sample batch, or for a minimum of 20% of all samples, analyze a fortified blank containing each analyte. Evaluate the accuracy as percent recovery.

E 108.262: Phosphate (ortho) and E 108.263: Phosphorous (total): To calibrate, make up standard

concentrations of 0.10, 0.20, 0.30, 0.50, 0.70 1.0 mg/L in 50 ml volumetric flasks. Dilute a 50mg/L phosphate as P standard as needed for standards and spikes. Also, measure 50 mls of DI water for the blank. Add 8.0 mls of mixed reagent, wait and read on the spectrophotometer after 10 minutes but no longer than 30 minutes. Also, calculate the correlation coefficient and if it is not .995 or better, rerun and/or troubleshoot. Document the standard concentration used for the standard curve and record the absorbances generated in the Spectrophotometer bound book. Calibration frequency is once yearly or sooner, if problems arise.

E 108.390: Turbidity: Perform a linear calibration once every three months with at least four standards from the same lot. The shelf life of an unopened lot is 1 year. Check with secondary standard. If the calibration has drifted more than 5% then put a new calibration in the turbidimeter.

E 108.421: Hardness: Primary stock solutions are used for the 2340 C EDTA titrimetric method. Values of blank samples are titrated and subtracted from sample results. A digital buret used for titrating the EDTA is tested for accuracy monthly and results are recorded.

E 108.430: Specific Conductance: A two point calibration is performed on the Corning conductivity meter. The first calibration is an air calibration and the second calibration is run by utilizing a primary standard with a value of 1413µs/cm. The electrode is stored in DI water when not in use.

E 108.442: Suspended Solids: The analytical balance receives an annual calibration by the Mettler service representative. Between visits check and document calibration weekly with the class S weights.

E 108.461 & E 108.464, Chlorine Residual: Standardize the 0.0282 N iodine titrant against the 0.00564 N phenylarsine oxide (PAO) solution.
Standardize the PAO solution upon opening a new bottle with 0.005N potassium biiodate solution by Section 5.9 of EPA method 330.2. Standardize FAS titrant against 0.100N primary standard potassium dichromate.

E 108.472: Total Cyanide by Distillation and Automated Color Reference: E 102.190 above

E 108.506: Ammonia - Ion Selective Electrode Method Using Known Addition, SM 18th Ed., 4500-NH_3 f.
A slope check should be performed daily to ensure that the electrode is working properly. The method used is as follows: Place electrode in 100 ml of distilled water. Add 2mL of I.S.A. Pipette 1 ml of 1000 mg/L standard into solution. When reading is stable, record mV value onto ammonia benchsheet. Pipette 10 ml of the same standard into solution. When mV is stable, record this value onto ammonia benchsheet. If the slope falls outside the range of -54.0 to -60.0, then the internal fill solution should be changed. If this doesn't resolve the faulty slope, the membrane should be replaced. More advanced troubleshooting can be found in the instrument's manual and the electrode's manual. Using 100 mls of sample and 1 ml of I.S.A. set Ion analyzer for standard addition analysis. Enter sample volume and slope. When electrode is stable press yes to continue. Add 1.0 of a 1000 mg/L NH3-N Standard and press yes to continue. Enter volume and concentration of standard used. Press yes to continue. When electrode is stable, the meter will again prompt "yes to continue". If so, press yes. The meter will now indicate the concentration of the sample. Record this value on the ammonia benchsheet.

E 108.510: Nitrite: To calibrate, make up standard concentrations of 0.01, 0.04, 0.10, 0.20, 0.40 mg/L from the 100ppm stock. Also, measure 50 mls of DI water for the blank. Add 1.0 ml of Sulfanilimide reagent and 1.0 ml of NED, wait 30 minutes and read on the spectrophotometer. Also, calculate the correlation coefficient, and if it is not .995 or better, rerun and/or troubleshoot. Document the standard concentration used for the standard curve and the absorbances generated in Spectrophotometer bound book. Calibration frequency is one year or sooner if problems arise.

E 108.531: Dissolved Oxygen: Calibrate the YSI field and laboratory DO meters when necessary by following manufacturer's instructions. Use air-saturated BOD dilution water for calibration by comparison with a Winkler titration.

E 108.580: Sulfide: Run internal calibration check according to instrument manuals. Analyze a known

reference standard with each batch. Analyze a DI blank and then zero on sample blank before sample analysis.

E 108.590: Biological Oxygen Demand: To 4 BOD bottles collect 300 mls of dilution water in each bottle and stopper. Place lab electrode in one bottle and start measurement. To the three other BOD bottles add 1 ml MnSO4 solution, followed by 1 ml alkali-iodide-azide reagent. Stopper carefully to exclude air bubbles and mix by inverting bottle a few times. When precipitate has settled sufficiently (to approximately half the bottle volume) to leave clear supernate above the manganese hydroxide floc, add 1.0 ml conc H2SO4. Restopper and mix by inverting several times until dissolution is complete. Titrate with 0.025M Na2S203 solution to a pale straw color. Add 1ml of starch solution and continue titration to first disappearance of blue color.

1ml of 0.025M Na2S2O3 = 1 mg DO/L

Adjust readings of the lab DO meter to read the same as the average of the Winkler BOD. Record results in the calibration book and the error between what the Winkler reading is and the DO meter reads.

E 108.660: Chemical Oxygen Demand: None

E 108.610: Organic Carbon: Calibration curve equations are automatically calculated and stored. To prepare curve: 1000 ppm TOC Standard and 1000 ppm TIC Standards are used. Make up 5, 10, 25 & 50 ppm TIC and TOC Standards. Make up standard curve template. Run samples. Standard curve must be .995 or better. Run an ERA reference to check calibration curve.

FoT E 109: Toxic Chemical Elements in Wastewater

E 109.190: Mercury (245.1): Refer to Section 2

E 109.010: ICP (200.7): Refer to Section 2.

FoT E 110: Organic Chemistry of Hazardous Waste (measurement by GC/MS combination)

E 116.080: EPA Method 624: Seven point calibration curves are prepared from 10 and 250 ug/mL secondary dilution calibration standards in blank water.

CALIBRATION LEVELS	MICROLITERS OF STANDARD PER 50 ML
0.5 ppb	2.5 uL of 10.0 ug/mL
1.0 ppb	5.0 uL of 10.0 ug/mL
5.0 ppb	25.0 uL of 10.0 ug/mL
10.0 ppb	2.0 uL of 250 ug/mL
20.0 ppb	4.0 uL of 250 ug/mL
40.0 ppb	8.0 uL of 250 ug/mL
80.0 ppb	16.0 uL of 250 ug/mL

Analyze calibration standards. Check calibration linearity by generating a Response Factor Report and examine the percent relative standard deviation (%RSD) of response factors at all levels. The %RSD should be less than 35% for each compound. A linear curve is allowed with an r of >0.995.

FoT E 114: Toxic Chemical Elements of Hazardous Waste

E 114.140 & E 114.141 Mercury (245.5): Refer to E 103.160.

E 114.221: Cyanide by Distillation and Automated Color: Reference: E 102.190 above

E 114.221: Cyanide by Distillation and Automated Color Reference: E 102.190 above

FoT E 116: Organic Chemistry of Hazardous Waste (measurement by GC/MS combination)

E 116.080: EPA Method 8260B: Seven point calibration curves are prepared from 10 and 250 ug/mL secondary dilution calibration standards in blank water.

CALIBRATION LEVELS	MICROLITERS OF STANDARD PER 50 ML
0.5 ppb	2.5 uL of 10 ug/mL
1.0 ppb	5.0 uL of 10 ug/mL
5.0 ppb	25.0 uL of 10 ug/mL
10.0 ppb	2.0 uL of 250 ug/mL
20.0 ppb	4.0 uL of 250 ug/mL
40.0 ppb	8.0 uL of 250 ug/mL
80.0 ppb	16.0 uL of 250 ug/mL

Check calibration linearity by generating a Response Factor Report and examine the percent relative standard deviation (%RSD) of response factors at all levels. The %RSD should be less than 15% for each compound. A linear calibration is allowed with an r of >0.995. However, the %RSD for each individual Calibration Check Compound (CCC) must be less than 30%.

Section 6: Analytical Procedures

FoT E 101.060 and E 107.010: Microbiology of Drinking Water and Wastewater

E 101.060: Total Coliforms and E.Coli in Drinking Water by MMO-MUG (40 CFR 141) are analyzed by a presence/absence (P/A) Colilert system: Samples are analyzed for E. coli whenever the presence of total coliforms is indicated.

E 101.010 & E 107.010: Heterotrophic Plate Count by Pour Plate Method (SM18th,9215B) uses 2.0 mL portions for sterility analysis on de-ionized water for media preparation. Set up duplicates and two controls. After depositing test portions, pour 10 to 12 mLs of culture medium and mix gently. Allow plates to solidify, invert, and incubate at 35 C for 48 hours. Count colonies on a Quebec colony counter.

FoT E 107.020: Total Coliforms in Wastewater by Multiple Tube Fermentation (MTF)(SM18th, 9221B)
Lauryl tryptose broth as a presumptive media, and brilliant green bile broth as a confirming media. Inoculation series is 5 tubes of 10 mL sample, 5 tubes of 1 mL sample, and 5 tubes of 1 mL diluted 1:10. Tubes are incubated at 35±.5 C for 24 ±2 hours, or 48 ± 3 hours if negative at 24 hours. A positive test is indicated by gas formation; a negative test by the absence of gas formation.

E 107.040: Fecal Coliforms in Wastewater by MTF (SM18th, 9221E) uses EC medium for inoculation from positive presumptive fermentation tubes within 48 hours of incubation. Tubes are incubated in a water bath at 44.5 ±0.2 C. Gas formation within 24 hours or less is a positive test.

FoT E 102: Inorganic Chemistry and Physical Properties of Drinking Water excluding Toxic Chemical Elements

E 102.030: Chloride, E 102.030: Fluoride, E 102.030: nitrate, E 102.030: sulfate by ion chromatography (EPA 300.0): Inject a small volume by syringe or autosampler. The developed method loads the 50 microliter loop, injects, and records peak areas and retention times as raw data.

E 102.100: Alkalinity by Titration (SM 18th, 2320B): Sample size: For alkalinity between 20 and 100 ppm, use 200 mL sample. For alkalinity above 100 ppm, use 50 mL sample. Titrant normality: Use 0.02 N standard sulfuric acid solution. End-point pH 4.5 or use color indicating reagent.

E 102.120: Hardness by Calculation from Ca/Mg (SM 18 2340B): Analyze calcium and magnesium as per method 200.7. Multiply calcium result in mg/L by 2.5 and magnesium result in mg/L by 4.12, add together for total hardness result as CaCO3 in mg/L. Samples with turbidities of 1.0 NTU or less do not have to be digested.

E 102.121: Corrosivity by Aggressive Index: from Corrosion Manual for Internal Corrosion of Water Distribution Systems, EPA 570/9-84-001: Analyze sample for pH, total alkalinity as CaCO3, and Calcium hardness as CaCO3. Calculate AI (Aggressive Index) by equation below:

$$AI = pH + \log [(\text{Alkalinity, mg/L})(\text{Ca Hardness, mg/L})$$

E 102.121: Hardness by EDTA Titration (SM 18th, 2340C). Units: Report hardness (EDTA) as mg CaCO3/L. Sampling: Collect in 500 mL plastic bottle. Sample size: Use a sample size that requires less than 15 mL EDTA titrant and complete titration within 5 minutes after buffer addition. Dilute sample size to 50 mL. Titrant normality: Use 0.01M EDTA titrant standardized against standard calcium solution (1.000 g CaCO3 per liter) to give1 mL = 1.00 mg CaCO3. Titration: Add 1 to 2 mL of buffer solution. Add 1 to 2 drops indicator solution. Add standard EDTA titrant slowly, with continuous stirring, until last reddish tinge disappears. Add the last few drops at 3- to 5-second intervals. The endpoint is blue in daylight or fluorescent light. The absence of a sharp end-point means either, 1. an inhibitor must be added or, 2. the indicator has deteriorated. Low-hardness sample: For softened waters and for natural waters of low hardness (less than 5 mg/L), use larger samples (100 to 1000 mL) and add proportionally more buffer, inhibitor, and indicator. Add titrant from a microburet. Run a blank of de-ionized water, subtracting volume of EDTA used for blank from volume used for sample.

Calculation:

Hardness (EDTA) as mg CaCO3/L = (A X B X 1000) / mL sample
A = mL titrant used for sample
B = mg CaCO3 equivalent to 1.00 mL EDTA titrant

E 102.140: Total Filterable Residue and 102.130: Conductivity (SM 18th, 2540C and 2510B):

1. Conductivity : place electrode in sample. Press Read: Run duplicate and record results.

2. Total Filterable Residue: Sample size: Choose sample volume to yield between 10 and 200 mg dried residue. If filtration takes more than 10 minutes, increase filter size or decrease volume but do not produce less than 10 mg residue.

Preparation of filter dish: Wash filter with three successive washes. Heat dish to 180 ± 2C for 1 hour in oven. Cool dish in desiccator and weigh just before use.

Analysis: Filter, wash three times, and continue suction for three minutes after filtration is complete. Evaporate filtrate to dryness in dish on a steam bath. Dry 1 hour in an oven at 180± 2C. Cool in desiccator and weigh. Repeat the cycle of drying, desiccating and weighing until a constant weight is obtained, or until a weight change of less than 4% of the previous weight or 0.5 mg is obtained, whichever is less.

Calculation:

mg TDS/L = [(A - B) X 1000] / sample volume, mL
A = weight of dried residue + dish, mg.
B = weight of dish, mg.

E 102.190: Cyanide by Automated Color: Prepare reagent and standards, setup manifold. Input data system parameters into the Method. Place samples and/or standards in the autosampler. Input the information required by the data system, such as concentration, replicates and QC scheme. Calibrate the instrument by injecting the standards via the autosampler.

Prepare Samples by the Lachat MidiDist Distillation Apparatus. It is designed to perform digestions and distillations of volatile analytes, such as cyanide, in accordance with USEPA Method 335.2 and USEPA 9012A. The advantage of the MidiDist System over a macro distillation system is that the reagent, sample and waste volumes have been scaled down by a factor of ten. As many as ten samples can be distilled simultaneously.

E 102.500: Sodium (EPA 273.1) , E 102.500 Potassium (EPA 258.1) by flame atomic absorption spectroscopy: Dilute samples to be within linear range of curves. Add 1000 mg/L final concentration of Cesium to all samples and standards as an ionization suppressant. Reduce the sensitivity for high concentrations of sodium by rotating the burner head to 45 degrees.

FoT E 103: <u>Analysis of Toxic Chemical Elements in Drinking Water</u>

E 103.130: ICP Analysis: For the determination of total elements choose a measured volume of the well-mixed acid-preserved sample appropriate for the expected level of elements (100 mls of DI sample was chosen for all the method detection limit and reporting limit studies). Transfer the sample to a Erlenmyer flask and add 1 ml concentrated Ultrapure HNO_3, 0.2 ml H_2O_2, and 0.5 ml HCl. Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil and that no area of the bottom of the beaker is allowed to go dry. Cool the beaker. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating until the digestion is complete (indicated when the digestate is light in color or does not change in appearance with continued refluxing). Allow to cool, wash down the beaker walls and watch glass with Type II water and filter the sample to remove insoluble material that could clog the nebulizer. Adjust the sample to a predetermined volume based on the expected concentrations of elements present (100 ml for all samples). Concentrations so determined shall be reported as "total." All sample prep is recorded on the digest sample prep sheet.

A peristaltic pump is utilized to introduce the standard or sample to the ultrasonic nebulizer at a uniform rate (1.8 ml/min). The sample or standard is aspirated for 130 sec before beginning integration of the background corrected signal. An average of three 5 sec background corrected integration periods as the atomic emission signal to be correlated to analyte concentration is utilized. Between each standard or sample run, the nebulizer and the solution uptake system is flushed with the rinse blank acid solution to ensure that analyte memory effects are not occurring. After the calibration has been performed the reference standards are introduced and analyzed which must fit in the 70% to 130% recovery bracket.

Copper and Lead in Drinking Water: Acidification without digestion is adequate for drinking water samples if turbidity is less than 1 NTU. Analyze with by ICP-MS.

E 103.140: ICP/MS: For the determination of total elements choose a measured volume of the well-mixed acid-preserved sample appropriate for the expected level of elements (50 mls of DI sample was chosen for all the method detection limit and reporting limit studies). Transfer the 1 ml concentrated Ultrapure HNO_3, into Digestion Vessel in Digestion Block and evaporate to near dryness (10mls) cautiously. Cover the beaker with a plastic watch glass, so that a gentle reflux action occurs. Continue heating until the digestion is complete (indicated when the digestate is light in color or does not change in appearance with continued refluxing). Allow to cool. If needed, filter the sample to remove insoluble material that could clog the nebulizer. Adjust the sample to a predetermined volume based on the expected concentrations of elements present (50ml for all samples). Concentrations so determined shall be reported as "total." All sample preps' are recorded on the digestion sample prep sheet.

A peristaltic pump is utilized to introduce the standard or sample to the nebulizer at a uniform rate. The sample or standard is aspirated for 130 sec before beginning integration. An average of three 5 sec corrected integration periods as the atomic mass signal to be correlated to analyte concentration is utilized. Between each standard or sample run, the nebulizer and the solution uptake system is flushed with the rinse blank acid solution (5 % HNO3) to ensure that analyte memory effects are not occurring. After the calibration has been performed, the reference standards are introduced and analyzed which must fit in the 90% to 110% recovery bracket.

Copper and Lead in Drinking Water: Acidification without digestion is adequate for drinking water samples if turbidity is less than 1 NTU.

Fot E 104: Organic Chemistry of Drinking Water (measurement by GC/MS combination)

E 104.040, E 104.045, E 104.050 EPA Method 524.2: Allow samples and standard solutions to warm to ambient temperature before analysis. BFB tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples.

Invert the VOA vial to verify there are no bubbles present. Place the room temperature 40 mL VOA vial in to the appropriate autosampler position. Edit the schedule to reflect a 10 mL volume of sample and 5 uL of a 100 ppm surrogate/internal standard.

Perform purge-and-trap. If the initial analysis of a sample or a dilution of the sample has a concentration of analyte(s) that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution.

Maintain a Sample Run Log/Sample Preparation Log with autosampler position number, data file name, sample identification and control number, sample volume, and concentration of internal standard/surrogate spiking solution. Opposite the sample preparation log make notes of corrective action taken.

FoT E 108: Wastewater Inorganic Chemistry, Nutrients and Demand

E 108.050: pH: To adjust for temperature effects, preferably use an automatic temperature compensator, or take the temperature separately and adjust manually. Stir samples gently to insure homogeneity and to avoid carbon dioxide entrainment. Rinse and blot electrode when moving from solution to solution.

E 108.171: Chlorine Residual, total by EPA method 330.2: Laboratory Method: Back titration is used on wastewater in order to eliminate the contact of the sample with high concentrations of liberated iodine. Total chlorine is measured at pH 4 or less. Standard 0.00564 N phenylarsine oxide (PAO) solution is added to 200 mL of sample in a known amount sufficient to reduce all the chlorine present.

Use 5.00 mLs if the chlorine residual is less than 5.0 mg/L. Use 10.0 mLs if the chlorine residual is between 5.0 and 10.0 mg/L. Dilute higher concentrations into this range. Add 4 mL of pH 4 buffer solution (or sufficient to adjust sample pH between 3.5 and 4.2). Add 1 g of potassium iodide, and mix. Add 1 mL of starch indicator solution. Titrate with 0.0282 N iodine solution from a 2 mL pipette (incremented to 0.01 mL) to a starch-iodide end-point, i.e. the first appearance of blue color that persists after complete mixing. Five times the volume of iodine solution used, subtracted from the volume of PAO added, gives the chlorine residual in mg/L. Field Testing: A short test is used in the field to determine nondetectability of chlorine. To a small amount of sample (about 10 mLs), add 1 mL each of pH 4 buffer solution, potassium iodide solution, and starch indicator. The absence of a blue color confirms the nondetectability of chlorine with a detection limit of 0.05 mg/L.

E 108.390: Turbidity: The Hach 2000 Turbidimeter should not be turned off. The light source must warm-up and stabilized before use. Samples should be well mixed and poured into sample cells before settling has occurred, but after air bubbles have disappeared. Fill a clean sample cell to the line with

dilution water. Wipe the cell clean and apply a thin film of silicone oil. After this, insert sample cell into turbidimeter and read NTU, after pressing ENTER. If the sample has a turbidity higher than 40.0, dilute and rerun.

E 108.410: Alkalinity (includes determination of bicarbonate, carbonate and hydroxide) (SM 18th, 2320B): For alkalinity above 100 mls, use 50 mLs sample. Use 0.02 Normal standard sulfuric acid titrant for alkalinity. Titrate to end-point (pH 4.5 or use color indicator).

E 108.442: Residue, Nonfilterable (TSS): Prepare standard glass fiber filters by placing wrinkled side up on a filter holder, and washing three separate times with DI water. Place in an aluminum weighing dish and dry for 1 hour in the drying oven at 103 to 105 degrees C. Cool and store in a desiccator. Weigh just before using. Use a well-mixed sample, avoiding gross floating or submerged inclusions. Filter a volume estimated to deposit 10 to 200 mg of residue on the filter. If less than 10 mg of residue is retained, increase the sample volume. Dry for at least 1 hour, cool and weigh. Confirm the drying time by repeating the cycle until a constant weight of less than 4% difference is achieved.

E 108.443: Residue, Settleable (SS): Fill an Imhoff cone to the 1 liter line with well-mixed sample. Settle for 45 minutes. Release residue on the sides by gently moving a glass rod around the inside of the cone. Settle for 15 minutes more, for a total of 1 hour. Subtract the estimated volume of any vacuoles in the settled residue. Measure in ml/L.

E 108.464: Chlorine Residual, Total by DPD-FAS Titrimetric Method. SM18, 4500-Cl F: This method is used for chlorine from 0.1 mg/L to 5.0 mg/L. Dilute samples of higher concentration. To 100 mL of sample, add 5.0 mL of phosphate buffer solution and 5.0 mL of DPD Indicator solution. Mix the sample, add 1.0 gram of potassium iodide, and then wait 2 minutes. Titrate rapidly with FAS titrant until red color is discharged / disappears. Record the volume of titrant used. This procedure gives a direct reading of chlorine residual concentration. Milliliters of FAS titrant used equals mg/L chlorine residual.

E 108.472: Total Cyanide by Distillation and Automated Color Reference: E 102.190 above

E 108.506: Ammonia by Ion-selective Electrode (SM 18th, 4500-NH_3 F): Select incremental technique mode. Use 2 mLs of pH adjusting ISA solution.

E 108.531: Oxygen, Dissolved: The membrane electrode method is suitable for field testing of wastewaters, effluents, and receiving waters. Calibrate against a Winkler titration of BOD dilution water as a laboratory standard. Provide sufficient sample flow across the membrane to eliminate erratic responses. In discharge streams and receiving waters, position the probe midstream and middepth. Allow sufficient time for the probe to stabilize to temperature and DO of sample before reading the dissolved oxygen in mg/L.

E 108.580: Sulfide: Warm up Hach 4000V Spectrophometer for 15 minutes. Scroll to Sulfide Method and activate. Measure 50 mL Blank, ERA reference Standard and samples. Add reagents according to SOP. Run a sample blank to zero before each sample analysis. Analyze a duplicate sample and record on control chart.

E 108.590: Biochemical Oxygen Demand (SM 18th, 5210B): Use one BOD nutrient buffer pillow to make 19 Liters of dilution water. Incubate duplicate dilution water blanks with each sample run. Seed all effluent samples. Adjust sample dilution so that a D.O. residual of at least 1 mg/L remains after and an uptake of at least 2 mg/L results from incubation. Add calculated volumes of sample directly to the BOD bottles. Do not overflow when making up volume with dilution water. Do not trap air when measuring initial D.O. or when stoppering. Stopper tightly, water-seal and incubate for five day at 19 to 21 C. After incubation discard bottles with gas bubbles trapped under stoppers. Avoid this condition by careful dilution water preparation, glassware maintenance, and by lowering D.O.s of supersaturated samples. Correct for seed depletion, but not for blank depletion.

E 108.610: Organic Carbon: Warm up instrument. Set up Analysis template. Run blank, Standard blank, sample duplicate and spike along with ERA reference standard. Press: Start Analysis.

E 108.660: Chemical Oxygen Demand: Homogenize samples before placing in the C.O.D. vials. This step ensures distribution of solids and improves accuracy and reproducibility. Pipet 2.0 ml (0.2 mL up to 2.0 mL for 0 to 15,000 range) of sample into vial. Replace the vial cap tightly. Invert several times to blend the contents. Place the vial in the preheated C.O.D. Reactor. Prepare a blank using deionized water. Heat the vials for 2-hours. Turn the reactor off. Wait 20 minutes for the vials to cool to 120 C or less. Invert each vial several times while still warm. Place the vials into a rack. Wait until the vials have cooled to room temperature. Set the Hach DR4000 Spectrophotometer to read C.O.D.'s. Allow to warm up for 15 minutes. Zero the Colorimeter with water blank. Place the sample vial in the adapter with the Hach logo facing the front of the instrument. Press: Read. The display will count down to zero. Then the display will show the results in mg/L C.O.D.

FoT E 110: Organic Chemistry of Wastewater (measurement by GC/MS combination)

E 110.040: EPA Method 624: Allow samples and standard solutions to warm to ambient temperature before analysis. BFB tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples.

Invert the VOA vial to verify there are no bubbles present. Place the room temperature 40 mL VOA vial in to the appropriate autosampler position. Edit the schedule to reflect a 10 mL volume of sample and 5 uL of a 100 ppm surrogate/internal standard.

To composite aqueous samples prior to GC/MS analysis add equal or flow-proportional volumes of each sample to a Tedlar bag. Composite samples while they are still cooled at 4 C. Mix well and fill a 40 mL VOA vial with a 50 mL syringe. Adjust schedule to reflect a 10 mL sample volume and 5 uL of internal standard/surrogate spiking solution.

Perform purge-and-trap. If the initial analysis of a sample or a dilution of the sample has a concentration of analyte(s) that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution.

Maintain a Sample Run Log/Sample Preparation Log with autosampler position number, data file name, sample identification and control number, and sample volume. Opposite the sample run log make notes of corrective action taken.

FoT E 113: Aquatic Toxicity Bioassays

E 113.003A: Wastewater Testing According to EPA/600/4-90/027F using Rainbow Trout (Onchorinchus mykiss)

FoT E 114: Inorganic Chemistry and Toxic Chemical Elements of Hazardous Waste:

E 114.221: Cyanide by Distillation and Automated Color Reference: E 102.190 above

FoT E 115: Extraction Tests of Hazardous Waste

E 115.030: California Waste Extraction Test (WET)(Title 22, CCR, 66261.100, Appendix II).

FoT E 116: Organic Chemistry of Hazardous Waste (measurement by GC/MS combination)

E 116.080: EPA Method 8260B: Allow samples and standard solutions to warm to ambient temperature before analysis. BFB tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples.

Invert the VOA vial to verify there are no bubbles present. Place the room temperature 40 mL VOA vial in to the appropriate autosampler position. Edit the schedule to reflect a 10 mL volume of sample and 5 uL of a 100 ppm surrogate/internal standard.

To composite aqueous samples prior to GC/MS analysis add equal or flow-proportional volumes of each sample to Tedlar bag. Maintaining zero headspace in a syringe, pull 50 mL from the bag. Composite samples while they are still cooled at 4 C. Mix well and fill a 40 mL VOA vial for analysis. Adjust schedule to reflect a 10 mL sample volume and 5 uL of internal standard/surrogate spiking solution.

Perform purge-and-trap. If the initial analysis of a sample or a dilution of the sample has a concentration of analyte(s) that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution.

Maintain a Sample Run Log/Sample Preparation Log with autosampler position number, data file name, sample identification and control number, and sample volume. Opposite the sample run log make notes of corrective action taken.

Section 7: Data Reduction, Validation and Reporting

FoT E 101 and 107: Microbiology of Drinking Water and Wastewater

E 101.060 and E 101.107: Results are reported as presence or absence of total coliforms or E. coli: The laboratory notifies the supplier within 24 hours whenever a presence is demonstrated or a sample is invalidated. The DOHS Office of Drinking Water (ODW) is notified when there is a presence of coliform bacteria. Notification is recorded in a notification logbook. Records documenting follow-up results are maintained. A monthly summary and the results of all samples for that month are reported to the ODW by the tenth day of the following month. A sample may be invalidated by laboratory accident or error. A letter requesting invalidation from the laboratory director shall include sample documentation, description of the accident or error, analytical and quality assurance documentation, and any observations noted by laboratory personnel.

E 107.020: Total Coliforms by Multiple Tube Fermentation: Bacterial density in MPN/100 mL is estimated by Table 9221-C on page 9-50 of the 18th edition of Standard Methods for combinations of positive results using five tubes per dilution. The MPN (most probable number) from combinations not in the table may be estimated by Thomas' formula if they occur 1% or less of the time.

$$MPN = \frac{no.positivetubes * 100}{\sqrt{mL(-)tubes * mLalltubes}}$$

Validate data by a review of sample log-in, incubator temperatures, autoclaving, media preparation, sterility and completed tests, and the quality of purified water used in microbiology. Record positive tubes on the microbiology tag, and in the green Microbiology Binder.
Report presumptive results to the operations staff daily. Input final test results in LIMS for preparation of monthly reports.

FoT E 102: Inorganic Chemistry and Physical Properties of Drinking Water excluding Toxic Chemical Elements

E 102.030: Chloride, E 102.030: Fluoride, E 102.030: nitrate, E 102.030: sulfate by ion chromatography: The raw data is integrated and processed by the parameters set forth in the developed method. Report nitrate as mgN/L. Use a midrange check standard from a different source than the

calibration standards to verify calibration to within 10 percent.

E 102.100: Calculation of total alkalinity (T):

A = mL standard acid used N = normality of std acid

$$Alkalinity, mg\ CaCO3/l = \frac{A\ X\ N\ X\ 50000}{mL\ sample}$$

Calculation of alkalinity relationships: Measure phenolphthalein alkalinity (P) by titration to pH end-point E 113.003A & E 113.003B. Use the following table for a breakdown into hydroxide (OH), carbonate (CO3), and bicarbonate (HCO3) alkalinities:

Result of Titration	Hydroxide Alkalinity	Carbonate Alkalinity	Bicarbonate Alkalinity
P = 0	0	0	T
P < 1/2 T	0	2P	T - 2P
P = 1/2 T	0	2P	0
P > 1/2 T	2P - T	2(T - P)	0
P = T	T	0	0

Units: Report alkalinity as mg CaCO3/L.

E 102.190: Cyanide by Automated Color: The data system will prepare a calibration curve by plotting instrument response against standard concentration. Sample concentration is calculated from the regression equation. Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed. This can be done two ways. One, let the auto-dilutor or Two, manually using the 0.25M NaOH in an Orange Top flat bottomed Corning Centrifuge Tube. Report results in mg CN/L.

E 102.500: Sodium (EPA 273.1) , E 102.500: Potassium (EPA 258.1) by flame atomic absorption spectroscopy: Check data for accuracy. If blank spikes pass acceptance criteria, data is accepted. Matrix spike/Matrix spike duplicate results are evaluated. Finished results are transferred to chain-of-custody reports and input into LABWORKS LIMS. Results are validated in LIMS; reports are issued and reviewed before distribution.

E 102.030: Chloride, E 102.030: Fluoride, E 102.030: nitrate, E 102.030: sulfate: Use a midrange check standard from a different source than the calibration standards to verify calibration to within 10 percent.

FoT E 104: <u>Organic Chemistry of Hazardous Waste (measurement by GC/MS combination)</u>

E 104.040 & E 104.045 & E 104.050: EPA Method 524.2: HP G1701B.01 EnviroQuant Compound Software on a 4.2 GB Intell Celeron 400 controls data acquisition, quantitation, reporting and file management. A Quantitation Report is produced with data file name and path; date and time acquisition begins; name, number and date of sample; and date and time of quantification. The autosampler position, analyst, method, instrument, and multiplier used in the result calculation are identified.

Quantitation results are reviewed and edited using Qedit, the quantitation editor. False positives are those results found not to be the identified compound by comparing the peak spectra with the library reference spectra, and GC retention time with a known standard. False positives are deleted from the quantitation results file. Isomers poorly separated by retention time are sorted by manual integration in Qedit mode. Poorly integrated peaks are reintegrated manually. An edited quantitation report is produced identifying internal standards, system monitoring compounds (surrogates), and target

compounds by retention time. The response and concentration based on quantitation target ion are given with the statistical quantitation value for identified compounds. Internal standards are monitored for deviation in retention times. Surrogates are checked for percent recovery. A chromatogram is produced with identified peaks labeled as to compound type, i.e. continuing calibration check compound (C), internal standard (I), matrix spike compound (M), system performance check compound (P), surrogate (S), and target compound (T).

FoT E 108: <u>Wastewater Inorganic Chemistry, Nutrients and Demand</u>

E 108.506: Ammonia: The test result is transferred to the data entry book and input into LIMS. Validate data by reviewing method used, i.e. direct calibration, standard addition, or double standard addition. Measure precision by calculating relative percent difference between duplicates:

Measure accuracy by calculating the percent recovery of a sample spike:

$$\%Recovery = \frac{spiked\ sample\ result - sample\ result}{spike\ added} X\ 100$$

$$\frac{dup1 - dup2}{mean} * 100$$

Determine the method detection limit (see endnote) [aa].

E 108.590: Biochemical Oxygen Demand: DO1 = the initial dissolved oxygen (DO) concentration measured immediately after setup. DO2 = The final DO measured after 5 days of incubation at 20 degrees C.
Discard the results from any sample dilution that does not (1) deplete at least 2 mg/L, and (2) leave a residual DO after incubation of at least 1 mg/L. VOL = volume of sample used to prepare a dilution. P = VOL/300 = decimal volumetric fraction of sample used. f = the ratio of volume of seed in a diluted sample to the volume of seed in the seed control.

Calculate the seed correction for dechlorinated samples based on a sample control setup as follows:

SC = (DO1-DO2) * f

The decimal volumetric fraction is based on a 300 mL BOD bottle. Calculate the BOD value of all dilutions that have passed the above criteria as follows: Calculate the average of all BOD values generated for each sample. Report to data entry book and input to LIMS.

E 108.660: Chemical Oxygen Demand: Sample concentration is read directly from the DR4000V Spectrophotometer. When High Range Plus C.O.D. Digestion Vials are used, multiply the display by 10.

<u>Data Validation</u>:

E 108.050: pH: Test results are recorded on field sample control sheets, transferred to data entry forms, and filed. Lab pH results are entered into LIMS.

E 108.171: Chlorine Residual, total by amperometric back-titration: The test result is recorded on the chlorine control sheet, transferred to the microbiology sample tag and to the data entry book, and entered into the LIMS. Computer report values are verified against the control sheet.

$$TEST\ RESULT = mLsPAO - (5 \times TESTmLs \times \frac{1.00}{STDmLS})$$

E 108.310: BOD: Validate accuracy with glucose-glutamic acid checks. Results must be within the limits established by <u>Standard Methods</u>, 18th edition. The upper limit is 228 mg/L and the lower limit is

167 mg/L. If the BOD value of a glucose-glutamic check is outside acceptable limits, begin corrective action to bring BOD testing into control. Validate precision by calculating the relative percent difference between duplicates. Set precision control limits based on 30 sets of duplicates, and calculate from the mean + or -3 standard deviations. Establish a detection limit based on the minimum depletion requirement of 2 mg/L in an undiluted sample.

E 108.390: Turbidity: Turbidity read out values are multiplied by the dilution factor and entered into Turbidity Log and LIMS.

E 108.442: Residue, Nonfilterable (TSS): To calculate a result expressed in mg/L, first subtract the weight of the dish from the weight of the dish plus the dried residue, and then divide the weight of the dried residue by a decimal percent calculated by dividing the volume of sample by 1000 (the mLs in 1 liter). Validate the data by verifying all calculations, by calculating the relative percent difference (RPD) between duplicates on at least one sample per analytical batch, and by running a blank with each analysis. Plot the RPD value on a control chart. Transfer acceptable data to the data entry book and enter the result into LIMS.

E 108.472: Total Cyanide by Distillation and Automated Color Reference: E 102.190 above

E 108.531: Oxygen, Dissolved: Test results are recorded on field sample control sheets, transferred to data entry forms, and filed. Data is validated by comparison of DO meters against samples measured by Winkler titration.

E 108.580: Sulfides: The digitally displayed value is divided by 1000 and multiplied by the dilution factor. Data is recorded in Sulfide log and in LIMS.

E 108.610: Organic Carbon: This instrument does most of the calculations internally, but analyst should be prepared to check instrument's calculations.

FoT E 109: <u>Toxic Chemical Elements in Wastewater</u>

The atomic absorption spectrometer generates absorbance and concentration data; and calculates averages, standard deviations, and relative standard deviations. Data is validated by blanks, blank spikes, duplicates, sample spikes and certified external standards. The data is evaluated by a senior lab tech, summarized and input into the computer file. Determine the method detection limit (see endnote 1.)

FoT E 110: <u>Organic Chemistry of Hazardous Waste (measurement by GC/MS combination)</u>

E 110.040: EPA Method 624: HP G1701B.01 EnviroQuant Compound Software on a 4.2 GB Intell Celeron 400 controls data acquisition, quantitation, reporting and file management. A Quantitation Report is produced with data file name and path; date and time acquisition begins; name, number and date of sample; and date and time of quantification. The autosampler position, analyst, method, instrument, and multiplier used in the result calculation are identified.

Quantitation results are reviewed and edited using Qedit, the quantitation editor. False positives are those results found not to be the identified compound by comparing the peak spectra with the library reference spectra and GC retention times with a known standard. False positives are deleted from the quantitation results file. Isomers poorly separated by retention time are sorted by manual integration in Qedit mode. Poorly integrated peaks are reintegrated manually. An edited quantitation report is produced identifying internal standards, system monitoring compounds (surrogates), and target compounds by retention time. The response and concentration based on quantitation target ion are given with the statistical quantitation value for identified compounds. Internal standards are monitored for deviation in retention times. Surrogates are checked for percent recovery. A chromatogram is produced with identified peaks labeled as to compound type, i.e. continuing calibration check compound (C), internal standard (I), matrix spike compound (M), system performance check compound (P), surrogate (S), and target compound (T)

FoT E 116: Organic Chemistry of Hazardous Waste (measurement by GC/MS combination)

E 116.080: EPA Method 8260B: HP G1701B.01 EnviroQuant Compound Software on a 4.2 GB Intell Celeron 400 controls data acquisition, quantitation, reporting and file management. A Quantitation Report is produced with data file name and path; date and time acquisition begins; name, number and date of sample; and date and time of quantification. The autosampler position, analyst, method, instrument, and multiplier used in the result calculation are identified.

Quantitation results are reviewed and edited using Qedit, the quantitation editor. False positives are those results found not to be the identified compound by comparing the peak spectra with the library reference spectra and GC retention time with a known standard. False positives are deleted from the quantitation results file. Isomers poorly separated by retention time are sorted by manual integration in Qedit mode. Poorly integrated peaks are reintegrated manually. An edited quantitation report is produced identifying internal standards, system monitoring compounds (surrogates), and target compounds by retention time. The response and concentration based on quantitation target ion are given with the statistical quantitation value for identified compounds. Internal standards are monitored for deviation in retention times. Surrogates are checked for percent recovery. A chromatogram is produced with identified peaks labeled as to compound type, i.e. continuing calibration check compound (C), internal standard (I), matrix spike compound (M), system performance check compound (P), surrogate (S), and target compound (T).

Section 8: Internal Quality Control Checks

FoT E 108: Wastewater Inorganic Chemistry, Nutrients and Demand

E 108.580: Sulfides: Use of an ERA Certified Reference Standard with every analysis.

E 108.590: Biological Oxygen Demand: Use of a Hach glucose-glutamic acid check with every analysis.

E 108.610: Organic Carbon: Use of an ERA Certified Reference Standard with every analysis.

Section 9: Performance and System Audits

FoT E 102: Inorganic Chemistry and Physical Properties of Drinking Water excluding Toxic Chemical Elements

E 102.190: Cyanide by Automated Color

Method Blank (MB) = Laboratory Reagent Blank (LRB) -- The laboratory must analyze at least one MB with each batch of samples. Data produced are used to assess contamination from the laboratory environment. Values that exceed the MDL indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing the analysis.

Method Blank Spike (MBS) = Laboratory Fortified Blank (LFB) -- The laboratory must analyze at least one MBS with each batch of samples. Calculate accuracy as percent recovery. If the recovery of any analyte falls outside the required control limits of 90-110%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

Continuing Calibration Verification (CCV) –(Mid Point Check Solution) -- For all determinations the

laboratory must analyze the CCV (a mid-range check standard) and a calibration blank immediately following daily calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run. Analysis of the CCV solution and calibration blank immediately following calibration must verify that the instrument is within +/-10% of calibration. Subsequent analyses of the CCV solution must verify the calibration is still within +/-10%. If the calibration cannot be verified within the specified limits, reanalyze the CCV solution. If the second analysis of the CCV solution confirms calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift, the **instrument to be recalibrated.** All samples following the last acceptable CCV solution must be reanalyzed. The analysis data of the calibration blank and CCV solution must be kept on file with sample analyses data.

Linear Calibration Range (LCR) -- The LCR must be determined initially and verified every 12 months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. For verification of linearity, you must use a minimum of a three (3) Standards and a blank. If any verification data exceeds the initial values by +/- 10%, linearity must be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

Sample Spike = Laboratory Fortified Sample Matrix (LFM) -- The laboratory must add a known amount of analyte to a minimum of 10% of routine samples. In each case, the LFM aliquot must be a duplicate of the aliquot used for sample analysis. The analyte concentration must be high enough to be detected above the original sample and should not be less than four times the MDL The added analyte concentration should be the same as that used in the laboratory fortified blank.

FoT E 108: Wastewater Inorganic Chemistry, Nutrients and Demand

E 108.472: Total Cyanide by Distillation and Automated Color
Reference: E 102.190 above

Performance Evaluation guidelines:

As part of the performance audit process, the laboratory participates annually in:

1. Discharge Monitoring Report-Quality Assurance (DMR-QA) Laboratory Performance Evaluation Study

2. California DOHS Microbiology Performance Evaluation Study

3. Water Pollution Laboratory Performance Evaluation Study

4. Water Supply Laboratory Performance Evaluation Study

Klem, Donald J., et. al., Manual for the Evaluation of Laboratories Performing Aquatic Toxicity Tests, EPA/600/4-90/031, October 1990.

Section 10: Preventive Maintenance

Analytical and toploader balances: An annual service of cleaning and calibration is performed by Mettler-Toledo. A certificate of test weight traceability to the National Institute of Standards and Technology is issued.

Dionex DX-100 Ion Chromatograph: Change inlet bed supports monthly if more than 30% system pressure increase has occurred. Every 6 months change piston seals, inspect port faces, and inspect slider. Every 12 months lubricate pump; replace back-up seal; check waste lines, eluent lines, and air tubing; replace

grippers, damaged lines, and port faces. Document in Maintenance Log.

Lachat FIA 8000: (1) For best results: daily change sample pump tubing and check Reagent levels. (2) Clean/Wipe the Cassette Pump Cartridges with Isopropyl alcohol. (3) Check for leaks at all union fittings.

Skalar, Formacs HT TOC Analyzer: (1) Weekly: Check level in the phosphoric acid bottle, fill as necessary. (2) Biannual: Replace tubing. Change the catalyst in the TC reactor. Replace the CO_2 scrubber. Replace the septum in the TC reactor. Check and replace the o-rings as necesary. Grease pump heads as necessary.

Varian 400 Flame AAS: (1) Daily: check gas supply, exhaust system, waste vessel, and burner head. Rinse spray chamber and liquid trap with DI water. (2)As needed: Clean lamp, windows, and instrument case. Check glass beads, nebulizer, and air filter assembly. Sonicate burner head with detergent solution (Acationix). (3) Yearly: arrange for Varian preventive maintenance service. When changing gas cylinders, check for leaks, test regulators and shut-off valves.

Thermo Jarrell Ash ICP: (1) Daily: change sample pump tubing. Replace torch and nebulizer when you see instability and counts falling. Check water recirculator for water levels.

Hewlett Packard ICP-MS: (1) Daily: change sample pump, internal standard and ISIS (Integrated Sample Introduction System) tubing. Replace torch and nebulizer when you see instability and counts falling. Check water chiller for water levels

Hewlett Packard 5890 Series II Plus Gas Chromatograph, Hewlett Packard 5372A Mass Spectrometer, Tekmar SolaTek 72 autosampler, Tekmar 3100 Concentrator:
(1) Scheduled preventive maintenance includes daily auto-sampler bake-out, weekly foreline pump fluid level check, semiannual replacement of foreline pump fluid and trap pellets, and, if necessary, replacement of diffusion pump fluid. Preventive maintenance on an as-needed basis includes trap and column change, ion source cleaning, carrier gas trap replacement, and replacement of worn parts such as filaments and electron multiplier.
(2) If the routine bake-out method is insufficient to remove sample-caused contamination, place the purge-and-trap system in BAKE for at least an hour. It may be necessary to replace the trap if contamination persists. If contamination is due to a bad gas tank, replace the tank and all hydrocarbon traps on the gas supply line. A solvent flush can be used to remove contaminants in the transfer lines. Use a solvent flush kit with water and methanol.
(3) Column bleed ions, elevated baseline, and shifting retention times indicate the need to change columns. Vent the MSD. Turn off the injector as well as the detector. Condition new columns before inserting into the detector for at least two hours at the highest analytical temperature. At the same time check the inlet liner. Clean or replace if necessary. Turn on the GC and the injection heating zone. Pump down the MSD. Wait 24 hours. Autotune the MSD and do an air and water check for leaks. Tighten connectors as necessary.
(4) Difficulties in passing BFB tune evaluation, especially the heavier ion ratios, may indicate a dirty source. Vent the MSD. Remove the analyzer, Remove, disassemble, and clean the ion source according to instructions in the Hardware Manual. Reassemble and reinstall. Turn on the GC and the injection heating zone. Pump down the MSD. Wait 24 hours. Autotune the MSD and do an air and water check for leaks.
(5) Maintenance logs are kept on the GC/MS and on the purge-and-trap. Spare parts kept in-house include vacuum pump fluid and trap absorbent, oxygen trap and gas filter, sample heater fuses, traps, ferrules, injector seals and liners, septums, o-rings, and a spare filament assembly.

General ICP Maintenance
(1) Daily, lenses and burners are cleaned, the nebulizer and premix chamber are flushed, and accumulated fluids are drained from the compressor/manifold assembly.
(2) Weekly, the burner compartment, the burner, and the burner/premix chamber are cleaned.
(3) Monthly, the air compressor filter and the fan filters in the electronics drawer are cleaned.
(4) Semi-annually, the oil-removing air filter is replaced.
(5) Annually, the air filter is replaced.

Section 11: Assessment of Precision and Accuracy

Precision is the relative percent difference (RPD) of duplicates.

RPD is the difference divided by the mean and multiplied by 100.

Accuracy is the percent recovery (PR) of a sample spiked with a known amount. PR is defined by the formula as the apparent spike concentration divided by its true value and expressed as a percent.

$$PR = \frac{spiked\ \ sample\ \ CONC\ \ - sample\ \ CONC}{spike\ \ true\ \ value} X\ 100$$

FoT E 102: Inorganic Chemistry and Physical Properties of Drinking Water excluding Toxic Chemical Elements.

E 102.190: Cyanide by Automated Color: The laboratory must use LFB analyses data to assess laboratory performance against the required control limits of 90-110%. When sufficient internal performance data become available (usually a minimum of 20-30 analyses), optional control limits can be developed from the percent mean recovery and the standard deviation (S) of the mean recovery. These data can be used to establish the upper and lower control limits as follows:

UPPER CONTROL LIMIT = + 3S

LOWER CONTROL LIMIT = - 3S

The optional control limits must be equal to or better than the required control limits of 90-110%. After each five to ten new recovery measurements, new control limits can be calculated using only the most recent 20-30 data points. Also, the standard deviation (S) data should be used to establish an on-going precision statement for the level of concentrations included in the LFB These data must be kept on file and be available for review.

Calculate accuracy as a function of percent recovery for each analyte, corrected for concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery range 90-110%. Percent recovery may be calculate using the following equation:

$$R_s = \frac{Cs-C}{} X\ 100$$

Where, ***R*** *= percent recovery,* ***Cs*** *= fortified sample concentration,* ***C*** *= sample background concentration,* ***s*** *= concentration equivalent of analyte added to sample.*

If the recovery of any analyte falls outside the designated LFM recovery range and the laboratory performance for that analyte is shown to be in control, the recovery problem encountered with the LFM is judged either matrix or solution related, not system related.
Where reference materials are available, they should be analyzed to provide additional performance data. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably.

E 102.500: Sodium (EPA 273.1), E 102.500 Potassium (EPA 258.1) by flame atomic absorption spectroscopy: Precision is % RSD calculated on a matrix spike and matrix spike duplicate. RSD must be <20% for data to be acceptable. Accuracy is percent recovery calculated on the average of the matrix spike and the matrix spike duplicate. Accuracy is also calculated on the blank spike. Blank spike must meet 80 to 120 % recovery limits. Matrix spike results should meet 80 to 120 % recoveries. *Acceptance criteria as per ELAP pre-inspection site manual guidelines.*

FoT E 104: Organic Chemistry of Drinking Water (measurement by GC/MS combination

E 104.040, E 104.045, E 104.050: EPA Method 524: Establish the ability to generate acceptable accuracy and precision by spiking matrix samples to contain 1.0 ug/L or less of each analyte. Analyze five replicates. Calculate the average recovery in ug/L and percent, and the standard deviation of the recovery (s) in ug/L and percent, for each analyte using the five results. Matrix spiking standards are prepared to test precision and accuracy of the method. The spike recovery compliance range is 75 to 125 %. The maximum limit of relative percent difference (RPD) is 20 %.

FoT E 108: Wastewater Inorganic Chemistry, Nutrients and Demand

E 108.472: Total Cyanide by Distillation and Automated Color
Reference: E 102.190 above

FoT E 110: Organic Chemistry of Wastewater (measurement by GC/MS combination)

E 110.040 EPA Method 624: Establish the ability to generate acceptable accuracy and precision by spiking matrix samples to contain 20 ug/L of each analyte. Analyze five replicates. Calculate the average recovery in ug/L and percent, and the standard deviation of the recovery (s) in ug/L and percent, for each analyte using the five results. Matrix spiking standards are prepared to test precision and accuracy of the method. The spike recovery compliance range is 71 to 138 %, or as listed in Table 5 of Method 624. The maximum limit of relative percent difference (RPD) is 26 %, or as listed in Table 5 of Method 624. Control charts are kept to establish laboratory accuracy and precision beyond that required by the method.

FoT E 116: Organic Chemistry of Hazardous Waste (measurement by GC/MS combination)

E 116.080: EPA Method 8260B: Establish the ability to generate acceptable accuracy and precision by spiking matrix samples to contain 20 ug/L or less of each analyte. Analyze four replicates. Calculate the average recovery in ug/L and percent, and the standard deviation of the recovery (s) in ug/L and percent, for each analyte using the four results. Matrix spiking standards are prepared to test precision and accuracy of the method. The matrix spike compounds are 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. The spike recovery compliance range is 75 to 125 %. The maximum limit of relative percent difference (RPD) is 30 %.

Section 12: Corrective Action

AMMONIA

1. If the electrode fails the slope check, resoak the electrode in internal filling solution. If it still doesn't pass, disassemble and check the inner body.

2. If the acceptance limit of the check standard is exceeded, prepare fresh standards by serial dilution. If the acceptance limit is still exceeded, perform the instrument checkout procedure.

3. If the electrode works in standards but exceeds precision and accuracy limits in samples, check for interferences. If complexing agents are present, use the method of standard additions. If working at low levels, use low-level measurement technique. If problems persist, review procedure or call Orion technical service (1-800-225-1480).

BIOCHEMICAL OXYGEN DEMAND

If the 5-day oxygen depletion of the dilution water (blank) exceeds 0.2 mg/L, then investigate other sources of water or improve the purification.

If the results of the glucose-glutamic acid check do not fall within the range of 167 to 228 mg/L, then check the dilution water quality, seed effectiveness, and analytical technique.

CHLORINE RESIDUAL-10 DOMETRIC

Recalculate the decimal correction factor weekly to correct for depletion in the normality of the reagent 0.0282 N iodine solution by dividing the mLs you expect to use (1.00 per 5.00 mLs PAO) by the actual mLs used.

CHLORINE RESIDUAL-DPD-FAS TITRATION

Discard DPD solution if discolored. Restandardize FAS solution with 0.100 N primary standard potassium dichromate after one month.

DISSOLVED OXYGEN

If the DO meter cannot be calibrated to the known value determined by a Winkler calibration on a stable water source, then check and change the batteries if necessary, or change and calibrate the membrane electrode.

pH

If pH meter does not calibrate to the standard calibration values, then clean, soak and recalibrate the electrode. Replace electrode when necessary.

SUSPENDED SOLIDS

If the acceptance limit of the relative percent difference between duplicates is exceeded, run a new set of duplicates on the same sample. Increase the sample volume for better precision if necessary.

EPA 524, 624, 8260B

If the tune evaluation report does not pass, (1) select a different spectrum one or two scans on either side of the peak apex, (2) prepare a fresh BFB standard and repeat the tune evaluation, (3) perform a Maximum Sensitivity Tune and repeat the evaluation. (3) Clean the source.

If the Continuing Calibration Verification (CCV) or System Performance Check Compound (SPCC) does not pass, remake and rerun the check standard. Besides standard mixture degradation, other possible problems are injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or in the purge-and-trap system. Clean and replace traps, liners, and sparge vessels. Flush the transfer lines with water and methanol. If the calibration check still doesn't pass, recalibrate with new standards.

Section 13: Quality Assurance Reports

FoT E 104: Organic Chemistry of Drinking Water (measurement by GC/MS combination)

E 104.040, E 104.045, E 104.050: EPA Method 524.2: Quality Assurance Reports are issued with analytical reports on drinking water quality. Analytical results from the analyses of laboratory reagent blanks, travel blanks, and field blanks measure interferences in the sampling and analytical procedures. The percent recovery calculations for all compounds in the continuing calibration checks measure accuracy.

FoT E 116: Organic Chemistry of Hazardous Waste (measurement by GC/MS combination)

E 116.080: EPA Method 8260B: Quality Assurance Reports are issued with analytical reports of Total Toxic Organics to the Industrial Waste section on industrial point sources. Percent recovery calculations for Calibration Check Compounds (CCCs) in reagent grade water and matrix spike compounds in sample matrices are provided as a measure of analytical accuracy. The calculated Relative Percent Differences between matrix spikes and matrix spike duplicates report on analytical precision.

ENDNOTES:

Definition and Procedure for the Determination of Method Detection Limit (Federal Register, vol. 49, no. 209, Friday, October 1984.

Estimate the MDL based on a signal to a noise ratio in the range of 2.5 to 5, on three times the standard deviation of replicates, on a break in the slope of the standard curve, on instrument limitations, or on a method of multiple sample duplicates. Based on the estimate, either prepare a standard in reagent water, or use a matrix sample, with a concentration between 1 to 5 times the estimated MDL. Take 7 replicates through the entire analytical method. Use a blank correction, or subtract an average blank measurement. Calculate the standard deviation (SD). The MDL is 3.14 times the SD.

1. Definition and Procedure for the Determination of Method Detection Limit (Federal Register, vol.49, no.209, Friday, October 26,1984.

Estimate the MDL based on a signal to a noise ratio in the range of 2.5 to 5, on three times the standard deviation of replicates, on a break in the slope of the standard curve, on instrument limitations, or on a method of multiple sample duplicates. Based on the estimate, either prepare a standard in reagent water, or use a matrix sample, with a concentration between 1 to 5 times the estimated MDL. Take 7 replicates through the entire analytical method. Use a blank correction, or subtract an average blank measurement. Calculate the standard deviation (SD). The MDL is 3.14 times the SD.