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Statistical Evaluation of Effluent Monitoring Data for the 200 Area Treated Effluent Disposal Facility

C. J. Chou
V. G. Johnson

March 2000

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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Richland, Washington 99352

Preface

An evaluation of 4 years of effluent monitoring data for the 200 Area Treated Effluent Disposal Facility (TEDF) at the Hanford Site was conducted by Pacific Northwest National Laboratory (PNNL) during fiscal year 1999. Findings of that evaluation were presented in a draft report (dated October 1999). The draft report was used by Washington State Department of Ecology as supporting information to revise effluent monitoring requirements for the new TEDF permit that will become effective in April 2000. This report is the unabridged version of the draft report that served as technical basis for the revised monitoring requirements.

Summary

This report updates the original effluent variability study for the 200 Area Treated Effluent Disposal Facility (TEDF) and provides supporting justification for modifying the effluent monitoring portion of the discharge permit (Ecology 1995). Four years of effluent monitoring data were evaluated and used to statistically justify changes in permit effluent monitoring conditions. The permit modifications will be used to regulate and monitor TEDF at a level appropriate to the environmental risk of the discharge.

Results of the statistical evaluation indicate the effluent is similar in composition to local drinking water (Columbia River water) with a little chloroform from the chlorinating process and some added chloride and iron (primarily particulate). Based on effluent data for four consecutive years, the probability of exceeding permit limits under normal operating conditions is less than one in a million, except for iron. Maximum monthly average concentrations of iron were exceeded twice for total iron.

Random transient increases in total iron and chloride occurred during the evaluation period. The iron transients are attributed to periodic flushing of rust particles from aging water and wastewater distribution and collection piping. The random spikes of chloride were due to ion-exchange column regeneration at the 200 Areas power plants that were shut down in 1998.

As a result of the 4-year period of effluent monitoring and data evaluation, the TEDF effluent composition and variability of the effluent waste stream are now well defined. Accordingly, a modified effluent monitoring program is proposed that is more tailored to contemporary 200 Area wastewater conditions. The low detection frequency for several permit constituents, the small number of actual permit limit exceedances and low exceedance probabilities for detected constituents indicate a significant reduction in the number and/or type of routine measurements can be made with no risk to the environment. The approach or strategy relies on (1) the use of gross alpha and gross beta in lieu of isotope specific analyses, (2) elimination of analytes with a history of non-detects, and (3) reduction in frequency of sampling where appropriate. Implementation of the proposed changes to the discharge permit will result in a more efficient and cost-effective effluent monitoring program.

Notice

This report is based on the effluent data that was available through June 28, 1999. However, high iron, manganese, and chromium concentrations for a sample collected on June 21, 1999, were validated after this report was completed. It was determined that these results may not adequately represent the typical composition of the original sample due to the presence of particulate material in the sample (i.e., non-homogeneous and highly variable). The excursions were the subject of a non-compliance report submitted to Washington State Department of Ecology (Ecology) on September 20, 1999. Therefore, the data set used for the statistical evaluation presented in this report did not include the anomalously high iron, manganese, and chromium concentrations that occurred on June 21, 1999.

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1.0 Introduction

1.1 Background

The 200 Area Treated Effluent Disposal Facility (TEDF) consists of a pair of infiltration basins that receive wastewater originating from the 200 West and 200 East Areas of the Hanford Site (Figure 1). TEDF has been in operation since 1995 and is regulated by State Waste Discharge Permit ST 4502 (Ecology 1995) under the authority of Chapter 90.48 Revised Code of Washington (RCW) and Washington Administrative Code (WAC) Chapter 173-216. The permit stipulates monitoring requirements for effluent (or end-of-pipe) discharges and groundwater monitoring for TEDF. Groundwater monitoring began in 1992 prior to TEDF construction. Routine effluent monitoring in accordance with the permit requirements began in late April 1995 when the facility began operations.

The State Waste Discharge Permit ST 4502 included a special permit condition (S.6). This condition specified a statistical study of the variability of permitted constituents in the effluent from TEDF during its first year of operation. The study was designed to (1) demonstrate compliance with the waste discharge permit; (2) determine the variability of all constituents in the effluent that have enforcement limits, early warning values, and monitoring requirements (WHC 1995); and (3) determine if concentrations of permitted constituents vary with season. Additional and more frequent sampling was conducted for the effluent variability study. Statistical evaluation results were provided in Chou and Johnson (1996). Parts of the original first year sampling and analysis plan (WHC 1995) were continued with routine monitoring required up to the present time.

1.2 Objectives and Scope

This report updates the original study of effluent variability (Chou and Johnson 1996) for TEDF. A major objective of this document is to provide supporting justification for modifying permit ST4502, Section S.9 regarding effluent monitoring and to propose a new monitoring regime in accordance with Section S.6. The first 4 years of effluent monitoring data were evaluated and used to statistically justify changes in permit effluent monitoring conditions. The permit modifications will be used to regulate and monitor TEDF at a level appropriate to the environmental risk of the discharge. Numerical and graphical results of the updated statistical evaluation are provided in Appendix A and B. The results are summarized and discussed in the following sections followed by recommendations for modifications to the existing monitoring program.

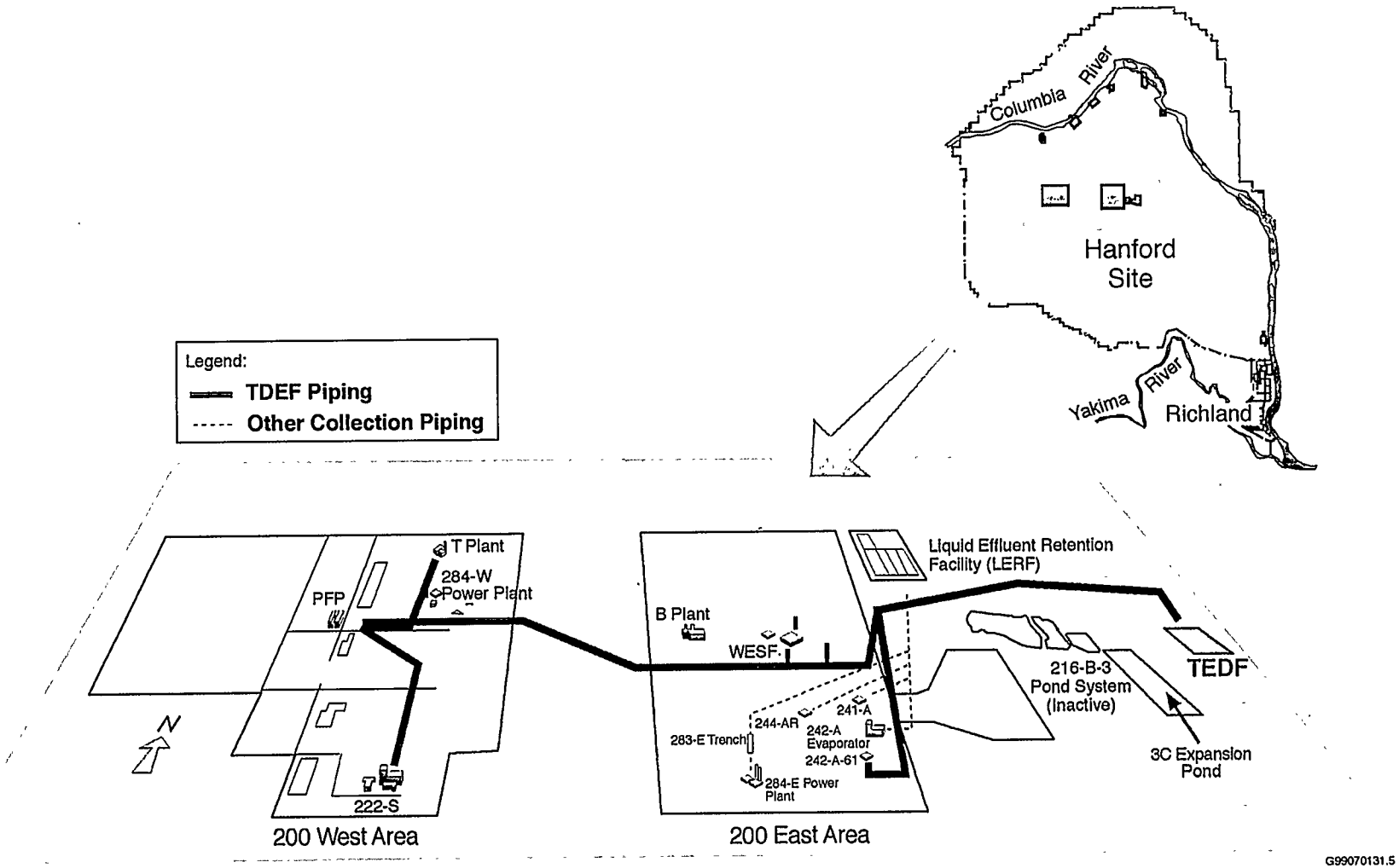


Figure 1. Schematic Diagram of the Effluent Collection System for TEDF

2.0 Detections

The sampling schedule and analyte list for the first year of TEDF operation (July 1995 through June 1996) are summarized in Table 1. More frequent sampling was conducted during this period to evaluate variability in analyte concentrations over time and to determine facility operational factors that might contribute to waste stream variability. At the conclusion of data collection for the variability analysis, sampling no longer included the samples and analytes required solely for the variability study. In subsequent years, only the routine monitoring indicated in Table 1 is required for permit compliance.

Continuous monitoring for pH, specific conductivity, and flow are also part of the overall monitoring program. The continuous measurements allow general water quality to be tracked on a day-to-day or real-time basis and indicate major changes in the effluent.

Current analytical methods and detection levels for constituents of interest are shown in Table 2. A detection frequency summary of all results to date (listed by years) is provided in Table 3. The detection limits improved for several constituents during the four-year period (e.g., arsenic, cadmium, chromium, lead, and radium-226) and account for the implied increase in detections. Even though the frequencies of detection for these constituents increased numerically, natural levels in river water account for most of the detections, as discussed later (Section 5.4).

Supporting details of Table 3 (by seasons of the year) are presented in Appendix A (Table A-1). A description of Table 3 (by constituent group) follows.

Volatile Organics. Total trihalomethane was the only significant volatile organic analyte (VOA) detected. Chloroform was the dominant trihalomethane with only occasional detections of bromodichloromethane. In addition, methylene chloride, a common laboratory contaminant, was reported as a detected constituent in 6 of the 237 samples analyzed for VOAs during the 4-year period. As noted in the previous variability study report (Chou and Johnson 1996), the trihalomethanes seem to be highest during the spring and summer. This seasonal factor is attributed to the increase in natural organics in river water that react with the chlorine to form the trihalomethanes. (Chlorine is added to river water from the 100 B Area at the water treatment plant to produce sanitary and drinking water for use in the 200 Areas.)

Semi-Volatiles. Except for the initial period of the variability study, phenol and bis (2-ethylhexyl) phthalate were analyzed in only the composite samples (see Table 1). Phenol was not detected during the 4-year period. The highest detection frequency (17% in grab samples) for bis (2-ethylhexyl) phthalate occurred during the first year of operation. The detection frequency for this constituent has declined in subsequent years to only a few percent (e.g., 2% or 1 detection in a total of 48 samples analyzed during the period from July 1998 to June 1999).

Table 1. Summary of Permit Requirements and Combined Monitoring Program Used During July 1995 through June 1996

Parameter	Permit Requirements		Combined Monitoring Program[a]	
	Routine	Variability Study	Summer-Winter[b]	Fall-Spring[c]
Volatile Organic Compounds				
Carbon tetrachloride Methylene chloride 1,1,1,-Trichloroethane Total trihalomethanes: Bromoform Bromodichloromethane Chloroform Dibromochloromethane	Grab 4/month	Random grab 10/month	Random grab 1/3 days	Random grab 1/week
Semivolatile Organic Compounds				
Bis(2-ethylhexyl)phthalate Phenol	Composite[d] 4/month	Composite 4/month	Random grab 1/3 days Composite 1/week	Random grab 1/week Composite 1/week
Total Metals				
Arsenic Cadmium Chromium Lead Mercury	Composite 4/month	Random grab 10/month Composite 4/month	Random grab 1/3 days Composite 1/week	Random grab 1/week Composite 1/week
Iron Manganese	Composite 1/month	Random grab 10/month Composite 4/month	Random grab 1/3 days Composite 1/week	Random grab 1/week Composite 1/week
Anions				
Chloride Nitrate Sulfate	Composite 1/month	Composite 4/month	Random grab 1/3 days Composite 1/week	Random grab 1/week Composite 1/week
Other Analyses				
Cyanide	Grab 4/month	---	Random grab 1/week	Random grab 1/week
WTPH-G	Grab 1/month	---	Random grab 1/month	Random grab 1/month
Oil and grease	Grab 1/month	Composite 4/month	Random grab 1/month Composite 1/week	Random grab 1/month
Total dissolved solids	Composite 1/month	---	Composite 1/month	Composite 1/month

Table 1. (contd)

Parameter	Permit Requirements		Combined Monitoring Program[a]	
	Routine	Variability Study	Summer-Winter[b]	Fall-Spring[c]
Gross alpha Gross beta Total radium (Radium-226 and Radium-228) Radium–226	Grab 1/month	---	Random grab 1/month	Random grab 1/month
In-Line Monitoring				
Flow Specific conductivity pH	Continuous	Continuous	Continuous	Continuous

(a) Combined monitoring program includes both the variability study and routine monitoring (performed from July 1995 through June 1996).
(b) Summer = July through September.
Winter = December through February.
(c) Fall = October through November.
Spring = March through June.
(d) Composite = a flow proportional composite sample obtained over a 24-hour period.

Table 2. Analytical Method and Detection Level Summary for Detected Constituents Analyzed for TEDF Effluent Variability Study

Parameter	Analytical Method	Detection Level
Volatile Organic Compound:		
Carbon tetrachloride (µg/L)	SW-846 8260A	0.7
Methylene chloride (µg/L)	SW-846 8260A	1.1
1,1,1-trichloroethane (µg/L)	SW-846 8260A	0.6
Total trihalomethanes: (µg/L)	SW-846 8260A	1.2
Bromoform (µg/L)	SW-846 8260A	1.9
Bromodichloromethane (µg/L)	SW-846 8260A	1.2
Chloroform (µg/L)	SW-846 8260A	0.9
Dibromochloromethane (µg/L)	SW-846 8260A	1.6
Semivolatile Organic Compound:		
Bis(2-ethylhexyl)phthalate (µg/L)	SW-846 8270B	3.5
Phenol (µg/L)	SW-846 8270B	2
Total Metals:		
Arsenic (µg/L)	EPA-600 200.8	0.4
Cadmium (µg/L)	EPA-600 200.8	0.21
Chromium (µg/L)	EPA-600 200.8	0.6
Lead (µg/L)	EPA-600 200.8	0.21
Mercury (µg/L)	EPA-600 200.8	0.2
Iron (µg/L)	SW-846 6010A	6.6
Manganese (µg/L)	SW-846 6010A	5
Anions:		
Chloride (µg/L)	EPA-600 300.0	420
Nitrate (as N) (µg/L)	EPA-600 300.0	20
Sulfate (µg/L)	EPA-600 300.0	500
Other Analyses:		
Cyanide (µg/L)	EPA-600 335.3	5
WTPH-G (µg/L)	WTPH-G (WA)	50
Oil and grease (µg/L)	SW-846 9070	5,000
Total dissolved solids (µg/L)	EPA-600 160.1	1,000
Gross alpha (pCi/L)	Laboratory Specific	1.8
Gross beta (pCi/L)	Laboratory Specific	1.8
Total radium, Radium-226 and Radium-228 (pCi/L)	Laboratory Specific	5
Radium-226 (pCi/L)	Laboratory Specific	1

Table 3. Detection Frequency Summary[a] for the Constituents Analyzed for the TEDF Effluent Variability Study

Parameter	July through June				
	Year 1 (95 - 96)	Year 2 (96 - 97)	Year 3 (97 - 98)	Year 4 (98 - 99)	Total (95 - 99)
Volatile Organic Compound[b]					
Carbon tetrachloride	0/86	0/52	0/50	0/49	0/237
Methylene chloride	0/86	0/52	1/50	5/49	6/237
1,1,1-trichloroethane	0/86	0/52	0/50	0/49	0/237
Total trihalomethanes:	86/86	35/52	24/50	39/49	184/237
Bromoform	0/86	0/52	0/50	0/49	0/237
Bromodichloromethane	19/86	0/52	0/50	9/49	28/237
Chloroform	86/86	36/52	26/50	45/49	193/237
Dibromochloromethane	0/86	0/52	0/50	0/49	0/237
Semivolatile Organic Compound					
Bis(2-ethylhexyl)phthalate					
Grab Sample	15/87	---	---	0/1	15/88
Composite Samples	5/50	3/52	2/50	1/48	11/200
Phenol					
Grab Sample	0/87	---	---	0/1	0/88
Composite Sample	0/50	0/52	0/50	0/48	0/200
Total Metals					
Arsenic					
Crab Sample	3/87	---	---	1/1	4/88
Composite Sample	4/51	17/52	44/50	46/48	111/201
Cadmium					
Grab Sample	0/87	---	---	0/1	0/88
Composite Sample	1/51	5/52	5/50	8/48	19/201
Chromium					
Grab Sample	8/87	---	---	1/1	9/88
Composite Sample	2/51	11/52	17/50	21/48	51/201
Lead					
Grab Sample	11/87	---	---	1/1	12/88
Composite Sample	9/51	30/52	22/50	38/48	99/201
Mercury					
Grab Sample	21/87	---	---	0/1	21/88
Composite Sample	8/51	11/52	3/50	4/48	26/201
Iron					
Grab Sample	87/87	---	---	1/1	88/88
Composite Sample	51/51	54/54	50/50	48/48	203/203
Manganese					
Grab Sample	50/87	---	---	1/1	51/88
Composite Sample	23/51	15/54	12/50	26/48	76/203

Table 3. (contd)

Parameter	July through June				
	Year 1 (95 - 96)	Year 2 (96 - 97)	Year 3 (97 - 98)	Year 4 (98 - 99)	Total (95 - 99)
Anions					
Chloride					
Grab Sample	87/87	---	---	1/1	88/88
Composite Sample	49/50	52/52	50/50	48/48	199/200
Nitrate (as N)					
Grab Sample	83/87	---	---	1/1	84/88
Composite	49/50	51/52	50/50	46/48	196/200
Sulfate					
Grab Sample	87/87	---	---	1/1	88/88
Composite	50/50	52/52	50/50	48/48	200/200
Other Analyses					
Cyanide[b]	9/50	7/52	0/50	0/49	16/201
WTPH-G[b]	4/12	1/12	0/12	0/13	5/49
Oil and grease					
Grab Sample	21/32	1/12	0/12	1/13	23/69
Composite Sample	27/43	---	---	---	27/43
Total dissolved solids					
Grab Sample	8/8	---	---	1/1	9/9
Composite Sample	12/12	45/45[c]	50/50	48/48	155/155
Gross Alpha					
Grab Sample	51/64	23/52	13/50	25/49	112/215
Composite Sample	26/39	---	---	---	26/39
Gross Beta					
Grab Sample	61/64	23/52	7/50	21/49	112/215
Composite Sample	36/39	---	---	---	36/39
Total radium[b]	0/12	0/12	0/12	0/13	0/49
Radium 226[b]	1/12	6/12	7/12	5/13	19/49

(a) Obtained from Table A-1 (Appendix A). Numbers in the table denote detection frequency, i.e., the number of times an analyte is detected over the total number of analyses performed during the period (e.g., from July 1995 through June 1996) where "---" indicates analysis is not required by the permit.
(b) Grab samples only.
(c) Monthly composite samples, rather than weekly samples, were analyzed during July and August 1996.

Metals. Metals were analyzed in both grab and composite samples during the first year. Based on the initial findings, composites were deemed adequate for subsequent monitoring purposes. The most commonly detected metals were iron, manganese and lead. Also, the detection frequencies of arsenic, chromium and lead have increased. As noted previously, this apparent increase in detection frequencies is attributed to the use of lower detection limits associated with a change in analytical methods from GFAA to ICP/MS. While arsenic, chromium and lead detection frequencies increased, the levels are comparable to concentrations reported for Columbia River water (see Section 5.4).

Anions. Chloride, nitrate, and sulfate are consistently detected because these common anions are found in the makeup water (Columbia River water). Likewise, total dissolved solids are always detected. Nitrate and most of the sulfate can be accounted for by river water whereas chloride is higher than average river water due to contributor inputs (see river water comparison in Section 5.4).

Other analyses (cyanide, WTPH-G, oil, and grease). Moderately frequent detections of these constituents occurred during the first and second year (1995-96, 1997) and not at all during the most recent two years (1998 and 1999).

Gross alpha and gross beta. These radionuclide indicators were frequently detected over the 4-year period although less so during the most recent two years. The detections are in part due to naturally occurring radionuclides present in Columbia River and due to occasional inputs from contributors.

Radium-226. No detections of total radium (the sum of radium-226 and radium-228) and only occasional detections of radium-226 were reported for the 4-year period. The detection frequency of radium-226 has increased during the last 3 years. This is attributed to the dramatic lowering of the detection limit from 1 pCi/L to less than 0.05 pCi/L after year one. Even though the detection frequency increased after year one, the maximum radium-226 concentration reported was only 0.14 pCi/L (sample date, October 8, 1997). This is consistent with previously reported radium-226 concentrations in Columbia River water (Table 5a).

3.0 Elevated Concentrations

Elevated concentrations of a few constituents exceeded either drinking water standards or, in only two cases, the permit limits. The effluent quality enforcement limits are based on maximum composite sample monthly averages for the analytes of interest. There are also daily maximum allowable limits for chloride and nitrate as well as a maximum monthly average limit for these two anions. The monthly average concentrations of permit required analyte measurements over the four-year period are tabulated in Table A-2 (Appendix A). It should be noted in calculating these averages that measurements below the practical quantification levels (PQL) were not replaced by zero as required for the Discharge Monitoring Report (DMR). Exceedances and elevated concentrations are discussed in the following section.

3.1 Iron

The iron measurements are made on unfiltered (digested) samples. Thus this total iron result includes both dissolved iron and particulate iron. Maximum monthly average concentrations were exceeded twice for total iron (~890 ppb for April 1996 and 526 ppb for January 1997 as compared to the enforcement limit of 258 ppb) (Figure 2a). The random transient increases in total iron (Figure 2b) are attributed to periodic flushing of rust particles from aging water and wastewater piping. Although high total iron concentrations and two exceedances occurred during the 4-year period, it is also noteworthy that the magnitude of the excursions in total iron concentration appears to have attenuated markedly since initial operation of TEDF (see Figure 2a). The contributors attribute this improvement to increased diligence and attention to operational factors. However, the iron transient occurrences are expected to continue to be a recurring issue as piping systems age. There are no plans to replace aging pipes to mitigate the sporadic release of particulate iron (presumably rust particles).

3.2 Gross Alpha

The permit sets no limit for gross alpha. The highest monthly average gross alpha concentration of 24.4 pCi/L occurred in January 1999. (Note: It was reported as 23.5 pCi/L in the DMR because in calculating the averages and variability, values below the PQL are not replaced by zeros.) This occurrence was attributed to breakthrough from an effluent treatment filter bed at the Plutonium Finishing Plant (PFP).

3.3 Chloride

In the 24-hour composite samples, the daily maximum concentration of chloride had no exceedances. While not a permit limit exceedance, one grab sample did have a concentration higher than the permit limit (Figure 3a). Most of the chloride excursions or spikes were due to ion-exchange column regeneration for the 200 Area Power House boilers. These sources have been eliminated and thus chloride concentrations have been reduced. The latter change is readily evident in a plot of the weekly chloride results over the 4-year period (see Figure 3a). Both the magnitude and frequency of concentration excursions have declined significantly since mid-1998 (Figures 3a and 3b).

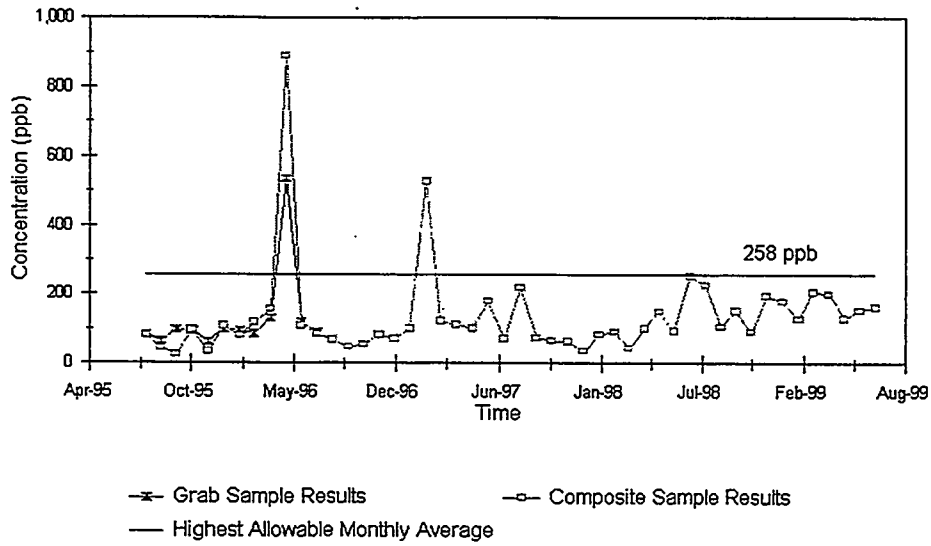


Figure 2a. TEDF Effluent Monitoring Result - Iron Monthly Averages

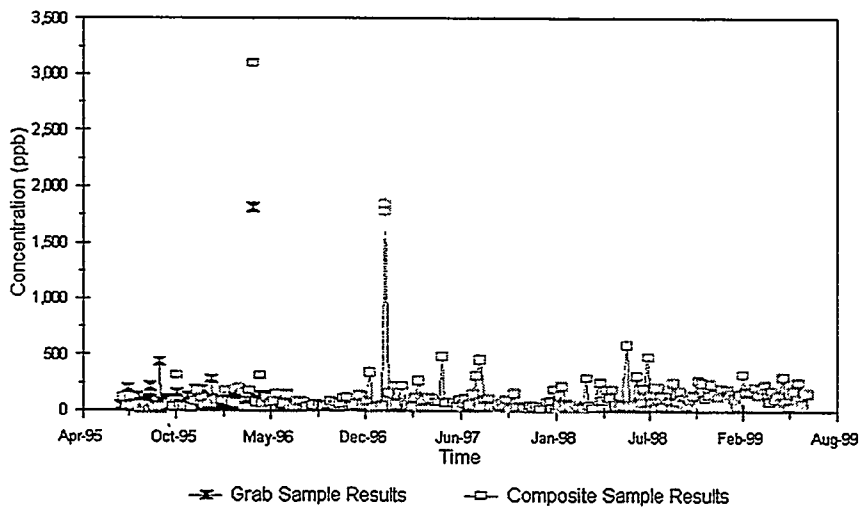


Figure 2b. TEDF Effluent Variability - Iron Grab and Composite Sample Results

3.4 Filtered versus Unfiltered Metals

The periodic iron spikes are most likely due to a particulate phase which is insoluble at pH 2 (acidity of preserved sample). For example, based on both filtered and unfiltered results for composite samples collected on April 7, 1996, and January 1, 1997 (dates when total or unfiltered iron was 3,100 and 1,780 µg/L, respectively), nearly all (>97%) of the iron was particulate (iron that passed through an 0.45 micron filter was 101 and 36 µg/L, respectively). The particulates in the unfiltered samples had to be "digested" in strong acid prior to analysis for total iron. Rust particles from old distribution lines that are periodically flushed are suspected to be the primary source for the particulate iron.

4.0 Trends

Time series trend plots of detected constituents are included in Appendix B. These plots indicate three general patterns:

- cyclic or seasonal variations
- random spike occurrences
- continuous or non-varying concentrations.

4.1 Seasonal Variation

Total trihalomethane and chloroform exhibit concentration maxima during the spring and summer months. This trend was noted in the initial effluent variability report (Chou and Johnson 1996). The cause was attributed to treatment of raw water from the Columbia River with chlorine in the water treatment plant. The chlorine reacts with natural dissolved organic matter in the river water to produce chloroform as a byproduct of the chlorination process. During the spring and summer dissolved organic matter typically increases along with increased phytoplankton densities. This produces increased amounts of chloroform. As noted in Chou and Johnson (1996), chloroform production is well known in municipal drinking water supplies where the raw water is drawn from lakes or rivers. It is noteworthy that higher concentrations of chloroform occur in drinking water supplies (nationally as well as at Hanford) than were observed in the TEDF effluent.

Nitrate also seems to exhibit a seasonal trend. For example, concentrations appear to be lower in summer and fall. The decrease in nitrate could be related to increased phytoplankton production (i.e., depletion of nitrate due to increased phytoplankton growth), as suggested in Chou and Johnson (1996).

4.2 Random Spikes

Iron, manganese, and lead exhibit random concentration spikes that seem to occur at the same time. Arsenic also exhibits random concentration spikes, but these do not coincide with iron, manganese and lead. Chromium exhibits a random spike pattern that does not seem to coincide with any of the other metals. As previously noted (Chou and Johnson 1996), the iron excursions probably occur as primarily particulate phases (rust particles). It is not known if the other metals that seem to coincide with iron spikes (e.g., manganese and lead) are also primarily particulate in nature.

Chloride also exhibits random spike occurrences. This feature was previously noted in the initial variability study (Chou and Johnson 1996) and was attributed to regeneration of water softener resin columns. However, the total amount of chloride discharged decreased considerably after mid-1998 (see Figures 3a and 3b) because the aging 200 Areas power plants were shut down and replaced with five high-efficiency "package" boilers. Thus chloride concentrations in TEDF effluent should be greatly diminished in the future.

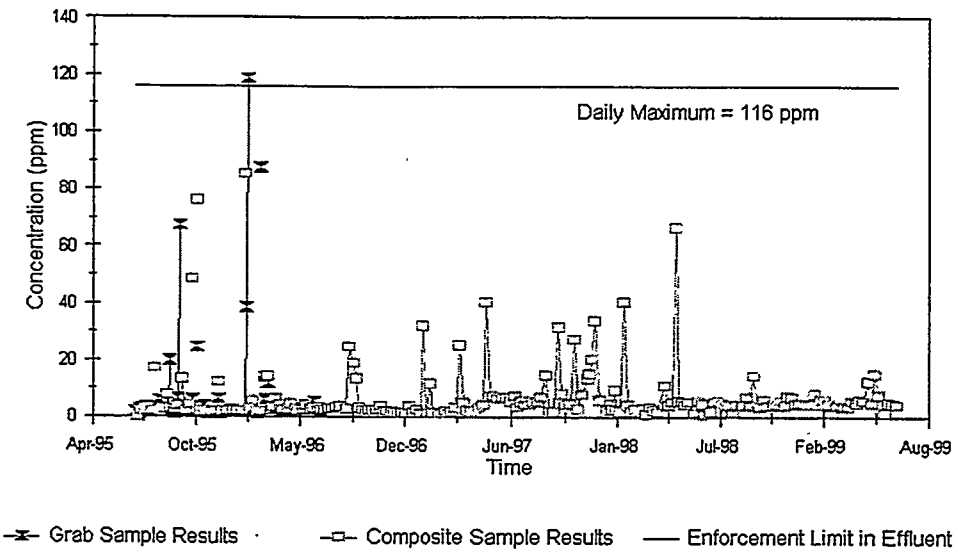


Figure 3a. TEDF Effluent Variability - Chloride Grab and Composite Sample Results

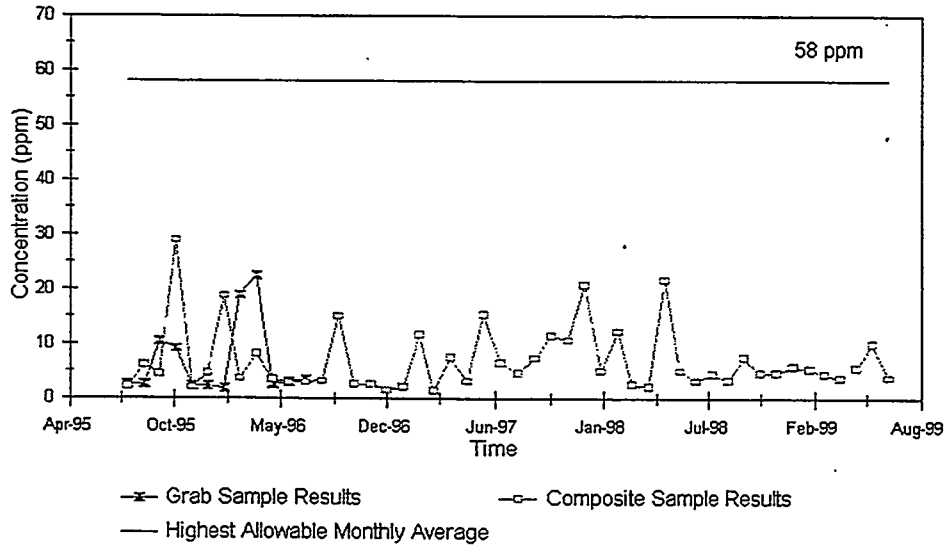


Figure 3b. TEDF Effluent Monitoring Result - Chloride Monthly Averages

Also, beginning in late 1997, the effluent flow rate shifted from a somewhat steady rate to more or less random fluctuations that approach or exceed 3,000 gpm for a few days or a week or two in duration for each event (Figure 4). These occurrences do not seem to coincide with either random increases in average metal or chloride concentrations discussed above. The dramatic change in effluent flow rate reflects operation of the 242-A Evaporator for short campaigns. This will be a common operational event for years into the future as Hanford Site cleanup continues. The primary effect of the periodic high-flow

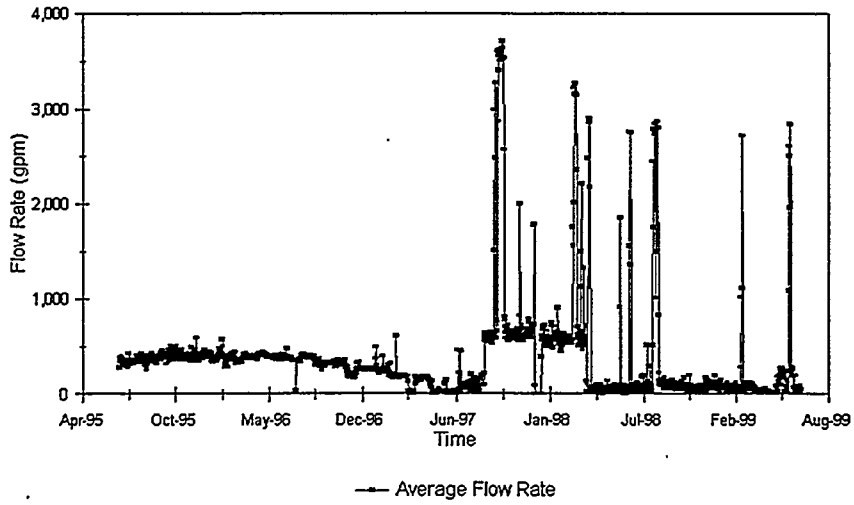


Figure 4. TEDF Continuous Monitoring Result - Daily Average Flow Rate

periods will be to produce an effluent that is essentially Columbia River water (i.e., condenser cooling water consisting of untreated Columbia River water from the 242-A Evaporator).

4.3 Steady or Stable Concentrations

Except for a short-term spike in gross beta in 1995, and one for gross alpha (which included some gross beta) in 1999, these two indicators exhibit relatively constant concentrations over time (see Appendix B) and are both similar to (but slightly higher) than gross alpha and gross beta concentrations reported for Columbia River water (see Section 5.4).

The average concentration of sulfate is somewhat higher than reported for the Columbia River (1998 annual average of ~9 mg/L in river water versus 16 mg/L in effluent, see Section 5.4). There does not seem to be a significant contribution of sulfate from operations over the 4-year period, although concentrations did reach as high as 25 mg/L in April 1999 and then declined. The small addition of sulfate is due to the use of sulfuric acid to neutralize wastewater from 222-S prior to discharge.

5.0 Summary of Statistical Results

A complete listing of results from the statistical evaluation and updates are provided in Appendix A and B. Statistical methods used are described in detail in the effluent variability study report (Chou and Johnson 1996). A summary of the salient features and findings of the statistical evaluation follows.

5.1 Standard Summary Statistics

The mean, standard deviation, 95% upper confidence limit (UCL) on mean concentration and 95% upper tolerance limit for detected analytes are provided (by season and by year) in the Appendix A (Table A-3). The variability is expressed as the coefficient of variation (CV) by season over the 4-year period is summarized in Table 4.

Chloride and iron have the largest variability of the detected analytes, as noted in the initial variability study. The high iron variability is attributed to random occurrences of particulate iron flushed from rusting cast iron pipe. The high chloride variability is due to the random disposal of ion exchange column regenerant. These transients were significantly reduced with closure of the 200 Area power plant facilities.

Sulfate exhibits the lowest CV. Except for two short-term releases previously discussed, gross beta and gross alpha exhibit relatively low variability.

5.2 Box and Whisker Plots

Box and whisker plots (Appendix B) of all detected analyte data for the 4-year period, segregated by season, provide a graphical indication of possible seasonal influences. Table 4 also provides a numerical summary of the same information.

Chloroform, nitrate and iron appear to vary seasonally. Chloroform concentration is highest in spring and summer (nitrate is highest in spring and winter), as previously discussed, and iron is highest in winter and spring. Gross alpha also appears to have a slight seasonal component with highest concentrations occurring in the spring and summer. No cause and effect relationship for the latter is evident at this time.

5.3 Exceedance Probability

The probability of exceeding a permit limit under normal operating conditions was calculated for each detected constituent. Results indicate there is a very low probability of exceeding any of the permit limits for the detected constituents of interest (see Table A-4, Appendix A). Except for iron, the exceedance probabilities were all less than one in one million. Iron had an exceedance probability of four in one thousand.

Table 4. Seasonal Effect and Variability Summary (July 1995 through June 1999) for TEDF Detected Constituents

Parameter	Season				Overall[e]
	Summer[a]	Fall[b]	Winter[c]	Spring[d]	
Volatile Organic Compounds: Grab Sample Results					
Total trihalomethanes					
Number of samples	38	35	48	67	178
Mean (ppb)	5.9	2.6	2.4	4.6	4.0
CV (%)	67	75	92	82	79
Chloroform					
Number of samples	70	33	67	67	237
Mean (ppb)	8.1	3.8	3.1	4.5	5.1
CV (%)	54	75	76	86	73
Total Metals: Composite Sample Results					
Iron[f]					
Number of samples	51	34	51	65	201
Mean (ppb)	96.3	83.5	110.0	137.1	110.8
CV (%)	102	89	71	77	85
Manganese[f]					
Number of samples	51	34	51	65	201
Mean (ppb)	6.4	6.1	5.8	7.1	6.4
CV (%)	71	77	44	111	76
Arsenic[g]					
Number of samples	38	25	38	49	150
Mean (ppb)	1.5	0.8	0.7	0.7	0.9
CV (%)	89	45	80	62	69
Anions: Composite Sample Results					
Chloride					
Number of samples	49	34	50	66	199
Mean (ppm)	6.0	9.8	6.6	6.6	7.0
CV (%)	103	160	201	144	152
Nitrate (as N)					
Number of samples	50	34	50	66	200
Mean (ppb)	167.6	147.9	178.0	201.4	178.1
CV (%)	62	44	29	47	46
Sulfate					
Number of samples	50	34	50	66	200
Mean (ppm)	13.6	13.5	13.1	17.9	14.9
CV (%)	27	27	44	46	36
Other Analyses: Composite Sample Results					
Total Dissolved Solids					
Number of samples	34	27	41	53	155
Mean (ppm)	80.9	85.2	78.3	90.5	84.2
CV (%)	31	25	44	30	33

Table 4. (contd)

Parameter	Season				Overall[e]
	Summer[a]	Fall[b]	Winter[c]	Spring[d]	
Other Analyses: Composite Sample Results					
Total Dissolved Solids					
Number of samples	34	27	41	53	155
Mean (ppm)	80.9	85.2	78.3	90.5	84.2
CV (%)	31	25	44	30	33
Radionuclides: Grab Sample Results					
Gross Alpha[h]					
Number of samples	47	33	63	67	210
Mean (pCi/L)	1.34	1.06	0.84	2.05	1.37
CV (%)	68	79	58	127	83
Gross Beta[i]					
Number of samples	38	31	68	57	194
Mean (ppb)	1.30	1.58	1.38	1.54	1.45
CV (%)	40	67	85	54	62

(a) Summer = July, August, and September of 1995, 1996, 1997, and 1998.
(b) Fall = October and November of 1995, 1996, 1997, and 1998.
(c) Winter = December, January, and February of 1995, 1996, 1997, and 1998.
(d) Spring = March, April, May, and June of 1996, 1997, 1998, and 1999.
(e) Overall = July 1995 through June 1999.
(f) Excluded data associated with iron excursions (April 7, 1996 and January 12, 1997).
(g) Data prior to July 1, 1996 were not used (mostly not detected).
(h) Excluded data collected between January 12, 1999 and February 17, 1999 due to PFP release.
(i) Excluded data collected prior to October 23, 1995 due to PUREX release.

5.4 Comparison of Effluent with River Water

The mean ±2 times the standard error of the mean of available constituents of interest in Columbia River water below Priest Rapids Dam and at the Richland pump house were compared with effluent data for calendar year (CY) 1998 (Tables 5a and 5b). The river water data were collected quarterly in connection with the Hanford Site Environmental Surveillance Program. Data for CY 1998 were selected for the primary comparison because analytical detection limits used for effluent and river water were the most comparable for most constituents during 1998. An important difference, however, is that gross alpha and gross beta detection limits were the most comparable for the earlier years (gross alpha and beta detection limits for effluent measurements increased in 1998 and 1999). Therefore, a comparison of radiological data for the years prior to 1998 is provided in Table 5c.

Tables 5a and 5b illustrate that concentrations of constituents of interest in river water account for most of the observed concentrations of these constituents in effluent. For example, natural levels in river water account for nearly all of the arsenic, nitrate, chromium, radium-226, uranium, gross alpha and gross beta in effluent. Deviations from this generalization are discussed as follows.

Table 5a. Concentrations of Selected Radionuclide Concentrations Measured in Columbia River Water Compared to Concentrations Measured in the 200 Area TEDF Effluent

Parameter	Calendar Year 1998		
	Number of Samples	Maximum	Average[a]
Gross Alpha (pCi/L)			
Columbia River Water at Priest Rapid Dam[b]	12	1.6	0.49 ± 0.26
Columbia River Water at Richland Pumphouse[b]	12	0.86	0.47 ± 0.12
200 Area TEDF Effluent	48	4.8	1.42 ± 0.24
Gross Beta (pCi/L)			
Columbia River Water at Priest Rapid Dam[b]	12	2.3	1.1 ± 0.36
Columbia River Water at Richland Pumphouse[b]	12	2.2	0.68 ± 0.50
200 Area TEDF Effluent	48	3.6	1.45 ± 0.14
Total Uranium (pCi/L)			
Columbia River Water at Priest Rapid Dam[b]	12	0.71	0.48 ± 0.056
Columbia River Water at Richland Pumphouse[b]	12	0.68	0.53 ± 0.040
200 Area TEDF Effluent[c]	48	0.41	0.24 ± 0.025
Radium-226 (pCi/L)			
Columbia River Water at Upstream of 300 Area TEDF[d]	1	<0.05	<0.05
Columbia River Water at Downstream of 300 Area TEDF[d]	1	<0.01	<0.01
200 Area TEDF Effluent	12	0.11	0.06 ± 0.016
Radium-228 (pCi/L)			
Columbia River Water at Upstream of 300 Area TEDF[d]	1	ND	ND
Columbia River Water at Downstream of 300 Area TEDF[d]	1	ND	ND
200 Area TEDF Effluent	12	ND	ND

(a) Averages are reported as mean concentration ± 2 standard error of the calculated mean.
(b) Obtained from Hanford Site Environmental Report for Calendar Year 1998 (Dirkes et al. 1999).
(c) Converted from µg/L to pCi/L by multiplying values reported by 0.68 pCi/µg (40 CFR 141, Vol. 56, No. 138, July 18, 1991, page 33068).
(d) Obtained from the 300 Area Treated Effluent Disposal Facility, Department of Natural Resources Land Lease Monitoring Report - September 1998 (WMH 1998).

Gross alpha and gross beta for CY 1998 (see Table 5a) appear to be slightly higher in effluent than in Columbia River water. However, for prior years there is no statistical difference between the mean values in effluent and river water (see Table 5c). The apparent higher effluent values for 1998 (see Table 5a) are an artifact of the higher detection limits used in 1998 for the effluent measurements. The mean of cadmium and lead was higher in effluent than in river water (see Table 5b). This is believed to be a result of higher detection limits for effluent (e.g., 0.01 µg/L for river water and 0.2 µg/L for effluent). The effluent detection limit for lead was higher for effluent than for river water (0.21 µg/L versus 0.01 µg/L), which contributed to the mean being higher for effluent than for the Columbia River water.

Table 5b. Concentrations of Selected Chemical Constituent Concentrations Measured in Columbia River Water Compared to Concentrations Measured in the 200 Area TEDF Effluent

Parameter	Calendar Year 1998		
	Number of Samples	Maximum	Average[a]
Chloride (ppm)			
Columbia River Water at Priest Rapid Dam[b]	15	1.09	0.925± 0.052
Columbia River Water at Richland Pumphouse[b]	40	2.06	1.053 ± 0.098
200 Area TEDF Effluent (all CY 1998 data)	48	66.48	6.389 ± 3.041
200 Area TEDF Effluent (spikes removed)[c]	44[c]	7.11[c]	3.965 ± 0.489[c]
Nitrate (as N) (ppm)			
Columbia River Water at Priest Rapid Dam[b]	15	0.161	0.096 ± 0.026
Columbia River Water at Richland Pumphouse[b]	40	0.494	0.124 ± 0.032
200 Area TEDF Effluent	48	0.443	0.177 ± 0.024
Sulfate (ppm)			
Columbia River Water at Priest Rapid Dam[b]	15	10.3	8.67 ± 0.63
Columbia River Water at Richland Pumphouse[b]	40	13.2	9.13 ± 0.48
200 Area TEDF Effluent	48	22.89	15.84 ± 1.24
Total Arsenic (ppb)			
Columbia River Water at Priest Rapid Dam[b]	17	0.96	0.709 ± 0.077
Columbia River Water at Richland Pumphouse[b]	42	1.102	0.721 ± 0.044
200 Area TEDF Effluent	48	5.91	1.029 ± 0.252
Total Cadmium (ppb)			
Columbia River Water at Priest Rapid Dam[b]	17	0.0698	0.027 ± 0.008
Columbia River Water at Richland Pumphouse[b]	42	0.0591	0.027 ± 0.004
200 Area TEDF Effluent[f]	48	0.61	0.208 ± 0.020
Total Chromium (ppb)			
Columbia River Water at Priest Rapid Dam[b]	17	8.112	0.838 ± 0.926
Columbia River Water at Richland Pumphouse[b]	42	1.016	0.324 ± 0.068
200 Area TEDF Effluent	48	2.4	0.976 ± 0.113
Total Lead (ppb)			
Columbia River Water at Priest Rapid Dam[b]	17	0.1672	0.100 ± 0.018
Columbia River Water at Richland Pumphouse[b]	42	0.2355	0.132 ± 0.015
200 Area TEDF Effluent	48	3.4	0.542 ± 0.170
Total Iron (ppb)			
Columbia River Water at Priest Rapids Dam[d]	10	24	<10
Columbia River Water at Richland Pumphouse[d]	4	<10	<10
200 Area TEDF Effluent	48	590	139 ± 34
200 Area TEDF Effluent (spikes removed)[e]	46[e]	313[e]	122 ± 25[e]

(a) Averages are reported as mean concentration ±2 standard error of the calculated mean.
(b) Obtained from Hanford Site Environmental Report for Calendar Year 1998 (Dirkes et al. 1999).
(c) Remove unrepresentative random spikes (chloride concentration >10 ppm).
(d) Obtained from Hanford Site Environmental Report for Calendar Year 1998 (Dirkes et al. 1999) based on USGS data (Table A.4).
(e) Remove unrepresentative random spikes (iron concentration >320 ppb).
(f) 42 samples analyzed during CY 1998 were non-detects.

Table 5c. Concentrations of Gross Alpha and Gross Beta Concentrations Measured in Columbia River Water Compared to Concentrations Measured in the 200 Area TEDF Effluent for Calendar Years 1995 to 1997

Parameter	Number of Samples	Maximum	Average[a]
Calendar Year 1995			
Gross Alpha (pCi/L)			
Columbia River Water at Priest Rapid Dam[b]	12	0.800	0.346 ± 0.158
Columbia River Water at Richland Pumphouse[b]	4	1.49	1.05 ± 0.30
200 Area TEDF Effluent (grab and composite combined)	42	2.9	0.72 ± 0.18
Gross Beta (pCi/L)			
Columbia River Water at Priest Rapid Dam[b]	12	3.36	1.46 ± 0.42
Columbia River Water at Richland Pumphouse[b]	4	3.63	1.95 ± 1.42
200 Area TEDF Effluent[c] (grab and composite combined)	26	2.10	0.85 ± 0.15
Calendar Year 1996			
Gross Alpha (pCi/L)			
Columbia River Water at Priest Rapid Dam[d]	13	1.1	0.38 ± 0.21
Columbia River Water at Richland Pumphouse[d]	13	1.7	0.43 ± 0.24
200 Area TEDF Effluent (grab and composite combined)	88	4.6	0.86 ± 0.14
Gross Beta (pCi/L)			
Columbia River Water at Priest Rapid Dam[d]	13	3.0	0.99 ± 0.47
Columbia River Water at Richland Pumphouse[d]	13	2.8	1.1 ± 0.49
200 Area TEDF Effluent (grab and composite combined)	88	3.4	1.23± 0.16
Calendar Year 1997			
Gross Alpha (pCi/L)			
Columbia River Water at Priest Rapid Dam[e]	12	0.82	0.35 ± 0.076
Columbia River Water at Richland Pumphouse[e]	12	2.2	0.58 ± 0.16
200 Area TEDF Effluent (grab only)	51	2.8	1.33 ± 0.12
Gross Beta (pCi/L)			
Columbia River Water at Priest Rapid Dam[e]	12	3.2	0.36 ± 0.40
Columbia River Water at Richland Pumphouse[e]	12	2.6	1.2 ± 0.21
200 Area TEDF Effluent (grab only)	51	5.3	1.65 ± 0.27

(a) Averages are reported as mean concentration ±2 standard error of the calculated mean.
(b) Obtained from Hanford Site 1995 Environmental Report (Dirkes and Hanf 1996).
(c) Excluded excursions from PUREX release (i.e., prior to October 23, 1995 data were removed).
(d) Obtained from Hanford Site 1996 Environmental Report (Dirkes and Hanf 1997).
(e) Obtained from Hanford Site 1997 Environmental Report (Dirkes and Hanf 1998).

Chloride and iron are higher in effluent than in Columbia River water for reasons previously discussed. The chloride concentration in effluent should approach the natural level in river water in the future. Iron spikes appear to be declining as well. It is also noteworthy that the maximum nitrate concentration observed for Columbia River water (0.49 mg/L) is close to the permit limit, suggesting that the permit limit should be raised.

In summary, the comparisons shown in Tables 5a and b indicate the current TEDF effluent is very similar to Columbia River water with a little added chloroform from the chlorinating process and some added chloride and iron (primarily particulate).

6.0 Justification for Permit Modification

The low detection frequency for several permit constituents, the small number of actual permit limit exceedances (i.e., two iron exceedances over the 4-year period) and low exceedance probabilities for detected constituents indicate that a significant reduction in the number and/or type of routine measurements can be made with no risk to the environment. The approach or strategy relies on (1) the use of gross alpha and gross beta in lieu of isotope specific analyses, (2) elimination of analytes with a history of non-detects, and (3) reduction in frequency of sampling where appropriate. The rationale for modifying the permit requirements by eliminating selected analytes and changing sampling frequencies is as follows.

6.1 Analyte Deletions

6.1.1 Radioisotopes

Gross alpha (and gross beta) measurements can account for the total radionuclide content of a sample. These total activity measurements can thus be used in lieu of routine isotopic analyses until an appropriate threshold level is exceeded.

The monitoring results for total radium (radium-226 + radium-228) and radium-226 for the 4-year period indicate that both were consistently less than 5 pCi/L and 1 pCi/L, respectively. (The detection limit for radium-226 is lower than for total radium.) The observed radium-226 in effluent is attributed to natural background sources that contribute to Columbia River water (see Table 5a) from upstream (e.g., uranium mining activities in the Spokane area). For the foregoing reasons, there is little to be gained by continuing routine total radium or radium-226 measurements. As long as gross alpha measurements are made, these isotope specific measurements can be eliminated from further routine monitoring.

The primary beta emitting radionuclides of concern are the moderately long-lived fission products, cesium-137 and strontium-90. The gross beta method can easily detect both of these radionuclides. The gross beta method is especially responsive for strontium-90 because two beta emissions occur for each strontium-90 disintegration. Thus gross beta activity or concentration should be double the strontium-90 concentration.

The mean gross beta for Columbia River water (CY 1998) is about 1 pCi/L (see Table 5a). As with the gross alpha, the gross beta of the effluent stream is very low, similar to the low natural background of Columbia River water (see Table 5a). The overall mean of the effluent data over 4-years is 1.45 pCi/L (see Table 4). This overall mean value includes a few elevated gross beta values due to strontium-90 that occurred during the 4-year period. The consistently low values, other than these short-term excursions, can be seen in the time series plots (Appendix B). The low and consistent background concentration indicates that gross beta should be a good indicator of any beta emitting radionuclides added to the waste stream at concentrations of regulatory concern. Thus strontium-90 and cesium-137 (gamma energy analysis) can be eliminated from the routine monitoring list.

6.1.2 WTPH-G/Oil and Grease

Petroleum products (hydrocarbons) are detected with the WTPH-G determination (light fraction or gasoline only). There were only 1 and 2 detected measurements out of a total of 37 analyses for WTPH-G and oil and grease, respectively, after June 1996 (see Table 3). The oil and grease method, which also involves a group determination of carbon compounds, was designed for biological lipids and mineral oils (APHA 1985, p. 496). These constituents are not likely to originate in Hanford facilities. Thus the oil and grease, as well as the WTPH-G analysis, can be removed from the analyte list.

6.1.3 Semivolatile Organic Analytes (Semi-VOA)

The semi-VOA group, phenol and bis(2-ethylhexyl)phthalate, can likewise be eliminated. Phenol was not detected in any of the samples analyzed during the study and bis(2-ethylhexyl)phthalate was detected only in 11 out of 200 composite sampling events in the 4-year period (see Table 3). Bis(2-ethylhexyl)phthalate is also ubiquitous (industrially) in plastics and is not associated with any past or current process or activity at Hanford.

6.1.4 Volatile Organic Analytes (VOAs)

Except for a few detections (6 out of a total 237 analyses or <3% for methylene chloride, a common laboratory contaminant), the only VOAs consistently detected in the TEDF wastestream are the trihalomethanes. As previously noted, these compounds, especially chloroform, are associated with the chlorination of raw water. The concentrations in TEDF discharges are lower than the national median concentrations for drinking water supplies. Thus detailed VOA analyses can also be deleted from routine monitoring because the source of the only significant detections (chloroform) is identified as a common disinfectant process (chlorination) used to sanitize potable water supplies. The resulting concentrations are at levels that poses no threat to groundwater.

6.1.5 Cyanide

Cyanide was detected in only 16 out of a total of 201 samples analyzed (see Table 3). The highest observed concentration was 27.2 ppb on May 12, 1997. This maximum value is only about half of the early warning value in effluent (50 ppb). It is also noteworthy that cyanide has not been detected since July 1997. Also, cyanide does not occur in any waste stream linked to TEDF. The only cyanide at Hanford is stored in single-shell tanks. However, the cyanide-containing waste from these tanks follows an entirely separate pathway, which is isolated from the TEDF waste streams. For the above reasons, cyanide can be eliminated from further routine monitoring.

6.2 Sampling Frequency and Type

6.2.1 Frequency

Results of the statistical evaluation indicated that an adequate effluent monitoring program could be achieved with fewer sampling events for the following reasons:

- a significant decline in the number and magnitude of spike concentrations of constituents that previously approached or exceeded permit limits (e.g., iron)
- elimination of the 200 Areas power plants as waste stream contributors of chloride and iron
- a bi-weekly sampling frequency at the PFP wastewater treatment plant (self monitoring), the most significant remaining contributor source
- statistical evaluation results (e.g., variability and exceedance probabilities) for the routine sampling phase (Appendix A and B) versus the more intensive sampling during the initial variability study (i.e., July 1995 through June 1996; Chou and Johnson 1996) are comparable. This suggests the less frequent sampling regime provided adequate temporal coverage.

The TEDF effluent monitoring program should now be viewed as an audit or periodic check on the efficacy of the contributor's effluent monitoring and control procedures. The audit function can therefore be accomplished with less frequent sample collections. Also, the original permit specified monthly rather than weekly grab sampling. Monthly is now deemed appropriate based on the 4-year period of observation and for the other reasons noted above.

6.2.2 Sample Type

Monthly results could be averaged over a quarter and the enforcement limits set on that basis rather than monthly averages of weekly grab samples or composite samples. The statistical evaluation also indicates there is little difference in observed (detected) analyte concentrations between a grab sample and a 24-hour composite sample. Thus a simple grab sample should provide the same temporal coverage as a composite run for only 24 hours where the objective is an overall monthly or quarterly average value.

7.0 Conclusions and Recommendations

Based on the updated statistical evaluation of effluent monitoring data for June 1995 through June 1999, it is concluded that the probability of exceeding permit limits under normal operating conditions is less than one in a million for all permitted constituents other than iron. The probability for the latter is four in one thousand. Except for iron (and two short-term releases of alpha and beta emitters), the current effluent is similar in composition to local drinking water (i.e., chlorinated Columbia River water). Results of the present study support the general findings and conclusions of the initial variability study (Chou and Johnson 1996).

As a result of the 4-year period of effluent monitoring and data evaluation, the TEDF effluent composition and variability of the effluent waste stream is now well defined. Accordingly, a revised or updated monitoring program that is specifically tailored to Hanford, and with fewer routine measurements, is deemed justified and appropriate.

Findings from the updated statistical evaluation of effluent monitoring data for TEDF lead to the following recommendations for a more efficient effluent monitoring program:

- Use gross alpha and gross beta in lieu of specific isotopic analyses (radium, cesium-137, and strontium-90) for routine monitoring. If the drinking water standards for gross alpha (15 pCi/L) or gross beta (50 pCi/L) are exceeded, then isotope specific measurements and an investigation of the exceedance can be conducted. Sufficient sample volume should be collected and archived to allow a later rerun if the gross count standards are exceeded.

- Eliminate unnecessary measurements. For example, VOAs, phenols and bis(2-ethylhexyl)phthalate, WTPH-G, oil and grease, and cyanide have been essentially undetected and are also unlikely based on process knowledge. Also, chloroform, the only VOA with significant or consistent detections, is a byproduct of a common water treatment process used in drinking water systems.

- Revise the nitrate limit to be consistent with groundwater protection standards (i.e., drinking water standard of 10 mg/L as nitrogen). The existing standard is too close to the background concentrations of nitrate in Columbia River water from agricultural activities.

- Use a roughing pre-filter or fine mesh screen to remove large particulates from the effluent samples collected for metal analyses. Rust particles are an inevitable consequence of the aging piping system. However, it is the colloidal and solute fractions that are of importance for groundwater protection purposes and not the flakes or rust particles that can be filtered out by the soil column. Thus it is not appropriate to include the large particles in the analysis of total iron (or other metals) by dissolving the large particulates for a "total" analysis. A more realistic effluent water sample is one that has been passed through a pre-filter or fine mesh screen prior to acidification and analysis. This modification in the sample collection procedure will more closely assess the potential impact on groundwater quality than the current procedure (digestion or dissolution of all particulates).

- Eliminate the 24-hour composite and use only monthly grab samples to calculate a quarterly average for permit compliance purposes.

- Add low level tritium (once per year) as an effluent tracer to detect the presence of effluent in the TEDF groundwater monitoring network wells (additional details are discussed in the groundwater monitoring plan for TEDF).

The recommended modifications noted above are shown in Table 6a together with the current program and the original permit-specified conditions. Table 6b summarizes the detection frequencies, variability and exceedance probabilities.

Implementation of the proposed changes (see Table 6a) will result in a more site-specific monitoring program and will improve the overall efficiency and cost effectiveness of TEDF monitoring activities.

Table 6a. Current and Proposed Effluent Monitoring Plan for the 200 Area TEDF

Parameter	Permit Requirement	Current Sampling Program	Proposed Effluent Monitoring Plan
Volatile Organic Compounds			
Carbon tetrachloride Methylene chloride 1,1,1,-Trichloroethane Total trihalomethanes Bromoform Bromodichloromethane Chloroform Dibromochloromethane	Grab 4/month	Grab 4/month	Eliminate
Semivolatile Organic Compounds			
Bis(2-ethylhexyl)phthalate Phenol	Composite 4/month	Composite 4/month	Eliminate
Metals			
Arsenic Cadmium Chromium Lead Mercury	Unfiltered, Composite 4/month	Unfiltered, Composite 4/month	Filtered, Grab 1/month
Iron Manganese	Unfiltered, Composite 1/month	Unfiltered, Composite 4/month	Filtered, Grab 1/month
Anions			
Chloride Nitrate Sulfate	Composite 1/month	Composite 4/month	Grab 1/month
Other Analyses			
Cyanide	Grab 4/month	Grab 4/month	Eliminate
WTPH-G	Grab 1/month	Grab 1/month	Eliminate
Oil and grease	Grab 1/month	Grab 1/month	Eliminate
Total dissolved solids	Composite 1/month	Composite 4/month	Grab 1/month
Other Analyses			
Gross alpha Gross beta Total radium (Radium-226 and Radium-228) Radium – 226 Tritium (Low-level)	Grab 1/month Grab 1/month Grab 1/month Grab 1/month Not required	Grab 4/month Grab 4/month Grab 1/month Grab 1/month ---	Grab 1/month Grab 1/month Eliminate Eliminate Grab 1/year
In-Line Monitoring			
Flow Specific conductivity pH	Continuous	Continuous	Continuous

Table 6b. Summary of TEDF Monitoring Results Based on Effluent Data Collected from July 1995 through June 1999

Parameter	Detection Status[a]			Variability[b] CV (%)	Exceedance Probability[c]
	Total Analyses	Detected Analyses (Grab)	Detected Analyses (Composite)		
Volatile Organic Compounds					
Carbon tetrachloride	237	0			
Methylene chloride	237	6			
1,1,1,-Trichloroethane	237	0			
Total trihalomethanes	237	184	NA	79%	<1 in 1,000,000
Bromoform	237	0			
Bromodichloromethane	237	28			
Chloroform	237	193		73%	<1 in 1,000,000
Dibromochloromethane	237	0			
Semivolatile Organic Compounds					
Bis(2-ethylhexyl)phthalate	288	15	11		
Phenol	288	0	0		
Total Metals					
Arsenic	289	4	111	69%	<1 in 1,000,000
Cadmium	289	0	19		
Chromium	289	9	51		
Lead	289	12	99		
Mercury	289	21	26		
Iron[d]	291	88	203	85%	4 in 1,000
Manganese	291	51	76	76%	<1 in 1,000,000
Anions					
Chloride	288	88	199	152%	<1 in 1,000,000
Nitrate	288	84	196	46%	<1 in 1,000,000
Sulfate	288	88	200	36%	<1 in 1,000,000
Other Analyses					
Cyanide	201	16	NA		
WTPH-G	49	5	NA		
Oil and grease	112	23	27		
Total dissolved solids	164	9	155	33%	<1 in 1,000,000

Table 6b. (contd)

Parameter	Detection Status[a]			Variability[b] CV (%)	Exceedance Probability[c]
	Total Analyses	Detected Analyses (Grab)	Detected Analyses (Composite)		
Other Analyses					
Gross alpha	254	112	26	83%	<1 in 1,000,000
Gross beta	254	112	36	62%	<1 in 1,000,000
Total radium (Radium-226 and Radium-228)	49	0	NA		
Radium – 226	49	19	NA		
In-Line Monitoring					
Flow Specific conductivity pH	NA	NA	NA	NA	NA

(a) Obtained from Table 2 Detection Frequency Summary (based on analyses performed from July 1995 through June 1999).
(b) Variability is expressed as coefficient of variation (CV) and is obtained from Table 4.
(c) Obtained from Table A-4 (Appendix A).
(d) Highest allowable average monthly concentration of 258 ppb was exceeded twice (April 7, 1996 and January 12, 1997) during the study period (July 1995 through June 1999).

8.0 References

40 CFR 141, Code of Federal Regulations, Title 40, Vol. 56, No. 138, July 18, 1991, p. 33068. *National Primary Drinking Water Regulations, Radionuclides.*

APHA. 1985. *Standard Methods for the Examination of Water and Wastewater*, Sixteenth Edition. American Public Health Association, Washington, D.C.

Chou, C. J. and V. G. Johnson. 1996. *Effluent Variability Study Results for the 200 Area Treated Effluent Disposal Facility.* WHC-SD-LEF-EV-001, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Dirkes, R. L. and R. W. Hanf (eds.). 1996. *Hanford Site 1995 Environmental Report.* PNNL-11139, Pacific Northwest National Laboratory, Richland Washington.

Dirkes, R. L. and R. W. Hanf (eds.) 1997. *Hanford Site 1996 Environmental Report.* PNNL-11472, Pacific Norwest National Laboratory, Richland Washington.

Dirkes, R. L. and R. W. Hanf (eds.) 1998. *Hanford Site 1997 Environmental Report.* PNNL-11795, Pacific Northwest National Laboratory, Richland Washington.

Dirkes, R. L., R. W. Hanf, and T. M. Poston. 1999. *Hanford Site Environmental Report for Calendar Year 1998.* PNNL-12088, Pacific Northwest National Laboratory, Richland, Washington.

Ecology. 1995. *State Waste Discharge Permit No. ST 4502.* U.S. Department of Energy, Richland Operations Office, Washington Department of Ecology, Olympia, Washington, April 18, 1995.

EPA-600/4-79-020. 1983. "Section 160.1, Physical Properties: Residue, Filterable, Gravimetric, Dried at 180°C." *Methods for Chemical Analysis of Water and Wastes.* U.S. Environmental Protection Agency, Washington, D.C.

EPA-600/4-79-020. 1983. "Section 335.3, Inorganic, Non-Metallics, Cyanide, Total, Colorimetric, Automated UV." *Methods for Chemical Analysis of Water and Wastes.* U.S. Environmental Protection Agency, Washington, D.C.

EPA-600/R-93-100. 1993. "Section 300.0, Determination of Inorganic Anions by Ion Chromatography - Revision 2.1." *Methods for the Determination of Inorganic Substances in Environmental Samples.* U.S. Environmental Protection Agency, Washington, D.C.

EPA-600/R-94-111. 1994. "Section 200.8, Determination of Trace Elements in Water and Wastes by Inductively Coupled Plasma - Mass Spectrometry - Revision 5.4." *Methods for the Determination of Metals in Environmental Samples - Supplement I.* U.S. Environmental Protection Agency, Washington, D.C.

RCW 90.48, as amended, Title 90, Chapter 105. "Water Pollution Control Act." *Revised Code of Washington*. Olympia, Washington.
SW-846. 1986. *Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods, 3rd ed.* Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

WAC 173-200. "Water Quality Standards for Ground Waters of the State of Washington." *Washington Administrative Code*. Olympia, Washington.

WAC 173-216. "State Waste Discharge Program." *Washington Administrative Code*. Olympia, Washington.

WHC. 1995. *200 Area TEDF Effluent Sampling and Analysis Plan*. WHC-SD-LEF-PLN-002, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

WMH. 1998. *Department of Natural Resources land Lease Monitoring Report – September 1998*. WMH-98651383.31, Waste Management Federal Services Hanford, Inc., Richland, Washington.

Appendix A

Statistical Data Tables

Appendix A

Statistical Data Tables

This appendix contains the results of statistical computations performed on the raw effluent monitoring data collected from July 1995 through June 1999. A description of statistical methods used and definitions of terms is available in the precursor to this report (Chou and Johnson 1996).

The statistical data tables contained herein are updated versions of tables presented in the initial variability study report (Chou and Johnson 1996) and are designed to be stand-alone tables. For example, footnotes are provided at either the bottom of the page or at the end of each table and provide additional clarification or references to other sources and explain how anomalous data were handled. The monthly average concentrations of permit required analyte measurements over the 4-year period are tabulated in Table A-2. It should be noted in calculating these averages that measurements below the practical quantification levels were not replaced by zero as required for the Discharge Monitoring Report.

The data are arranged by year, sample type (grab versus composite) and by season (Fall, Winter, Spring or Summer). This format is a continuation of the format used for the variability study report referenced above. The original intent was to identify variations that might be attributable to either sample type or season of the year. The individual years are shown separately since changes in analytical methods and operations that occurred during the 4-year period of data collection could influence the observed variability.

It should also be noted that both grab and 24-hour composites were collected and a more intensive sampling frequency was performed only during the first year for the effluent variability study. Thereafter sampling no longer included the samples and analytes required solely for the variability study. After June 1995 only routine monitoring to demonstrate compliance with the discharge limits was required. Accordingly, only one sample type was collected, depending on the analyte group involved. For example, grab samples are no longer collected for metals and anions.

A.1 References

Chou, C. J. and V. G. Johnson. 1996. *Effluent Variability Study Results for the 200 Area Treated Effluent Disposal Facility*. WHC-SD-LEF-EV-001, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

WAC 173-200. "Water Quality Standards for Ground Waters of the State of Washington." *Washington Administrative Code*. Olympia, Washington.

Table A-1. Detection[a] Status of Constituents Analyzed for the TEDF Effluent Variability Study (July 1995 through June 1996)

Parameter	Grab Samples				Composite Samples			
	Summer	Fall	Winter	Spring	Summer	Fall	Winter	Spring
Volatile Organic Compound								
Carbon tetrachloride	0/32	0/8	0/29	0/17	---	---	---	---
Methylene chloride	0/32	0/8	0/29	0/17	---	---	---	---
1,1,1, - Trichloroethane	0/32	0/8	0/29	0/17	---	---	---	---
Total trihalomethanes:	32/32	8/8	29/29	17/17	---	---	---	---
Bromoform	0/32	0/8	0/29	0/17	---	---	---	---
Bromodichloromethane	17/32	0/8	0/29	2/17	---	---	---	---
Chloroform	32/32	8/8	29/29	17/17	---	---	---	---
Dibromochloromethane	0/32	0/8	0/29	0/17	---	---	---	---
Semivolatile Organic Compound								
Bis(2-ethylhexyl)pathalate	5/32	2/8	4/30	4/17	0/12	1/9	2/12	2/17
Phenol	0/32	0/8	0/30	0/17	0/12	1/9	0/12	0/17
Total Metals								
Arsenic	3/32	0/8	0/30	0/17	4/13	0/9	0/12	0/17
Cadmium	0/32	0/8	0/30	0/17	0/13	0/9	0/12	1/17
Chromium	0/32	0/8	5/30	3/17	1/13	0/9	0/12	1/17
Lead	7/32	0/8	1/30	3/17	3/13	1/9	0/12	5/17
Mercury	7/32	4/8	10/30	0/17	0/13	4/9	4/12	0/17
Iron	32/32	8/8	30/30	17/17	13/13	9/9	12/12	17/17
Manganese	20/32	3/8	17/30	10/17	3/13	2/9	9/12	9/17
Anions								
Chloride	32/32	8/8	30/30	17/17	11/12	9/9	12/12	17/17
Nitrate (as N)	28/32	8/8	30/30	17/17	11/12	9/9	11/12	17/17
Sulfate	32/32	8/8	30/30	17/17	12/12	9/9	12/12	17/17
Other Analyses								
Cyanide	2/13	4/8	1/13	2/16	---	---	---	---
WTPH-G	0/3	0/2	0/3	4/4	---	---	---	---
Oil and grease	2/4	0/2	2/9	17/17	6/13	1/1	3/12	17/17
Total dissolved solids	---	1/1	3/3	4/4	3/3	2/2	3/3	4/4
Gross Alpha	9/9	7/8	26/30	9/17	3/3	7/8	9/12	7/16
Gross Beta	9/9	8/8	30/30	14/17	3/3	8/8	11/12	14/16
Total radium	0/3	0/2	0/3	0/4	---	---	---	---
Radium-226	1/3	0/2	0/3	0/4	---	---	---	---

(a) Numbers in the table denote detection frequency (= the number of times an analyte is detected over the total number of analyses performed during the period from July 1995 through June 1996) where "---" indicates analysis is not required by the permit.

Table A-1. Detection[a] Status of Constituents Analyzed for the TEDF Effluent Variability Study (July 1996 through June 1997)

Parameter	Grab Samples				Composite Samples			
	Summer	Fall	Winter	Spring	Summer	Fall	Winter	Spring
Volatile Organic Compound								
Carbon tetrachloride	0/13	0/9	0/13	0/17	---	---	---	---
Methylene chloride	0/13	0/9	0/13	0/17	---	---	---	---
1,1,1, - Trichloroethane	0/13	0/9	0/13	0/17	---	---	---	---
Total trihalomethanes:	13/13	6/9	2/13	14/17	---	---	---	---
Bromoform	0/13	0/9	0/13	0/17	---	---	---	---
Bromodichloromethane	0/13	0/9	0/13	0/17	---	---	---	---
Chloroform	13/13	7/9	2/13	14/17	---	---	---	---
Dibromochloromethane	0/13	0/9	0/13	0/17	---	---	---	---
Semivolatile Organic Compound								
Bis(2-ethylhexyl)pathalate	---	---	---	---	1/13	1/9	0/13	1/17
Phenol	---	---	---	---	0/13	0/9	0/13	0/17
Total Metals								
Arsenic	---	---	---	---	3/13	1/9	4/13	9/17
Cadmium	---	---	---	---	0/13	1/9	2/13	2/17
Chromium	---	---	---	---	1/13	0/9	4/13	6/17
Lead	---	---	---	---	0/13	6/9	7/13	17/17
Mercury	---	---	---	---	0/13	1/9	2/13	8/17
Iron	---	---	---	---	13/13	9/9	15/15	17/17
Manganese	---	---	---	---	4/13	3/9	5/15	3/17
Anions								
Chloride	---	---	---	---	13/13	9/9	13/13	17/17
Nitrate (as N)	---	---	---	---	12/13	9/9	13/13	17/17
Sulfate	---	---	---	---	13/13	9/9	13/13	17/17
Other Analyses								
Cyanide	2/13	1/9	2/13	2/17	---	---	---	---
WTPH-G	1/3	0/2	0/3	0/4	---	---	---	---
Oil and grease	1/3	0/2	0/3	0/4	---	---	---	---
Total dissolved solids	---	---	---	---	6/6	9/9	13/13	17/17
Gross Alpha	7/13	3/9	5/13	8/17	---	---	---	---
Gross Beta	6/13	7/9	5/13	5/17	---	---	---	---
Total radium	0/3	0/2	0/3	0/4	---	---	---	---
Radium-226	0/3	2/2	1/3	3/4	---	---	---	---

(a) Numbers in the table denote detection frequency (= the number of times an analyte is detected over the total number of analyses performed during the period from July 1996 through June 1997 where "---" indicates analysis is not required by the permit.

Table A-1. Detection[a] Status of Constituents Analyzed for the TEDF Effluent Variability Study (July 1997 through June 1998)

Parameter	Grab Samples				Composite Samples			
	Summer	Fall	Winter	Spring	Summer	Fall	Winter	Spring
Volatile Organic Compound								
Carbon tetrachloride	0/13	0/8	0/13	0/16	---	---	---	---
Methylene chloride	0/13	0/8	0/13	1/16	---	---	---	---
1,1,1, - Trichloroethane	0/13	0/8	0/13	0/16	---	---	---	---
Total trihalomethanes:	10/13	3/8	1/13	10/16	---	---	---	---
Bromoform	0/13	0/8	0/13	0/16	---	---	---	---
Bromodichloromethane	0/13	0/8	0/13	0/16	---	---	---	---
Chloroform	10/13	3/8	1/13	12/16	---	---	---	---
Dibromochloromethane	0/13	0/8	0/13	0/16	---	---	---	---
Semivolatile Organic Compound								
Bis(2-ethylhexyl)pathalate	---	---	---	---	1/13	0/8	1/13	0/16
Phenol	---	---	---	---	0/13	0/8	0/13	0/16
Total Metals								
Arsenic	---	---	---	---	11/13	7/8	11/13	15/16
Cadmium	---	---	---	---	0/13	1/8	2/13	2/16
Chromium	---	---	---	---	1/13	0/8	4/13	12/16
Lead	---	---	---	---	6/13	1/8	6/13	9/16
Mercury	---	---	---	---	0/13	0/8	2/13	1/16
Iron	---	---	---	---	13/13	8/8	13/13	16/16
Manganese	---	---	---	---	5/13	1/8	2/13	4/16
Anions								
Chloride	---	---	---	---	13/13	8/8	13/13	16/16
Nitrate (as N)	---	---	---	---	13/13	8/8	13/13	16/16
Sulfate	---	---	---	---	13/13	8/8	13/13	16/16
Other Analyses								
Cyanide	0/13	0/8	0/13	0/16	---	---	---	---
WTPH-G	0/3	0/2	0/3	0/4	---	---	---	---
Oil and grease	0/3	0/2	0/3	0/4	---	---	---	---
Total dissolved solids	---	---	---	---	13/13	8/8	13/13	16/16
Gross Alpha	2/13	1/8	3/13	7/16	---	---	---	---
Gross Beta	0/13	4/8	1/13	2/16	---	---	---	---
Total radium	0/3	0/2	0/3	0/4	---	---	---	---
Radium-226	3/3	1/2	1/3	2/4	---	---	---	---

(a) Numbers in the table denote detection frequency (= the number of times an analyte is detected over the total number of analyses performed during the period from July 1997 through June 1998 where "---" indicates analysis is not required by the permit.

Table A-1. Detection[a] Status of Constituents Analyzed for the TEDF Effluent Variability Study (July 1998 through June 1999)

Parameter	Grab Samples				Composite Samples			
	Summer	Fall	Winter	Spring	Summer	Fall	Winter	Spring
Volatile Organic Compound								
Carbon tetrachloride	0/12	0/8	0/12	0/17	---	---	---	---
Methylene chloride	1/12	0/8	1/12	3/17	---	---	---	---
1,1,1, - Trichloroethane	0/12	0/8	0/12	0/17	---	---	---	---
Total trihalomethanes:	11/12	8/8	10/12	10/17	---	---	---	---
Bromoform	0/12	0/8	0/12	0/17	---	---	---	---
Bromodichloromethane	2/12	2/8	5/12	0/17	---	---	---	---
Chloroform	11/12	8/8	11/12	15/17	---	---	---	---
Dibromochloromethane	0/12	0/8	0/12	0/17	---	---	---	---
Semivolatile Organic Compound								
Bis(2-ethylhexyl)pathalate	---	---	---	0/1	0/12	0/8	0/12	1/16
Phenol	---	---	---	0/1	0/12	0/8	0/12	0/16
Total Metals								
Arsenic	---	---	---	1/1	12/12	8/8	10/12	16/16
Cadmium	---	---	---	0/1	1/12	3/8	1/12	3/16
Chromium	---	---	---	1/1	9/12	4/8	2/12	6/16
Lead	---	---	---	1/1	10/12	6/8	9/12	13/16
Mercury	---	---	---	0/1	0/12	0/8	2/12	2/16
Iron	---	---	---	1/1	12/12	8/8	12/12	16/16
Manganese	---	---	---	1/1	7/12	2/8	8/12	9/16
Anions								
Chloride	---	---	---	1/1	12/12	8/8	12/12	16/16
Nitrate (as N)	---	---	---	1/1	12/12	7/8	12/12	15/16
Sulfate	---	---	---	1/1	12/12	8/8	12/12	16/16
Other Analyses								
Cyanide	0/12	0/8	0/12	0/17	---	---	---	---
WTPH-G	0/3	0/2	0/3	0/5	---	---	---	---
Oil and grease	0/3	1/2	0/3	0/5	---	---	---	---
Total dissolved solids	---	---	---	1/1	12/12	8/8	12/12	16/16
Gross Alpha	4/12	2/8	8/12	11/17	---	---	---	---
Gross Beta	4/12	3/8	6/12	8/17	---	---	---	---
Total radium	0/3	0/2	0/3	0/5	---	---	---	---
Radium-226	1/3	1/2	1/3	2/5	---	---	---	---

(a) Numbers in the table denote detection frequency (= the number of times an analyte is detected over the total number of analyses performed during the period from July 1998 through June 1999 where "---" indicates analysis is not required by the permit.

Table A-2. Monthly Averages[a] for Detected Analytes

Parameter	July 1995	Aug 1995	Sept 1995	Oct 1995	Nov 1995	Dec 1995	Jan 1996	Feb 1996	Mar 1996	Apr 1996	May 1996	June 1996
Chloroform[b]												
Grab	14.00	9.64	8.64	8.25	6.75	5.60	4.20	4.44	8.40	7.50	12.50	8.75
Composite	---	---	---	---	---	---	---	---	---	---	---	---
Total trihalomethanes[b]												
Grab	NA	NA	NA	NA	NA	NA	NA	4.44	8.40	7.85	12.50	8.75
Composite	---	---	---	---	---	---	---	---	---	---	---	---
Iron[c]												
Grab	83.70	64.45	96.73	94.00	62.00	98.30	93.64	84.78	130.40	535.75	118.00	89.50
Composite	80.75	42.00	25.60	95.80	33.75	106.75	79.20	117.67	156.40	891.25	106.25	83.50
Manganese[d, e]												
Grab	7.80	5.45	7.36	5.25	6.00	4.89	4.91	4.38	4.40	15.50	5.25	5.75
Composite	6.25	4.25	4.00	6.00	4.00	6.75	6.40	4.67	4.60	14.00	6.00	5.25
Arsenic[f, e]												
Grab	0.22	0.17	0.25	0	0	0	0	0	0	0.75	1.50	1.50
Composite	0	0.43	1.08	0	0	0	0	0	0	0.75	1.50	1.50
Lead[g, e]												
Grab	0	1.45	0.35	0	0	0.16	0	0	0	0.50	0.58	0.55
Composite	0	1.33	0.48	0.20	0	0	0	0	0.20	0.73	0.53	0.50
Chloride[h]												
Grab	2.47	2.50	10.46	9.15	2.35	2.36	1.93	18.98	22.48	2.49	3.07	3.45
Composite	2.07	6.03	4.34	28.93	2.01	4.64	18.75	3.58	8.04	3.44	2.90	2.93
Nitrate[i] (as N)												
Grab	53.8	48.1	86.4	110.0	112.8	160.8	140.2	222.8	160.8	169.5	109.3	166.0
Composite	115.0	57.0	92.0	98.0	121.8	180.8	153.4	173.3	182.8	176.3	105.5	168.5
Sulfate[j] (ppm)												
Grab	11.81	10.47	12.05	12.24	11.40	11.88	11.31	9.89	10.67	24.28	12.65	15.00
Composite	9.24	10.91	12.80	11.64	11.30	10.24	12.04	10.20	11.32	22.55	12.20	20.95
TDS[k] (ppm)												
Grab	---	---	---	---	129	84	56	46	121	141	70	71
Composite	61.5	104	115	99	125	64	67	75	123	127	72	91
Gross Alpha[l] (pCi/L)												
Grab	0.34	0.38	1.22	0.97	0.36	0.54	0.37	0.53	1.15	1.03	1.05	1.12
Composite	---	---	0.87	1.12	0.29	0.56	0.37	1.18	0.88	0.96	1.30	0.75
Gross Beta[m] (pCi/L)												
Grab	---	---	42.83[n]	25.33[n]	0.79	0.98	0.50	1.37	1.84	1.44	1.32	0.92
Composite	---	---	30.63[n]	25.88[n]	0.67	0.86	0.56	2.04	1.31	1.43	1.55	1.31

Table A-2. (contd)

Parameter	July 1996	Aug 1996	Sept 1996	Oct 1996	Nov 1996	Dec 1996	Jan 1997	Feb 1997	Mar 1997	Apr 1997	May 1997	June 1997
Chloroform[b]												
Grab	7.80	13.00	7.25	4.00	0.90	0	0.93	0.93	1.54	4.00	5.25	4.50
Composite	---	---	---	---	---	---	---	---	---	---	---	---
Total trihalomethanes[b]												
Grab	7.80	13.00	7.25	4.00	0.90	0	1.00	1.00	1.54	4.00	5.25	4.50
Composite	---	---	---	---	---	---	---	---	---	---	---	---
Iron[c]												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	66.80	47.00	54.25	82.00	71.00	100.60	526.00	121.33	111.40	99.50	178.50	70.5
Manganese[d, e]												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	5.36	5.00	5.75	6.20	4.75	6.20	16.29	5.00	5.40	5.00	8.35	5.00
Arsenic[f, e]												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	1.50	3.63	1.50	0.84	0.43	0.46	0.40	1.23	0.52	0.45	0.40	0.50
Lead[g, e]												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	0.50	0.50	0.50	0.38	0.30	0.44	1.03	0.60	0.58	0.35	1.88	0.43
Chloride[h]												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	3.09	14.96	2.58	2.57	1.53	2.06	11.54	1.46	7.53	3.12	15.38	6.48
Nitrate[i] (as N)												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	274.2	239.8	322.8	242.4	171.0	177.0	178.8	217.0	230.0	279.5	392.5	212.8
Sulfate[j] (ppm)												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	12.93	13.71	12.38	11.80	8.98	8.63	8.71	9.64	11.56	13.93	24.08	25.49
TDS[k] (ppm)												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	38	88	63.25	64	89.25	49.8	65.5	67.75	64.2	95.25	99.25	105.75
Gross Alpha[l] (pCi/L)												
Grab	1.75	0.70	0.89	1.04	0.26	1.13	1.26	0.88	1.42	1.07	1.83	1.19
Composite	---	---	---	---	---	---	---	---	---	---	---	---
Gross Beta[m] (pCi/L)												
Grab	1.20	1.00	0.68	1.36	1.98	1.60	1.28	1.24	2.16	1.25	1.60	2.31
Composite	---	---	---	---	---	---	---	---	---	---	---	---

Table A-2. (contd)

Parameter	July 1997	Aug 1997	Sept 1997	Oct 1997	Nov 1997	Dec 1997	Jan 1998	Feb 1998	Mar 1998	Apr 1998	May 1998	June 1998
Chloroform[b]												
Grab	3.80	4.73	0.95	1.45	1.18	1.12	0.90	0.90	1.05	2.00	4.50	2.20
Composite	---	---	---	---	---	---	---	---	---	---	---	---
Total trihalomethanes[b]												
Grab	3.80	4.73	0.95	1.50	1.25	1.20	1.00	1.00	1.65	2.05	4.50	2.60
Composite	---	---	---	---	---	---	---	---	---	---	---	---
Iron[c]												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	217.40	72.50	64.00	63.00	35.25	82.46	91.23	41.80	99.50	149.85	92.65	254.00
Manganese[d, e]												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	11.00	5.00	5.25	11.00	5.00	5.36	4.55	4.55	4.40	5.76	5.15	23.90
Arsenic[f, e]												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	0.56	0.58	0.65	0.73	0.80	0.82	0.83	0.78	0.65	0.83	0.93	1.14
Lead[g, e]												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	0.90	0.30	0.20	0.20	0.20	0.28	0.35	0.23	0.20	0.55	0.45	0.60
Chloride[h]												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	4.55	7.32	11.39	10.60	20.59	5.00	12.16	2.57	2.06	21.69	5.01	3.09
Nitrate[i] (as N)												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	164.8	151.8	145.3	134.5	153.3	168.8	236.0	185.5	204.5	323.3	212.0	146.5
Sulfate[j] (ppm)												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	16.28	15.59	10.99	13.80	12.48	11.63	9.50	11.43	11.38	19.17	18.24	13.38
TDS[k] (ppm)												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	84.4	92.25	67.75	76.75	91.5	80.6	131.5	82.75	83	119.75	95	74.5
Gross Alpha[l] (pCi/L)												
Grab	1.18	1.13	1.73	1.53	1.20	1.48	1.03	0.98	1.18	1.33	1.19	1.72
Composite	---	---	---	---	---	---	---	---	---	---	---	---
Gross Beta[m] (pCi/L)												
Grab	1.41	1.68	1.48	1.88	2.26	1.30	1.30	1.28	1.50	1.98	1.33	1.23
Composite	---	---	---	---	---	---	---	---	---	---	---	---

Table A-2. (contd)

Parameter	July 1998	Aug 1998	Sept 1998	Oct 1998	Nov 1998	Dec 1998	Jan 1999	Feb 1999	Mar 1999	Apr 1999	May 1999	June 1999
Chloroform[b]												
Grab	6.75	3.10	5.50	3.25	4.25	4.50	5.00	2.35	2.75	1.48	4.23	1.94
Composite	---	---	---	---	---	---	---	---	---	---	---	---
Total trihalomethanes[b]												
Grab	7.05	3.30	5.50	3.25	4.55	4.83	5.40	2.56	2.75	1.60	4.35	2.32
Composite	---	---	---	---	---	---	---	---	---	---	---	---
Iron[c]												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	224.68	105.33	150.50	90.60	194.25	178.50	127.98	205.0	200.75	128.33	152.83	161.15
Manganese[d, e]												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	11.58	6.88	6.50	4.40	7.09	6.54	4.64	9.26	5.06	4.40	9.27	11.37
Arsenic[f, e]												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	1.02	2.36	1.48	1.00	0.82	0.53	0.50	0.90	0.69	0.87	0.58	0.78
Lead[g, e]												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	1.35	0.40	0.83	0.36	0.74	0.46	0.25	0.42	0.28	0.26	0.89	1.70
Chloride[h]												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	4.39	3.31	7.39	4.60	4.57	5.82	5.28	4.39	3.70	5.54	10.02	3.79
Nitrate[i] (as N)												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	153.8	125.5	147.3	127.5	122.5	140.0	152.5	182.5	160.0	117.5	185	122.5
Sulfate[j] (ppm)												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	15.03	15.28	18.17	18.03	20.48	19.97	23.55	22.56	22.58	24.79	23.40	15.08
TDS[k] (ppm)												
Grab	---	---	---	---	---	---	---	---	---	---	---	---
Composite	84.25	90.75	82.25	88	93.5	66.5	87.25	86.5	88.25	88.00	102.50	64.25

Table A-2. (contd)

Parameter	July 1998	Aug 1998	Sept 1998	Oct 1998	Nov 1998	Dec 1998	Jan 1999	Feb 1999	Mar 1999	Apr 1999	May 1999	June 1999
Gross Alpha[l] (pCi/L)												
Grab	2.53	1.31	1.49	1.98	1.18	1.14	24.4[o]	7.55	3.40	7.45	6.43	0.94
Composite	---	---	---	---	---	---	---	---	---	---	---	---
Gross Beta[m] (pCi/L)												
Grab	1.35	1.18	1.73	1.98	1.28	1.24	4.33	2.35	1.25	1.28	1.63	1.03
Composite	---	---	---	---	---	---	---	---	---	---	---	---

(a) Units are in parts per billion (ppb) unless otherwise specified.
(b) Early warning value in effluent for total trihalomethanes is 66 ppb.
(c) Highest allowable average monthly effluent limit for total iron (unfiltered) is 258 ppb.
(d) Highest allowable average monthly effluent limit for total manganese (unfiltered) is 50 ppb.
(e) For the purpose of demonstrating permit compliance, non-detects were replaced with the applicable detection limit:
(f) Highest allowable average monthly effluent limit for total arsenic (unfiltered) is 15 ppb.
(g) Early warning value in effluent for total lead (unfiltered) is 10 ppb.
(h) Highest allowable average monthly effluent limit for chloride is 58 ppm.
(i) Highest allowable average monthly effluent limit for nitrate (as N) is 620 ppb.
(j) No permit limit is set for sulfate; the WAC 173-200 groundwater quality standard is 250 ppm.
(k) Highest allowable average monthly effluent limit for total dissolved solids (TDS) is 250 ppm.
(l) No permit limit is set for gross alpha; the WAC 173-200 groundwater quality standard is 15 pCi/L.
(m) No permit limit is set for gross beta; the WAC 173-200 groundwater quality standard for beta activity is 50 pCi/L.
(n) Anomalous values were attributed to strontium-90 and cesium-137 from a one-time Plutonium-Uranium Extraction Plant (PUREX) release.
(o) Anomalous value was attributed to Plutonium Finishing Plant (PFP) release.

Table A-3. Summary Statistics, Upper 95 Percent Confidence Limits (UCL) and Upper 95 Percent Tolerance Limits (UTL) for Detected Analytes

Summary Statistics[a]	Period (July 1995 through June 1996)							
	Summer (July, Aug, Sept)		Fall (Oct, Nov)		Winter (Dec, Jan, Feb)		Spring (Mar, Apr, May, June)	
	Grab	Composite	Grab	Composite	Grab	Composite	Grab	Composite
Chloroform (ppb)								
Number of samples	32	NA	8	NA	29	NA	17	NA
Mean	10.67		7.52		4.79		9.32	
Standard Deviation	3.33		1.64		1.73		3.60	
CV (%)	30.9		21.8		36.0		38.7	
95% UCL	11.8		8.8		5.4		11.2	
95% UTL	19.8		14.6		9.8		22.0	
Total trihalomethanes (ppb)								
Number of samples	---	NA	---	NA	10	NA	17	NA
Mean	---		---		4.35		9.40	
Standard Deviation	---		---		1.73		3.66	
CV (%)	---		---		39.8		38.9	
95% UCL	---		---		5.7		11.3	
95% UTL	---		---		12.3		22.3	
Iron (ppb)								
Number of samples	32	13	8	9	30	12	16[b]	16[b]
Mean	78.8	48.6	79.3	61.3	91.6	98.2	113.1[b]	126.1[b]
Standard Deviation	62.7	36.6	52.4	53.4	41.8	39.6	37.8[b]	73.8[b]
CV (%)	79.6	75.3	66.1	87.1	45.7	40.3	33.4[b]	58.5[b]
95% UCL	102.7	76.3	142.3	127.6	106.6	124.2	132.7[b]	169.3[b]
95% UTL	287.6	232.3	450.6	451.0	219.0	263.2	243.9[b]	428.1[b]
Manganese (ppb)								
Number of samples	32	13	8	9	30	12	16[b]	16[b]
Mean	6.68	4.70	5.62	5.04	4.68	6.05	5.06[b]	5.37[b]
Standard Deviation	3.74	1.58	2.38	2.05	1.10	2.63	0.92[b]	1.36[b]
CV (%)	56.0	33.7	42.3	40.6	23.5	43.4	18.2[b]	25.3[b]
95% UCL	8.0	5.7	7.9	6.8	5.1	7.8	5.5[b]	6.0[b]
95% UTL	18.3	10.7	18.9	15.3	7.6	17.9	7.8[b]	9.8[b]
Chloride (ppm)								
Number of samples	32	11	8	9	30	12	17	17
Mean	3.92	4.33	5.41	17.40	3.92	7.05	6.14	4.40
Standard Deviation	3.77	3.15	6.22	49.51	4.68	11.39	6.92	2.76
CV (%)	96.2	72.8	115.0	284.6	119.4	161.6	112.7	62.6
95% UCL	5.4	7.1	17.0	161.8	5.9	22.4	10.9	6.0
95% UTL	16.7	21.9	66.2	521.3	20.4	82.4	38.7	15.6

Table A-3. (contd)

Summary Statistics[a]	Period (July 1995 through June 1996)							
	Summer (July, Aug, Sept)		Fall (Oct, Nov)		Winter (Dec, Jan, Feb)		Spring (Mar, Apr, May, June)	
	Grab	Composite	Grab	Composite	Grab	Composite	Grab	Composite
Nitrate (as N, ppb)								
Number of samples	29	10	8	9	30	12	17	17
Mean	72.08	101.18	113.85	109.06	169.68	168.91	152.13	160.15
Standard Deviation	45.68	72.64	14.68	16.83	57.58	39.03	68.80	72.61
CV (%)	63.4	71.8	12.9	15.4	33.9	23.1	45.2	45.3
95% UCL	89.9	171.0	124.8	120.7	189.7	192.1	188.3	198.3
95% UTL	219.4	537.0	170.0	171.6	334.4	307.2	405.1	427.3
Sulfate (ppm)								
Number of samples	32	11[c]	8	9	30	12	16[b]	1[b]
Mean	11.44	11.92[c]	12.24	11.49	11.07	11.00	12.40[b]	13.81[b]
Standard Deviation	2.35	1.20[c]	1.11	1.22	1.22	1.79	2.36[b]	4.79[b]
CV (%)	20.6	10.0[c]	9.1	10.6	11.0	16.3	19.0[b]	34.7[b]
95% UCL	12.2	12.6[c]	13.1	12.3	11.5	12.0	13.5[b]	16.3[b]
95% UTL	17.5	15.6[c]	16.3	15.7	14.1	16.9	19.6[b]	30.5[b]
Total Dissolved Solids (ppm)								
Number of samples	---	3	1	2	3	3	4	4
Mean	---	95.51	NC	112.77	62.93	68.74	102.44	104.28
Standard Deviation	---	33.03	NC	18.72	19.79	5.62	38.28	28.54
CV (%)	---	34.6	NC	16.6	31.4	8.2	37.4	27.4
95% UCL	---	NC	NC	NC	NC	NC	NC	NC
95% UTL	---	NC	NC	NC	NC	NC	NC	NC
Gross Alpha (pCi/L)								
Number of samples	9	2	8	9	30	12	17	16
Mean	1.06	0.99	0.67	0.66	0.47	0.65	1.09	0.99
Standard Deviation	0.79	0.77	0.52	0.60	0.24	0.56	0.38	0.46
CV (%)	74.5	77.8	77.0	90.2	49.9	87.1	34.7	46.0
95% UCL	1.95	NC	1.36	1.43	0.56	1.14	1.28	1.25
95% UTL	6.4	NC	4.7	5.1	1.2	3.8	2.4	2.7
Gross Beta (pCi/L)								
Number of samples	NC[d]	NC[d]	6[d]	6[d]	30	12	17	16
Mean			0.82[d]	0.66[d]	0.91	0.78	1.42	1.41
Standard Deviation			0.24[d]	0.35[d]	0.53	0.46	0.62	0.60
CV (%)			28.8[d]	53.5[d]	58.2	58.5	43.8	42.2
95% UCL			1.09[d]	1.21[d]	1.11	1.12	1.74	1.73
95% UTL			2.2[d]	3.7[d]	2.6	3.0	3.7	3.6

Table A-3. (contd)

Summary Statistics[a]	Period (July 1996 through June 1997)							
	Summer (July, Aug, Sept)		Fall (Oct, Nov)		Winter (Dec, Jan, Feb)		Spring (Mar, Apr, May, June)	
	Grab	Composite	Grab	Composite	Grab	Composite	Grab	Composite
Chloroform (ppb)								
Number of samples	13	NA	9	NA	13	NA	17	NA
Mean	9.30		2.76		ND		3.86	
Standard Deviation	4.11		2.94		NC		3.01	
CV (%)	44.2		106.4		NC		78.1	
95% UCL	11.9		7.0		NC		5.7	
95% UTL	26.2		26.4		NC		16.9	
Total trihalomethanes (ppb)								
Number of samples	13	NA	9	NA	13	NA	17	NA
Mean	9.30		2.76		ND		3.86	
Standard Deviation	4.11		2.94		NC		3.01	
CV (%)	44.2		106.4		NC		78.1	
95% UCL	11.9		7.0		NC		5.7	
95% UTL	26.2		26.4		NC		16.9	
Iron (ppb)								
Number of samples	NA	13	NA	9	NA	14[e]	NA	17
Mean		57.1		78.1		104.0[e]		5.79
Standard Deviation		21.7		40.5		107.5[e]		1.98
CV (%)		38.1		51.8		103.3[e]		34.2
95% UCL		70.4		115.9		190.7[e]		6.8
95% UTL		142.5		304.4		671.2[e]		12.5
Manganese (ppb)								
Number of samples	NA	13	NA	9	NA	14[e]	NA	17
Mean		5.37		5.57		5.41[e]		5.79
Standard Deviation		1.04		1.13		1.15[e]		1.98
CV (%)		19.3		20.2		21.3[e]		34.2
95% UCL		5.9		6.4		6.0[e]		6.8
95% UTL		8.8		10.0		9.2[e]		12.5
Chloride (ppm)								
Number of samples	NA	13	NA	9	NA	13	NA	17
Mean		6.22		2.11		3.91		7.62
Standard Deviation		6.33		0.70		5.32		7.40
CV (%)		101.8		33.0		136.0		97.2
95% UCL		11.7		2.7		9.2		12.5
95% UTL		41.4		5.3		35.6		41.5

Table A-3. (contd)

Summary Statistics[a]	Period (July 1996 through June 1997)							
	Summer (July, Aug, Sept)		Fall (Oct, Nov)		Winter (Dec, Jan, Feb)		Spring (Mar, Apr, May, June)	
	Grab	Composite	Grab	Composite	Grab	Composite	Grab	Composite
Nitrate (as N, ppb)								
Number of samples	NA	12	NA	9	NA	13	NA	17
Mean		302.48		211.21		189.95		274.93
Standard Deviation		60.45		70.73		29.79		92.99
CV (%)		20.0		33.5		15.7		33.8
95% UCL		337.6		267.8		206.0		321.2
95% UTL		509.7		538.0		284.5		590.2
Sulfate (ppm)								
Number of samples	NA	13	NA	9	NA	9	NA	17
Mean		13.00		10.56		8.97		18.39
Standard Deviation		1.25		1.74		0.82		7.35
CV (%)		9.6		16.5		9.2		39.9
95% UCL		13.6		11.8		9.4		22.2
95% UTL		16.7		17.1		11.4		44.4
Total Dissolved Solids (ppm)								
Number of samples	NA	6	NA	9	NA	13	NA	17
Mean		63.70		77.22		60.80		90.33
Standard Deviation		18.74		39.67		28.42		34.08
CV (%)		29.4		51.4		46.7		37.7
95% UCL		85		114.0		79.2		107.6
95% UTL		177.8		297.8		180.5		209.3
Gross Alpha (pCi/L)								
Number of samples	13	NA	7	NA	13	NA	17	NA
Mean	1.12		1.22		1.10		1.38	
Standard Deviation	0.69		1.60		0.40		0.46	
CV (%)	61.3		131.4		36.5		33.1	
95% UCL	1.60		5.5		1.4		1.6	
95% UTL	4.3		22.2		2.7		2.9	
Gross Beta (pCi/L)								
Number of samples	12	NA	9	NA	13	NA	17	NA
Mean	1.15		1.93		1.39		1.81	
Standard Deviation	0.99		2.40		0.62		0.88	
CV (%)	86.3		123.9		44.9		48.7	
95% UCL	2.01		5.80		1.79		2.28	
95% UTL	6.4		22.6		4.0		5.2	

Table A-3. (contd)

Summary Statistics[a]	Period (July 1997 through June 1998)							
	Summer (July, Aug, Sept)		Fall (Oct, Nov)		Winter (Dec, Jan, Feb)		Spring (Mar, Apr, May, June)	
	Grab	Composite	Grab	Composite	Grab	Composite	Grab	Composite
Chloroform (ppb)								
Number of samples	13	NA	8	NA	13	NA	16	NA
Mean	3.32		ND		ND		2.76	
Standard Deviation	3.43		NC		NC		3.93	
CV (%)	103.4		NC		NC		142.5	
95% UCL	6.3		NC		NC		5.9	
95% UTL	22.5		NC		NC		22.6	
Total trihalomethanes (ppb)								
Number of samples	13	NA	8	NA	13	NA	16	NA
Mean	3.32		ND		ND		2.71	
Standard Deviation	3.43		NC		NC		1.78	
CV (%)	103.4		NC		NC		65.8	
95% UCL	6.3		NC		NC		3.8	
95% UTL	22.5		NC		NC		10.3	
Iron (ppb)								
Number of samples	NA	13	NA	8	NA	13	NA	16
Mean		127.5		47.6		73.0		151.2
Standard Deviation		134.4		30.8		65.7		174.5
CV (%)		105.4		64.8		90.0		115.4
95% UCL		245.8		84.2		126.8		279.9
95% UTL		934.0		263.4		424.1		1,008.9
Manganese (ppb)								
Number of samples	NA	13	NA	8	NA	13	NA	16
Mean		7.22		7.56		4.86		8.45
Standard Deviation		3.79		5.19		0.81		7.54
CV (%)		52.6		68.7		16.6		89.3
95% UCL		9.8		14.0		5.3		13.5
95% UTL		23.9		45.2		7.5		43.5
Chloride (ppm)								
Number of samples	NA	13	NA	8	NA	13	NA	16
Mean		7.30		17.31		5.57		6.75
Standard Deviation		6.37		18.78		5.63		9.43
CV (%)		87.4		108.5		101.0		139.6
95% UCL		12.4		50.4		10.4		14.2
95% UTL		41.0		195.3		36.8		54.2

Table A-3. (contd)

Summary Statistics[a]	Period (July 1997 through June 1998)							
	Summer (July, Aug, Sept)		Fall (Oct, Nov)		Winter (Dec, Jan, Feb)		Spring (Mar, Apr, May, June)	
	Grab	Composite	Grab	Composite	Grab	Composite	Grab	Composite
Nitrate (as N, ppb)								
Number of samples	NA	13	NA	8	NA	13	NA	16
Mean		155.21		144.09		193.91		224.07
Standard Deviation		33.38		21.56		57.75		94.67
CV (%)		21.5		15.0		29.8		42.2
95% UCL		173.8		160.4		227.6		275.2
95% UTL		267.7		229.0		404.7		573.8
Sulfate (ppm)								
Number of samples	NA	13	NA	8	NA	13	NA	16
Mean		14.50		13.14		10.92		15.64
Standard Deviation		4.12		1.14		1.36		5.03
CV (%)		28.4		8.7		12.4		32.2
95% UCL		16.9		14.0		11.6		18.2
95% UTL		29.3		17.3		15.1		32.9
Total Dissolved Solids (ppm)								
Number of samples	NA	13	NA	8	NA	13	NA	16
Mean		89.41		84.25		95.88		92.95
Standard Deviation		18.38		12.05		31.95		24.04
CV (%)		20.6		14.3		33.3		25.9
95% UCL		99.6		93.3		114.9		104.9
95% UTL		150.8		131.3		216.3		171.0
Gross Alpha (pCi/L)								
Number of samples	13	NA	8	NA	13	NA	16	NA
Mean	1.33		1.36		1.19		1.34	
Standard Deviation	0.35		0.36		0.34		0.40	
CV (%)	26.2		26.2		28.8		30.2	
95% UCL	1.53		1.66		1.39		1.55	
95% UTL	2.6		3.0		2.4		2.7	
Gross Beta (pCi/L)								
Number of samples	13	NA	8	NA	13	NA	16	NA
Mean	1.51		2.06		1.30		1.50	
Standard Deviation	0.26		1.40		0.26		0.44	
CV (%)	17.0		67.9		20.2		29.6	
95% UCL	1.65		3.77		1.44		1.72	
95% UTL	2.3		12.1		2.2		3.0	

Table A-3. (contd)

Summary Statistics[a]	Period (July 1998 through June 1999)							
	Summer (July, Aug, Sept)		Fall (Oct, Nov)		Winter (Dec, Jan, Feb)		Spring (Mar, Apr, May, June)	
	Grab	Composite	Grab	Composite	Grab	Composite	Grab	Composite
Chloroform (ppb)								
Number of samples	12	NA	8	NA	12	NA	17	NA
Mean	5.89		3.81		4.47		2.52	
Standard Deviation	5.69		2.03		4.70		2.81	
CV (%)	96.7		53.4		105.1		111.4	
95% UCL	11.1		6.0		9.0		4.4	
95% UTL	39.1		16.6		32.6		15.7	
Total trihalomethanes (ppb)								
Number of samples	12	NA	8	NA	12	NA	17	NA
Mean	5.47		3.97		4.43		2.58	
Standard Deviation	3.25		2.25		3.32		1.94	
CV (%)	59.5		56.6		74.9		75.2	
95% UCL	7.9		6.4		7.1		3.7	
95% UTL	21.2		18.5		22.0		10.9	
Iron (ppb)								
Number of samples	NA	12	NA	8	NA	12	1	16
Mean		167.3		146.1		173.7	NC	165.2
Standard Deviation		152.8		92.9		82.4	NC	96.0
CV (%)		91.3		63.6		47.5	NC	58.1
95% UCL		303.5		255.6		230.6	NC	221.2
95% UTL		1,040.1		790.0		538.6	NC	556.8
Manganese (ppb)								
Number of samples	NA	12	NA	8	NA	12	1	16
Mean		8.12		5.66		6.79	NC	7.43
Standard Deviation		5.26		2.54		3.08	NC	4.00
CV (%)		64.8		44.9		45.5	NC	53.9
95% UCL		12.2		8.2		8.9	NC	9.7
95% UTL		34.4		20.3		20.2	NC	23.4
Chloride (ppm)								
Number of samples	NA	12	NA	8	NA	12	1	16
Mean		5.11		4.59		5.34	NC	5.81
Standard Deviation		3.37		0.85		2.69	NC	3.40
CV (%)		65.9		18.6		50.4	NC	58.6
95% UCL		7.7		5.3		7.2	NC	7.8
95% UTL		22.1		8.1		17.5	NC	19.7

Table A-3. (contd)

Summary Statistics[a]	Period (July 1998 through June 1999)							
	Summer (July, Aug, Sept)		Fall (Oct, Nov)		Winter (Dec, Jan, Feb)		Spring (Mar, Apr, May, June)	
	Grab	Composite	Grab	Composite	Grab	Composite	Grab	Composite
Nitrate (as N, ppb)								
Number of samples	NA	12	NA	8	NA	12	1	16
Mean		144.59		136.87		159.29	NC	149.25
Standard Deviation		72.21		119.85		57.77	NC	62.59
CV (%)		49.9		87.6		36.3	NC	41.9
95% UCL		195.2		313.2		196.5	NC	183.0
95% UTL		470.4		1,140.9		391.8	NC	380.0
Sulfate (ppm)								
Number of samples	NA	12	NA	8	NA	12	1	16
Mean		16.26		19.26		22.17	NC	21.62
Standard Deviation		4.42		1.54		5.76	NC	6.40
CV (%)		27.2		8.0		26.0	NC	29.6
95% UCL		18.9		20.4		25.6	NC	24.9
95% UTL		32.6		24.8		43.2	NC	43.1
Total Dissolved Solids (ppm)								
Number of samples	NA	12	NA	8	NA	12	1	16
Mean		86.51		90.77		80.26	NC	88.07
Standard Deviation		25.63		4.82		17.57	NC	39.24
CV (%)		29.6		5.3		21.9	NC	44.6
95% UCL		102.3		94.2		90.6	NC	109.5
95% UTL		183.4		107.4		141.7	NC	235.4
Gross Alpha (pCi/L)								
Number of samples	12	NA	8	NA	7[f]	NA	17	NA
Mean	1.77		1.59		1.36[f]		4.84	
Standard Deviation	1.05		0.99		0.67[f]		7.04	
CV (%)	59.7		62.5		49.6[f]		145.4	
95% UCL	2.55		2.75		2.15[f]		10.44	
95% UTL	6.9		8.4		6.0[f]		38.8	
Gross Beta (pCi/L)								
Number of samples	12	NA	8	NA	12	NA	17	NA
Mean	1.42		1.63		2.62		1.28	
Standard Deviation	0.35		0.55		2.07		0.36	
CV (%)	24.7		34.1		79.2		28.5	
95% UCL	1.63		2.12		4.35		1.46	
95% UTL	2.7		3.8		13.9		2.5	

Table A-3. (contd)

Summary Statistics[a]	Period (July 1997 through June 1998)							
	Summer (July, Aug, Sept)		Fall (Oct, Nov)		Winter (Dec, Jan, Feb)		Spring (Mar, Apr, May, June)	
	Grab	Composite	Grab	Composite	Grab	Composite	Grab	Composite
Arsenic[g] (ppb)								
Number of samples	NA	13	NA	8	NA	13	NA	16
Mean		0.59		0.77		0.81		0.88
Standard Deviation		0.20		0.28		0.43		0.55
CV (%)		34.2		36.3		52.8		62.9
95% UCL		0.7		1.0		1.1		1.2
95% UTL		1.4		2.2		2.7		3.2
	Period (July 1998 through June 1999)							
	Summer (July, Aug, Sept)		Fall (Oct, Nov)		Winter (Dec, Jan, Feb)		Spring (Mar, Apr, May, June)	
	Grab	Composite	Grab	Composite	Grab	Composite	Grab	Composite
Arsenic[g] (ppb)								
Number of samples	NA	12	NA	8	NA	12	1	16
Mean		1.56		0.91		0.67	NC	0.73
Standard Deviation		0.93		0.20		0.48	NC	0.33
CV (%)		59.9		21.4		71.6	NC	44.5
95% UCL		2.3		1.1		1.0	NC	0.9
95% UTL		6.1		1.8		3.1	NC	2.0

(a) Calculated based on assumed lognormal distribution (see WHC-SD-LEF-EV-001, Rev. 0, Appendix A).
(b) Excluded excursion occurred on April 7, 1996 (see WHC-SD-LEF-EV-001, Rev. 0, Appendix C).
(c) Outlier (July 6, 1995) removed.
(d) Excluded anomalous data (collected prior to October 23, 1995) due to a one-time PUREX release.
(e) Excluded excursion occurred on January 12, 1997.
(f) Excluded anomalous data (collected from January 22, 1999 to February 17, 1999) due to a PFP release.
(g) Summary statistics not calculated for period covered from July 1995 through June 1997 (most data were non-detects).

Table A-4. Probability of Exceeding Average Monthly Concentration for TEDF Detected Constituents Under Normal Operating Conditions

Parameter	Summer	Fall	Winter	Spring	Overall
Chloroform: Grab Sample Results (ppb)					
Permit limit[a]	66	66	66	66	66
Number of Observations	12	8	12	16	48
Average	7.1	3.75	2.57	4.54	4.56
Standard Deviation	3.87	2.67	2.02	3.25	3.41
Minimum	0.95	0.9	0	1.05	0
Maximum	14	8.25	5.6	12.5	14
Exceedance Probability[b]	≅ 0	≅ 0	≅ 0	≅ 0	≅ 0
Total Trihalomethanes: Grab Sample Results (ppb)					
Permit limit	66	66	66	66	66
Number of Observations	9	6	10	16	41
Average	5.93	2.58	2.24	4.66	4.05
Standard Deviation	3.43	1.56	1.94	3.18	3.06
Minimum	0.95	0.9	0	1.54	0
Maximum	13	4.55	5.4	12.5	13
Exceedance Probability[b]	≅ 0	≅ 0	≅ 0	≅ 0	≅ 0
Iron[c]: Composite Sample Results (ppb)					
Permit limit	258	258	258	258	258
Number of Observations	12	8	12	16	48
Average	95.9	83.21	112.4	137.51	111.78
Standard Deviation	66.76	50.5	43.85	48.24	55.18
Minimum	25.6	33.75	41.8	70.5	25.6
Maximum	224.68	194.25	205	254	254
Exceedance Probability	0.0076	0.0003	0.0004	0.0063	0.004
Manganese[c]: Composite Sample Results (ppb)					
Permit limit	50	50	50	50	50
Number of Observations	12	8	12	16	48
Average	6.4	6.06	5.74	7.18	6.44
Standard Deviation	2.44	2.25	1.39	4.86	3.24
Minimum	4	4	4.55	4.4	4
Maximum	11.58	11	9.26	23.9	23.9
Exceedance Probability[b]	≅ 0	≅ 0	≅ 0	≅ 0	≅ 0
Arsenic[d]: Composite Sample Results (ppb)					
Permit limit	15	15	15	15	15
Number of Observations	9	6	9	15	39
Average	1.44	0.77	0.72	0.81	0.93
Standard Deviation	1.00	0.19	0.27	0.34	0.60
Minimum	0.56	0.43	0.4	0.4	0.4
Maximum	3.63	1	1.23	1.5	3.63
Exceedance Probability[b]	≅ 0	≅ 0	≅ 0	≅ 0	≅ 0

Table A-4. (contd)

Parameter	Summer	Fall	Winter	Spring	Overall
Lead[d]: Composite Sample Results (ppb)					
Permit limit[e]	10	10	10	10	10
Number of Observations	9	6	9	15	39
Average	0.61	0.36	0.45	0.66	0.56
Standard Deviation	0.36	0.20	0.25	0.49	0.39
Minimum	0.2	0.2	0.23	0.2	0.2
Maximum	1.35	0.74	1.03	1.88	1.88
Exceedance Probability[b]	≅ 0	≅ 0	≅ 0	≅ 0	≅ 0
Chloride: Composite Sample Results (ppm)					
Permit limit	58	58	58	58	58
Number of Observations	12	8	12	16	48
Average	5.95	9.42	6.44	6.55	6.85
Standard Deviation	3.85	10.12	5.12	5.30	5.94
Minimum	2.07	1.53	1.46	2.06	1.46
Maximum	14.96	28.93	18.75	21.69	28.93
Exceedance Probability[b]	≅ 0	0.000001	≅ 0	≅ 0	≅ 0
Nitrate (as N): Composite Sample Results (ppb)					
Permit limit	620	620	620	620	620
Number of Observations	12	8	12	16	48
Average	165.78	146.38	178.8	201.2	177.61
Standard Deviation	76.56	44.54	26.58	76.62	64.01
Minimum	57	98	140	105.5	57
Maximum	322.8	242.4	236	392.5	392.5
Exceedance Probability[b]	≅ 0	≅ 0	≅ 0	≅ 0	≅ 0
Sulfate[c]: Composite Sample Results (ppm)					
Drinking Water Standard[f]	250	250	250	250	250
Number of Observations	12	8	12	16	48
Average	13.61	13.56	13.18	17.46	14.78
Standard Deviation	2.57	3.82	5.50	5.43	4.89
Minimum	9.24	8.98	8.63	11.32	8.63
Maximum	18.17	20.48	23.55	25.49	25.49
Exceedance Probability[b]	≅ 0	≅ 0	≅ 0	≅ 0	≅ 0
Total Dissolved Solids: Composite Sample Results (ppb)					
Permit limit[f]	250	250	250	250	250
Number of Observations	12	8	12	16	48
Average	80.95	90.88	77.01	93.29	85.73
Standard Deviation	20.67	17.61	20.34	19.43	20.32
Minimum	38	64	49.8	64.2	38
Maximum	115	125	131.5	127	131.5
Exceedance Probability[b]	≅ 0	≅ 0	≅ 0	≅ 0	≅ 0

Table A-4.(contd)

Parameter	Summer	Fall	Winter	Spring	Overall
Gross Alpha[g]: Grab Sample Results (pCi/L)					
Drinking Water Standard[f]	15	15	15	15	15
Number of Observations	12	8	12	16	48
Average	1.22	1.07	1.28	2.09	1.50
Standard Deviation	0.62	0.57	0.98	1.99	1.34
Minimum	0.34	0.26	0.37	0.94	0.26
Maximum	2.53	1.98	4.07	7.45	7.45
Exceedance Probability[b]	≅ 0	≅ 0	≅ 0	≅ 0	≅ 0
Gross Beta[h]: Grab Sample Results (pCi/L)					
Drinking Water Standard[f]	50	50	50	50	50
Number of Observations	9	8	12	16	45
Average	1.30	1.57	1.56	1.50	1.49
Standard Deviation	0.33	0.53	0.97	0.39	0.60
Minimum	0.68	0.79	0.5	0.92	0.50
Maximum	1.73	2.26	4.33	2.31	4.33
Exceedance Probability[b]	≅ 0	≅ 0	≅ 0	≅ 0	≅ 0

(a) Early warning value in effluent for total trihalomethanes is used.
(b) Exceedance probability ≅ 0 means $<10^{-6}$ (or less than 1 in one million).
(c) Excluded April 7, 1996 and January 12, 1997 excursions for iron and manganese; excluded April 7, 1996 excursion for sulfate.
(d) Data from April 21, 1996 and later (prior to April 21, 1996 arsenic and lead data are essentially not detected).
(e) Early warning value in effluent of 10 ppb is used.
(f) No applicable permit limit, the limit used is based on WAC 173-200 groundwater quality standard.
(g) Excluded anomalous data collected between January 22, 1999 to February 10, 1999 due to release from PFP.
(h) Excluded anomalous data collected prior to October 22, 1995 due to a one time release from PUREX.

Appendix B

Graphical Display of Effluent Monitoring Data

Appendix B

Graphical Display of Effluent Monitoring Data

This appendix includes time series plots and box and whisker plots of effluent monitoring data for the detected constituents. The figures are intended to stand alone. However, explanatory notes are added where appropriate. The main text can also be used for additional discussion that may clarify the graphical displays and indicate caveats of the data presented.

Continuous monitoring data (flow rate, specific conductivity, and pH) are presented first (Figures B-1 through B-3). Time versus concentration plots for detected constituents based on individual grab and/or composite samples are present next (Figures B-4 through B-12) followed by the monthly averages (Figures B-13 through B-21). The presence of temporal cycles (seasonality) was examined visually by using multiple box and whisker plots (Figures B-22 through B-30) where the distribution of effluent concentrations (for a particular constituent) over different seasons is displayed. Similarly, it was used to examine the effect of sample types (grab versus composite) on effluent concentrations (Figure B-31 through B-38).

In a box and whisker plot, the upper (Q_3) and lower (Q_1) quarters of the data are shown by the top and bottom of a box and the median (Q_2) is indicated by a line segment within the box. The box covers the middle 50 percent of the data values. The 'whiskers' extend out to the extremes (minimum and maximum observations). When extremely large or small values occur, these values are plotted as individual points. The whiskers extend only to those points that are within 1.5 times the interquartile range, IQR (Q_3 - Q_1). The median and IQR are analogous to the more common mean and standard deviation of a data set. The median is a measure of 'central tendency' or 'location,' whereas the IQR is a measure of 'variability.' Any data point that falls outside the whisker could be classified as a suspected outlier (Ostle and Malone 1988).

It should be noted that within each data display category, volatile organic compound is shown first, followed by metals, anions, other analysis, and radionuclides. Also, anomalous data that correlated to excursions (e.g., iron exceedances observed on April 7, 1996 and January 12, 1997) were not used in the multiple box and whisker plots depicting seasonal effects. Their inclusion would make the range covered by the vertical concentration scale so large that the seasonal effects would not be discernable. Additionally, only individual grab and composites samples collected for the variability study (from July 1995 through June 1996) are used to generate the box and whisker plots depicting possible sample type effects (Figures B-31 through B-38). This is because after June 1996 only one type of samples was collected and analyzed for the constituent of interest. Finally, the specific conductivity and pH data are subject to a flow rate limitation. When the flow rate drops below 50 gpm, water from the effluent stream can no

longer flow through the measurement cell. Thus during very low flow periods, the values recorded are for stagnant water in the cell and do not reflect ambient conditions in the effluent stream. This is a problem that is under study.

Explanatory notes and a brief discussion of the salient features of the concentration versus time plots and the box and whisker plots are as follows.

Figure B-1

The marked change in flow conditions after 1997 is due to evaporator campaigns that last for a few days to a week or two. The high flow rates are required to cool the evaporator condensers. The specific conductance of effluent during the high flow periods is similar to Columbia River water (~140 μS/cm).

Figure B-2

Most of the large peaks are due to calibration problems. Also, during low flow (<50 gpm) the conductivity and pH probes are immersed in stagnant water. This is because the monitoring system requires at least 50 gpm to ensure water flows through the measurement cell. Most of the readings shown cluster around the average or typical river water value of 140 μS/cm.

Figure B-3

The same caveats concerning low flow conditions apply to pH as well as conductivity. The most common or most frequent values are in the range of typical river water.

Figure B-4

The original variability study (Chou and Johnson 1996) indicated that the minima during the winter and fall and maxima during spring and summer are readily recognizable as illustrated in the box and whisker plots in Figure B-22. However, there also appears to be an overall trend of declining chloroform concentrations during the 4-year period of record.

Figure B-5

The random spike occurrences of iron are readily apparent. The general trend, however, appears to be for spikes or excursions that are smaller in magnitude during 1998 and 1999 than in previous years. Grab samples and composite samples are shown together for comparison. In most cases, the grab samples and 24-hour composite samples are comparable.

Figure B-6

Manganese is not detected much of the time as indicated by a line corresponding to the method detection limit (~4.4 ppb). Manganese, a co-variate with iron, exhibits the same spike occurrences as iron and probably has a similar origin (rusting carbon steel pipe). The grabs and 24-hour composites are comparable.

Figure B-7

The short term or spike occurrences for chloride have clearly been attenuated since 1998. This is due to elimination of the water softeners associated with the old 200 Areas Power Plants that were shut down in 1998. The grab samples and composite samples both reflected the excursion that occurred February 6, 1996.

Figure B-8

In general, the grab samples and composite samples are comparable for this constituent. As with several other detected constituents, nitrate appears to have declined since 1998. The cyclic nature of the concentrations is also evident in this plot. The highest concentrations shown are far below the drinking water standard (10,000 ppb as N) even though the daily maximum limit is only 1,240 ppb.

Figure B-9

Grab samples and composite samples seem to be generally comparable. Overall there appears to be a gradual upward trend over the last two years. Nevertheless, the average concentrations are not much higher than the average Columbia River water of 11 mg/L and are well below either the drinking water standard or the permit limits.

Figure B-10

Total dissolved solids (TDS) is equivalent to conductivity. The overall pattern is similar to chloride that has been a dominant contributor to TDS in the past. Grab samples and 24-hour composite samples also seem to track each other fairly closely.

Figure B-11

Grab sample results for gross alpha track well with composite samples. Except for the excursion January 22, 1999, and for a short period thereafter, gross alpha is consistently close to the natural background for Columbia River water. The excursion in 1999 was attributed to breakthrough of treatment columns at the Plutonium Finishing Plant (PFP) water treatment plant.

Figure B-12

As noted for gross alpha, grab and composite samples for gross beta yield similar results. Except for an early excursion due to strontium-90, gross beta is consistently near the natural background level of river water. The consistent and low background levels for both gross alpha and gross beta make these constituents good overall indicators for alpha and beta emitters.

Figure B-13

The monthly average for chloroform reflects the same general trend as the grab samples except the variability is greatly attenuated. The average is well below the early warning value in effluent (set for total trihalomethanes).

Figure B-14

The highest allowable monthly average of 258 ppb was exceeded twice during the 4-year monitoring period (July 1995 through June 1996). The monthly averaging process also greatly smoothes the individual data for total iron as illustrated by comparing this plot with Figure B-5. There is a close correspondence between the grab and composite sample data.

Figure B-15

The averaging process has the same effect on manganese as on iron and chloroform. Likewise, the grabs and composite averages are in good agreement.

Figure B-16

The monthly averaging process also attenuates the chloride concentrations (see Figure B-7). However, the monthly averages of grab and composite samples appear to be out of phase with each other during the first year of operation. This may be a result of frequent spike occurrences that were "captured" by the 24-hour composite sample but not by the grab samples. Also, the effect of reduced input of chloride beginning in 1998 (200 Areas Power Plant shutdown) is clearly evident in comparison to the previous three years.

Figure B-17

The cyclic nature of nitrate is clearly evident in the monthly average data as shown in this plot. Grab samples and composite samples are also in good agreement.

Figure B-18

In contrast to chloride, the monthly averages of grab and composite sample results are in close agreement for sulfate. As with the other constituents, averaging smoothes the data and makes the cyclic trends more recognizable.

Figure B-19

The monthly averaging process smoothed the TDS results as with the other constituents. Grab and composite sample data are in agreement as noted for sulfate.

Figure B-20

The monthly averaging process did not alter gross alpha very much because the individual weekly samples did not exhibit much variability.

Figure B-21

As with gross alpha, the monthly averaging of individual weekly data for this constituent did not have much of an effect because it was so consistent (excluding the initial excursion).

Figure B-22

The box plots for the complete 4-year data set, segregated by season, indicate there are lower concentrations in fall and winter and higher concentrations in spring and summer. This has been attributed to enhanced chlorination of organics produced by phytoplankton during the annual maxima in their growth cycle. The spread in the data (range of concentrations) is in part due to the overall decline in concentrations during 1998 and 1999.

Figure B-23

The anomalously high iron values that exceeded the permit standard are shown as +s. The median concentrations are slightly higher in winter and spring. Also, variability is larger in the winter and spring seasons.

Figure B-24

In contrast to iron, the manganese box plots suggest there is a high concentration group co-mingled with a low concentration group that has a very narrow range (flattened boxes). The low concentration group represents data that were near and/or at the detection limit (see Figure B-6). The higher concentration could be a result of the hypothesized occurrence of particulate releases from rusting cast iron pipe.

Figure B-25

Chloride exhibits a bimodal population as noted in the initial variability study report (Chou and Johnson 1996). There appears to be two chloride populations: (1) a large group of typically low concentrations (172 out of total 200 analyses) that occur over a rather narrow range (<10 ppm) with most samples (134 sample) between 1 to 5 ppm; and (2) a smaller group consisting of much higher concentrations scattered over a wide range (up to 85.2 ppm). The higher concentration group (≥10 ppm) is attributed to periodic (random) regeneration of resin beds for water softeners at the old power plants. The low concentration population is close to the natural background of river water.

Figure B-26

The seasonal variation (highest median concentrations in winter and spring) is evident for nitrate. This pattern is shifted from the chloroform maxima that occur in spring and summer.

Figure B-27

The most noticeable feature for sulfate is the apparent larger variability and higher concentration in composite samples collected during the spring season. The "+s" shown outside the box plot for winter correspond to samples collected during January and February of 1999 (see Figure B-9)

Figure B-28

Total dissolved solids tend to follow the same seasonal pattern as sulfate, with lowest concentration median occurring in winter and higher median concentration in spring.

Figure B-29

There appears to be a seasonal effect for the gross alpha data with lower concentration in winter and higher concentration in spring. The narrow widths of the boxes for gross alpha indicate a relatively low variability over all seasons. The outliers (+s) shown for spring are due to a treatment column operational problem at the PFP that occurred only in 1999.

Figure B-30

There does not appear to be a seasonal component in the gross beta data. The outliers (+s) shown outside of the box plot for winter could be related to the PFP release that occurred during January 1999.

Figure B-31

The grab and composite samples yield similar results. The highest concentration shown as + in the composite (3,100 ppb) as well as grab sample (1,850 ppb) corresponded to the event occurred on April 7, 1996 where permit limit was exceeded.

Figure B-32

Manganese in the 24-hour composite and grab samples are similar. Both indicate a low concentration group (boxes) which are comprised primarily of non-detects, and a population of higher concentrations that occur as random spikes (co-variate with iron).

Figure B-33

Both grab samples and composite samples for chloride exhibit similar distributions (bimodal, see discussion in Figure B-25).

Figure B-34

Both grab and composite samples for nitrate yield similar results (similar in median concentration and variability).

Figure B-35

Both grab and composite samples for sulfate yield similar results (similar in median concentration and variability).

Figure B-36

Both grab and composite samples for total dissolved solids yield similar results. Larger variability as shown for the grab samples were due to fewer data (8 observations) points.

Figure B-37

Both grab and composite samples for gross alpha yield similar results (similar in median concentration and variability).

Figure B-38

Both grab samples and composite samples yield similar results for gross beta. The outliers (shown as +s outside of the boxes) were excursion due to strontium-90 of one time release from PUREX.

B.1 References

Chou and Johnson. 1996. *Effluent Variability Study Results for the 200 Area Treated Effluent Disposal Facility*. WHC-SD-LEF-EV-001, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Ostle and Malone. 1988. *Statistics in Research*, fourth edition, Iowa State University Press, Ames, Iowa, pp. 66-67.

Continuous Monitoring Data

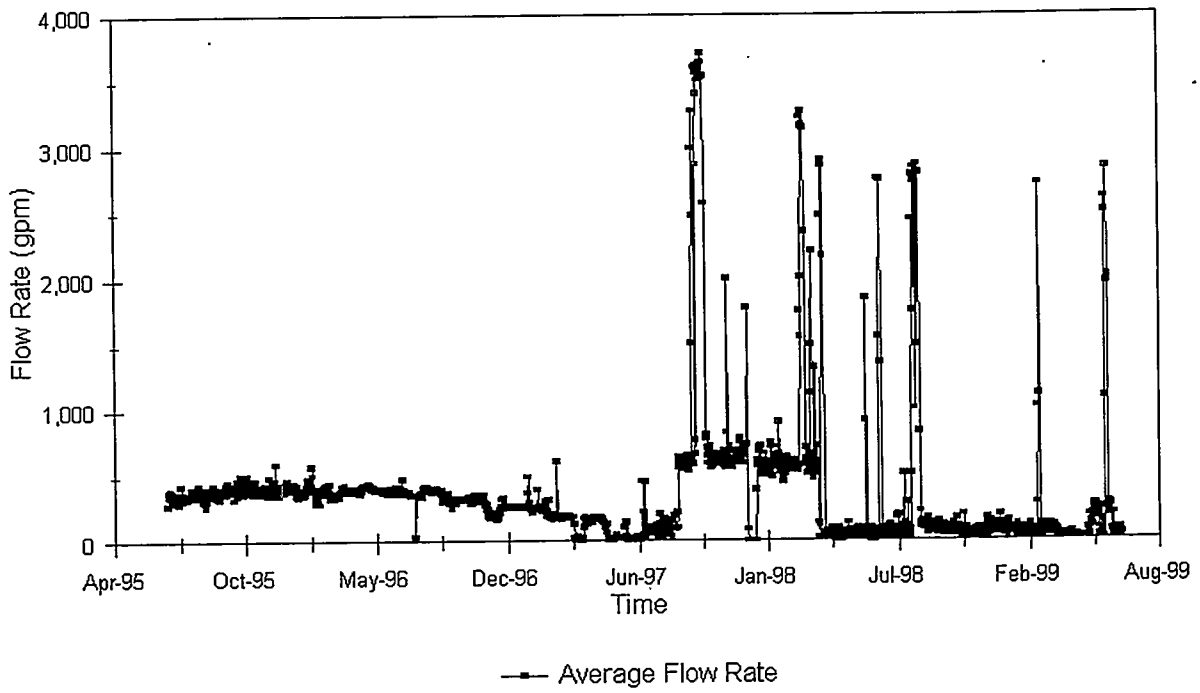


Figure B-1. TEDF Continuous Data – Average Daily Rate Flow Rate

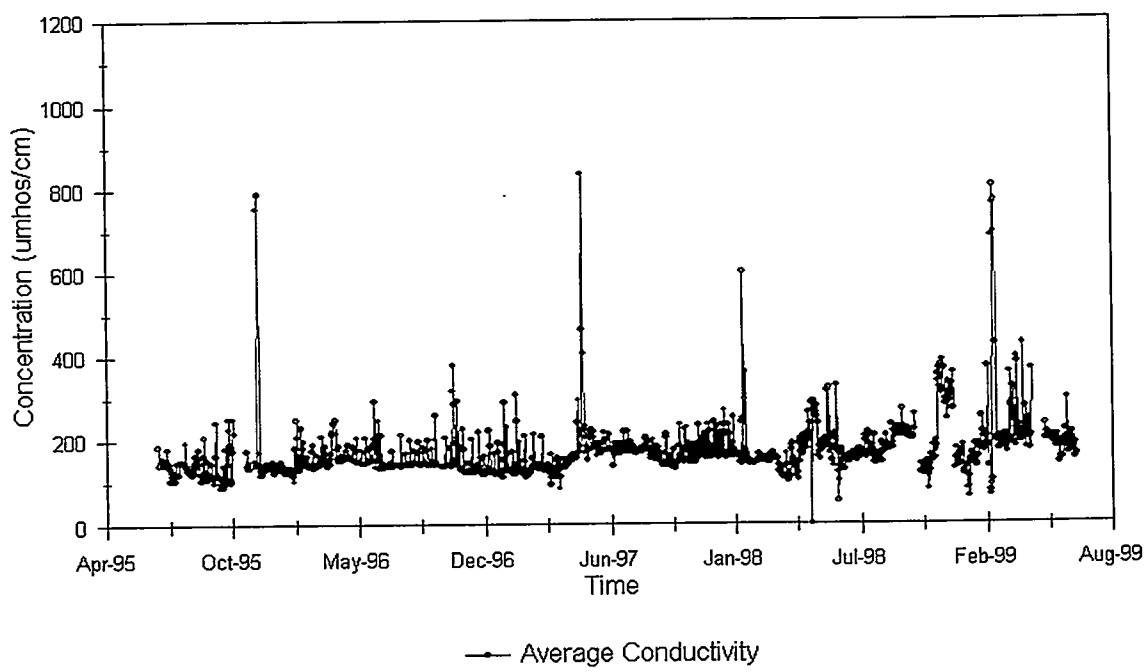


Figure B-2. TEDF Continuous Monitoring Data - Average Daily Specific Conductivity

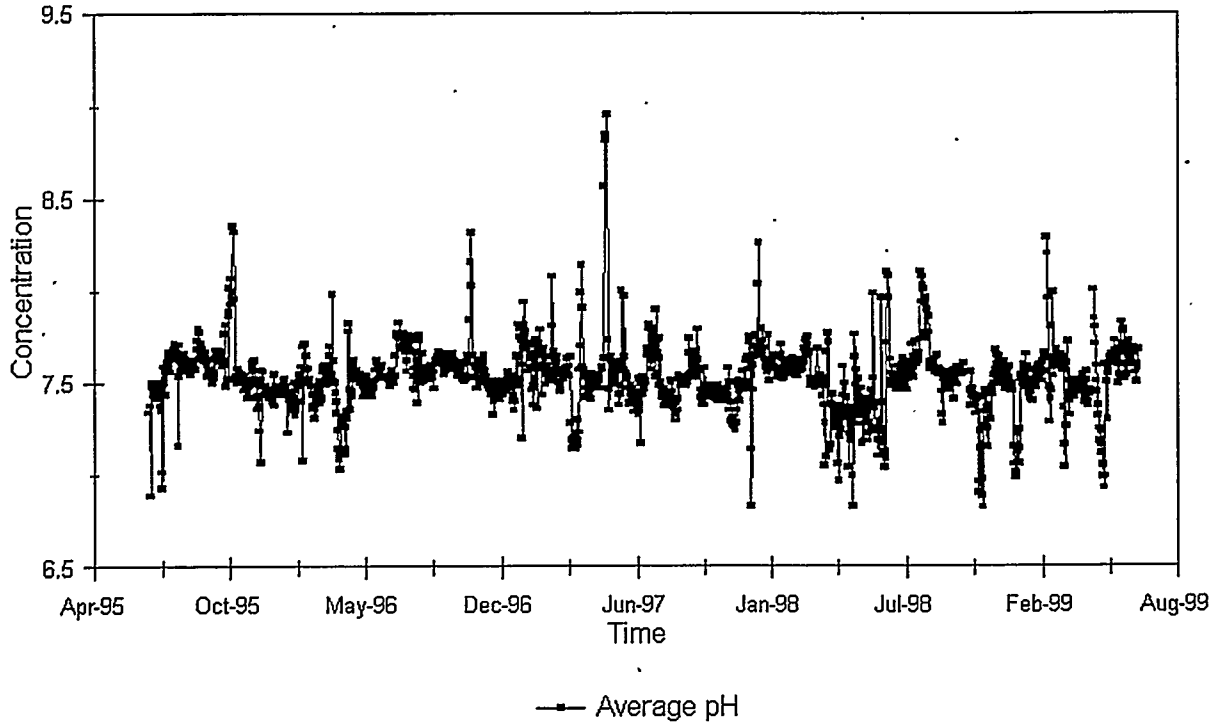


Figure B-3. TEDF Continuous Monitoring Data - Average Daily pH

Time Versus Concentration Plots - Weekly Grab and/or Composite Sample Results

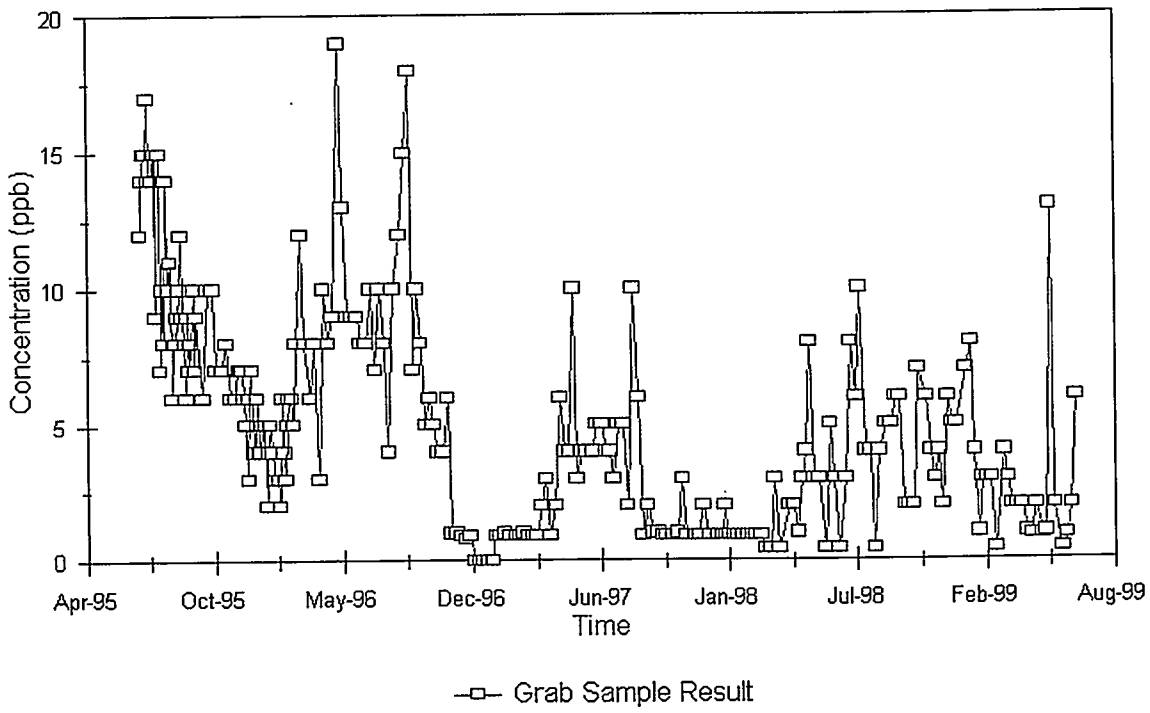


Figure B-4. TEDF Effluent Variability - Chloroform

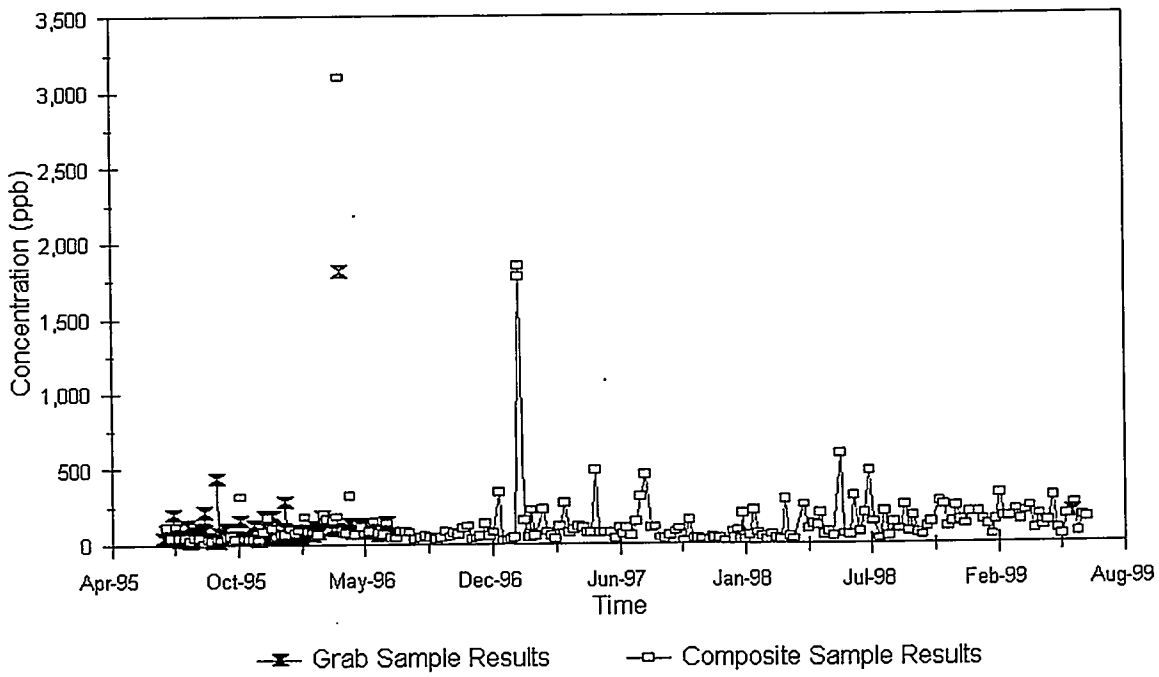


Figure B-5. TEDF Effluent Variability - Iron

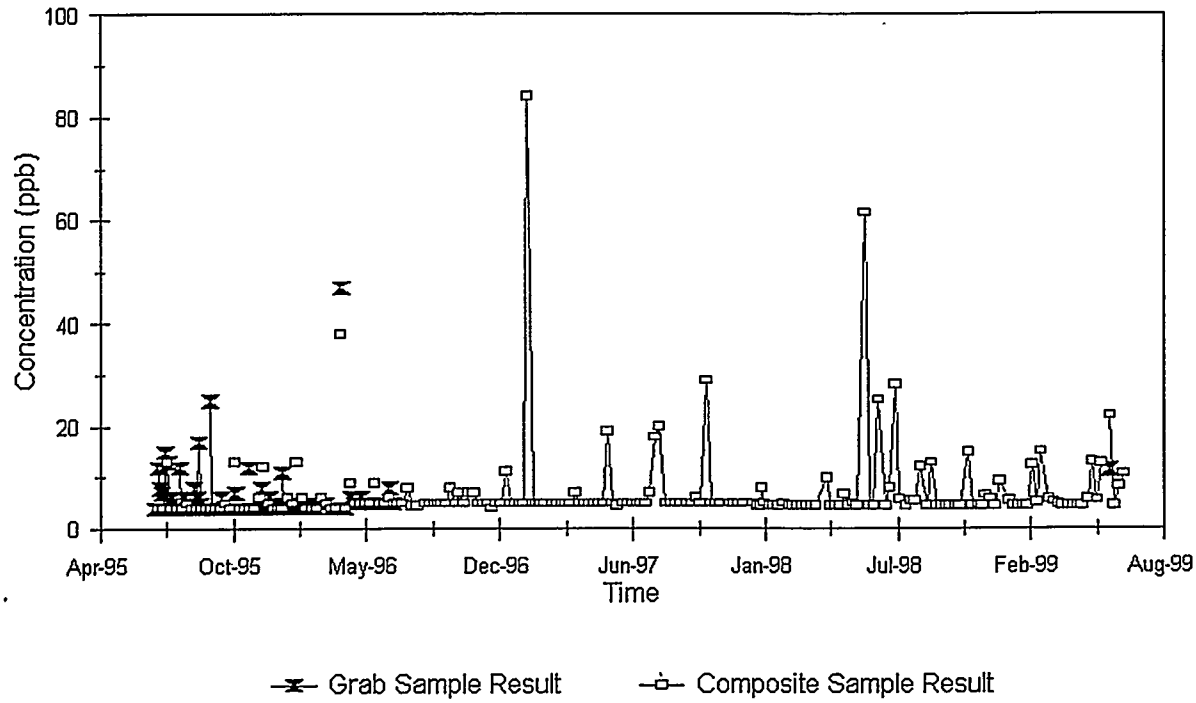


Figure B-6. TEDF Effluent Variability – Manganese

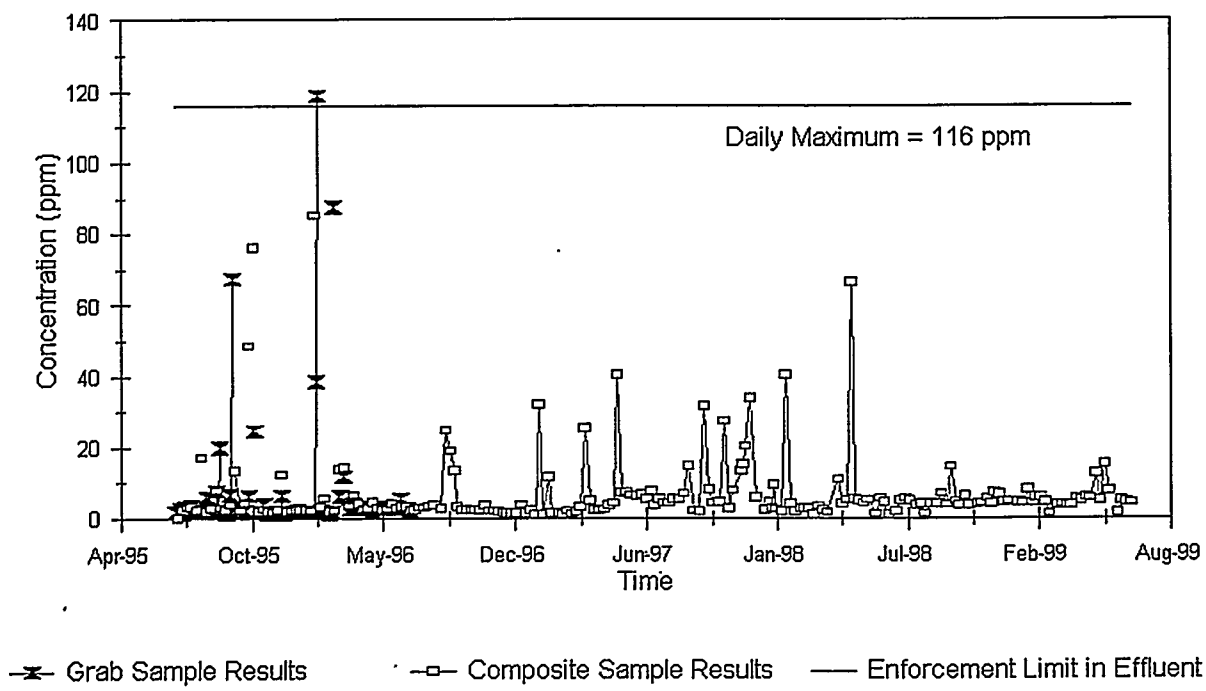


Figure B-7. TEDF Effluent Variability – Chloride

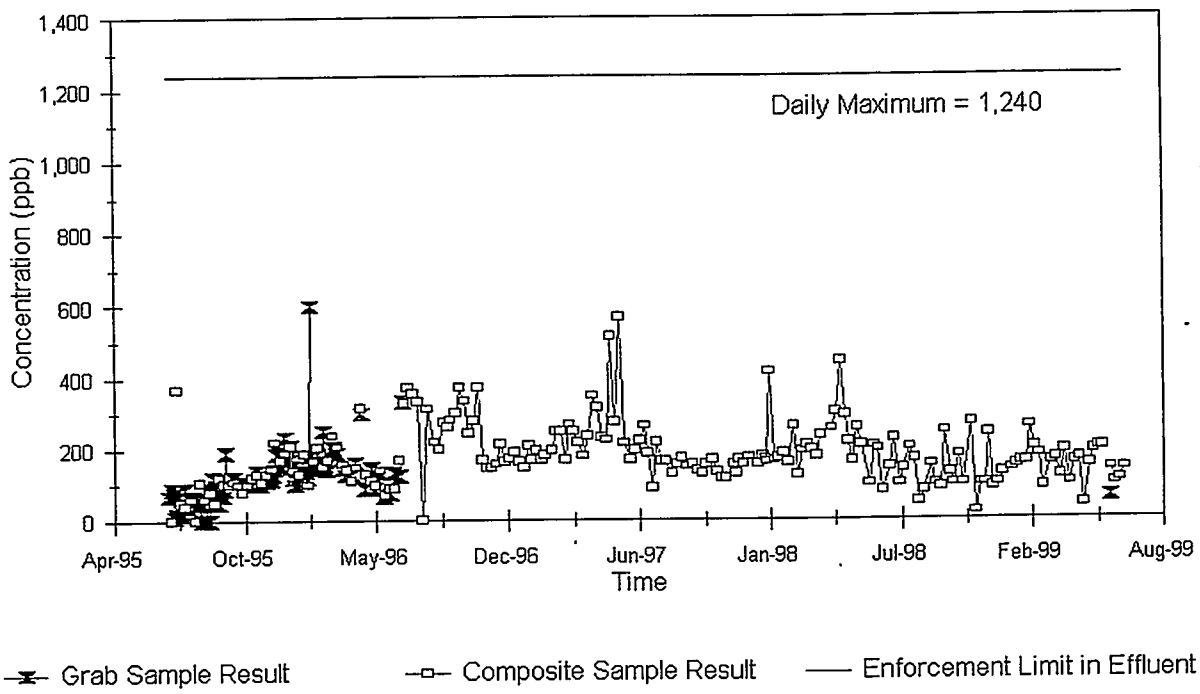


Figure B-8. TEDF Effluent Variability - Nitrate (as N)

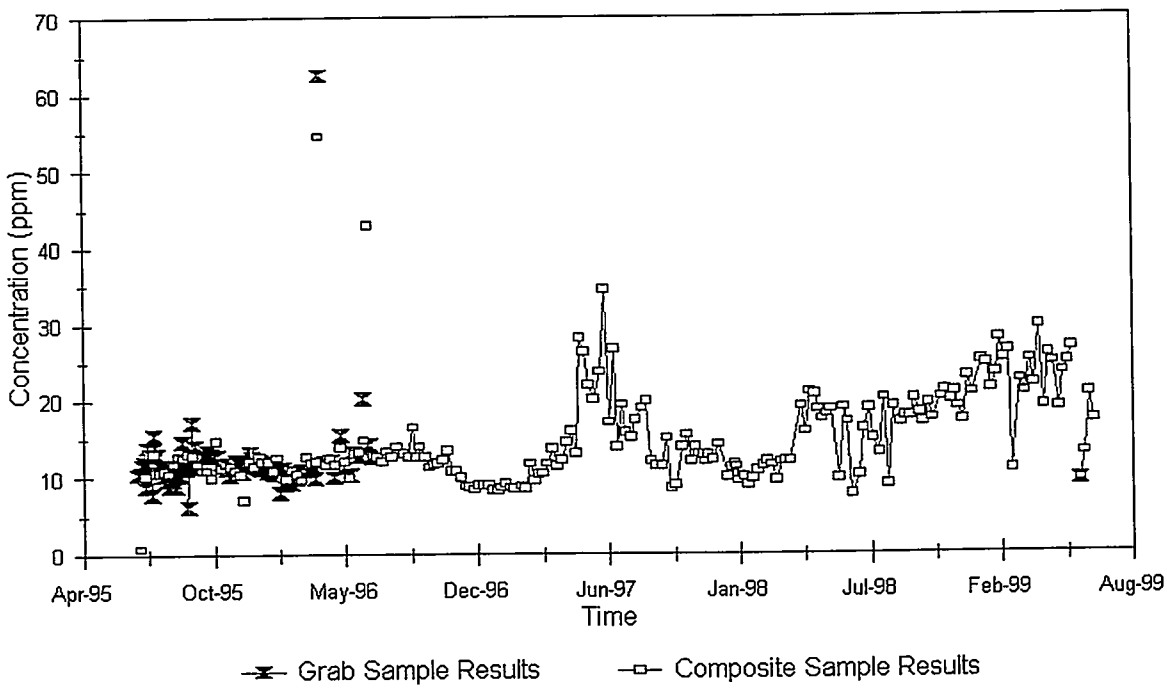


Figure B-9. TEDF Effluent Variability – Sulfate

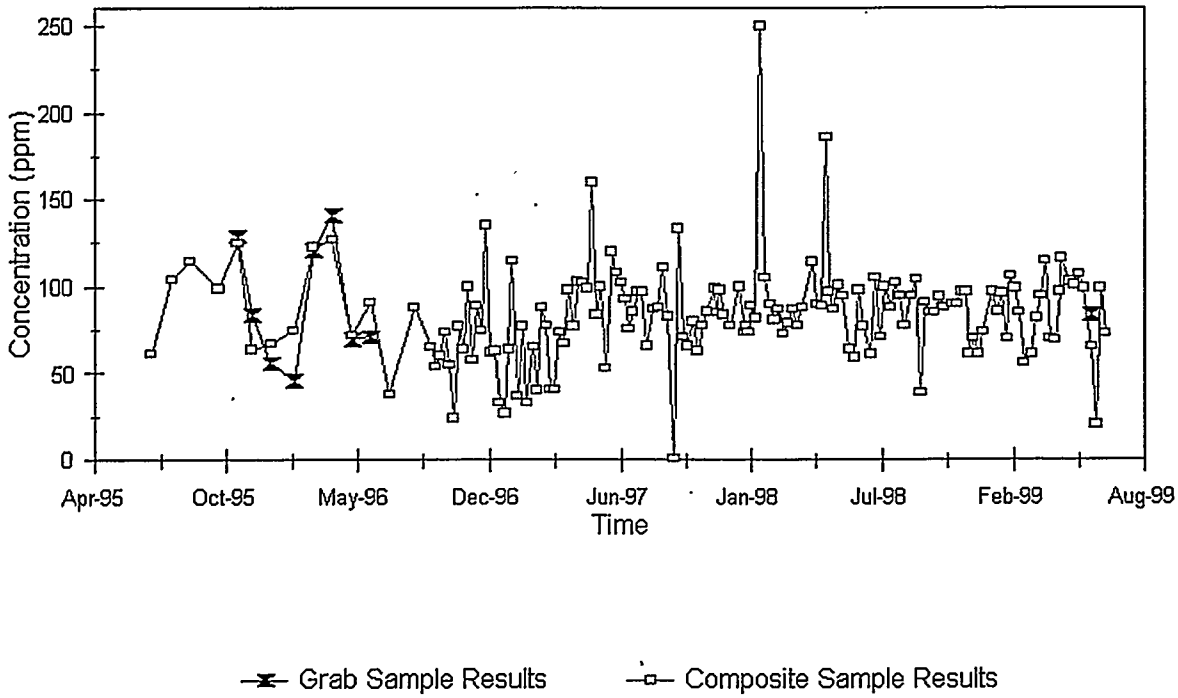


Figure B-10. TEDF Effluent Variability - Total Dissolved Solids

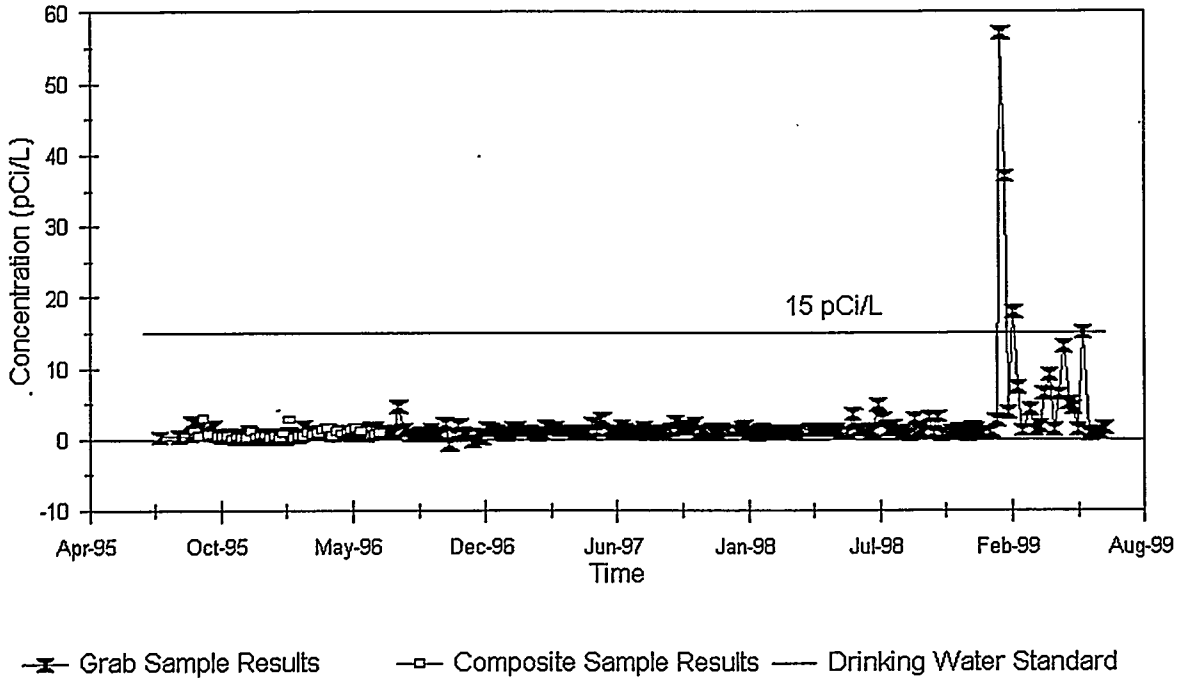


Figure B-11. TEDF Effluent Variability - Gross Alpha

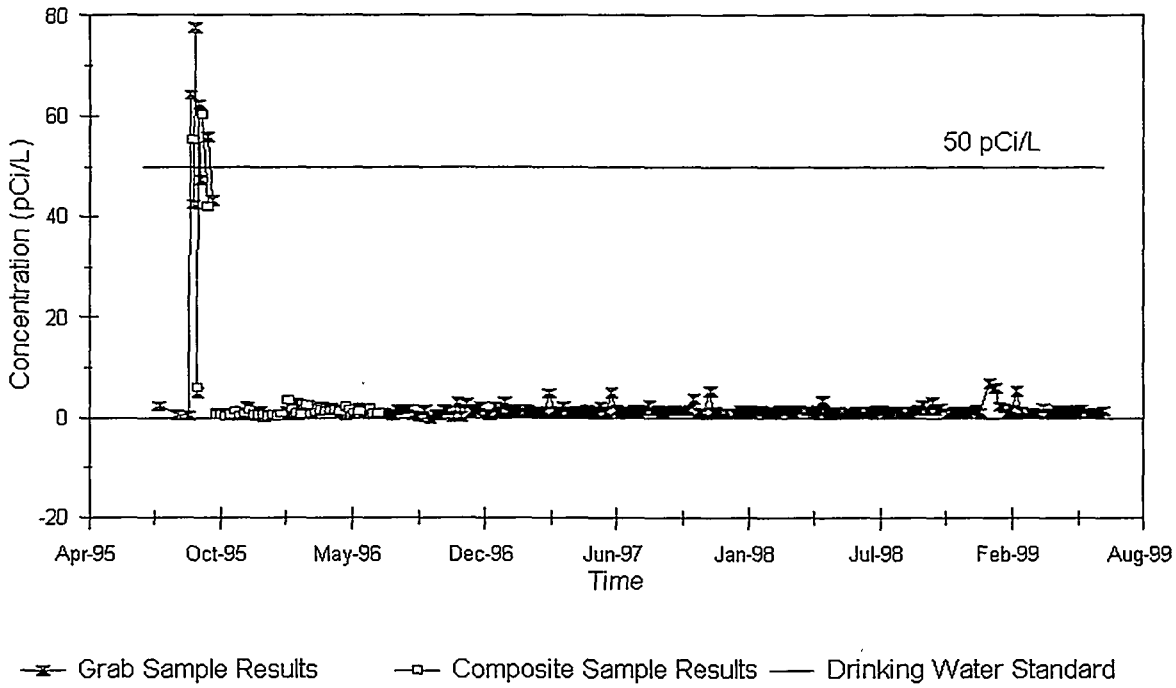


Figure B-12. TEDF Effluent Variability - Gross Beta

Time versus Concentration Plots - Average Monthly Data

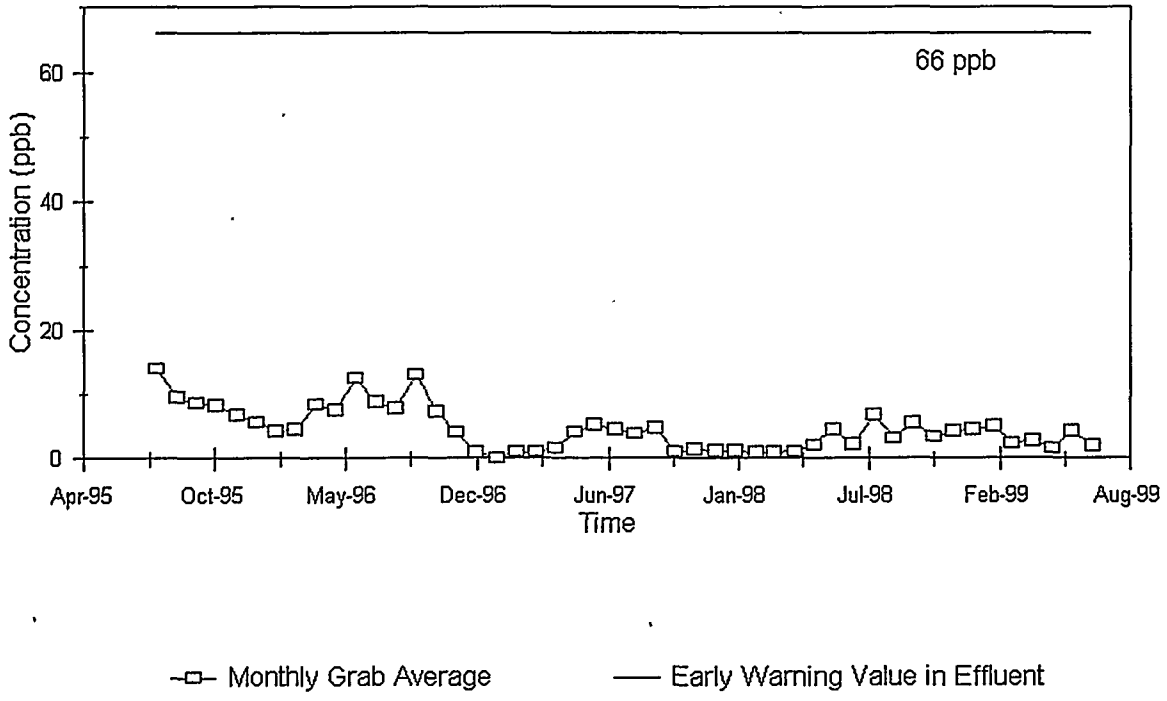


Figure B-13. TEDF Effluent Monitoring Result - Chloroform Monthly Averages

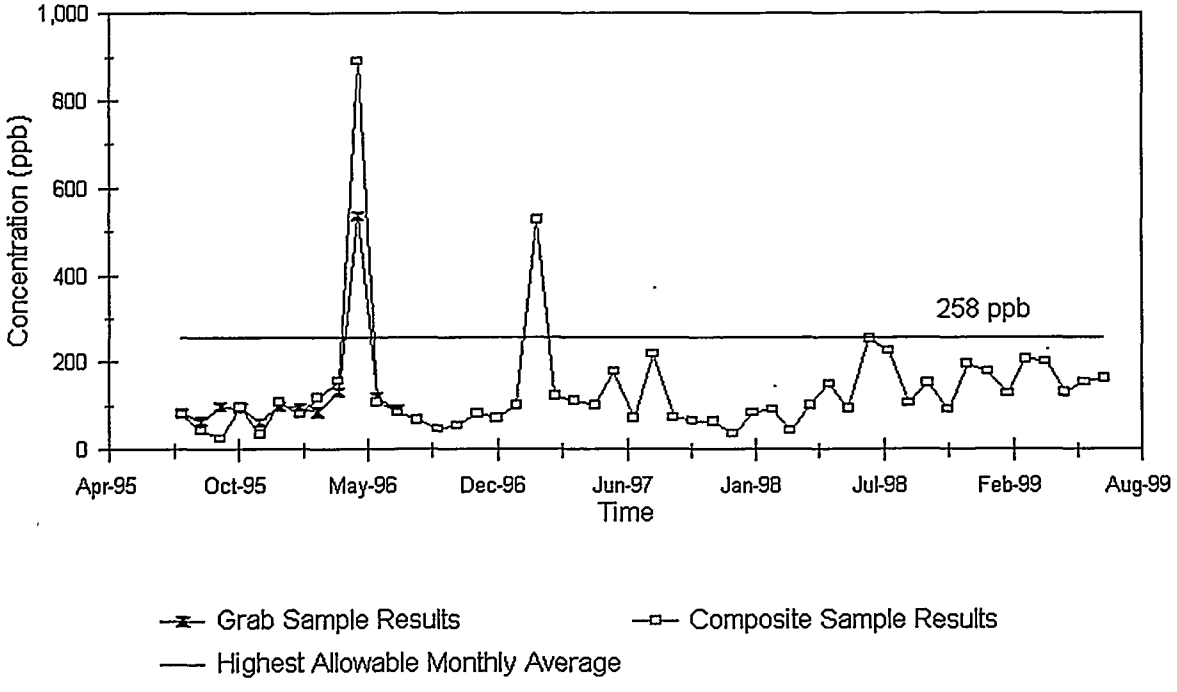


Figure B-14. TEDF Effluent Monitoring Result - Iron Monthly Averages

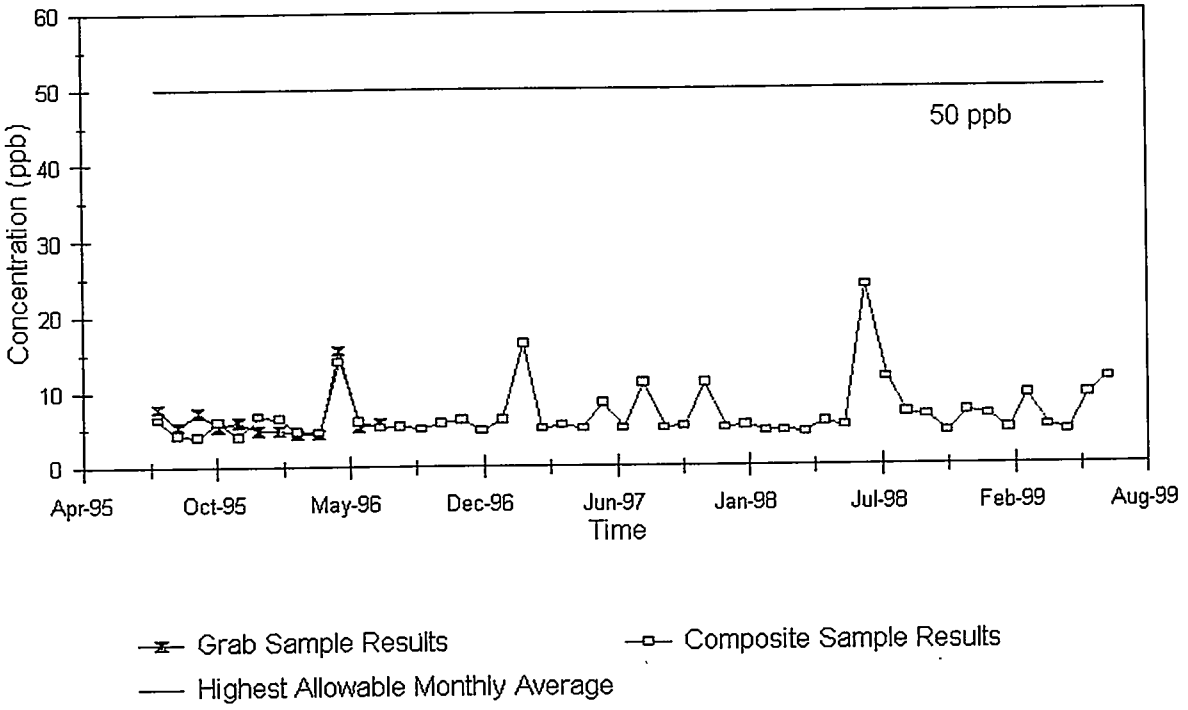


Figure B-15. TEDF Effluent Monitoring Result - Manganese Monthly Averages

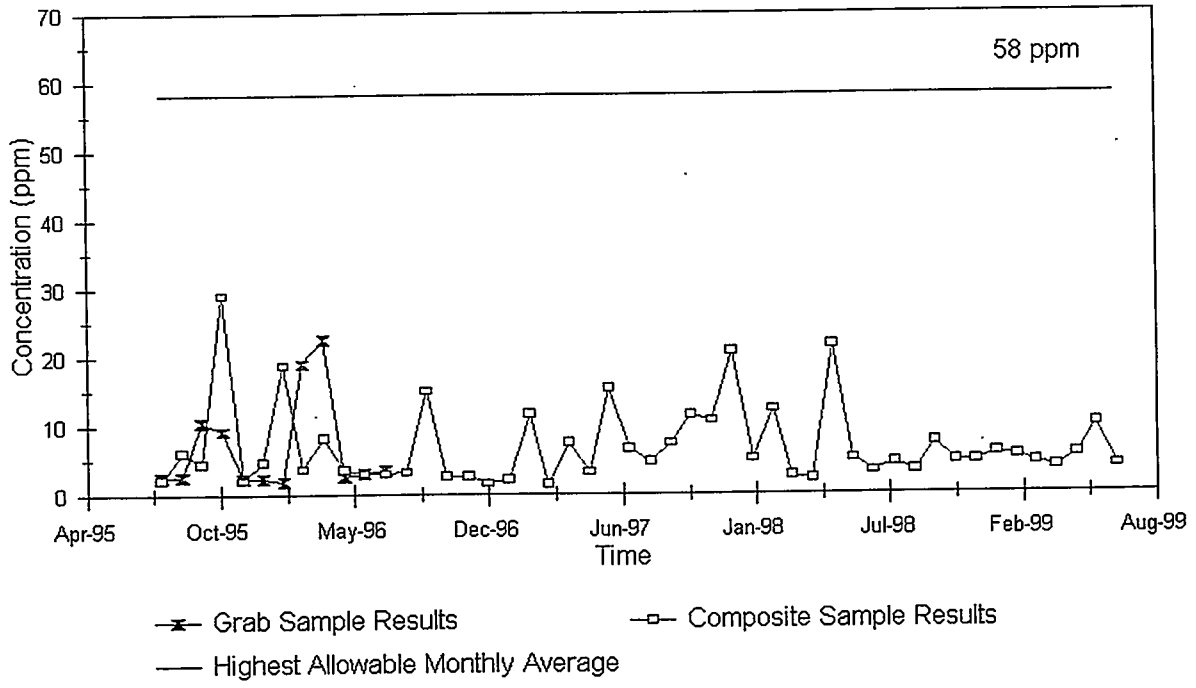


Figure B-16. TEDF Effluent Monitoring Result - Chloride Monthly Averages

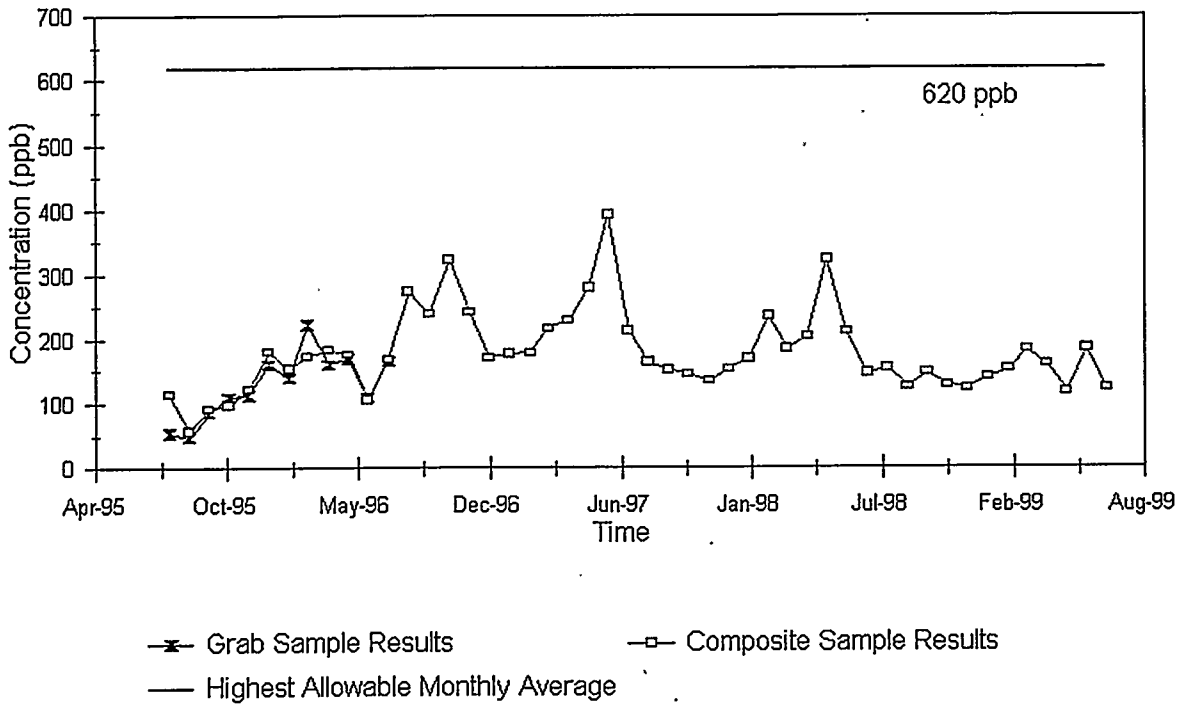


Figure B-17. TEDF Effluent Monitoring Result - Nitrate (as N) Monthly Averages

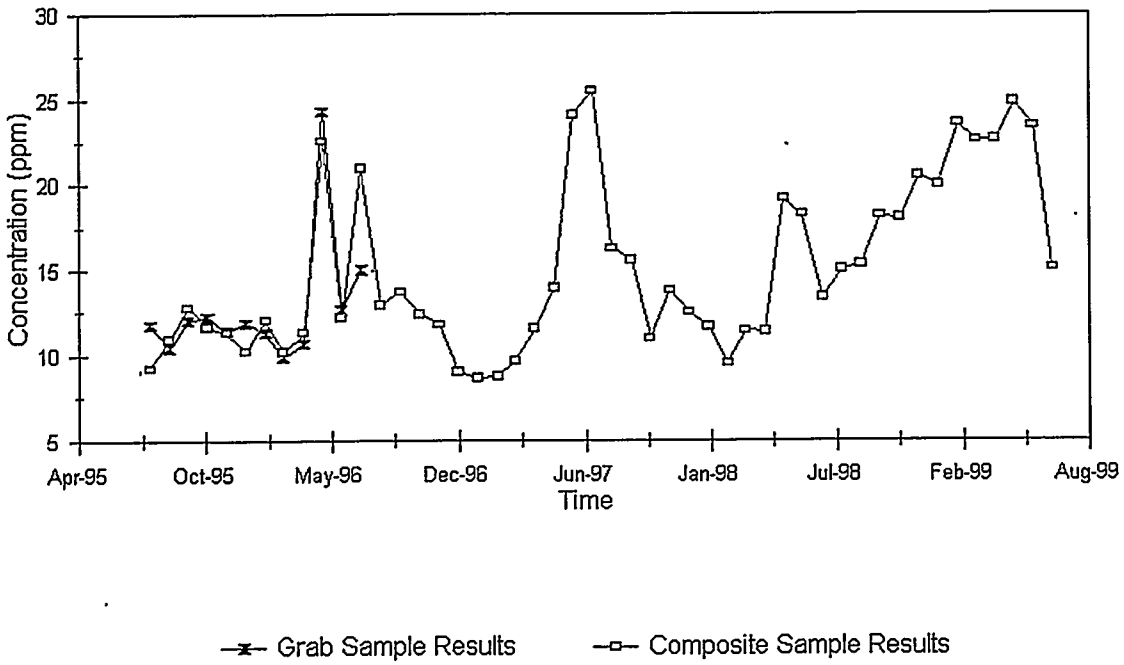


Figure B-18. TEDF Effluent Monitoring Result - Sulfate Monthly Averages

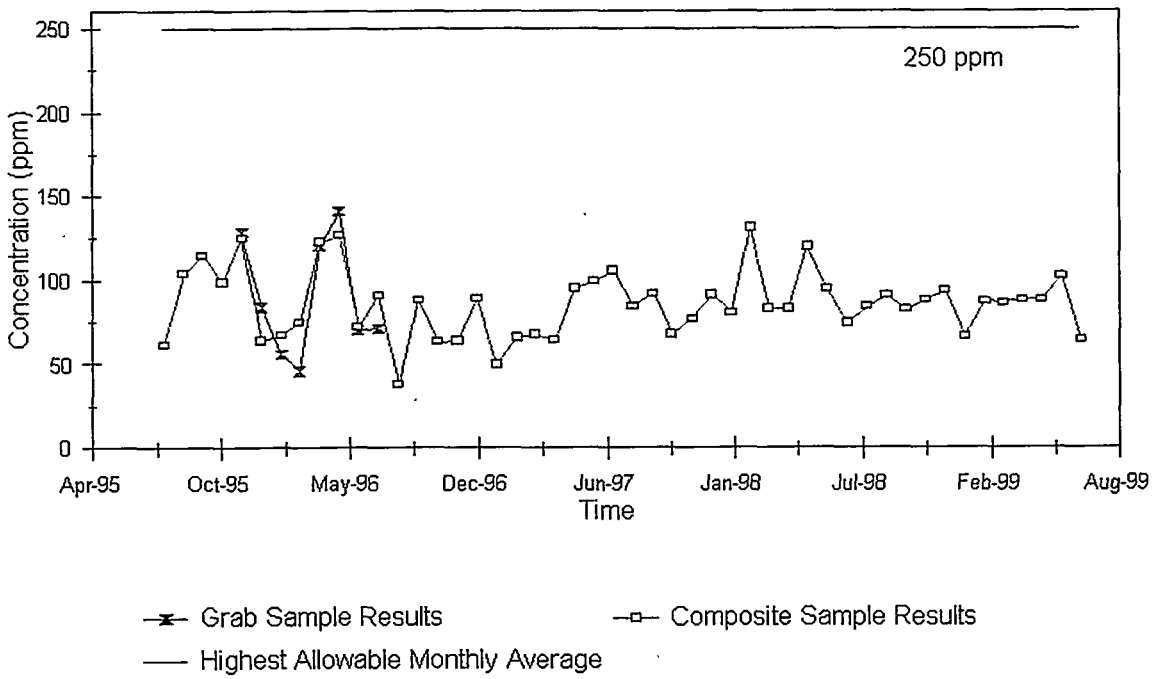


Figure B-19. TEDF Effluent Monitoring Result - Total Dissolved Solids (TDS) Monthly Averages

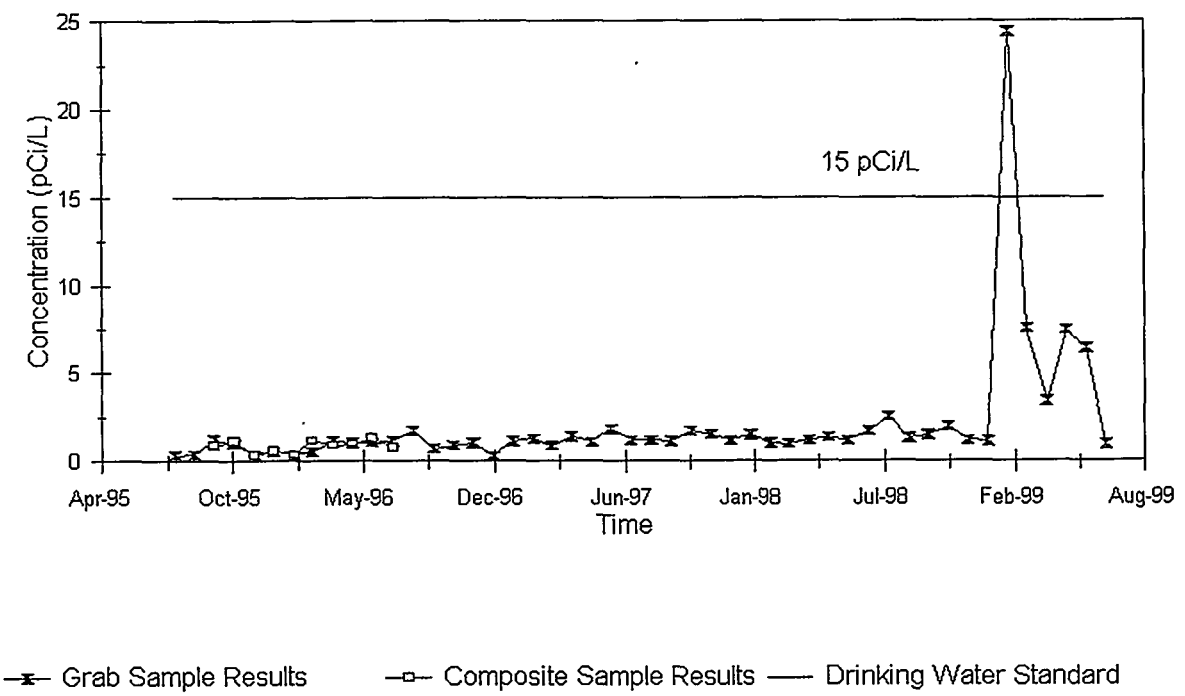


Figure B-20. TEDF Effluent Monitoring Result - Gross Alpha Monthly Averages

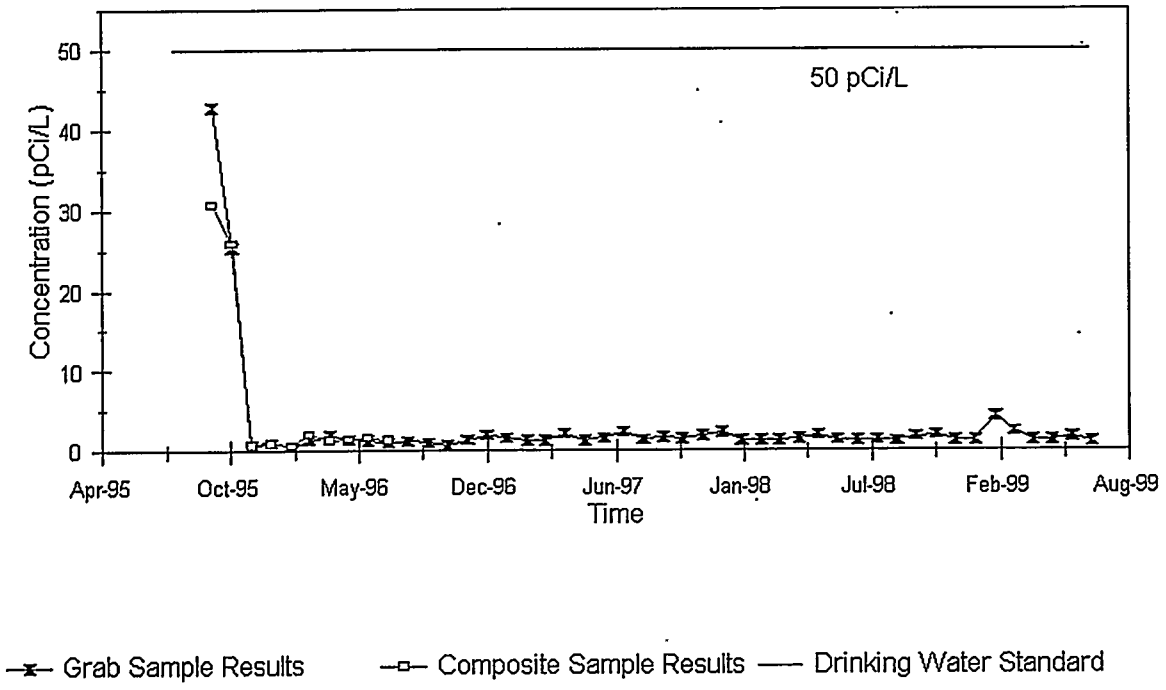


Figure B-21. TEDF Effluent Monitoring Result - Gross Beta Monthly Averages

Multiple Box and Whiskers Plots - Seasonal Effects

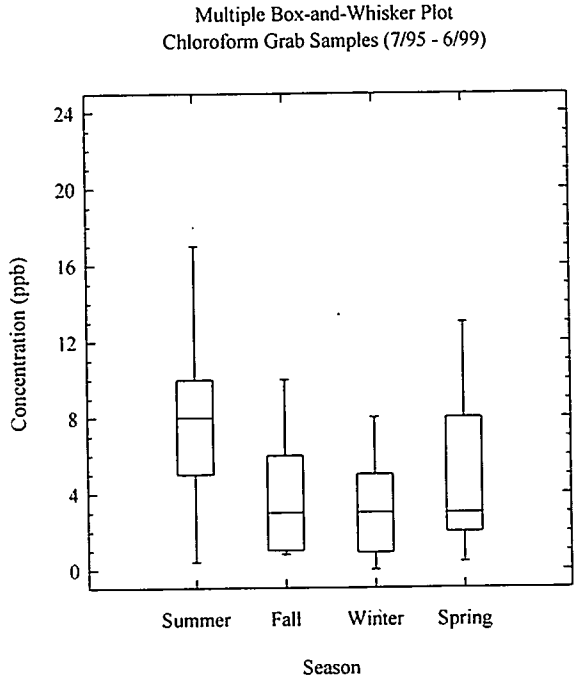
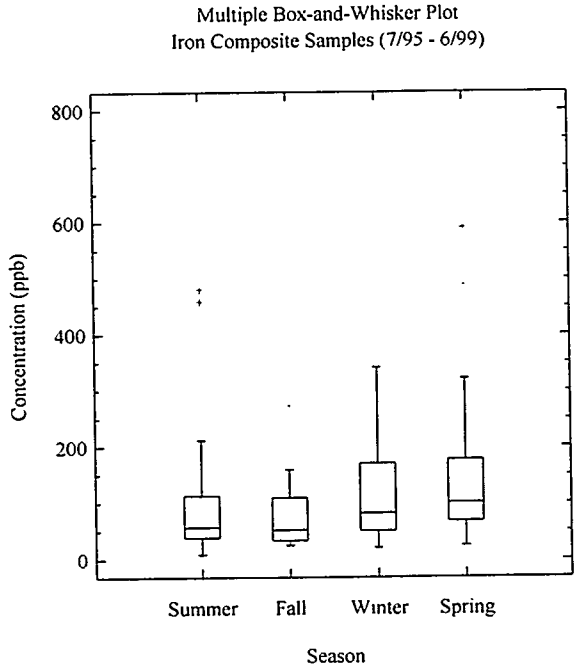
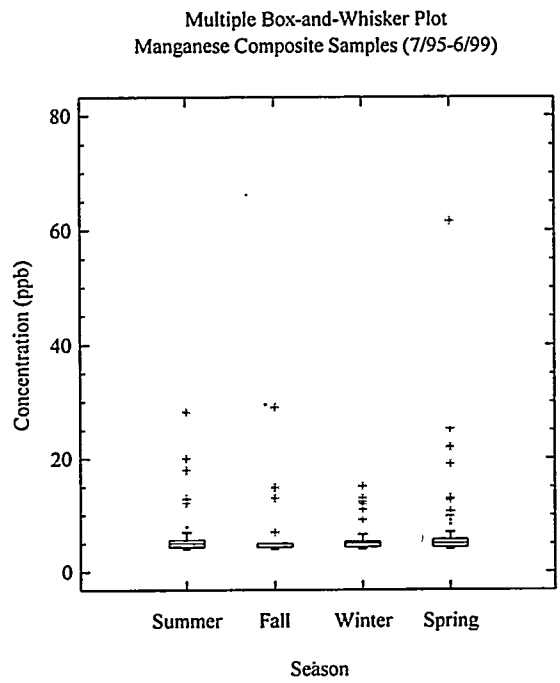


Figure B-22. Chloroform Grab Sample Results Shown by Season



Excursions (4/7/96 & 1/12/97) Excluded

Figure B-23. Iron Composite Sample Results Shown by Season



Exluded Data (4/7/96 & 1/12/97)

Figure B-24. Manganese Composite Sample Results Shown by Season

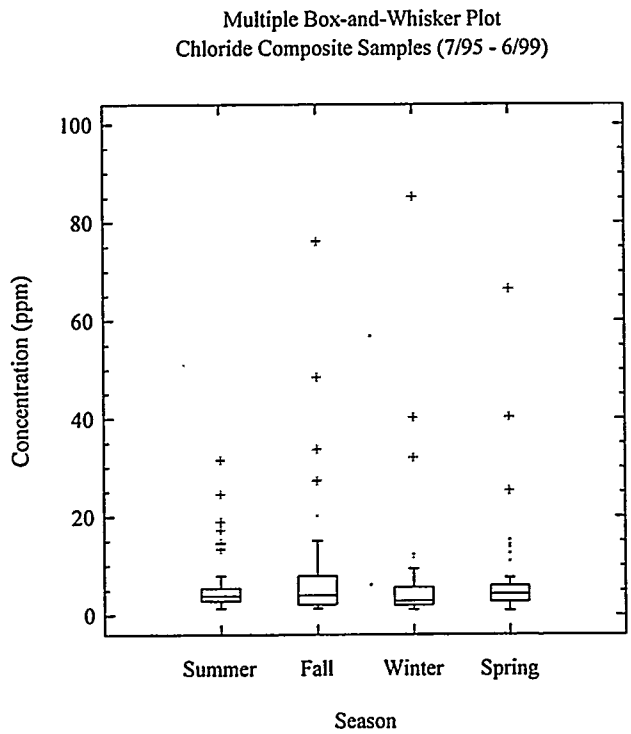


Figure B-25. Chloride Composite Sample Results Shown by Season

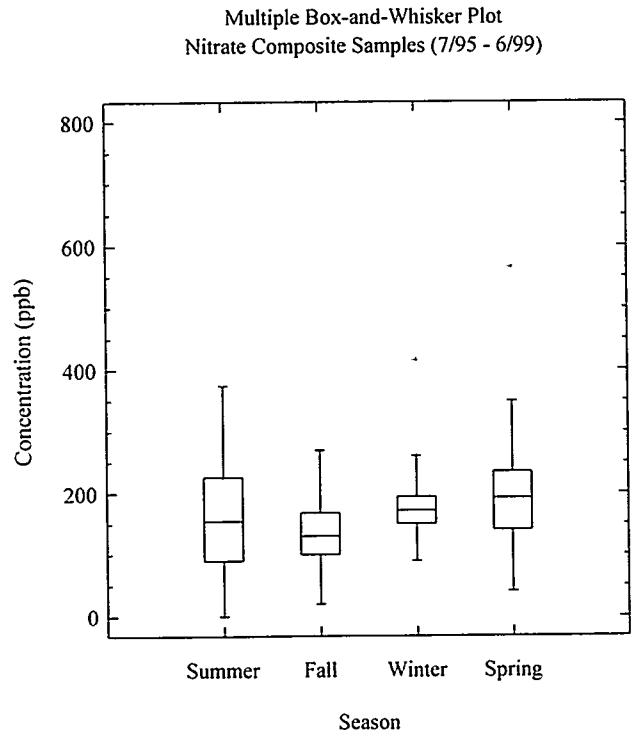


Figure B-26. Nitrate (as N) Composite Sample Results Shown by Season

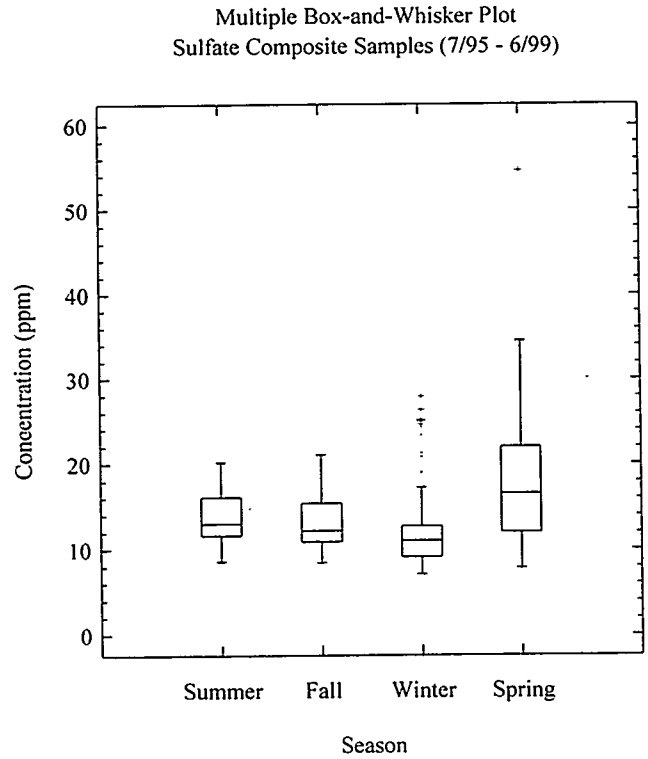


Figure B-27. Sulfate Composite Sample Results Shown by Season

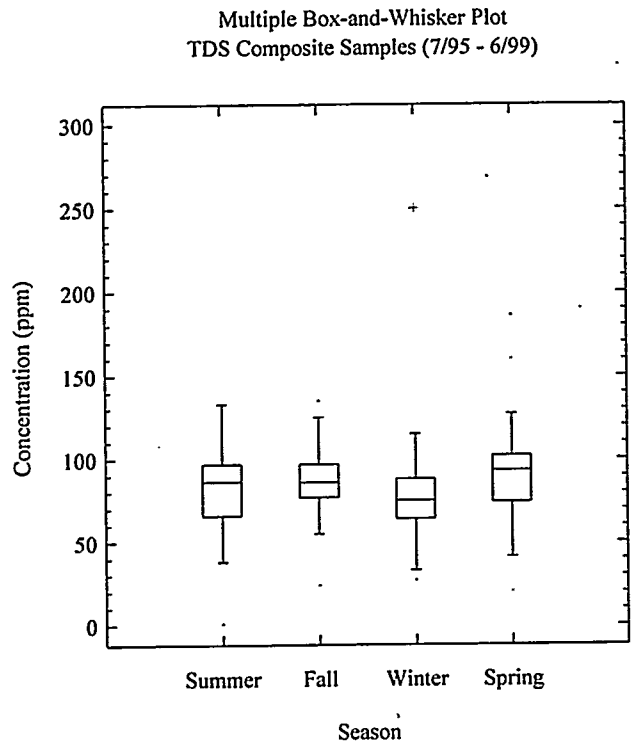
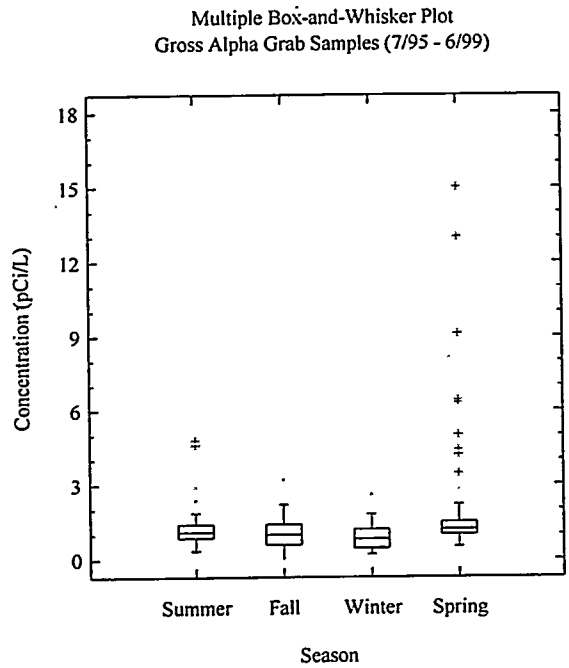
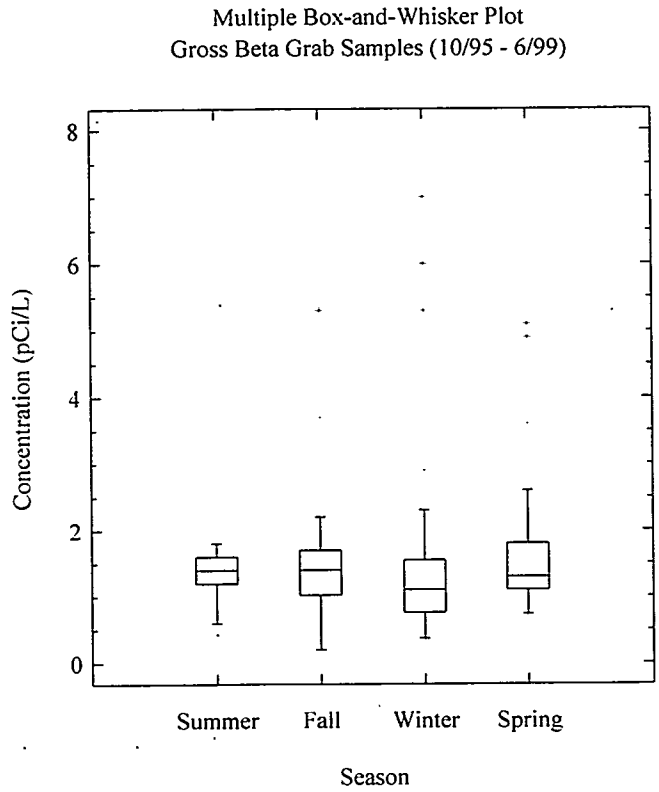


Figure B-28.. Total Dissolved Solids Composite Sample Results Shown by Season



Excluded Data From 1/22/99 to 2/17/99

Figure B-29. Gross Alpha Grab Sample Results Shown by Season



Exclude Data Prior to 10/23/95

Figure B-30. Gross Beta Grab Sample Results Shown by Season

Multiple Box and Whisker Plots - Sample Type Effects

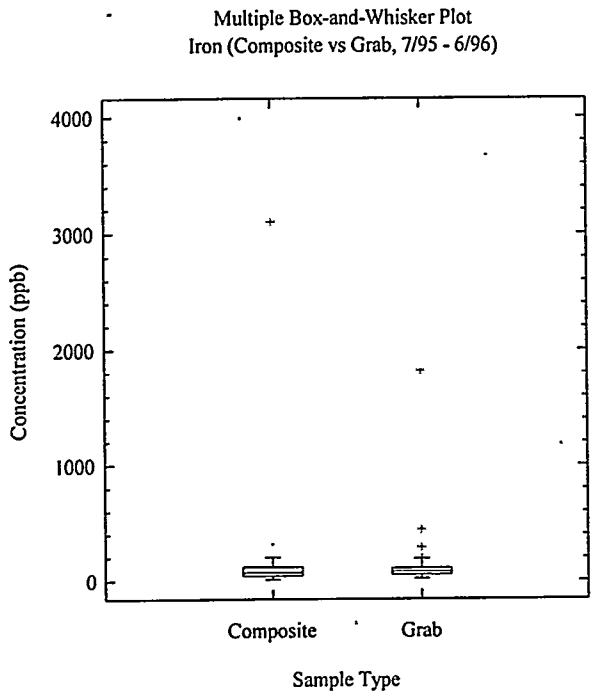


Figure B-31. Multiple Box and Whisker Plot - Iron (Composite versus Grab Sample Results)

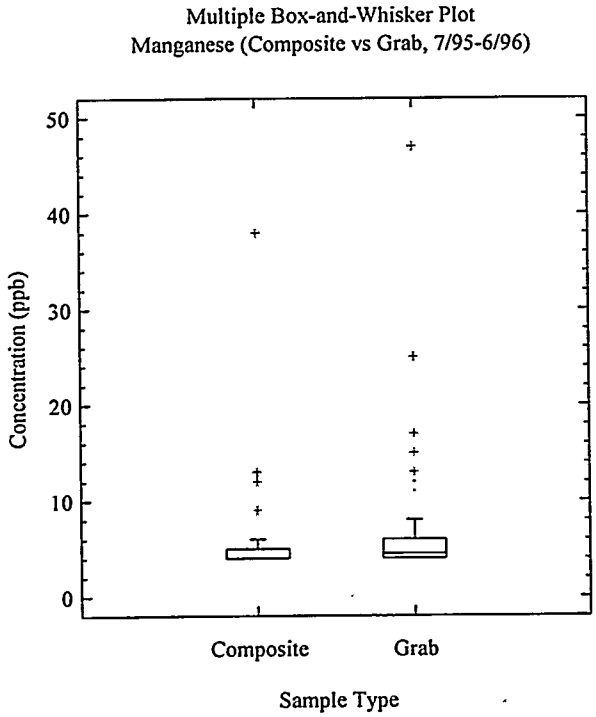


Figure B-32. Multiple Box and Whisker Plots - Manganese (Composite versus Grab Sample Results)

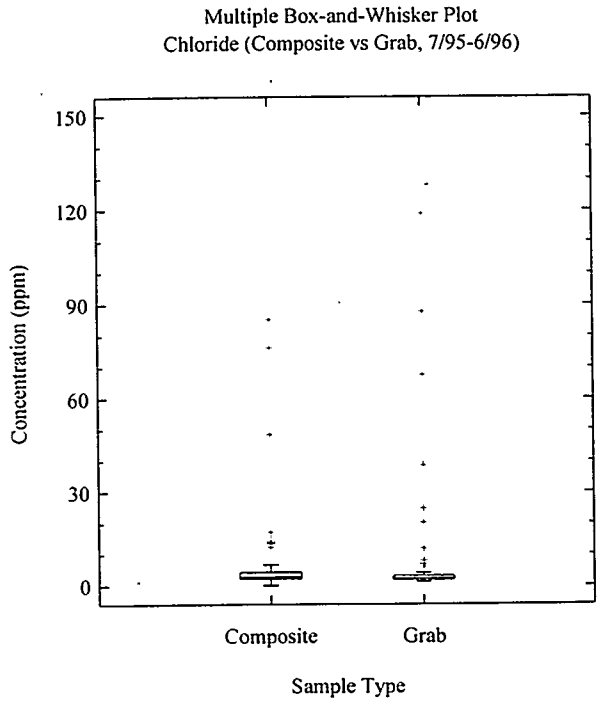


Figure B-33. Multiple Box and Whisker Plots - Chloride (Composite versus Grab Sample Results)

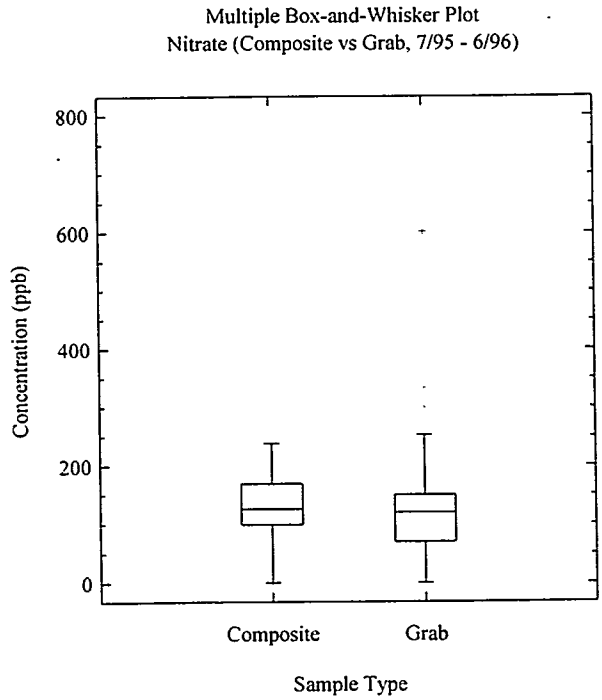


Figure B-34. Multiple Box and Whisker Plots - Nitrate (Composite versus Grab Sample Results)

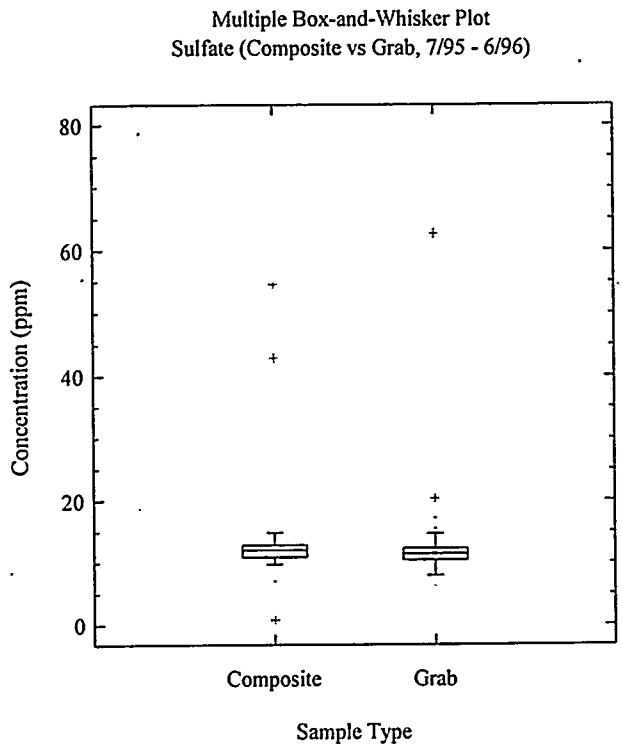


Figure B-35. Multiple Box and Whisker Plots - Sulfate (Composite versus Grab Sample Results)

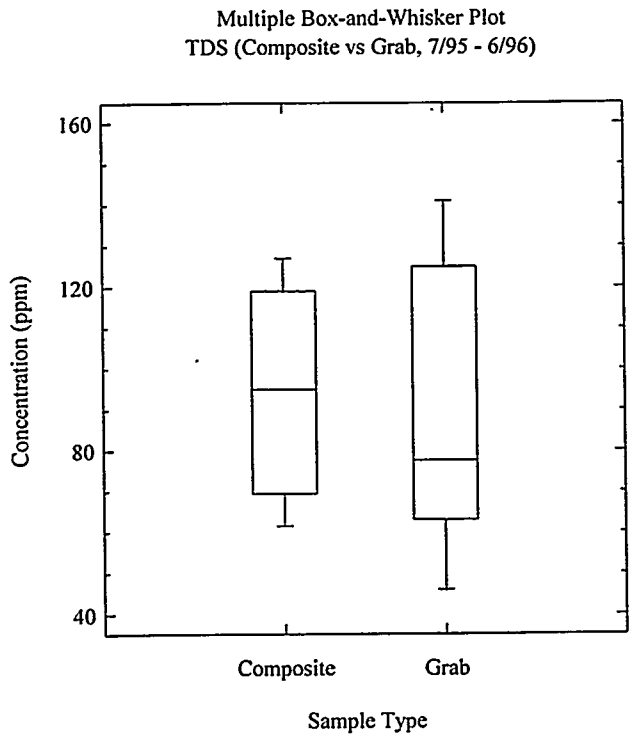


Figure B-36. Multiple Box and Whisker Plots - Total Dissolved Solids (Composite versus Grab Samples)

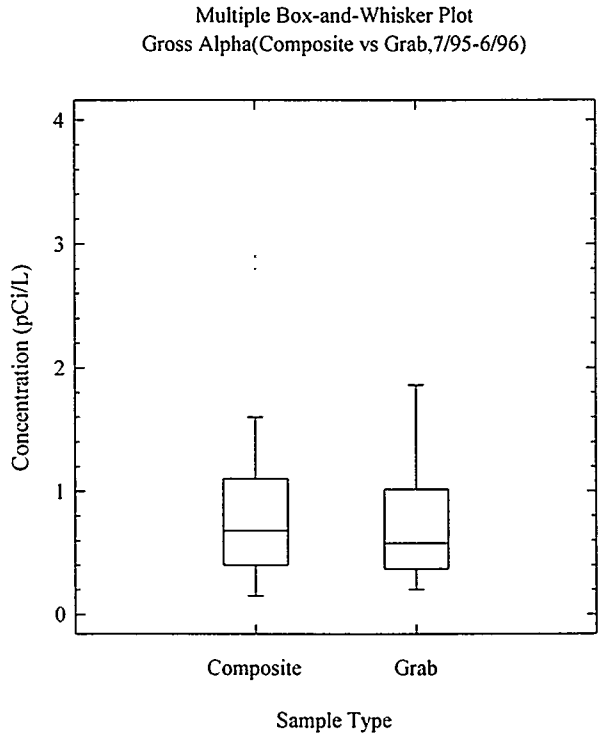


Figure B-37. Multiple Box and Whisker Plots - Gross Alpha (Composite versus Grab Sample Results)

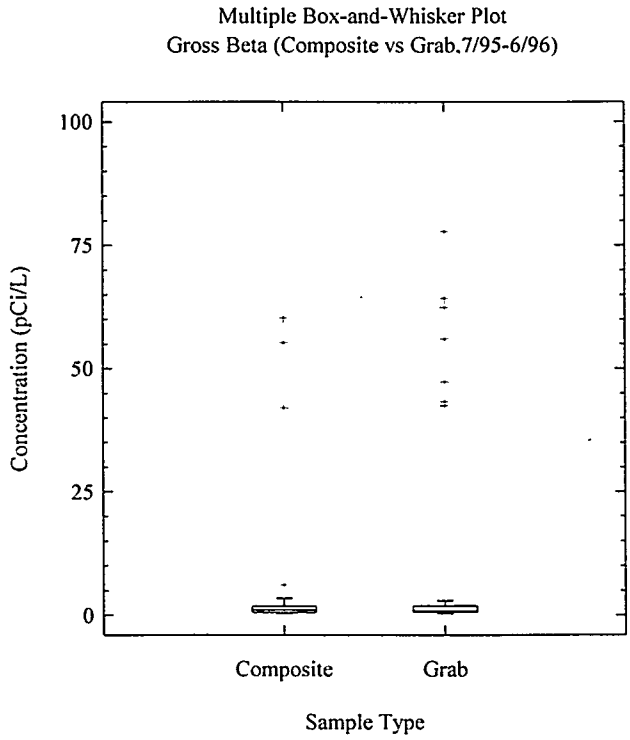


Figure B-38. Multiple Box and Whisker Plots - Gross Beta (Composite versus Grab Sample Results)

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