

**Memorandum**

MAY 09 2001

**MWQI Copy**

Date :  
To : Municipal Water Quality Investigations Committee

**Photocopy and RETURN**

Rich Breuer, Chief *Richard S Breuer*  
Municipal Water Quality Investigations Program  
From : **Department of Water Resources**

Subject : Sievers Organic Carbon Analyzer Pilot Study

Please find enclosed, a copy of the report on the pilot study on field use of the Sievers Model 800 organic carbon auto-analyzer at the Hood field facility. The study was to evaluate the Sievers equipment's ability to provide representative data during automated field operation over an extended period of time. The Sievers Model 800 is intended for bench-top use in a lab setting.

The analyzer was purchased and installed at the Hood Field Station on the Sacramento River. Initial operation and testing of the unit began in January 1999. Preliminary tests on the analyzer and its system components were conducted for approximately five months. Various operational modifications and changes in system components were implemented during this period to refine and improve the performance of the analyzer. The initial evaluation indicated that the analyzer, the connected components, and the water delivery system were dependable and operating satisfactorily.

The next step in the study was to begin a year-long pilot study to evaluate the ability of the analyzer to provide representative data over a sustained period of automated operation. During this pilot study a series of samples were collected weekly to evaluate the accuracy and reliability of the auto-analyzer and performance of the water delivery system. The attached report contains details of how this pilot study was conducted, with a discussion of the sample data collected for the study and an evaluation of the Sievers equipment's performance in field use.

The study showed the Sievers analyzer to be a generally dependable instrument capable of providing consistently representative data. However, some limitations were encountered with the analyzer, most critically, the instrument's inability to accommodate raw high turbidity surface water. This instrument continues to be in operation at the Hood Field Station and the analytical data it produces is now uploaded weekly and is available on the California Data Exchange Center web site.

Enclosure

State of California  
The Resources Agency  
DEPARTMENT OF WATER RESOURCES  
Division of Planning and Local Assistance

**Pilot Study on the Analytical Performance  
of a Total Organic Carbon Analyzer  
in Operation at a Field Station on  
the Sacramento River**

Memorandum Report

May 2001

# Table of Contents

<b>INTRODUCTION</b> .....	<b>3</b>
History of Organic Carbon Issues .....	3
Selection of Analyzer .....	4
Monitoring Site Selection and Requirements .....	5
Study Objective .....	6
<b>INSTRUMENTATION INSTALLATION AND OPERATION</b> .....	<b>6</b>
Water Delivery System .....	6
Analyzer System Components .....	7
Operation of Analyzer .....	10
Water Delivery System Modifications .....	11
Sample Criteria .....	14
<b>QUALITY ASSURANCE/QUALITY CONTROL</b> .....	<b>15</b>
Quality Control Samples .....	15
Data Assessment .....	16
<b>RESULTS/DISCUSSION</b> .....	<b>17</b>
Average Daily Results .....	17
Grab Sample Results .....	23
<b>QUALITY CONTROL SAMPLES</b> .....	<b>56</b>
Performance Evaluation Samples .....	56
<b>CONCLUSIONS AND RECOMMENDATIONS</b> .....	<b>59</b>
<b>ACKNOWLEDGEMENTS</b> .....	<b>63</b>

## Tables

Table 1. Sacramento River Particle Size vs. Turbidity .....	13
Table 2. Three Month Daily Precipitation Total vs. Daily TOC Average, 1/1/2000 through 3/31/2000 .....	21
Table 3. Comparison of Bryte Chemical Laboratory Analysis of River Grab and Filter Outlet Grab Samples to Evaluate TOC Influence the Water Delivery System has on Water Quality .....	24
Table 4. Relative Percent Difference in Analysis of River Grab Samples by the Bryte Chemical Laboratory and Sievers Analyzer On-line Analysis .....	28
Table 5. Relative Percent Difference in TOC Analysis by Bryte Chemical Laboratory of River Grab Samples and the Sievers Analyzer On-line Analysis .....	31
Table 6. Comparison of Bryte Chemical Laboratory DOC Analysis of Filter Inlet and Filter Outlet Grab Samples .....	36
Table 7. Comparison of Bryte Chemical Laboratory DOC and TOC Analysis of Grab Samples from Filter Inlet and Outlet to River Samples to Evaluate Water Quality Impacts of Water Delivery System .....	41
Table 8. Comparison of Weekly Duplicate Filter Outlet Grab Sample TOC and DOC Analysis by the Bryte Chemical Laboratory and the Sievers Analyzer On-line Analysis .....	46
Table 9. Results of Weekly Duplicate Filter Outlet Grab Sample TOC Analysis by the Bryte Chemical Laboratory and the Sievers Analyzer On-line Analysis .....	49
Table 10. Comparison of Sievers Analyzer On-line Analysis to Bryte Chemical Laboratory Filter Outlet and River Grab Sample TOC Results for Estimation of 2 Standard Deviations Using One Way ANOVA Analysis of Variance .....	54
Table 11. Round 1 - Performance Evaluation TOC Sample Results between the Sievers Analyzer and the Bryte Chemical Laboratory O/I Analytical 1010 Analyzer .....	57
Table 12. Round 2 - Performance Evaluation TOC Sample Results between the Sievers Analyzer and the Bryte Chemical Laboratory O/I Analytical 1010 Analyzer .....	58
Table 13. Bryte Chemical Laboratory Replicate Analysis Variability of DOC and TOC Samples .....	60

## Figures

Figure 1. Real-Time TOC Monitoring System at the Hood Field Station .....	8
Figure 2. Sievers Model 800 Analyzer Daily Average TOC for the Sacramento River at the Hood Facility for One Year .....	19
Figure 3. Sievers Model 800 Analyzer TOC Values of Four Sampling Event Averages per Day During 1999/2000 Winter Season .....	20
Figure 4. Daily TOC Values vs. Daily Precipitation Totals .....	22
Figure 5. Comparison of River Grab and Filter Outlet Grab Samples to Evaluate TOC Influence of the Water Delivery System on Water Quality .....	26
Figure 6. Comparison of Bryte Chemical Laboratory DOC/TOC Analysis of River Grab Samples and Sievers Analyzer On-line Analysis .....	30
Figure 7. Comparison of TOC Analysis of Bryte Chemical Laboratory of River Grab Samples and the Sievers Analyzer On-line Analysis .....	34
Figure 8. Comparison of Bryte Chemical Laboratory DOC Analysis of Filter Inlet and Filter Outlet Grab Samples .....	38
Figure 9. Comparison of Filter Inlet and Filter Outlet DOC Grab Samples to River DOC Grab Samples .....	39
Figure 10. Comparison of Bryte Chemical Laboratory Filter Inlet and Filter Outlet TOC Grab Sample Analysis .....	40
Figure 11. Comparison of Bryte Chemical Laboratory Analysis of Filter Inlet and Filter Outlet TOC Samples to River TOC Grab Samples .....	44
Figure 12. Comparison of Weekly Duplicate Filter Outlet Grab Sample TOC and DOC Analysis by the Bryte Chemical Laboratory and the Sievers Analyzer On-line Analysis .....	48
Figure 13. Comparison of Weekly Duplicate Filter Outlet Grab Sample TOC Analysis by the Bryte Chemical Laboratory and the Sievers Analyzer On-line Analysis .....	51
Figure 14. Estimated Range in RPD Between Bryte Chemical Laboratory TOC Analysis of River Grab Sample and Sievers Analyzer On-line Analysis .....	53

## INTRODUCTION

### History of Organic Carbon Issues

Natural organic matter (NOM) in the waters of the Sacramento-San Joaquin Delta is an important issue for the health of aquatic ecosystems and for the production of quality drinking water. The aquatic ecosystems depend on a combination of photosynthesis and NOM to initiate energy transference through the trophic levels of the food chain. In this application, the organic matter is considered a beneficial water quality component of the aquatic system.

Organic matter can create problems in the production of drinking water. Organic matter, in the form of organic carbon, with bromide ions adversely impacts drinking water quality because they act as precursors to the formation of trihalomethanes (THMs) and other disinfection byproducts (DBPs). These byproducts are formed during the treatment of water with chlorine or ozone to remove harmful microorganisms.<sup>1,2</sup> DBPs are undesirable products in drinking water because they are potential carcinogens in humans and are regulated by State and federal regulations. The higher the amounts of organic carbon and bromide in the source water, the greater the amount of pre-treatment conditioning required prior to chlorination/ozonation to minimize DBP formation.

Identifying the contributing sources of organic carbon in the Delta and estimating the relative amount from these sources is a complex process. One way is to measure organic carbon in the Sacramento and San Joaquin Rivers that flow into the Delta and also to evaluate the processes at work within the Delta that contribute organic carbon to the system. Numerous studies have shown that factors such as the physical design, soil composition, biological organisms, agricultural practices, urban development, and hydrological processes play critical roles in the water quality and carbon cycle of the Delta.

The Municipal Water Quality Investigations Program was established in 1990 to monitor organic carbon and other parameters of concern for drinking water in Delta channels and agricultural drains that provide source water for the State Water Project. Through the years, MWQI has compiled extensive water quality data from a number of Delta sites. Most of the organic carbon occurrence and distribution data in the Delta are based on monthly sampling events with the exception of a few studies that were based on weekly events. A monthly or a weekly grab sample cannot provide a representative picture of the variability or pulses in organic carbon loading that result from storm events, agricultural or urban discharges, or other activities that can affect water quality. To get this data, samples would have to be collected daily or hourly. The associated additional costs from the required increased staff time and analytical fees would prohibit such a high frequency grab sample collection schedule.

---

<sup>1</sup> Krasner, S.W., et. al. June 1996. Three approaches for characterizing NOM. Journal of American Water Works Association.

<sup>2</sup> Pomes, Michael, et al. 1999. DBP formation potential of aquatic humic substances. AWWA Journal, Vol. 91



## **Selection of Analyzer**

To provide more continuous real-time total organic carbon (TOC) data, it was proposed that MWQI staff investigate the feasibility of using portable TOC analyzers at sites within the Delta. The criteria for the analyzer were that it be able to operate in an unattended autosampling mode, employ an approved Environmental Protection Agency method of TOC analysis, have telemetry capabilities, allow routine calibration and maintenance to be performed in the field by staff, and be easily moved from site to site if needed. After reviewing the set-up and operation requirements of models meeting the criteria available at the time of this study, the Sievers Model 800 was selected for this project.

The instrument is manufactured by Sievers Instruments. When purchased in 1996, the instrument was considered state of the art for a portable organic carbon analyzer. It uses a digestion method of analysis that is based on the oxidation of organic compounds to form carbon dioxide by adding an oxidizing agent (ammonium persulfate), an acid (phosphoric acid) to lower the pH, and UV radiation. During an analysis, the instrument first measures the total inorganic carbon, then determines the total carbon content of the sample after oxidation of the organic compounds. The total organic carbon concentration is calculated by measuring the difference between the total carbon and total inorganic carbon concentrations ( $TOC = TC - TIC$ ).

After an analysis, the unit will immediately repeat the analytical procedure on a new sample and continue this process for the duration of the sampling program that has been entered by the operator. The instrument can perform one analytical cycle every six minutes. The instrument can be configured to operate in an on-line flow-through mode where it is connected to a pressurized water delivery line, or in a grab sample mode where an operator manually provides samples to the analyzer.

Another important consideration was how this instrument would be field operated compared with how it would be routinely used in standard applications. The target applications for the instrument are in the pharmaceutical and electronic chip manufacturing sectors and others areas that require high quality finished water. DWR's application used the instrument in the analysis of raw surface water. Because this was the first time this model was used in this application, staff worked closely with Sievers to ensure optimal field performance of the analyzer. Several meetings were held with Sievers technicians and representatives to discuss the type of water that would be analyzed and to request advice on the best way to install and operate the instrument. The manufacturer provided assistance in planning the initial equipment installation and operational design of the study and it was decided to take a conservative approach in the initial operational stage of the study.

The main concern was the unknown effect of running unfiltered raw water through the analyzer for an extended period. It was not known if suspended material and sediment in the water, especially during storm events, would be problematic to the instrument or clog the small-bore tubing and analytical components of the analyzer. Although the analyzer is factory equipped with a 60 micron ( $\mu\text{m}$ ) on-line filter, the Sievers representatives thought it best to begin the study with a 1  $\mu\text{m}$  on-line filter unit before

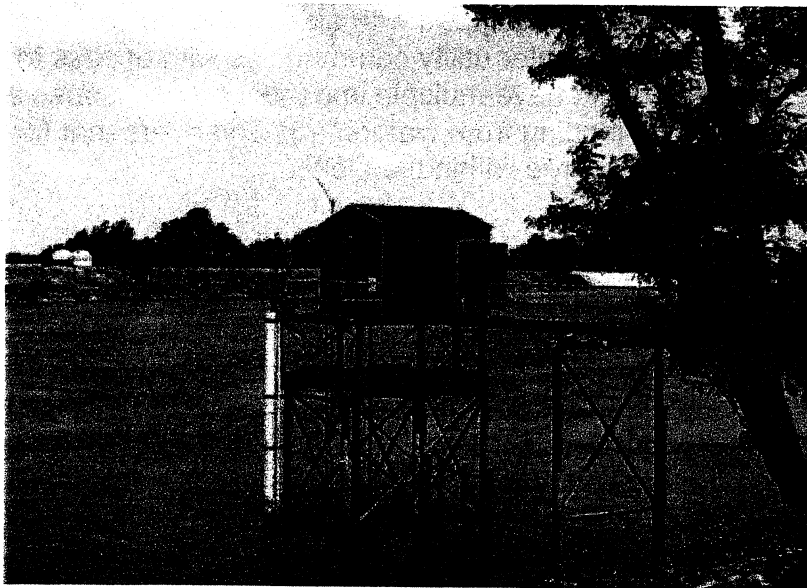
the water entered the analyzer. This change was recommended because of the small size and limited capacity of the analyzer's on-line filter. The Sievers representatives suggested that filters of larger pore size be tried later if the instrument operated successfully with the 1  $\mu\text{m}$  filter.

### **Monitoring Site Selection and Requirements**

Another important issue was selecting the location to install the analyzer. The site had to meet criteria to assure the proper installation and operation of the unit. These criteria included:

- Security – The instrument had to be installed in a structure that had a high degree of resistance to trespassers and vandalism. DWR has experienced the loss of, and damage to expensive equipment because of vandals.
- Availability of Utilities and Climate Control - At a minimum, the site needed dependable electrical service and access to telephone service or some system that could be used for the telemetry of data. The structure needed to have heating and air conditioning.
- Site Location and Accessibility – Because this was a pilot study that would require frequent visits, a site was needed with a minimum commute time from the DWR field office in West Sacramento. The site also needed to have access especially during severe weather with little risk of flooding.
- Easy Access to Surface Water Source - The site needed a source of surface water that was easily accessible for the installation of a water delivery system to the analyzer.

While investigating the feasibility of potential sites, it was learned that DWR's Environmental Services Office was building a permanent monitoring facility at the DWR site on the Sacramento River in the town of Hood. This site and facility met all the criteria needed for the analyzer. An agreement was made with ESO to allow MWQI to use this facility for the installation of the analyzer.



*Field facility at Hood located on the Sacramento River*

## **Study Objective**

Because this instrument model had never been used for raw water analysis, MWQI conducted a pilot study to assess the field performance of the instrument and the quality of TOC data it produced. This information was needed before operating the instrument in a telemetered mode. This study was designed to address multiple issues about the performance of this instrument and determine whether an organic carbon analyzer could function at a remote DWR operational facility and produce reliable results and representative data.

The first objective was to evaluate the reliability of the instrument. MWQI needed to know if the instrument would successfully perform the programmed sampling regime over an extended period when sampling raw water. This included evaluating the instrument's mechanical and electronic components and its ability to maintain calibration.

The second objective was to see if the system used in delivering water from the river to the instrument affects the TOC content of the sample. The water would need to pass through approximately 21 meters of line and tubing to reach the intake port of the analyzer. The water would also need to pass through a filtering device installed into the system. If the water delivery system and filtration device introduced bias into the data, a determination was needed whether the bias was consistent and predictable, or random in nature.

Finally, MWQI wanted to assess the instrument's ability to provide data that were comparable to the data from corresponding river grab samples and be more cost effective than data produced from river grab samples collected by field staff.

The ability of the analyzer to perform successfully and provide quality data in this pilot study could verify the feasibility of installing similar instruments at key locations in the Delta. A network of field stations equipped with autoanalyzers connected to telemetry could provide the scientific and water utility communities with access to continuous real-time TOC data. This data could have multiple impacts on such issues as understanding temporal patterns of carbon loading from watersheds and rivers that flow into the Delta and agricultural drainage discharge within the Delta.

## **INSTRUMENTATION INSTALLATION AND OPERATION**

### **Water Delivery System**

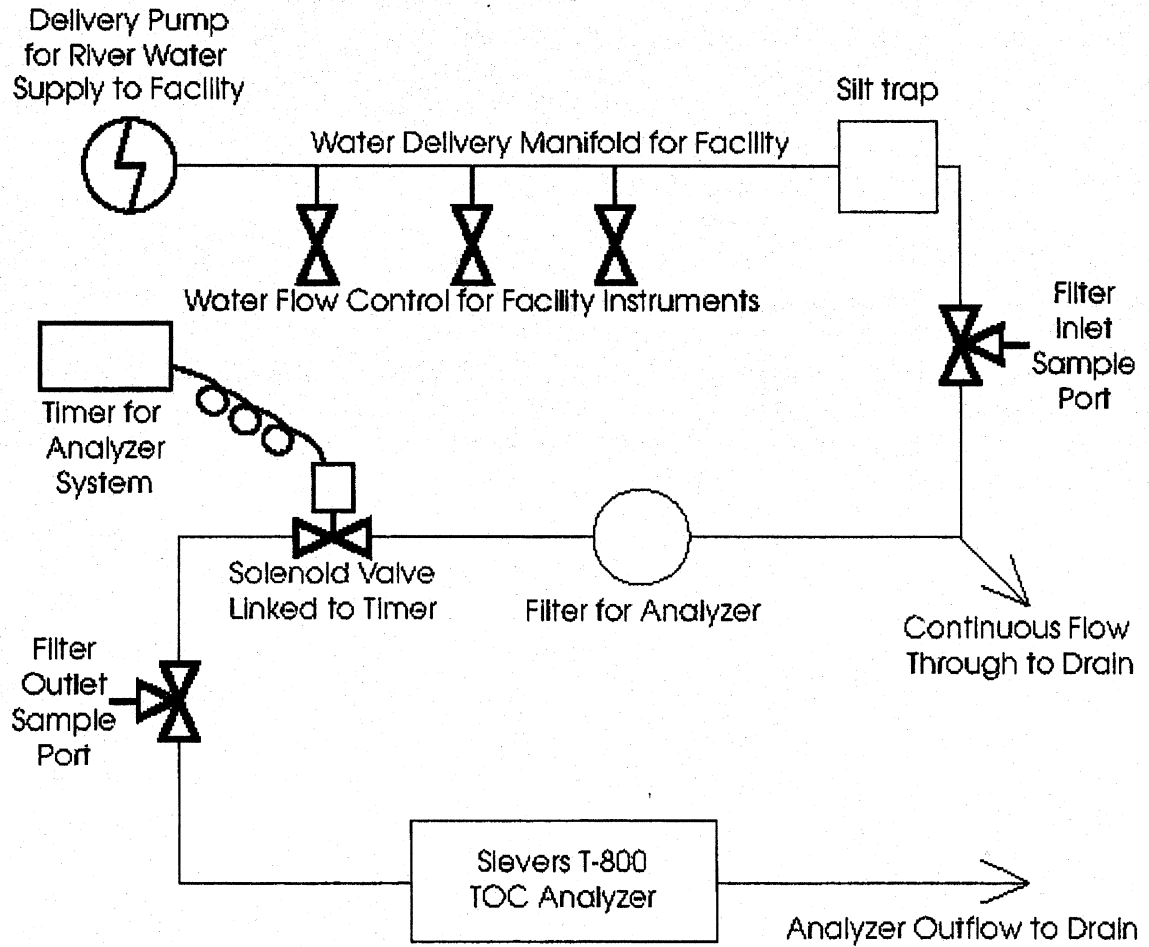
The TOC analyzer was installed at the Hood facility in January 1999. The facility is equipped with a pressurized water delivery manifold connected to a submersible pump positioned 1 meter below the river surface. This pump provides water to the system at a pressure that does not exceed 10 pounds per square inch. This pressurized system provides water to the TOC analyzer and to other instrumentation at the facility that monitors and records various water quality parameters.

### **Analyzer System Components**

Installing the analyzer required additional components be incorporated into the system design to allow the required operation of the instrument. These components included an electronic timer for programming the sampling event schedule, a solenoid valve for controlling the water flow to the analyzer, and a filter for controlling the size of particles entering the analyzer (see Figure 1). While the analyzer is capable of continuous analysis when installed in the on-line operation mode, this routine was not considered appropriate for this application. There was concern that if the filter was installed to a continuous flow-through system, the filter could load to its filtering capacity in a short time. This would require field staff to make frequent site visits for filter changes to prevent a clogged filter from blocking water flow to the analyzer.

Staff decided that the best way to resolve this problem was to control the sampling events of the analyzer with a remote timer and solenoid valve. The timer was programmed to start and stop the analyzer; it determined the duration and frequency of the sampling events. When the timer signals the start of a sampling event, it actuates the solenoid valve, opening the flow of water through the filter unit and into the analyzer. When a sensor on the analyzer detects pressure in the water line, the analyzer shifts from pause mode to analyze mode.

**Figure 1. Real-Time TOC Monitoring System at the Hood Field Station**



At the end of the scheduled sampling event, the timer signals the solenoid valve to close, stopping the water flow to the analyzer. When the analyzer senses the lack of pressure in the line, it enters the pause mode until the next sampling event is triggered. When the analyzer is in the pause mode, the water continues to flow through the line by means of a Y connector installed in the line just before the filter unit. The solenoid valve stops the water flow through the arm of the Y connector that is attached to the filter unit, bypassing and extending the life of the filter. The water line attached to the other arm of the Y connector is left open to allow water to continuously flow through the return drain line where it is discharged into the river. This minimizes the sedimentation and deposition of particulates within the water line.

After the system had been operating for a few months, the solenoid valve developed a problem with closing after the timer had turned off the system. It was necessary to clean the solenoid valve every two weeks to remove the fine silts and particles clogging the water ports in the valve, which shut the valve when given a signal from the solenoid. To correct this problem, the location of the solenoid valve was moved and positioned after the filter. The move enabled the filter to remove the silts and fines before the water entered the valve. After switching the location, there were no further problems with the solenoid valve and timer.

Selecting an appropriate filter and housing was critical to the study's success. A filter was needed that had the capacity to accommodate a large volume of water before clogging and did not contribute organic carbon to the water. The filter housing also could not contribute to the carbon load of the sample.

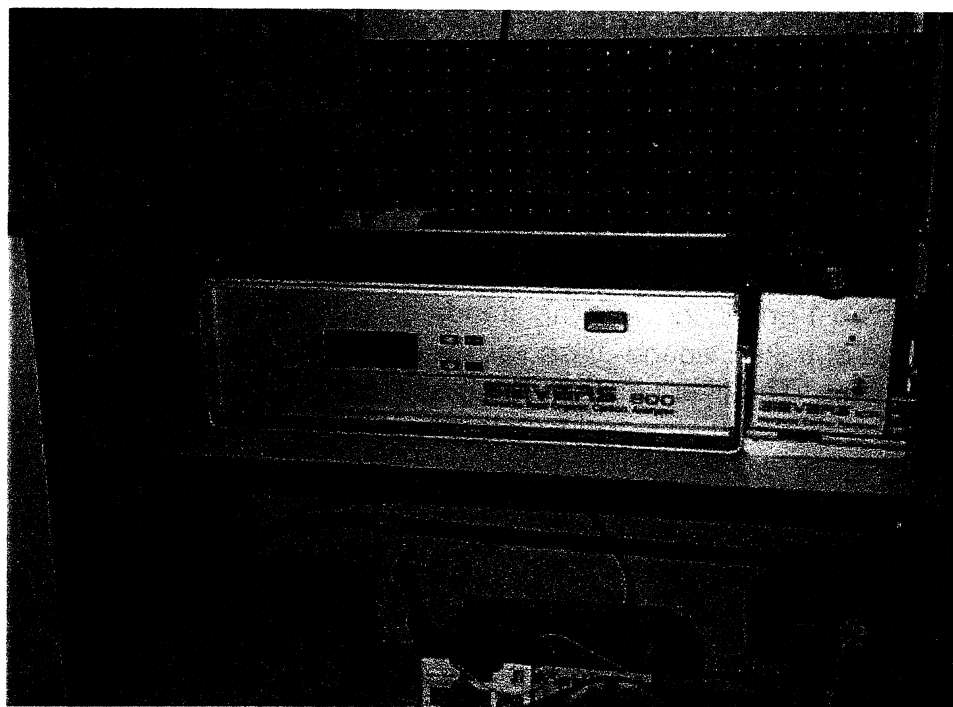
After researching the composition of available filters and housings, a filter housing and three different filters were selected for testing. They were tested for the ability to filter water without contributing a significant amount of organic carbon to the sample water. Two filter media and the filter housing were selected that were clean of organic carbon leaching. The two 1  $\mu\text{m}$  filters were the standard 10-inch cylindrical types. One filter was constructed of baked wound-glass yarn and the other was a melt-blown polypropylene filter. The filter housing was made of virgin polypropylene. The filtering capacity of these filters requires replacement once a week during times of peak river turbidities, and every two weeks with lower turbidities.

During the first months of monitoring, high concentrations of inorganic carbon were detected in the source water. The difference between the organic and inorganic carbon in the Sacramento River fluctuates throughout the year. When the difference between the organic and inorganic is greater than 10 to 1, the analyzer posts a warning message on the display screen. This warning indicates that the difference exceeds recommended operating ratios between the two carbon sources. This could cause the instrument to produce erroneous data. The Sievers representative recommended installing an inorganic carbon remover. After the ICR was installed, the inorganic carbon level went from 12.0 – 14.0 mg/L down to 20.0  $\mu\text{g/L}$  and this resulted in eliminating the warning message.

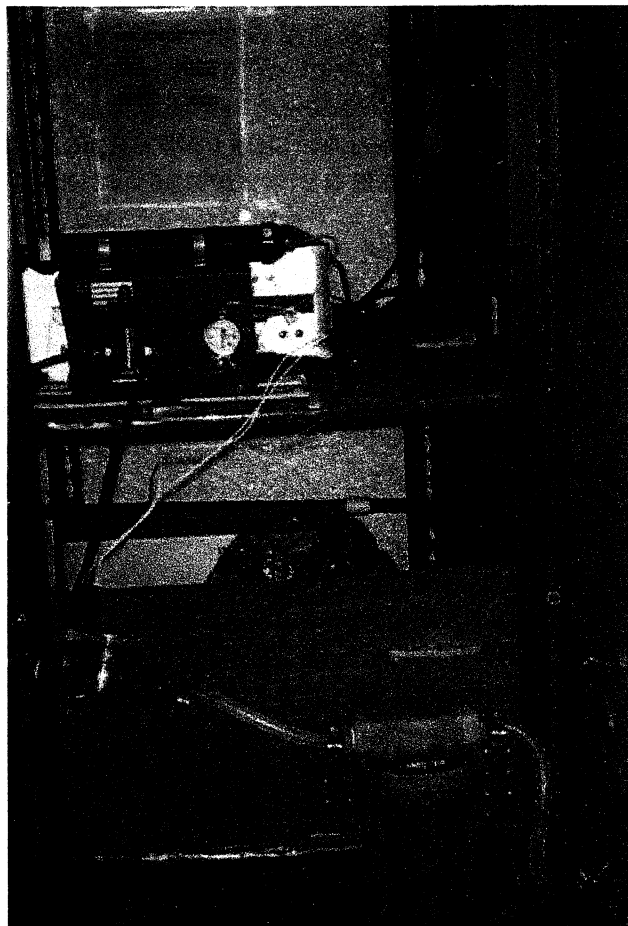
### **Operation of Analyzer**

The analyzer and timer were programmed to run four sampling events every 24 hours. The sampling event was timed to allow the analyzer to perform six analyses during each event. The results of the first two analyses of each sampling event were discarded to provide time for the filtration system to purge water in the system that remained from the previous sampling event. This provided four analyses in each event that represented fresh river water, and these were used in the data analysis process.

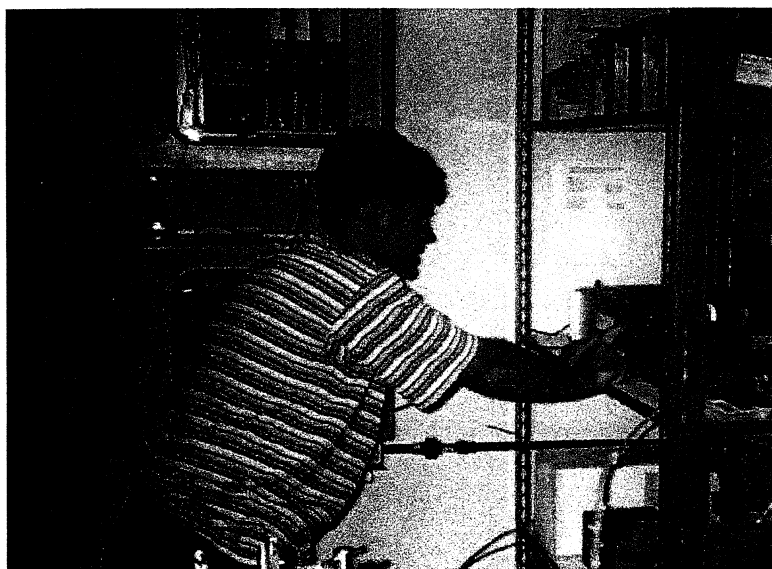
Because of the need for a filter, it was necessary to know the size range of the particles suspended in the river water, which could provide information on the percentage of particles retained by the 1.0-micron filter. River water samples were collected for particle size analysis. The samples were sent to Core Labs Inc. in Bakersfield, California for analysis by laser diffraction methodology. To ensure the data collected were not biased by the filtration media, seasonal particle size analyses were collected. The samples were initially collected seasonally (in June and August 1999, and in November 1999), then switched to a weekly collection on January 21, 2000. The first heavy rains in 2000 started during the third week of January and continued for several weeks into February.



*Front view of Sievers 800 organic carbon analyzer with inorganic carbon removal unit located to the right of analyzer. Automated timer located in upper left corner.*



*Side view of analyzer showing inorganic carbon removal unit, filtration unit, and solenoid valve.*



*Staff programming analyzer for sampling event.*



The weekly particle size analyses continued weekly through the end of March then switched to monthly analyses in April 2000 and were continued over the summer months. These analyses provided information on the size of the particles present and the percentage each size category represents of the total suspended load in the sample. Monthly samples continue to be collected until the next heavy rainstorms when the schedule will change to accommodate a more intense sampling regimen.

The results from the Sacramento River at the Hood facility exhibited a range of turbidity. Turbidity measurements are made in the field by staff with a Hach model 2100P Turbidity Meter. The turbidity increased as the flows of the Sacramento River increased during high flows and rainfall. From June 1, 1999, through June 30, 2000, the turbidities ranged between 5.5 NTU and 81.1 NTU during peak rains. A comparison of the Sacramento River particle size and turbidity shows the seasonal and weather pattern changes. This data is shown in Table 1.

### **Water Delivery System Modifications**

The filter component of this study is important because of the issue of how to classify the resulting analytical data. It was uncertain whether to treat the Sievers analysis as TOC or dissolved organic carbon (DOC) data. DOC is the fraction of TOC that will pass through a 0.45 $\mu$ m filter. The higher the percentage of particles retained by the filter, the greater the instrument analyses would reflect a DOC value. Conversely, the greater the percentage of particles >0.45 $\mu$ m passing through the filter, the more the analysis reflected a true TOC value. The TOC and DOC grab sample data were compared to the Sievers analyzer data to determine effects the 1 $\mu$ m filter may have had on the samples results.

**Table 1. Sacramento River Particle Size vs. Turbidity**

Date	Sacramento River Turbidity	Mean Particle Size, (microns)	Particle Size, Range (microns)
6/22/99	24.6	1.7	0.2 - 3.5
9/10/99	11.4	1.8	0.2 - 3.5
11/16/99	10.2	1.7	0.2 - 3.6
1/21/00	8.4	5.3	0.4 - 10.7
1/28/00	12.2	7.7	0.5 - 15.6
2/4/00	8.3	19.4	0.7 - 60.8
2/11/00	8.2	7.4	0.5 - 15.5
2/18/00	7.4	6.2	0.3 - 14.9
2/25/00	40.7	5.0	0.4 - 10.4
3/3/00	31.9	1.7	0.2 - 3.6
3/10/00	32.1	3.0	0.2 - 7.2
3/20/00	24.1	3.6	0.3 - 7.4
3/24/00	22.0	1.8	0.2 - 3.6
3/31/00	24.0	1.8	0.2 - 3.6
4/28/00	13.5	1.7	0.2 - 3.6
5/26/00	14.0	1.7	0.2 - 3.5
6/30/00	14.5	1.8	0.2 - 3.5

The 1.0 $\mu$ m filters were replaced on December 10, 1999 with a 50.0 $\mu$ m (nominal) filter. The 50.0 $\mu$ m filter was selected to replace the 1.0 $\mu$ m filter when the mean particle size of suspended material in the water did not exceed 20.0 $\mu$ m. The change to a larger pore-sized filter helps clarify the question of whether the data represents TOC or DOC. Since the mean particle sizes did not exceed the 50 $\mu$ m filter pore size, it was assumed the data can be used as TOC. The results of the particle size analysis indicated that the possibility of particles >50 $\mu$ m entering the analyzer existed only during periods of heavy storm events. The Sievers analyzer has a maximum allowable particle size limit of 60.0 $\mu$ m. The manufacturer considers particles >60 $\mu$ m to have an adverse impact on the instrument's ability to perform properly. This 50 $\mu$ m filter was still below the pore size of the 60 $\mu$ m on-line filter that came factory installed on the analyzer from Sievers. The 50.0-micron filter would protect the analyzer from particles >60.0 $\mu$ m and not impart organic carbon into the system.

Besides changes in the filter component, a silt trap was added to the water delivery line. The silt trap was a standard 10-inch filter housing without a filter. This allowed a place for larger suspended particles to settle out instead of depositing in the water delivery line. The silt trap is removed and cleaned weekly. Before the silt trap is replaced the water line is turned on and flushed at maximum flow rate. This flushes and cleans the water line from the pump intake to the silt trap valve. After flushing the water line, the silt trap is replaced. This process has helped reduce the amount of sedimentation in the line and reduce the turbidity of the water entering the solenoid valve and filter.

### **Sample Criteria**

A series of preliminary tests were conducted on the water delivery system, timer, and analyzer to assess the equipment's ability to perform the programmed sampling scenario for the required duration. These tests evaluated the filtering capacity of the filters to determine how often they would have to be changed. These tests were conducted for a one-month period during the winter storm season to confirm the equipment performed to our requirements and to provide the high turbidity water needed to test the filters.

After determining the operational ability of the delivery system and analyzer, a scheduled grab sampling study was initiated to compare and evaluate the Sievers instrument's analytical results to the grab samples analyzed by Bryte Chemical Laboratory. All data produced by the Sievers analyzer were from the on-line water delivery configuration with filter in place unless noted. The grab samples were collected to provide data for a series of evaluations. The grab sample results were compared to the Sievers analyzer data to determine if the 21 meters of water delivery line affected the TOC levels in the water. The grab samples were collected from three locations to evaluate components of the water delivery system. The first location was adjacent to the intake pump that provides river water to the delivery system for the analyzer. River grab samples were collected with a stainless steel bucket attached to a stainless steel cable. This river grab sample site provided background data on the water before entering the delivery system, and also served as a direct comparison to the on-line data

produced by the Sievers analyzer and the corresponding Bryte Chemical Laboratory river grab sample analysis. The other two sampling sites were located on the water delivery line to the analyzer. One sampling port was located before the filter assembly unit. This site provided an evaluation of the system up to the filtration device. The other site was located after the filter assembly and before the water line enters the analyzer. This site evaluated possible TOC contributions from the filtration device.

This series of grab samples provided data for the evaluation of the performance the Sievers analyzer and its ability to provide representative data. These samples were collected to compare the Bryte Chemical Laboratory analyses of water samples from the pump intake site with the Sievers instrument's analyses of the water after it had passed through the entire delivery system. These grab samples also provided an evaluation and a means to monitor the water delivery system.

Because a 1.0  $\mu\text{m}$  filter was in place before water entered the analyzer during the first six months of this study, the analyses during that period did not reflect a true TOC value. Therefore, it was necessary to analyze the grab samples for total and dissolved organic carbon. The results of these grab sample analyses from the Bryte Chemical Laboratory were compared to the on-line analyses of the Sievers instrument to determine the degree of change, if any, the filtration process had on the TOC value. The grab sample data and Sievers analyzer data are discussed in the Results section of this report.

Initially, a set of grab samples was collected twice a week to monitor the stability of the water delivery system, to detect problems associated with filter loading, and to evaluate the instrument performance. This schedule was followed through June 1999. At that time, the sampling schedule was reduced to once a week because of the consistency of the data, and the reliability of system components.

### **QUALITY ASSURANCE/QUALITY CONTROL**

Components of Quality Assurance/Quality Control were incorporated into the study to ensure the quality of data produced. These components included the development of the Quality Assurance Project Plan to establish the Quality Control criteria for the study. This plan included the Data Quality Objectives for the study. Another feature of the Quality Control program was the scheduled maintenance including the replacement of date-specific components and the calibration checks recommended by the manufacture. Duplicate samples were collected with each grab sample event to evaluate the precision of the laboratory analyses. The filtering equipment used to collect the DOC samples was evaluated on each grab sampling event by passing deionized water through the equipment and collecting a sample of the filtered water. A sample of the unfiltered deionized water was also collected for comparative analysis.

### **Quality Control Samples**

Many series of Quality Control samples were analyzed by the Sievers instrument and Bryte Chemical Laboratory to evaluate the performance of the analyzer and to acquire a statistical comparison of the analytical results by the two analyzers. All Bryte Chemical

Laboratory samples, including the Quality Control samples and field grab samples, were analyzed on an O/I Analytical model 1010 organic carbon analyzer that uses the digestion method of analysis similar to the Sievers instrument.

To analyze the Quality Control samples, the Sievers instrument was disconnected from the pressurized water delivery line and reconfigured to the grab sample mode. While in the grab sample mode it was programmed to perform a fixed number of replicate analyses for each Quality Control sample.

Two sets of performance evaluation TOC samples supplied by Environmental Research Associates, a commercial vendor of quality control samples, were analyzed by the Sievers autoanalyzer and by the Bryte Chemical Laboratory. One set contained certified commercially prepared stock samples, and the other set contained blind matrix spike samples prepared by ERA. Duplicate check standards prepared by Bryte Chemical Laboratory were analyzed by the Sievers analyzer and by the Bryte Chemical Laboratory instrument for performance comparison. The check standards were prepared by Bryte Chemical Laboratory chemists to specified concentrations and evaluated by both analyzers. The standards are made up with potassium hydrogen phthalate, or KHP, which is an accepted calibration standard for organic carbon analyzers. The calibration checks were another way of validating the data quality.

For further Quality Control and performance testing, three sets of surface water samples were collected for analysis. Bryte Chemical Laboratory analyzed each sample three times and achieved a result that was reported. The Sievers 800 analyzer was disconnected from the on-line mode and placed into the grab sample mode to analyze five replicates for each sample. The results of the first two analyses of the five were rejected. The water from the first two analyses is for purging the system before to accepting the results of the remaining three analyses.

To evaluate the analytical intra-variability of Bryte Chemical Laboratory results, samples from varying matrix waters were collected in four sets of ten replicates. The purpose of these analyses was to evaluate the precision of the Bryte Chemical Laboratory instrumentation. The four sets of ten replicates were submitted to Bryte Chemical Laboratory as single blind samples to determine the variability within each set of ten samples and to evaluate the precision of the laboratory's instrumentation. The matrix of these samples ranged from blank water to Sacramento River water with relatively low TOC levels (1.6 mg/L).

Bryte Chemical Laboratory blank water was also evaluated for this set of analyses. One set of unfiltered blank water was evaluated and one set of filtered blank water was evaluated with the Sacramento River water to evaluate the range of results. The results of the Quality Control sample analysis are shown in the Results section of this report.

### **Data Assessment**

This study measured agreement in the data produced by the autoanalyzer with the grab sample data provided by Bryte Chemical Laboratory. This determined if the

autoanalyzer produced data that were representative of the river water. The method used to determine the agreement in these data was to calculate the relative percent difference between the Sievers autoanalyzer and Bryte Chemical Laboratory data. The relative percentage difference is a measure of precision, which compares two values based on the mean of the two values, and is reported as an absolute value.<sup>3</sup> The higher the RPD value, the greater the amount of difference or error in the data. The RPD was calculated using the following equation:

$$RPD = \frac{(C_1 - C_2)}{(C_1 + C_2)/2} \quad \text{where;}$$

$C_1$  = the larger of the two observed values  
 $C_2$  = the smaller of the two observed values

The Bryte Chemical Laboratory established the maximum acceptable RPD level of precision between the O/I Analytical model 1010 and Sievers T-800 autoanalyzer was not to exceed 30 percent. This figure was derived from Bryte Chemical Laboratory statistical analysis of data from samples collected during the first three months of this project and prior to the start of this study.

## RESULTS/DISCUSSION

The purpose of the study was to determine whether an organic carbon autoanalyzer could function at a DWR remote operational facility and produce reliable and repeatable results, and representative data. The analyzer data from the first six months of this study were obtained with a 1.0 $\mu$ m filter in place. After comparing the results of the TOC and DOC grab sample data to this six months of analyzer data, no significant relative percentage differences were observed in the Bryte Chemical Laboratory TOC data and Sievers analyzer data. Therefore, for this study, all the data produced by the Sievers analyzer are reported as TOC with the caveat that a 1.0 $\mu$ m filter was in use for the first six months.

### Average Daily Results

The data collected from June 1, 1999 through June 30, 2000 show the TOC data trend for a typical water year. The daily averages of the analyzer are shown in Figure 2. This figure displays the raw daily average of TOC data analyzed and compiled by the Sievers analyzer. To see more detail in the daily and monthly changes of organic carbon after storm and environmental changes in the Sacramento River, four months of winter data were isolated and expanded to show the responses to these events. These data are shown in Figure 3. Each data point represents the simple mean of the four sub-samples of each daily sampling event. Four sampling events per day result in four mean data points. Figure 3 shows the analyzer's ability to detect and record abrupt and gradual changes in the river's TOC content.

---

<sup>3</sup> Wagner R.E., et.al. 1992. Guide to environmental analytical methods. 2<sup>nd</sup>. Ed. Genium Publishing Corp. Appendix D-9

Rainfall daily totals for the first three months of 2000 were compared with the daily TOC levels in the river. Three months of rainfall data was chosen due to the number of days rainfall was detected by the weather station for the first months of the year. Table 2 shows the days' rainfall as measured by the National Weather Service in Sacramento, and compares it to the daily average of TOC from the Sievers analyzer in the Sacramento River. Figure 4 shows the time between the onset of the rainfall to the time the analyzer picks up the change in TOC levels at the Hood facility. This series of tables and graphs demonstrates the responsiveness of the Sievers analyzer to detect the changes in the TOC levels in the river during storm events. During the study, it was made evident that there was a direct correlation between the amount of rainfall and TOC levels in the Sacramento River. These data are incidental to the primary purpose of this study, yet they illustrate the ability of the Sievers analyzer at the Hood facility to act as an early-warning station to the TOC levels in source drinking waters.

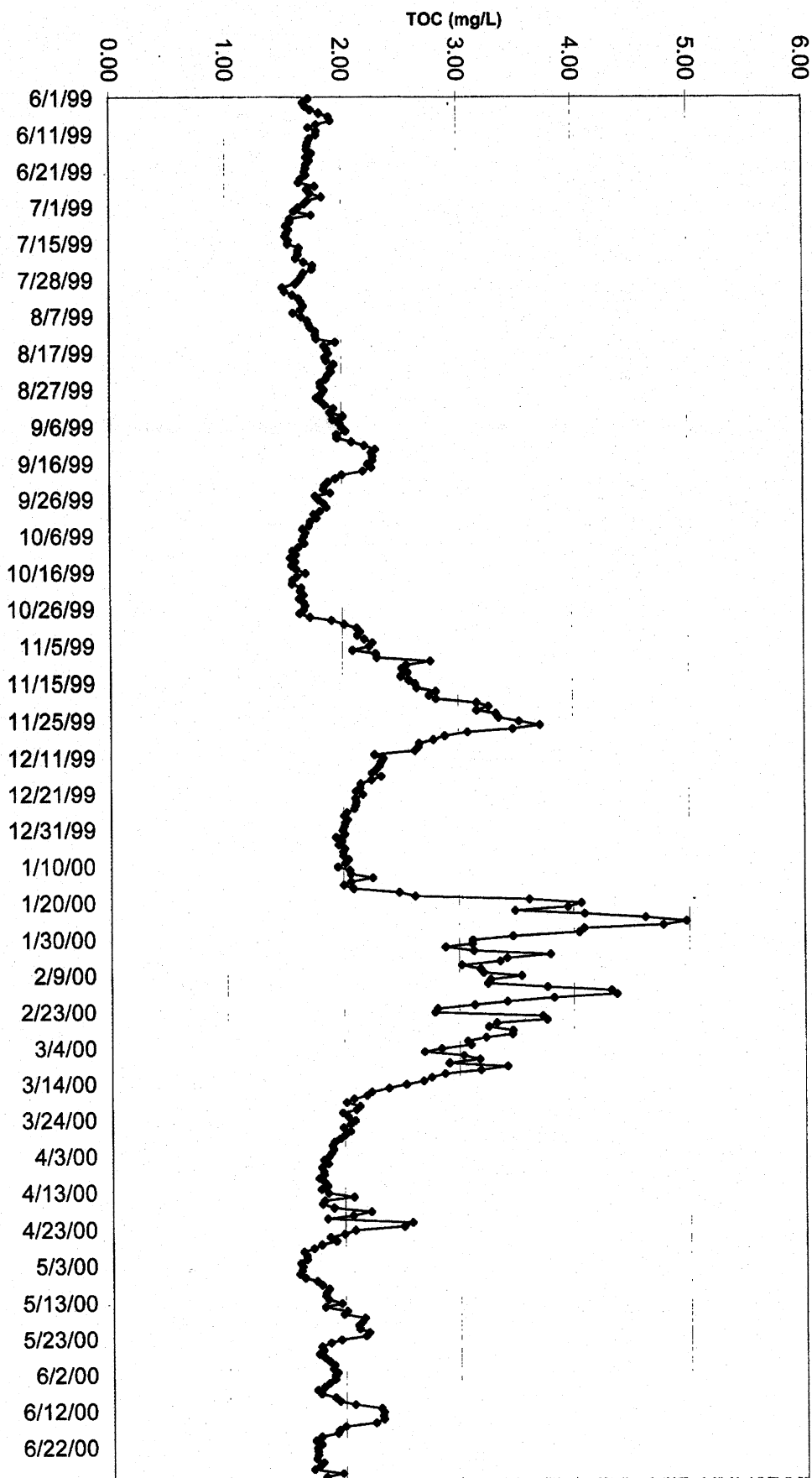
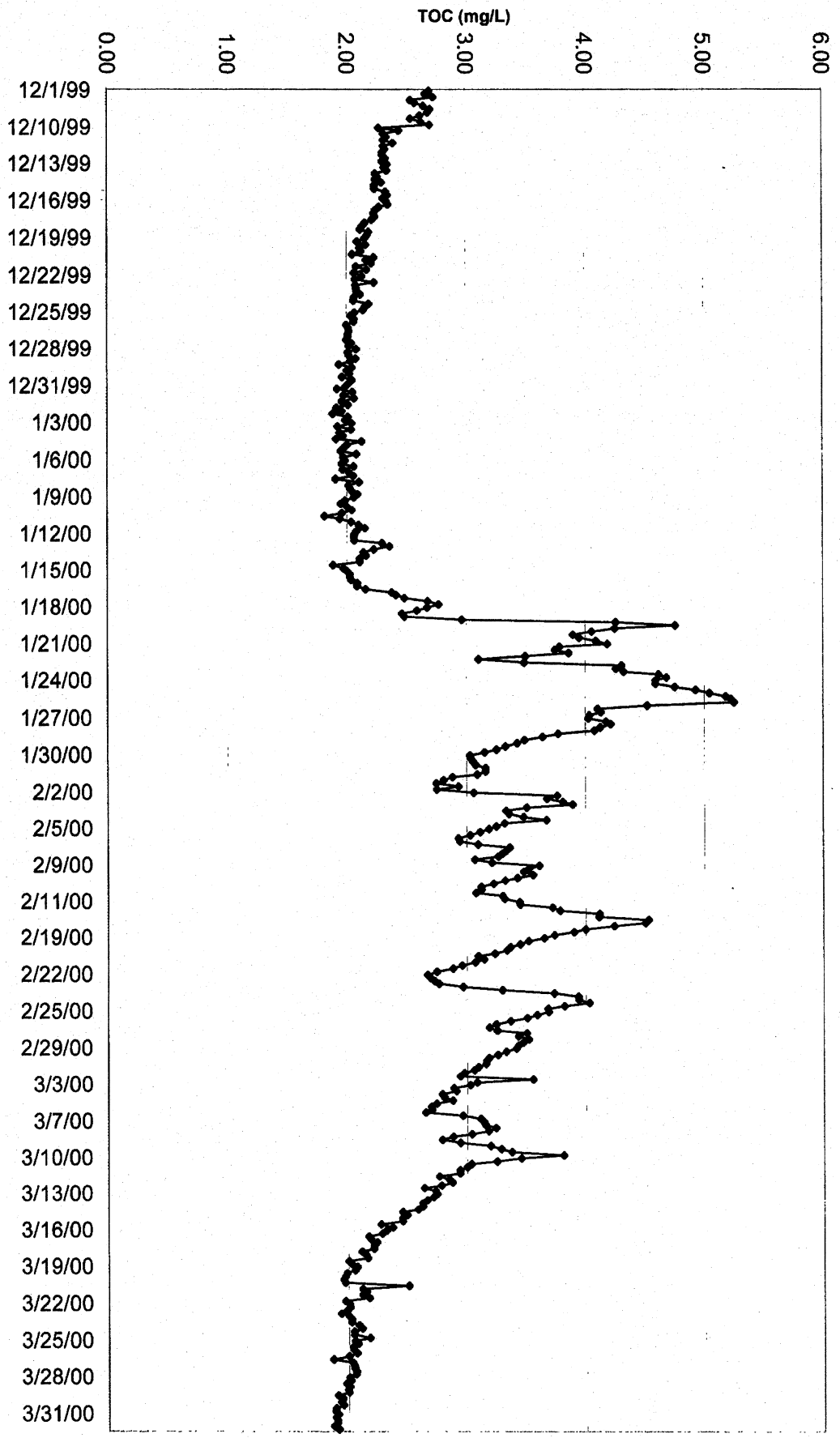


Figure 2. Sievers Model 800 Analyzer Daily Average TOC for the Sacramento River at the Hood Facility for One Year



Figure 3. Sievers Model 800 Analyzer TOC Values of Four Sampling Event Averages per Day During the 1999/2000 Winter Season\*



\* Each data point represents the average of one of the four daily sampling events. Each calendar day is represented by four data points.

**Table 2. Three Month Daily Precipitation Total vs.  
Daily TOC Average, 1/1/2000 through 3/31/200**

Date	Daily Precipitation total, inches	Daily TOC Average, (mg/L)
1/11/00	0.42	2
1/15/00	0.15	1.98
1/16/00	0.35	2.05
1/17/00	0.23	2.45
1/18/00	0.72	2.6
1/19/00	0.13	3.39
1/22/00	0.02	3.46
1/23/00	1.15	3.95
1/24/00	3.11	4.53
1/25/00	0.02	4.77
1/30/00	0.86	3.11
1/31/00	0.04	3.09
2/3/00	0.41	3.72
2/4/00	0.01	3.41
2/5/00	0.03	3.34
2/9/00	0.11	3.47
2/10/00	0.69	3.26
2/11/00	1.26	3.23
2/12/00	0.34	3.64
2/13/00	1.13	4.21
2/14/00	0.83	4.23
2/16/00	0.5	4.29
2/17/00	0.01	4.32
2/20/00	0.53	3.4
2/21/00	0.02	3.11
2/22/00	1.05	2.8
2/23/00	0.25	2.73
2/24/00	0.01	3.61
2/26/00	0.91	3.3
2/27/00	0.38	3.19
2/29/00	0.44	3.42
3/2/00	0.06	3.05
3/4/00	0.28	2.82
3/5/00	0.66	2.68
3/7/00	0.39	3.12
3/8/00	0.53	2.88
3/9/00	0.32	3.37
3/10/00	0.01	3.15
3/11/00	0.01	2.85

mg/L TOC & Inches of rain

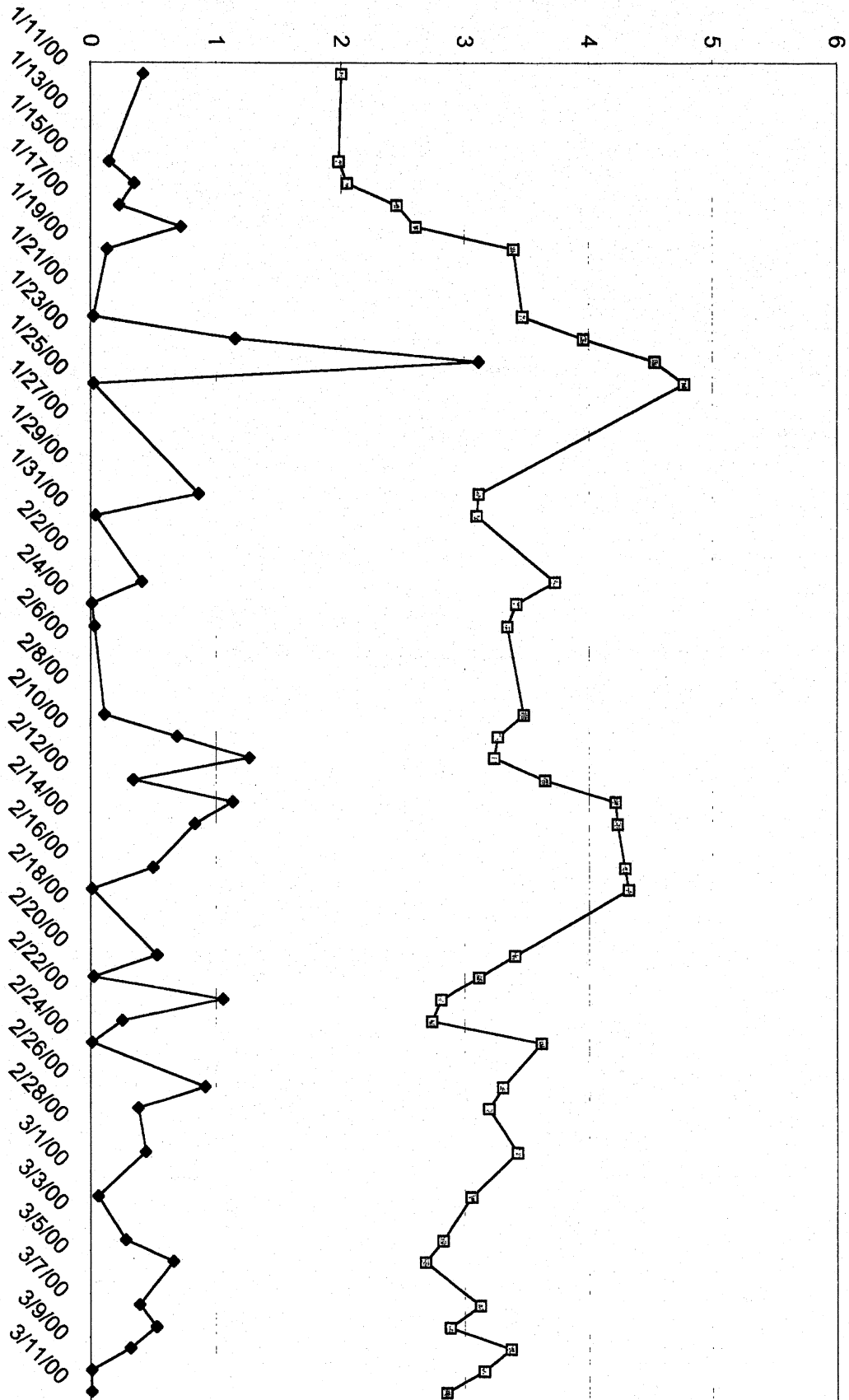


Figure 4. Daily TOC Average vs Daily Precipitation Totals

—◆— Daily TOC Average, (mg/L) —□— Daily Precipitation total, inches

## **Grab Sample Results**

Three types of grab samples were routinely collected for comparison with the data produced by the Sievers analyzer.

### **1. *River Grab Sample vs. Filter Outlet Comparison***

The filter outlet grab sample represents the water that is entering the Sievers analyzer. The filter outlet TOC grab sample is a measure of the water after it has passed through the entire water delivery system, including the filter. The river grab samples provide the baseline data of the TOC level in the water before it enters the water delivery system. A comparison of the river grab sample and filter outlet grab sample analysis for TOC level from the Bryte Chemical Laboratory was made to determine the effects, if any, the water delivery system imparts on the TOC concentration of the water. Comparisons of these data are shown in Table 3. These data are in close agreement, as shown in Figure 5, and are a good indicator that the water delivery system does not provide significant impacts to the TOC content of the water. The 30 percent RPD acceptance level was never exceeded during this study.

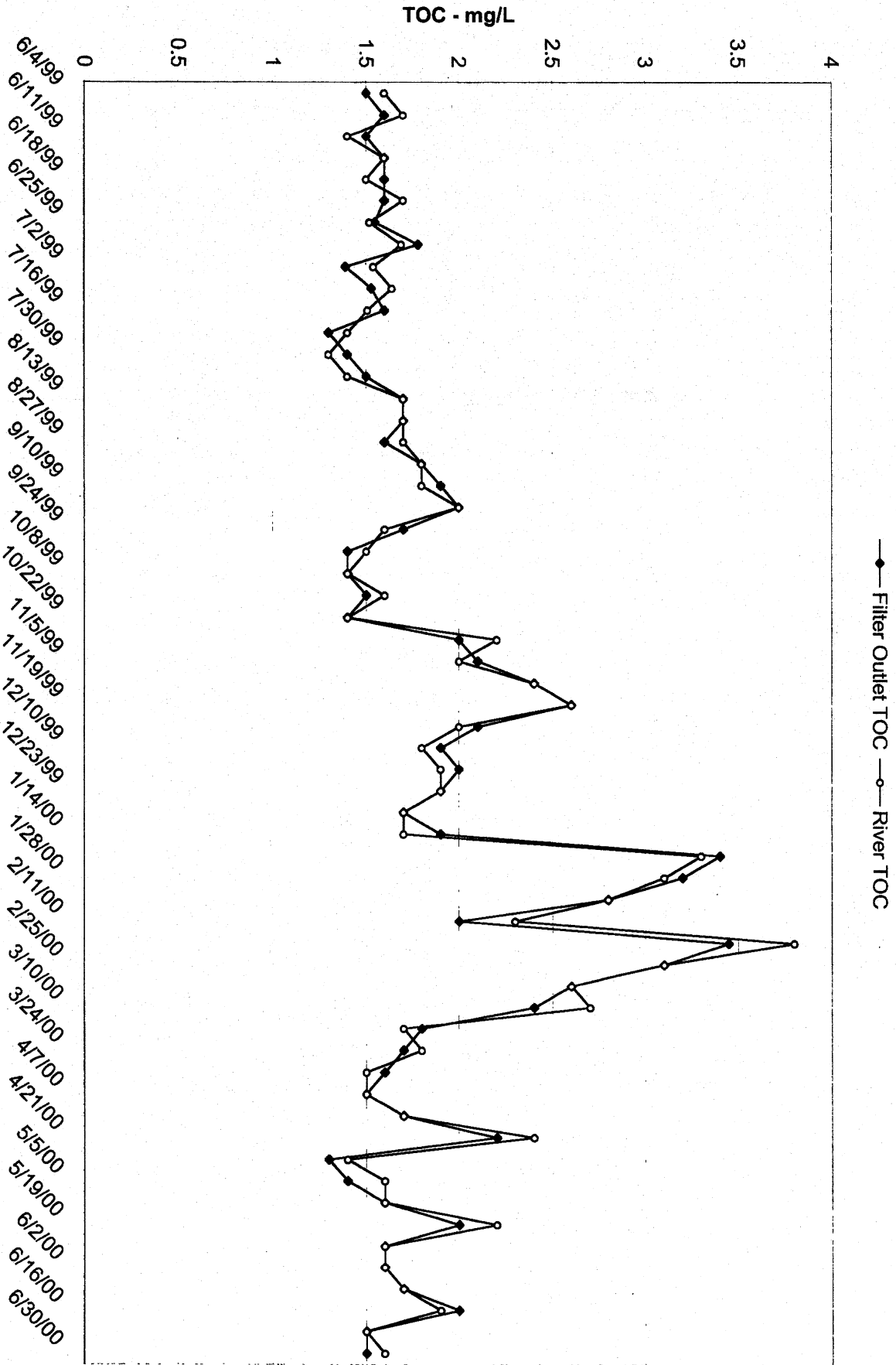
**Table 3. Comparison of Bryte Chemical Laboratory Analysis of River Grab and Filter Outlet Grab Samples to Evaluate TOC Influence the Water Delivery System has on Water Quality**

Date	Filter Outlet TOC-mg/L	River TOC mg/L	River/Outlet TOC - RPD
6/4/99	1.5	1.6	6.45%
6/7/99	1.6	1.7	6.06%
6/11/99	1.5	1.4	6.90%
6/14/99	1.6	1.6	0.00%
6/18/99	1.6	1.5	6.45%
6/21/99	1.6	1.7	6.06%
6/25/99	1.55	1.52	1.95%
6/28/99	1.78	1.69	5.19%
7/2/99	1.39	1.54	10.24%
7/9/99	1.53	1.64	6.94%
7/16/99	1.6	1.51	5.79%
7/23/99	1.3	1.4	7.41%
7/30/99	1.4	1.3	7.41%
8/6/99	1.5	1.4	6.90%
8/13/99	1.7	1.7	0.00%
8/20/99	1.7	1.7	0.00%
8/27/99	1.6	1.7	6.06%
9/3/99	1.8	1.8	0.00%
9/10/99	1.9	1.8	5.41%
9/17/99	2	2	0.00%
9/24/99	1.7	1.6	6.06%
10/1/99	1.4	1.5	6.90%
10/8/99	1.4	1.4	0.00%
10/15/99	1.5	1.6	6.45%
10/22/99	1.4	1.4	0.00%
10/29/99	2	2.2	9.52%
11/5/99	2.1	2	4.88%
11/12/99	2.4	2.4	0.00%
11/19/99	2.6	2.6	0.00%
12/3/99	2.1	2	4.88%
12/10/99	1.9	1.8	5.41%
12/16/99	2	1.9	5.13%
12/23/99	1.9	1.9	0.00%
1/7/00	1.7	1.7	0.00%
1/14/00	1.9	1.7	11.11%
1/21/00	3.4	3.3	2.99%
1/28/00	3.2	3.1	3.17%

**Table 3 continued. Comparison of Bryte Chemical Laboratory Analysis of River Grab and Filter Outlet Grab Samples to Evaluate TOC Influence the Water Delivery System has on Water Quality**

Date	Filter Outlet TOC-mg/L	River TOC mg/L	River/Outlet TOC - RPD
2/4/00	2.8	2.8	0.00%
2/11/00	2	2.3	13.95%
2/18/00	3.45	3.8	9.66%
2/25/00	3.1	3.1	0.00%
3/3/00	2.6	2.6	0.00%
3/10/00	2.4	2.7	11.76%
3/17/00	1.8	1.7	5.71%
3/24/00	1.7	1.8	5.71%
3/31/00	1.6	1.5	6.45%
4/7/00	1.5	1.5	0.00%
4/14/00	1.7	1.7	0.00%
4/21/00	2.2	2.4	8.70%
4/28/00	1.3	1.4	7.41%
5/5/00	1.4	1.6	13.33%
5/12/00	1.6	1.6	0.00%
5/19/00	2	2.2	9.52%
5/26/00	1.6	1.6	0.00%
6/2/00	1.6	1.6	0.00%
6/9/00	1.7	1.7	0.00%
6/16/00	2	1.9	5.13%
6/23/00	1.5	1.5	0.00%
6/30/00	1.5	1.6	6.45%

Figure 5. Comparison of River Grab and Filter Outlet Grab Samples to Evaluate TOC Influence the Water Delivery System has on Water Quality



## 2. *River Grab Samples vs. Autoanalyzer*

River grab sample data were compared with the autoanalyzer sample data. The river grab sample data set used here is a compilation of the samples collected for this pilot study and other river grab sample data collected at the same site for other studies. The collection times for these other grab samples were within two hours of the date and time of the corresponding analyzer data. Comparing the river grab sample data, which served as the baseline, with the analyzer data provided information on whether the analyzer data were representative of the TOC concentrations in the river as measured by the instrumentation of Bryte Chemical Laboratory. First, a comparison was made of the Bryte Chemical Laboratory DOC and TOC river grab sample data with the analyzer on-line data. This comparison was necessary to see if the on-line filter to the analyzer created a bias in the on-line data to make it resemble the DOC data rather than the TOC data. Examining these data showed that the filtering device did not reduce the TOC concentration of the water. These data are shown in tabular form including the relative percentage difference in Table 4 and in Figure 6. In a more direct comparison, only the TOC data from the Bryte Chemical Laboratory river grab samples were compared with the corresponding on-line analyzer data to determine the relative percentage difference. This comparison revealed that the maximum allowable RPD of 30 percent had been exceeded twice during the year of monitoring. These data are shown in Table 5 and in Figure 7.



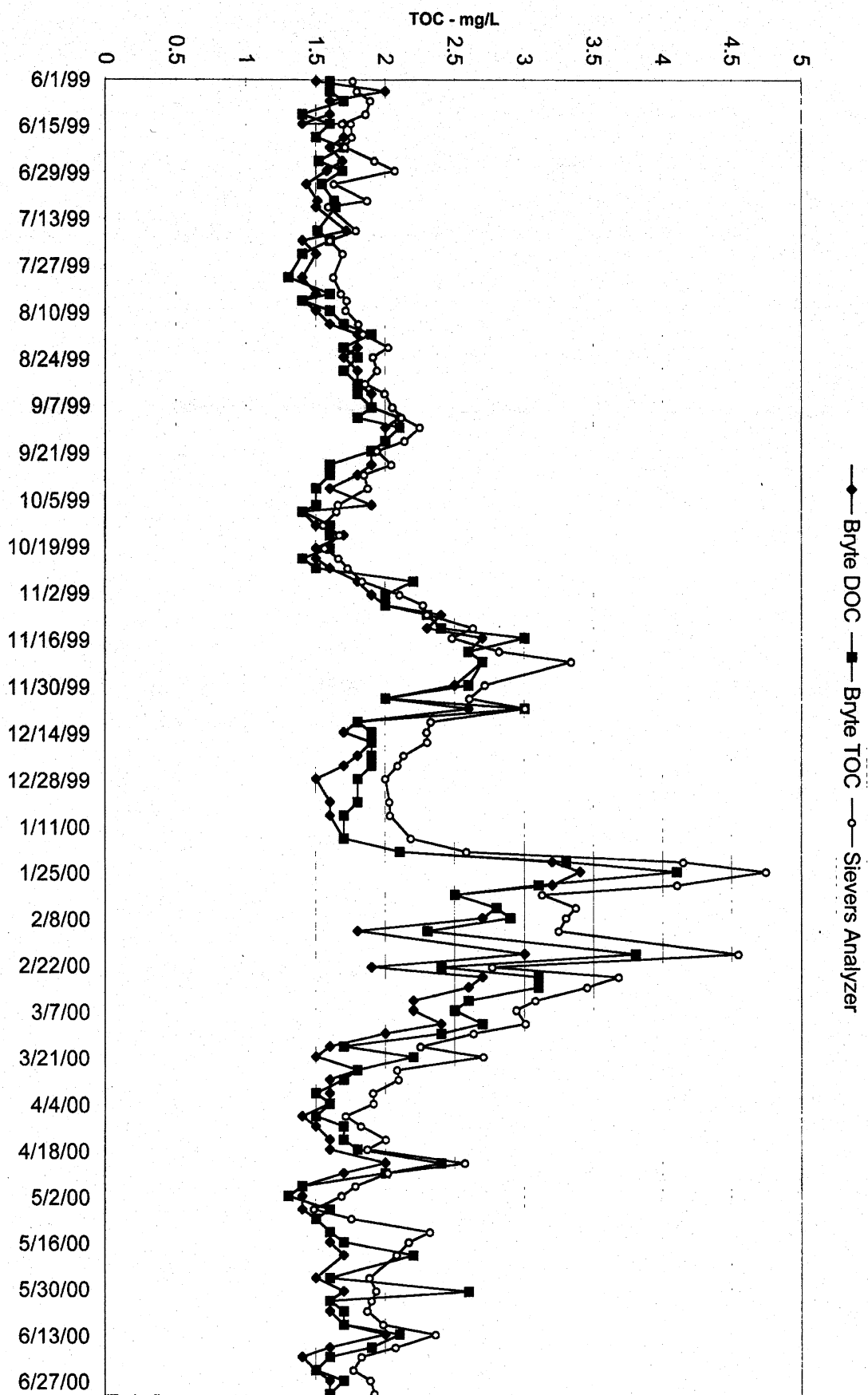
**Table 4. Relative Percent Difference in Analysis of River Grab Samples by the Bryte Chemical Laboratory and Sievers Analyzer On-line Analysis**

Collection Date	Bryte - River	Bryte - River	Sievers TOC	Bryte DOC-Sievers TOC	Bryte / Sievers TOC
	DOC mg/L	TOC mg/L	mg/L	RPD	RPD
06/01/99	1.5	1.6	1.77	16.28%	9.86%
06/04/99	2	1.6	1.8	10.69%	11.60%
06/07/99	1.6	1.7	1.89	16.62%	10.58%
06/11/99	1.6	1.4	1.86	15.03%	28.22%
06/14/99	1.4	1.6	1.69	18.77%	5.47%
06/14/99	1.7	1.6	1.75	2.90%	8.96%
06/18/99	1.7	1.5	1.76	3.47%	15.95%
06/21/99	1.6	1.7	1.71	6.65%	0.59%
06/25/99	1.69	1.52	1.92	12.74%	23.26%
06/28/99	1.58	1.69	2.07	26.85%	20.21%
07/02/99	1.43	1.54	1.63	13.04%	5.65%
07/07/99	1.51	1.63	1.87	21.30%	13.71%
07/09/99	1.5	1.64	1.59	5.83%	3.10%
07/16/99	1.72	1.51	1.79	3.99%	16.97%
07/19/99	1.4	1.6	1.6	13.33%	0.00%
07/23/99	1.5	1.4	1.69	11.99%	18.85%
07/30/99	1.4	1.3	1.63	14.97%	22.32%
08/04/99	1.5	1.6	1.68	11.30%	4.86%
08/06/99	1.4	1.4	1.72	20.60%	20.60%
08/09/99	1.5	1.6	1.72	13.41%	6.97%
08/13/99	1.6	1.7	1.81	12.10%	6.05%
08/16/99	1.8	1.9	1.84	2.24%	3.17%
08/20/99	1.8	1.7	2.02	11.59%	17.27%
08/23/99	1.7	1.8	1.91	11.57%	5.86%
08/27/99	1.8	1.7	1.94	7.45%	13.15%
08/31/99	1.8	1.8	1.85	2.92%	2.92%
09/03/99	1.9	1.8	1.99	4.81%	10.21%
09/07/99	1.9	1.9	2.05	7.68%	7.68%
09/10/99	2.1	1.8	2.12	0.75%	16.13%
09/13/99	2	2.1	2.25	11.69%	6.82%
09/17/99	2	2	2.14	6.70%	6.70%
09/20/99	1.9	1.9	1.94	2.13%	2.13%
09/24/99	1.9	1.6	2.04	7.20%	24.27%
09/27/99	1.8	1.6	1.85	2.52%	14.27%
10/01/99	1.6	1.5	1.87	15.73%	22.12%
10/06/99	1.9	1.5	1.66	13.59%	10.02%
10/08/99	1.4	1.4	1.65	16.19%	16.19%

**Table 4 continued. Relative Percent Difference in Analysis of  
River Grab Samples by the Bryte Chemical Laboratory and  
Sievers Analyzer On-line Analysis**

<b>Collection Date</b>	<b>Bryte - River</b>	<b>Bryte - River</b>	<b>Sievers TOC</b>	<b>Bryte DOC- Sievers TOC</b>	<b>Bryte / Sievers TOC</b>
	<b>DOC mg/L</b>	<b>TOC mg/L</b>	<b>mg/L</b>	<b>RPD</b>	<b>RPD</b>
10/12/99	1.5	1.6	1.55	3.39%	3.06%
10/15/99	1.7	1.6	1.67	1.86%	4.20%
10/19/99	1.5	1.6	1.56	4.18%	2.28%
10/22/99	1.5	1.4	1.66	10.36%	17.23%
10/25/99	1.6	1.5	1.73	7.80%	14.23%
10/29/99	1.8	2.2	1.83	1.85%	18.17%
11/02/99	1.9	2	2.1	10.04%	4.92%
11/05/99	2	2	2.27	12.64%	12.64%
11/08/99	2.4	2.3	2.3	4.20%	0.06%
11/12/99	2.3	2.4	2.63	13.50%	9.26%
11/15/99	2.7	3	2.48	8.38%	18.86%
11/19/99	2.6	2.6	2.82	8.15%	8.15%
11/22/99	2.7	2.7	3.34	21.13%	21.13%
11/29/99	2.5	2.6	2.72	8.39%	4.47%
12/03/99	2	2	2.61	26.29%	26.29%
12/06/99	2.6	3	3.01	14.51%	0.23%
12/10/99	1.8	1.8	2.33	25.60%	25.60%
02/18/00	3	3.8	4.55	40.99%	17.90%
02/22/00	1.9	2.4	2.77	37.28%	14.33%
02/25/00	2.7	3.1	3.68	30.68%	17.07%
02/28/00	2.6	3.1	3.45	28.10%	10.69%
03/03/00	2.2	2.6	3.08	33.33%	16.90%
03/06/00	2.2	2.5	2.94	28.84%	16.22%
03/10/00	2.4	2.7	3.01	22.53%	10.84%
03/13/00	2	2.4	2.64	27.41%	9.35%
03/17/00	1.6	1.7	2.25	33.96%	28.04%
03/20/00	1.5	2.2	2.71	57.42%	20.70%
03/24/00	1.8	1.8	2.08	14.52%	14.52%
03/27/00	1.6	1.7	2.1	26.83%	20.86%
03/31/00	1.6	1.5	1.91	17.61%	23.99%
04/03/00	1.6	1.6	1.91	17.83%	17.83%
04/07/00	1.4	1.5	1.72	20.28%	13.43%
04/10/00	1.5	1.7	1.83	19.64%	7.18%
04/14/00	1.6	1.7	2	22.35%	16.35%
04/17/00	1.6	1.8	1.87	15.49%	3.74%

Figure 6. Comparison of Bryte Chemical Laboratory DOC/TOC Analysis of River Grab Samples and Sievers Analyzer On-line Analysis



**Table 5. Relative Percent Difference in TOC Analysis by  
Bryte Chemical Laboratory of River Grab Samples and  
the Sievers Analyzer On-line Analysis**

Collection Date	Bryte TOC mg/L	Sievers TOC mg/L	Bryte TOC-Sievers TOC RPD
06/01/99	1.6	1.77	9.86%
06/04/99	1.6	1.8	11.60%
06/07/99	1.7	1.89	10.58%
06/11/99	1.4	1.86	28.22%
06/14/99	1.6	1.69	5.47%
06/14/99	1.6	1.75	8.96%
06/18/99	1.5	1.76	15.95%
06/21/99	1.7	1.71	0.59%
06/25/99	1.52	1.92	23.26%
06/28/99	1.69	2.07	20.21%
07/02/99	1.54	1.63	5.65%
07/07/99	1.63	1.87	13.71%
07/09/99	1.64	1.59	3.10%
07/16/99	1.51	1.79	16.97%
07/19/99	1.6	1.6	0.00%
07/23/99	1.4	1.69	18.85%
07/30/99	1.3	1.63	22.32%
08/04/99	1.6	1.68	4.86%
08/06/99	1.4	1.72	20.60%
08/09/99	1.6	1.72	6.97%
08/13/99	1.7	1.81	6.05%
08/16/99	1.9	1.84	3.17%
08/20/99	1.7	2.02	17.27%
08/23/99	1.8	1.91	5.86%
08/27/99	1.7	1.94	13.15%
08/31/99	1.8	1.85	2.92%
09/03/99	1.8	1.99	10.21%
09/07/99	1.9	2.05	7.68%
09/10/99	1.8	2.12	16.13%
09/13/99	2.1	2.25	6.82%
09/17/99	2	2.14	6.70%
09/20/99	1.9	1.94	2.13%
09/24/99	1.6	2.04	24.27%
09/27/99	1.6	1.85	14.27%
10/01/99	1.5	1.87	22.12%
10/06/99	1.5	1.66	10.02%
10/08/99	1.4	1.65	16.19%

**Table 5 continued. Relative Percent Difference in TOC Analysis  
by Bryte Chemical Laboratory of River Grab Samples and  
the Sievers Analyzer On-line Analysis**

Collection Date	Bryte TOC mg/L	Sievers TOC mg/L	Bryte TOC-Sievers TOC RPD
10/12/99	1.6	1.55	3.06%
10/15/99	1.6	1.67	4.20%
10/19/99	1.6	1.56	2.28%
10/22/99	1.4	1.66	17.23%
10/25/99	1.5	1.73	14.23%
10/29/99	2.2	1.83	18.17%
11/02/99	2	2.1	4.92%
11/05/99	2	2.27	12.64%
11/08/99	2.3	2.3	0.06%
11/12/99	2.4	2.63	9.26%
11/15/99	3	2.48	18.86%
11/19/99	2.6	2.82	8.15%
11/22/99	2.7	3.34	21.13%
11/29/99	2.6	2.72	4.47%
12/03/99	2	2.61	26.29%
12/06/99	3	3.01	0.23%
12/10/99	1.8	2.33	25.60%
12/13/99	1.9	2.3	18.95%
12/16/99	1.9	2.3	19.06%
12/20/99	1.9	2.13	11.53%
12/23/99	1.9	2.09	9.36%
12/27/99	1.8	2.	10.45%
01/03/00	1.8	2.03	11.92%
01/07/00	1.7	2.03	17.73%
01/14/00	1.7	2.18	24.85%
01/18/00	2.1	2.58	20.67%
01/21/00	3.3	4.15	22.80%
01/24/00	4.1	4.74	14.56%
01/28/00	3.1	4.1	27.89%
01/31/00	2.5	3.13	22.28%
02/04/00	2.8	3.37	18.50%
02/07/00	2.9	3.3	12.89%
02/11/00	2.3	3.25	34.24%
02/18/00	3.8	4.55	17.90%
02/22/00	2.4	2.77	14.33%
02/25/00	3.1	3.68	17.07%
02/28/00	3.1	3.45	10.69%

**Table 5 continued. Relative Percent Difference in TOC Analysis  
by Bryte Chemical Laboratory of River Grab Samples and  
the Sievers Analyzer On-line Analysis**

Collection Date	Bryte TOC	Sievers TOC	Bryte TOC-Sievers TOC
	mg/L	mg/L	RPD
03/03/00	2.6	3.08	16.90%
03/06/00	2.5	2.94	16.22%
03/10/00	2.7	3.01	10.84%
03/13/00	2.4	2.64	9.35%
03/17/00	1.7	2.25	28.04%
03/20/00	2.2	2.71	20.70%
03/24/00	1.8	2.08	14.52%
03/27/00	1.7	2.1	20.86%
03/31/00	1.5	1.91	23.99%
04/03/00	1.6	1.91	17.83%
04/07/00	1.5	1.72	13.43%
04/10/00	1.7	1.83	7.18%
04/14/00	1.7	2.	16.35%
04/17/00	1.8	1.87	3.74%
04/21/00	2.4	2.58	7.04%
04/24/00	2	2.02	0.77%
04/28/00	1.4	1.78	24.10%
05/01/00	1.3	1.69	25.84%
05/05/00	1.6	1.48	7.51%
05/08/00	1.5	1.76	15.68%
05/12/00	1.6	2.32	36.70%
05/15/00	1.7	2.17	24.15%
05/19/00	2.2	2.08	5.61%
05/26/00	1.6	1.89	16.40%
05/30/00	2.6	1.93	29.48%
06/02/00	1.6	1.9	17.05%
06/05/00	1.7	1.87	9.47%
06/09/00	1.7	1.98	15.39%
06/12/00	2.1	2.36	11.58%
06/16/00	1.9	2.07	8.63%
06/19/00	1.6	1.83	13.29%
06/23/00	1.5	1.77	16.58%
06/26/00	1.7	1.89	10.63%
06/30/00	1.6	1.92	18.32%

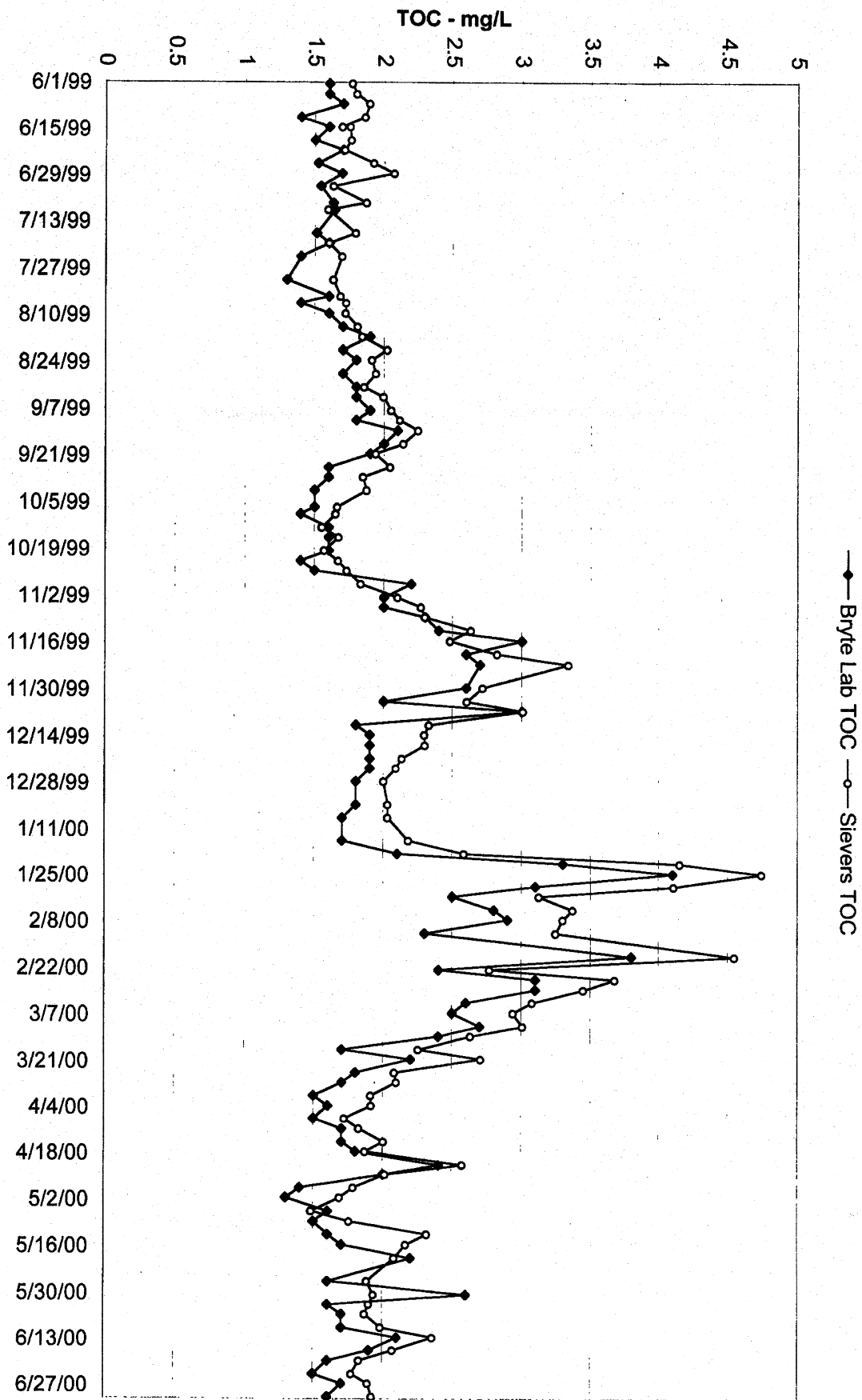


Figure 7. Comparison of TOC Analysis by Bryte Chemical Laboratory of River Grab Samples and the Sievers Analyzer On-line Analysis

—●— Bryte Lab TOC —○— Sievers TOC

### 3. *Filter Inlet vs. Filter Outlet Comparison*

This comparison provided an evaluation of the DOC and TOC levels in the water at the point before it entered the filter and after passing through the filter. This evaluation was performed to determine any effects the filter might have had on the TOC and DOC levels in the water, and to evaluate the influence the water delivery lines may have had on the water before it entered the filter. This comparison revealed a new component that was not apparent from observing previous data. The comparison of the filter inlet and filter outlet DOC data showed strong agreement in the two data sets (Table 6 and Figure 8). Additional confirmation of this agreement continues when the DOC comparison includes the river DOC grab sample data. The data show little variation in the DOC concentration of the water as it travels from the river and through the water delivery system. This comparison is shown in Figure 9. However, when the filter inlet and outlet grab sample TOC data were plotted, a different pattern was revealed. The data shown in Figure 10 indicate events of considerable TOC differences in the filter inlet and filter outlet water. The maximum allowable RPD of 30 percent was exceeded three times and the RPD warning level of 25 percent was exceeded three times. A comparison of the DOC and TOC data values and their associated relative percentage differences for these samples is shown in Table 7. Since the comparison of the river grab samples to the filter outlet grab samples showed the water delivery system after filtration did not contribute TOC to the water, then other factors prior to filtration must be responsible for the



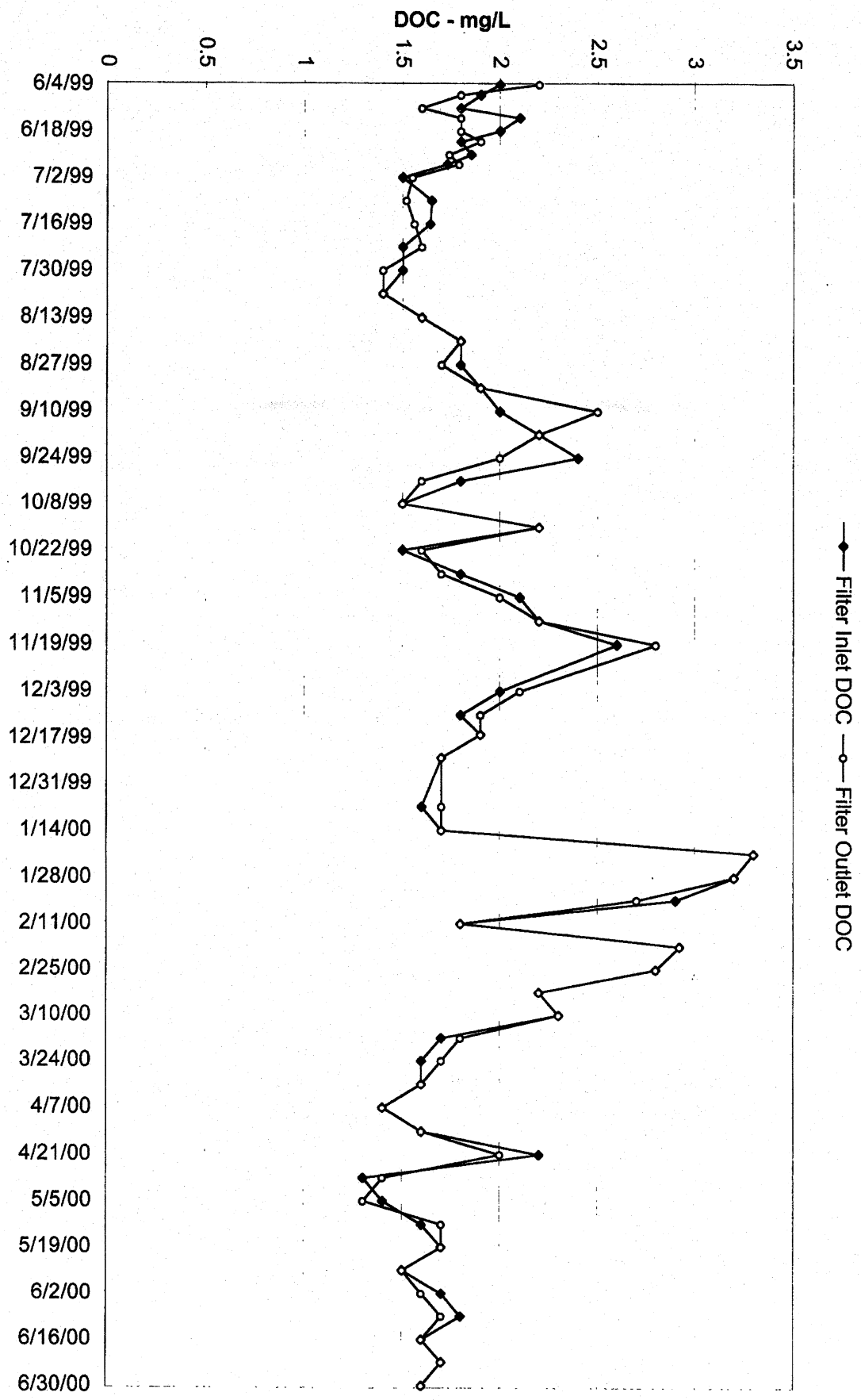
**Table 6. Comparison of Bryte Chemical Laboratory DOC  
Analysis of Filter Inlet and Filter Outlet Grab Samples**

Collection Date	Filter Inlet DOC - mg/L	Filter Outlet DOC - mg/L	DOC Inlet Vs Outlet RPD
06/04/99	2	2.2	9.52%
06/07/99	1.9	1.8	5.41%
06/11/99	1.8	1.6	11.76%
06/14/99	2.1	1.8	15.38%
06/18/99	2	1.8	10.53%
06/21/99	1.8	1.9	5.41%
06/25/99	1.85	1.74	6.13%
06/28/99	1.73	1.79	3.41%
07/02/99	1.5	1.55	3.28%
07/09/99	1.65	1.52	8.20%
07/16/99	1.64	1.56	5.00%
07/23/99	1.5	1.6	6.45%
07/30/99	1.5	1.4	6.90%
08/06/99	1.4	1.4	0.00%
08/13/99	1.6	1.6	0.00%
08/20/99	1.8	1.8	0.00%
08/27/99	1.8	1.7	5.71%
09/03/99	1.9	1.9	0.00%
09/10/99	2	2.5	22.22%
09/17/99	2.2	2.2	0.00%
09/24/99	2.4	2	18.18%
10/01/99	1.8	1.6	11.76%
10/08/99	1.5	1.5	0.00%
10/15/99	2.2	2.2	0.00%
10/22/99	1.5	1.6	6.45%
10/29/99	1.8	1.7	5.71%
11/05/99	2.1	2	4.88%
11/12/99	2.2	2.2	0.00%
11/19/99	2.6	2.8	7.41%
12/03/99	2	2.1	4.88%
12/10/99	1.8	1.9	5.41%
12/16/99	1.9	1.9	0.00%
12/23/99	1.7	1.7	0.00%
01/07/00	1.6	1.7	6.06%
01/14/00	1.7	1.7	0.00%
01/21/00	3.3	3.3	0.00%
01/28/00	3.2	3.2	0.00%
02/04/00	2.9	2.7	7.14%

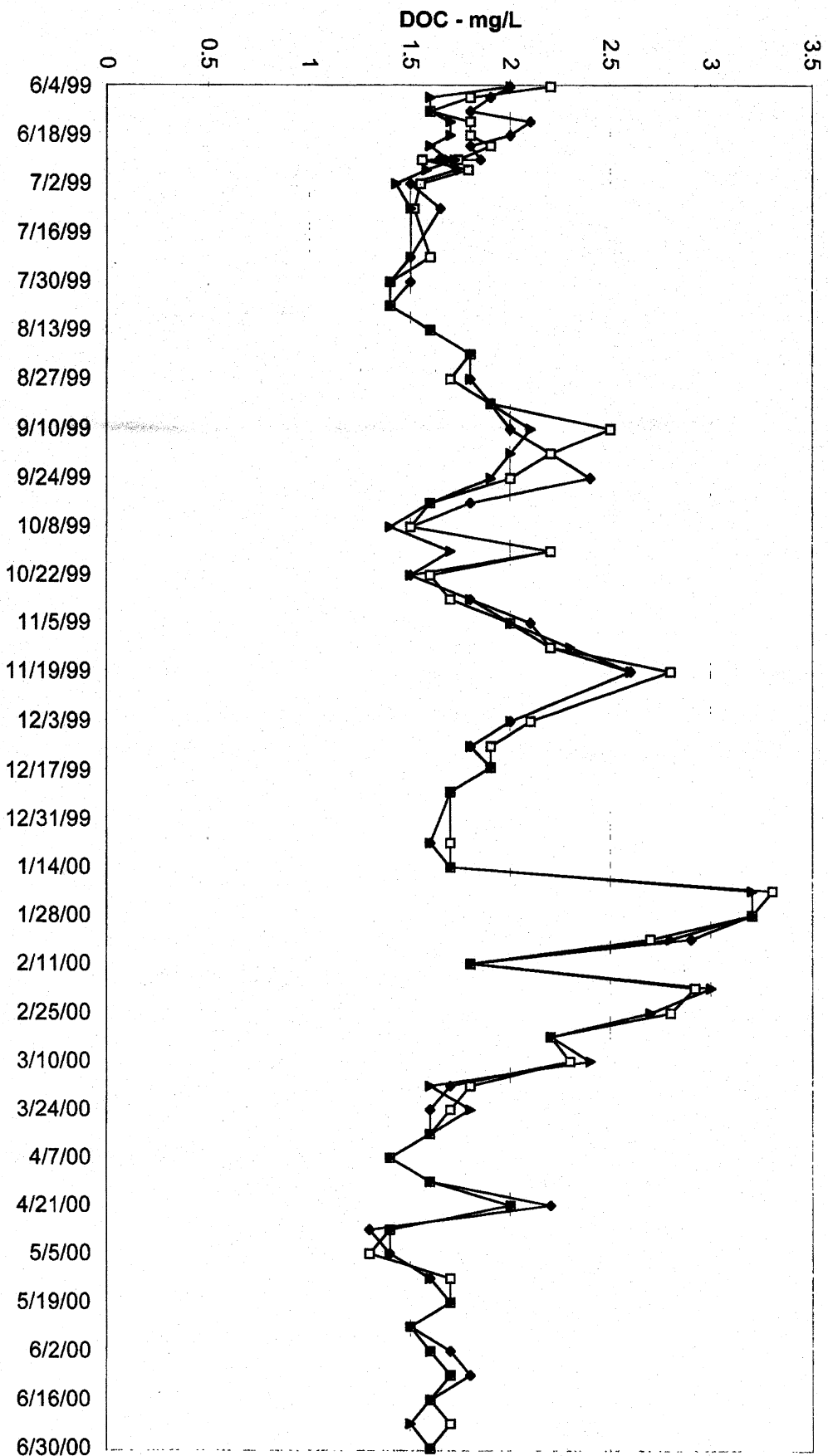
**Table 6 continued. Comparison of Bryte Chemical Laboratory  
DOC Analysis of Filter Inlet and Filter Outlet Grab Samples**

Collection Date	Filter Inlet DOC - mg/L	Filter Outlet DOC - mg/L	DOC Inlet Vs Outlet RPD
02/11/00	1.8	1.8	0.00%
02/18/00	2.92	2.92	0.00%
02/25/00	2.8	2.8	0.00%
03/03/00	2.2	2.2	0.00%
03/10/00	2.3	2.3	0.00%
03/17/00	1.7	1.8	5.71%
03/24/00	1.6	1.7	6.06%
03/31/00	1.6	1.6	0.00%
04/07/00	1.4	1.4	0.00%
04/14/00	1.6	1.6	0.00%
04/21/00	2.2	2	9.52%
04/28/00	1.3	1.4	7.41%
05/05/00	1.4	1.3	7.41%
05/12/00	1.6	1.7	6.06%
05/19/00	1.7	1.7	0.00%
05/26/00	1.5	1.5	0.00%
06/02/00	1.7	1.6	6.06%
06/09/00	1.8	1.7	5.71%
06/16/00	1.6	1.6	0.00%
06/23/00	1.7	1.7	0.00%
06/30/00	1.6	1.6	0.00%

**Figure 8. Comparison of Bryte Chemical Laboratory DOC Analysis of Filter Inlet and Filter Outlet Grab Samples**



**Figure 9. Comparison of Filter Inlet and Filter Outlet DOC Grab Samples to River DOC Grab Samples**



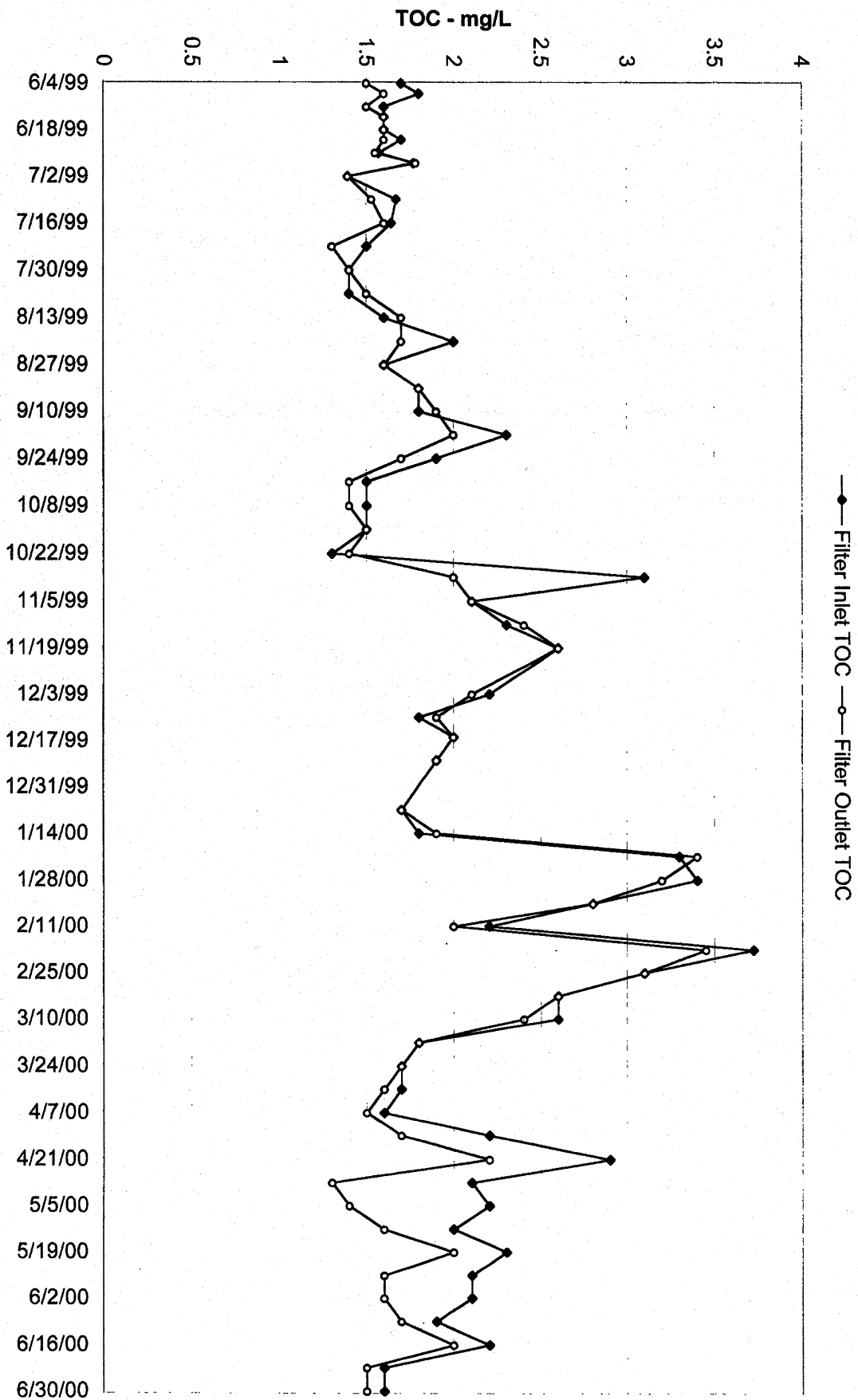


Figure 10. Comparison of Bryte Chemical Laboratory Filter Inlet and Filter Outlet TOC Grab Sample Analysis

—●— Filter Inlet TOC —○— Filter Outlet TOC

Table 7. Comparison of Blythe Chemical Laboratory DOC and TOC Analysis of Grab Samples from Filter Inlet and Outlet to River Grab Samples to Evaluate Water Quality Impacts of Water Delivery System

Date	Filter Inlet DOC-mg/L	Filter Outlet DOC-mg/L	River DOC mg/L	Inlet/Outlet DOC-RPD	River/Outlet DOC-RPD	River/Inlet DOC-RPD	Filter Inlet TOC-mg/L	Filter Outlet TOC-mg/L	River TOC mg/L	Inlet/Outlet TOC-RPD	River/Outlet TOC-RPD	River/Inlet TOC-RPD
06/04/99	2	2.2	2	9.52%	9.52%	0.00%	1.7	1.5	1.6	12.50%	6.45%	6.06%
06/07/99	1.9	1.8	1.6	5.41%	11.76%	17.14%	1.8	1.6	1.7	11.76%	6.06%	5.71%
06/11/99	1.8	1.6	1.6	11.76%	0.00%	11.76%	1.6	1.5	1.4	6.45%	6.90%	13.33%
06/14/99	2.1	1.8	1.7	15.38%	5.71%	21.05%	1.6	1.6	1.6	0.00%	0.00%	0.00%
06/18/99	2	1.8	1.7	10.53%	5.71%	16.22%	1.6	1.6	1.5	0.00%	6.45%	6.45%
06/21/99	1.8	1.9	1.6	5.41%	17.14%	11.76%	1.7	1.6	1.7	6.06%	6.06%	0.00%
06/25/99	1.85	1.74	1.69	6.13%	2.92%	9.04%	1.57	1.55	1.52	1.28%	1.95%	3.24%
06/28/99	1.73	1.79	1.58	3.41%	12.46%	9.06%	1.77	1.78	1.69	0.56%	5.19%	4.62%
07/02/99	1.5	1.55	1.43	3.28%	8.05%	4.78%	1.39	1.39	1.54	0.00%	10.24%	10.24%
07/09/99	1.65	1.52	1.5	8.20%	1.32%	9.52%	1.67	1.53	1.64	8.75%	6.94%	1.81%
06/25/99	1.64	1.56	1.72	5.00%	9.76%	4.76%	1.64	1.6	1.51	2.47%	5.79%	8.25%
07/23/99	1.5	1.6	1.5	6.45%	6.45%	0.00%	1.5	1.3	1.4	14.29%	7.41%	6.90%
07/30/99	1.5	1.4	1.4	6.90%	0.00%	6.90%	1.4	1.4	1.3	0.00%	7.41%	7.41%
08/06/99	1.4	1.4	1.4	0.00%	0.00%	0.00%	1.4	1.5	1.4	6.90%	6.90%	0.00%
08/13/99	1.6	1.6	1.6	0.00%	0.00%	0.00%	1.6	1.7	1.7	6.06%	0.00%	6.06%
08/20/99	1.8	1.8	1.8	0.00%	0.00%	0.00%	2	1.7	1.7	16.22%	0.00%	16.22%
08/27/99	1.8	1.7	1.8	5.71%	5.71%	0.00%	1.6	1.6	1.8	0.00%	6.06%	6.06%
09/03/99	1.9	1.9	1.9	0.00%	0.00%	0.00%	1.8	1.8	1.8	0.00%	0.00%	0.00%
09/10/99	2	2.5	2.1	22.22%	17.39%	4.88%	1.8	1.9	1.8	5.41%	5.41%	0.00%
09/17/99	2.2	2.2	2	0.00%	9.52%	9.52%	2.3	2	2	13.95%	0.00%	13.95%
09/24/99	2.4	2	1.9	18.18%	5.13%	23.26%	1.9	1.7	1.6	11.11%	6.06%	17.14%
10/01/99	1.8	1.6	1.6	11.76%	0.00%	11.76%	1.5	1.4	1.5	6.90%	6.90%	0.00%
10/08/99	1.5	1.5	1.4	0.00%	6.90%	6.90%	1.5	1.4	1.4	6.90%	0.00%	6.90%
10/15/99	2.2	2.2	1.7	0.00%	25.64%	25.64%	1.5	1.5	1.6	0.00%	6.45%	6.45%
10/22/99	1.5	1.6	1.5	6.45%	6.45%	0.00%	1.3	1.4	1.4	7.41%	0.00%	7.41%
10/29/99	1.8	1.7	1.8	5.71%	5.71%	0.00%	3.1	2	2.2	43.14%	9.52%	33.96%
11/05/99	2.1	2	2	4.88%	0.00%	4.88%	2.1	2.1	2	0.00%	4.88%	4.88%
11/12/99	2.2	2.2	2.3	0.00%	4.44%	4.44%	2.3	2.4	2.4	4.26%	0.00%	4.26%
11/19/99	2.6	2.8	2.6	7.41%	7.41%	0.00%	2.6	2.6	2.6	0.00%	0.00%	0.00%
12/03/99	2	2.1	2	4.88%	4.88%	0.00%	2.2	2.1	2	4.65%	4.88%	9.52%
12/10/99	1.8	1.9	1.8	5.41%	5.41%	0.00%	1.8	1.9	1.8	5.41%	5.41%	0.00%
12/16/99	1.9	1.9	1.9	0.00%	0.00%	0.00%	2	2	1.9	0.00%	5.13%	5.13%
12/23/99	1.7	1.7	1.7	0.00%	0.00%	0.00%	1.9	1.9	1.9	0.00%	0.00%	0.00%
01/07/00	1.6	1.7	1.6	6.06%	6.06%	0.00%	1.7	1.7	1.7	0.00%	0.00%	0.00%
01/14/00	1.7	1.7	1.7	0.00%	0.00%	0.00%	1.8	1.9	1.7	5.41%	11.11%	5.71%
01/21/00	3.3	3.3	3.2	0.00%	3.08%	3.08%	3.3	3.4	3.3	2.99%	2.99%	0.00%
01/28/00	3.2	3.2	3.2	0.00%	0.00%	0.00%	3.4	3.2	3.1	6.06%	3.17%	9.23%
02/04/00	2.9	2.7	2.8	7.14%	3.64%	3.51%	2.8	2.8	2.8	0.00%	0.00%	0.00%

Table 7 continued. Comparison of Bryte Chemical Laboratory DOC and TOC Analysis of Grab Samples from Filter Inlet and Outlet to River Samples to Evaluate Water Quality Impacts of Water Delivery System

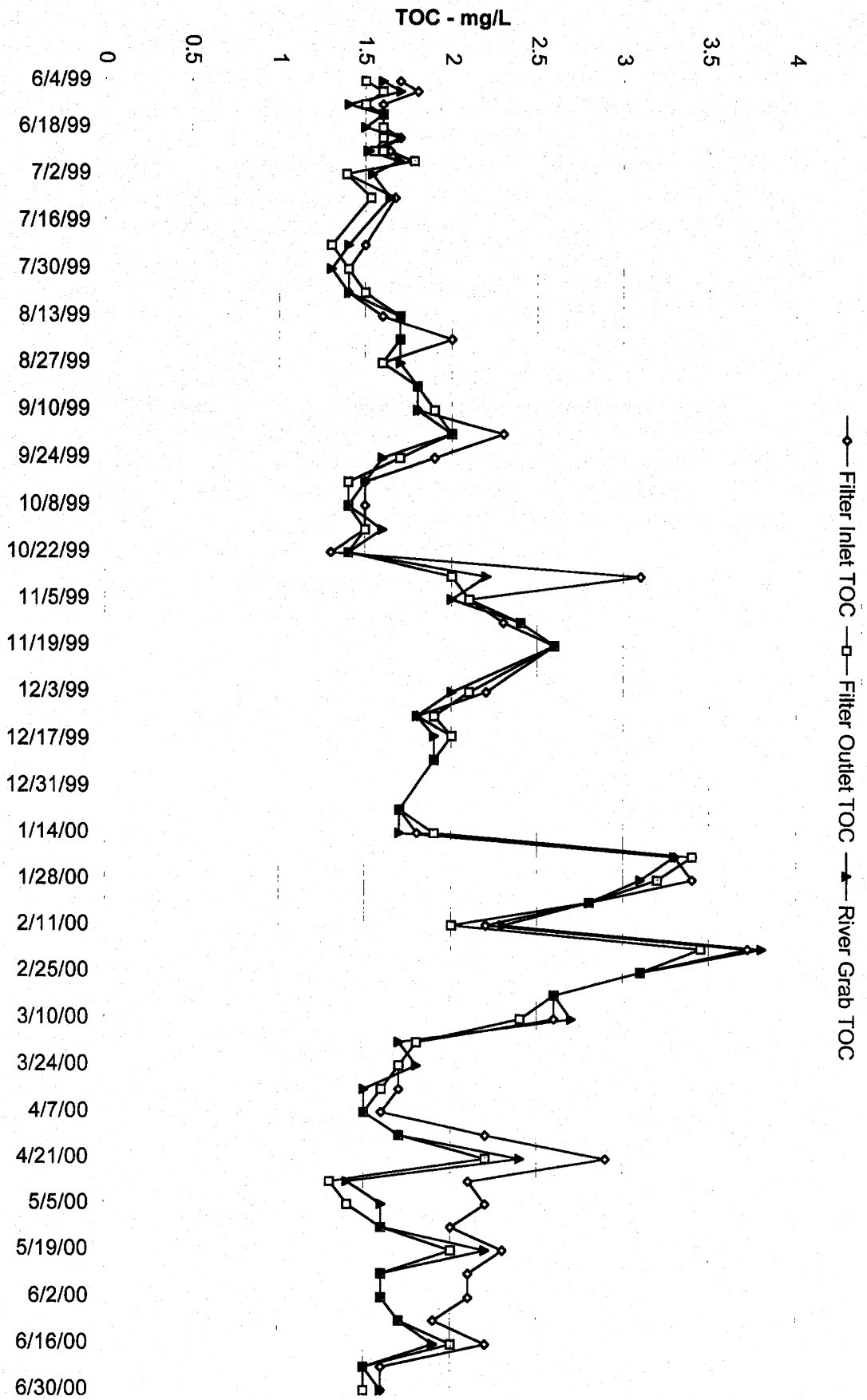
Date	Filter Inlet DOC-mg/L	Filter Outlet DOC-mg/L	River DOC mg/L	Inlet vs Outlet DOC - RPD	River vs Outlet DOC - RPD	River vs Inlet DOC - RPD	Filter Inlet TOC-mg/L	Filter Outlet TOC-mg/L	River TOC mg/L	Inlet vs Outlet TOC - RPD	River vs Outlet TOC - RPD	River vs Inlet TOC - RPD
02/11/00	1.8	1.8	1.8	0.00%	0.00%	0.00%	2.2	2	2.3	9.52%	13.95%	4.44%
02/18/00	2.92	2.92	3	0.00%	2.70%	2.70%	3.72	3.45	3.8	7.53%	9.66%	2.13%
02/25/00	2.8	2.8	2.7	0.00%	3.64%	3.64%	3.1	3.1	3.1	0.00%	0.00%	0.00%
03/03/00	2.2	2.2	2.2	0.00%	0.00%	0.00%	2.6	2.6	2.6	0.00%	0.00%	0.00%
03/16/00	2.3	2.3	2.4	0.00%	4.26%	4.26%	2.6	2.4	2.7	8.00%	11.76%	3.77%
03/17/00	1.7	1.8	1.6	5.71%	11.76%	6.06%	1.8	1.8	1.7	0.00%	5.71%	5.71%
03/24/00	1.6	1.7	1.8	6.06%	5.71%	11.76%	1.7	1.7	1.8	0.00%	5.71%	5.71%
04/07/00	1.6	1.6	1.6	0.00%	0.00%	0.00%	1.7	1.6	1.5	6.06%	6.45%	12.50%
04/14/00	1.4	1.4	1.4	0.00%	0.00%	0.00%	1.6	1.5	1.5	6.45%	6.45%	6.45%
04/21/00	1.6	1.6	1.6	0.00%	0.00%	0.00%	2.2	1.7	1.7	25.64%	0.00%	25.64%
04/28/00	2.2	2	2	9.52%	0.00%	9.52%	2.9	2.2	2.4	27.45%	8.70%	18.87%
05/05/00	1.3	1.4	1.4	7.41%	0.00%	7.41%	2.1	1.3	1.4	47.06%	7.41%	40.00%
05/12/00	1.4	1.3	1.4	7.41%	7.41%	0.00%	2.2	1.4	1.6	44.44%	13.33%	31.58%
05/19/00	1.6	1.7	1.6	6.06%	6.06%	0.00%	2	1.6	1.6	22.22%	0.00%	22.22%
05/26/00	1.7	1.7	1.7	0.00%	0.00%	0.00%	2.3	2	2.2	13.95%	9.52%	4.44%
06/02/00	1.5	1.5	1.5	0.00%	0.00%	0.00%	2.1	1.6	1.6	27.03%	0.00%	27.03%
06/09/00	1.7	1.6	1.6	6.06%	0.00%	6.06%	2.1	1.6	1.6	27.03%	0.00%	27.03%
06/16/00	1.8	1.7	1.7	5.71%	0.00%	5.71%	1.9	1.7	1.7	11.11%	0.00%	11.11%
06/23/00	1.6	1.6	1.6	0.00%	0.00%	0.00%	2.2	2	1.9	9.52%	5.13%	14.63%
06/30/00	1.7	1.7	1.5	0.00%	12.50%	12.50%	1.6	1.5	1.5	6.45%	0.00%	6.45%
	1.6	1.6	1.6	0.00%	0.00%	0.00%	1.6	1.5	1.6	6.45%	6.45%	0.00%

differences in TOC values seen in the filter inlet and filter outlet grab samples. It was concluded that the probable cause for the higher TOC values in the filter inlet samples was due to algae and other organic matter suspended in the inlet water line. This was based on the observation of large amounts of algae and other organic matter that was expelled from the water line during routine maintenance and servicing which included cleaning the silt trap and changing the filter. The data show that the incidences and the degree of these differences increase over time. The continued build-up of algae growth and other organic matter on the inside wall of the water lines would reach a point where some of the material would slough-off the wall surface and become suspended in the water flow. The filter was sufficient in retaining these particles of algae and matter while not impacting the TOC content of the water prior to its entering the autoanalyzer.

The type and quality of the carbon present was not investigated as in the form of UVA 254 or THMFP analyses. Evaluating the type or quality of carbon present was not a goal of this study, which was designed to assess the adequacy of the equipment. Further studies could be designed to evaluate carbon quality. Figure 11 shows the comparison of the TOC values in the filter inlet, filter outlet, and river grab samples where the increased filter inlet TOC values were observed. In summary, although the water delivery system at times appeared to contribute to increased TOC levels in the water, the filter device was efficient in removing these system contributions without impacting the measured TOC concentrations of the river water.



**Figure 11. Comparison of Bryte Chemical Laboratory Analysis of Filter Inlet and Filter Outlet TOC Samples to River TOC Grab Samples**



#### 4. *Filter Outlet vs. Autoanalyzer*

Another component of our evaluation was the comparison of the on-line river water data collected by the Sievers analyzer to the Bryte Chemical Laboratory analysis of filter outlet grab sample data. These grab samples were collected while the analyzer was in active sampling mode so they could be considered duplicate samples to the analyzer on-line analysis. The Sievers analyzer on-line data were compared with the corresponding filter outlet DOC and TOC grab sample data. This was done to check if the filtration device had any effect on the TOC levels in the water going into the autoanalyzer. A review of the data shown in Table 8 and Figure 12 indicates the filter did not create a bias in the autoanalyzer data. The data shows occasions where the DOC values are greater than the TOC. These differences in values are most likely the result of a combination of factors. These factors could include, contamination introduced in the field sampling procedure or from the equipment or filtering material, the natural variability inherent in the river water, and to some extent, the variability within laboratory analytical procedures.

When just the Sievers analyzer on-line TOC data are compared to the filter outlet TOC grab sample data, it is found that the maximum acceptable RPD value of 30 percent was exceeded only once during the year of the study. This occurred during storm events with the corresponding increased turbidity and higher TOC values. The Sievers analyzer consistently reported TOC values higher than the Bryte Chemical Laboratory during these storm events. These data are shown in Table 9 and Figure 13.

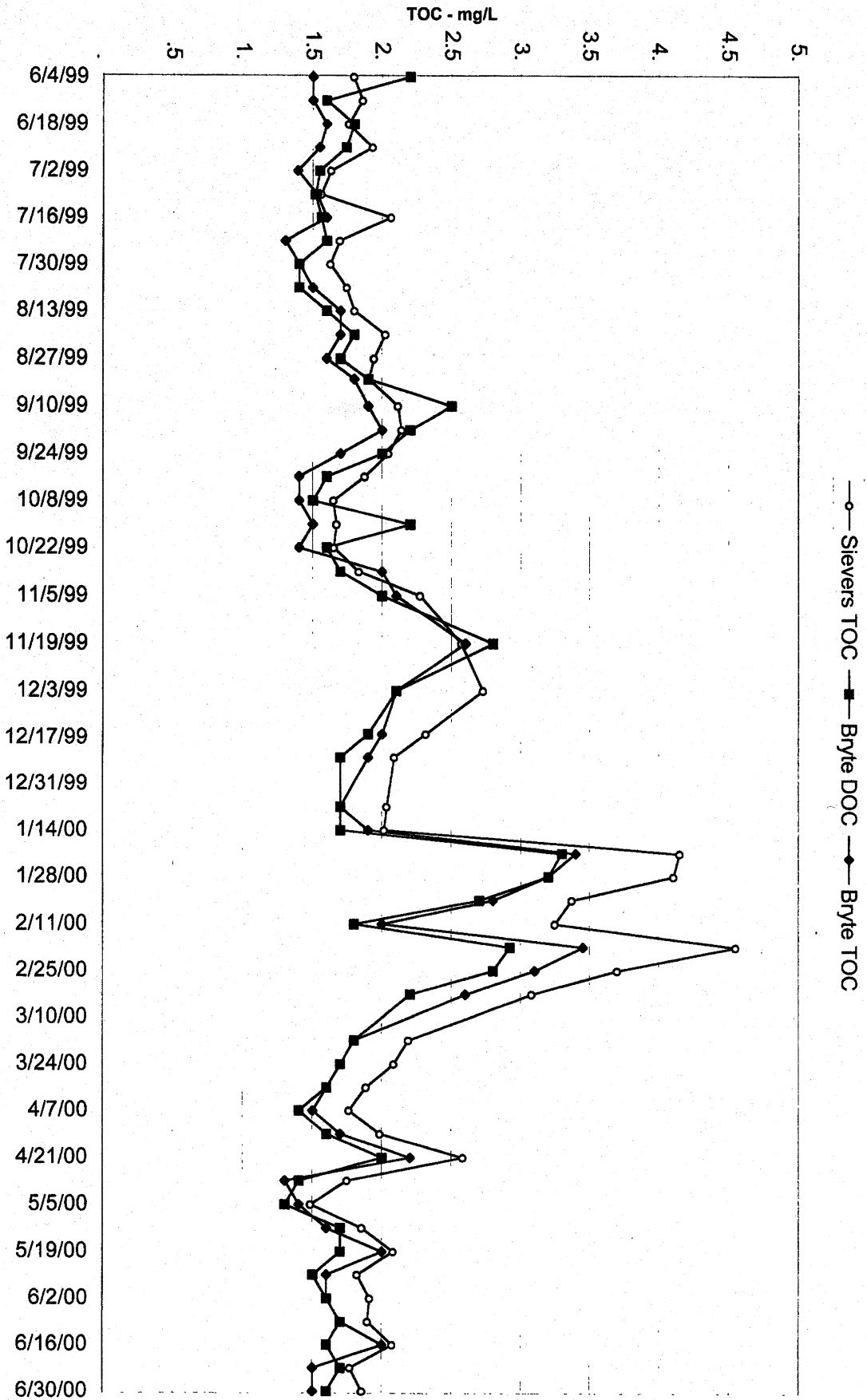
**Table 8. Comparison of Weekly Duplicate Filter Outlet Grab Sample TOC and DOC Analysis by the Bryte Chemical Laboratory and the Sievers Analyzer On-line Analysis**

Collection Date	Sievers TOC	Bryte DOC	Bryte TOC	Bryte DOC/Sievers TOC	Bryte / Sievers TOC
	mg/L	mg/L	mg/L	RPD	RPD
06/04/99	1.8	2.2	1.5	20.16%	18.02%
06/11/99	1.86	1.6	1.5	15.03%	21.43%
06/18/99	1.76	1.8	1.6	2.25%	9.52%
06/25/99	1.93	1.74	1.55	10.35%	21.84%
07/02/99	1.63	1.55	1.39	5.00%	15.86%
07/09/99	1.56	1.52	1.53	2.60%	1.94%
07/16/99	2.06	1.56	1.6	27.62%	25.14%
07/23/99	1.69	1.6	1.3	5.55%	26.17%
07/30/99	1.63	1.4	1.4	14.97%	14.97%
08/06/99	1.75	1.4	1.5	21.99%	15.15%
08/13/99	1.8	1.6	1.7	11.69%	5.64%
08/20/99	2.02	1.8	1.7	11.59%	17.27%
08/27/99	1.94	1.7	1.6	13.15%	19.17%
09/02/99	1.9	1.9	1.8	0.17%	5.57%
09/10/99	2.11	2.5	1.9	16.77%	10.62%
09/17/99	2.14	2.2	2	2.83%	6.70%
09/24/99	2.04	2	1.7	2.08%	18.28%
10/01/99	1.87	1.6	1.4	15.73%	28.91%
10/08/99	1.65	1.5	1.4	9.32%	16.19%
10/15/99	1.67	2.2	1.5	27.47%	10.65%
10/22/99	1.65	1.6	1.4	3.19%	16.50%
10/29/99	1.83	1.7	2	7.56%	8.68%
11/05/99	2.27	2	2.1	12.64%	7.77%
11/19/99	2.57	2.8	2.6	8.57%	1.16%
12/03/99	2.72	2.1	2.1	25.88%	25.88%
12/16/99	2.31	1.9	2	19.50%	14.41%
12/23/99	2.09	1.7	1.9	20.42%	9.36%
01/07/00	2.03	1.7	1.7	17.73%	17.73%
01/14/00	2.01	1.7	1.9	16.87%	5.79%
01/21/00	4.15	3.3	3.4	22.80%	19.85%
01/28/00	4.1	3.2	3.2	24.77%	24.77%
02/04/00	3.37	2.7	2.8	22.10%	18.50%
02/11/00	3.25	1.8	2	57.43%	47.63%
02/18/00	4.55	2.92	3.45	43.58%	27.43%
02/25/00	3.7	2.8	3.1	27.69%	17.64%
03/03/00	3.08	2.2	2.6	33.33%	16.90%

**Table 8 continued. Comparison of Weekly Duplicate Filter Outlet  
Grab Sample TOC and DOC Analysis by the Bryte Chemical  
Laboratory and the Sievers Analyzer On-line Analysis**

Collection Date	Sievers TOC	Bryte DOC	Bryte TOC	Bryte DOC/Sievers TOC	Bryte / Sievers TOC
	mg/L	mg/L	mg/L	RPD	RPD
03/24/00	2.08	1.7	1.7	20.19%	20.19%
03/31/00	1.89	1.6	1.6	16.39%	16.39%
04/07/00	1.76	1.4	1.5	22.93%	16.10%
04/14/00	1.98	1.6	1.7	21.33%	15.32%
04/21/00	2.58	2	2.2	25.35%	15.92%
04/28/00	1.75	1.4	1.3	22.09%	29.38%
05/05/00	1.48	1.3	1.4	13.23%	5.84%
05/12/00	1.85	1.7	1.6	8.61%	14.65%
05/19/00	2.08	1.7	2	20.10%	3.91%
05/26/00	1.82	1.5	1.6	19.39%	12.98%
06/02/00	1.91	1.6	1.6	17.65%	17.65%
06/09/00	1.9	1.7	1.7	10.94%	10.94%
06/16/00	2.07	1.6	2	25.68%	3.51%
06/23/00	1.77	1.7	1.5	4.10%	16.58%
06/30/00	1.86	1.6	1.5	14.83%	21.23%

Figure 12. Comparison of Weekly Duplicate Filter Outlet Grab Sample TOC and DOC Analysis by the Bryte Chemical Laboratory and the Sievers Analyzer On-line Analysis



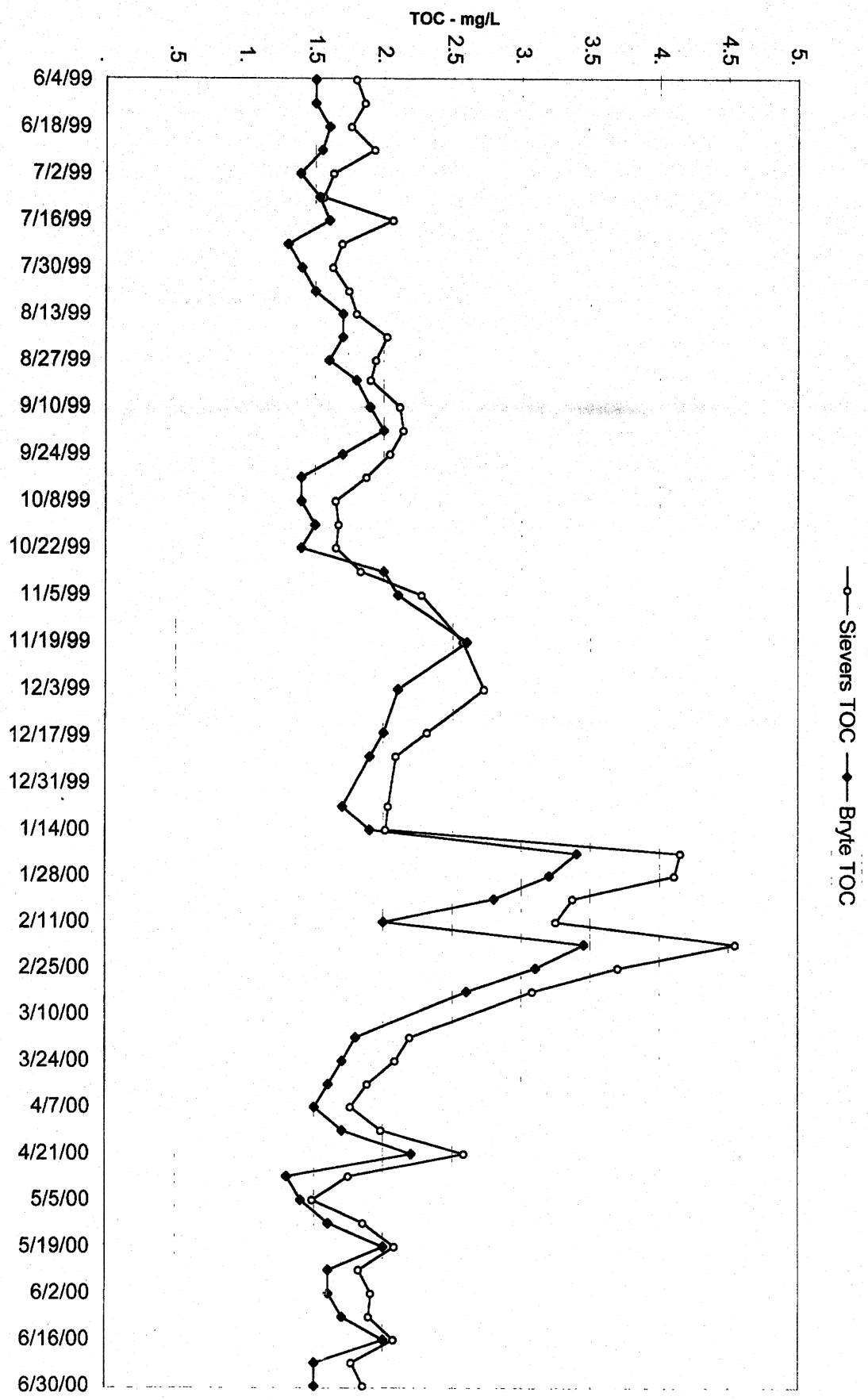
**Table 9. Results of Weekly Duplicate Filter Outlet Grab Sample TOC Analysis by the Bryte Chemical Laboratory and the Sievers Analyzer On-line Analysis**

Collection Date	Sievers Analyzer TOC mg/L	Bryte - Outlet TOC mg/L	Bryte TOC/Sievers TOC RPD
06/04/99	1.8	1.5	18.02%
06/11/99	1.86	1.5	21.43%
06/18/99	1.76	1.6	9.52%
06/25/99	1.93	1.55	21.84%
07/02/99	1.63	1.39	15.86%
07/09/99	1.56	1.53	1.94%
07/16/99	2.06	1.6	25.14%
07/23/99	1.69	1.3	26.17%
07/30/99	1.63	1.4	14.97%
08/06/99	1.75	1.5	15.15%
08/13/99	1.8	1.7	5.64%
08/20/99	2.02	1.7	17.27%
08/27/99	1.94	1.6	19.17%
09/02/99	1.9	1.8	5.57%
09/10/99	2.11	1.9	10.62%
09/17/99	2.14	2	6.70%
09/24/99	2.04	1.7	18.28%
10/01/99	1.87	1.4	28.91%
10/08/99	1.65	1.4	16.19%
10/15/99	1.67	1.5	10.65%
10/22/99	1.65	1.4	16.50%
10/29/99	1.83	2	8.68%
11/05/99	2.27	2.1	7.77%
11/19/99	2.57	2.6	1.16%
12/03/99	2.72	2.1	25.88%
12/16/99	2.31	2	14.41%
12/23/99	2.09	1.9	9.36%
01/07/00	2.03	1.7	17.73%
01/14/00	2.01	1.9	5.79%
01/21/00	4.15	3.4	19.85%
01/28/00	4.1	3.2	24.77%
02/04/00	3.37	2.8	18.50%
02/11/00	3.25	2	47.63%
02/18/00	4.55	3.45	27.43%
02/25/00	3.7	3.1	17.64%
03/03/00	3.08	2.6	16.90%
03/17/00	2.19	1.8	19.53%

**Table 9 continued. Results of Weekly Duplicate Filter Outlet Grab Sample TOC Analysis by the Bryte Chemical Laboratory and the Sievers Analyzer On-line Analysis**

Collection Date	Sievers Analyzer TOC mg/L	Bryte - Outlet TOC mg/L	Bryte TOC/Sievers TOC RPD
03/24/00	2.08	1.7	20.19%
03/31/00	1.89	1.6	16.39%
04/07/00	1.76	1.5	16.10%
04/14/00	1.98	1.7	15.32%
04/21/00	2.58	2.2	15.92%
04/28/00	1.75	1.3	29.38%
05/05/00	1.48	1.4	5.84%
05/12/00	1.85	1.6	14.65%
05/19/00	2.08	2	3.91%
05/26/00	1.82	1.6	12.98%
06/02/00	1.91	1.6	17.65%
06/09/00	1.9	1.7	10.94%
06/16/00	2.07	2	3.51%
06/23/00	1.77	1.5	16.58%
06/30/00	1.86	1.5	21.23%

Figure 13. Comparison of Weekly Duplicate Filter Outlet Grab Sample TOC Analysis by the Bryte Chemical Laboratory and the Sievers Analyzer On-line Analysis



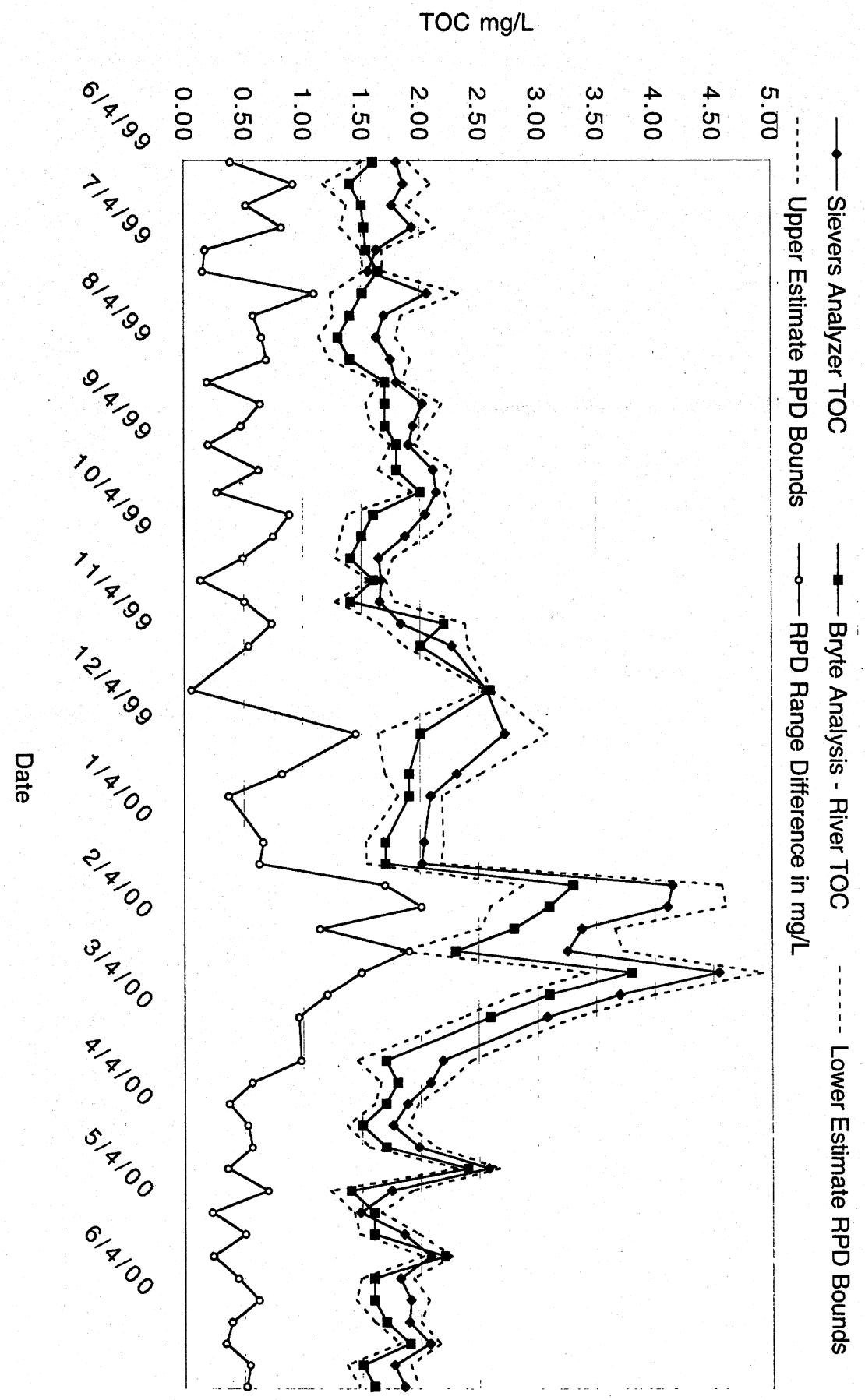


#### 5. *Estimation of RPD Range*

Finally, an analysis of the data from two key components allowed estimation of range in the RPD between the river grab sample analysis data from the Bryte Chemical Laboratory and the Sievers on-line analysis data. These river grab data are from samples collected while the Sievers analyzer was in active sampling mode so a direct comparison could be made to the Sievers data. The river grab sample data was selected because it represents the background water that is the common factor in all components of this sample investigation. The Sievers analyzer data are included because they are the object of interest in this pilot study. RPD normally expresses the difference between measurement as a percent. To calculate the RPD spread, each RPD was converted to a  $\pm$  range expressed in mg/L.

This analysis shows the range in the spread of the RPD values to be 1 mg/L or less for 85 percent of the data. The occurrence of when the spread in RPD range value is greater than 1 mg/L is predominately during periods of storm events. These data are shown in Figure 14. The data for the estimation of RPD and RPD range are shown in Table 10. These analyses provide support in the ability of the Sievers analyzer to provide representative data while in operation at a field facility.

Figure 14. Estimated Range in RPD Between Bryte Chemical Laboratory TOC Analysis of River Grab Sample and Sievers Analyzer On-line Analysis



**Table 10. Comparison of Sievers Analyzer On-line Analysis to Bryte Chemical Laboratory Filter Outlet and River Grab Sample TOC Results for Estimation of 2 Standard Deviations Using One Way ANOVA Analysis of Variance**

Collection Date	Sievers Analyzer TOC mg/L	Bryte - Outlet TOC mg/L	Bryte - River TOC mg/L	Average TOC mg/L	ANOVA Variance	Point Estimate of 2 Std. Deviations mg/L	Spread of Std. Deviation
6/4/99	1.80	1.50	1.60	1.63	0.02	0.30	0.60
6/11/99	1.86	1.50	1.40	1.59	0.06	0.48	0.97
6/18/99	1.76	1.60	1.50	1.62	0.02	0.26	0.52
6/25/99	1.93	1.55	1.52	1.67	0.05	0.46	0.91
7/2/99	1.63	1.39	1.54	1.52	0.01	0.24	0.48
7/9/99	1.56	1.53	1.64	1.58	0.00	0.11	0.23
7/16/99	2.06	1.60	1.51	1.72	0.09	0.59	1.18
7/23/99	1.69	1.30	1.40	1.46	0.04	0.41	0.81
7/30/99	1.63	1.40	1.30	1.44	0.03	0.33	0.67
8/6/99	1.75	1.50	1.40	1.55	0.03	0.36	0.71
8/13/99	1.80	1.70	1.70	1.73	0.00	0.11	0.23
8/20/99	2.02	1.70	1.70	1.81	0.03	0.37	0.74
8/27/99	1.94	1.60	1.70	1.75	0.03	0.35	0.70
9/2/99	1.90	1.80	1.80	1.83	0.00	0.12	0.24
9/10/99	2.11	1.90	1.80	1.94	0.03	0.32	0.64
9/17/99	2.14	2.00	2.00	2.05	0.01	0.16	0.32
9/24/99	2.04	1.70	1.60	1.78	0.05	0.46	0.93
10/1/99	1.87	1.40	1.50	1.59	0.06	0.50	1.00
10/8/99	1.65	1.40	1.40	1.48	0.02	0.28	0.57
10/15/99	1.67	1.50	1.60	1.59	0.01	0.17	0.34
10/22/99	1.65	1.40	1.40	1.48	0.02	0.29	0.58
10/29/99	1.83	2.00	2.20	2.01	0.03	0.37	0.73
11/5/99	2.27	2.10	2.00	2.12	0.02	0.27	0.55
11/19/99	2.57	2.60	2.60	2.59	0.00	0.03	0.07
12/3/99	2.72	2.10	2.00	2.27	0.15	0.79	1.57
12/16/99	2.31	2.00	1.90	2.07	0.05	0.43	0.86
12/23/99	2.09	1.90	1.90	1.96	0.01	0.22	0.43
1/7/00	2.03	1.70	1.70	1.81	0.04	0.38	0.76
1/14/00	2.01	1.90	1.70	1.87	0.03	0.32	0.63
1/21/00	4.15	3.40	3.30	3.62	0.22	0.93	1.86
1/28/00	4.10	3.20	3.10	3.47	0.31	1.11	2.21
2/4/00	3.37	2.80	2.80	2.99	0.11	0.66	1.32
2/11/00	3.25	2.00	2.30	2.52	0.43	1.31	2.61
2/18/00	4.55	3.45	3.80	3.93	0.31	1.12	2.24

**Table 10 continued. Comparison of Sievers Analyzer On-line Analysis to Bryte Chemical Laboratory Filter Outlet and River Grab Sample TOC Results for Estimation of 2 Standard Deviations Using One Way ANOVA Analysis of Variance**

Collection Date	Sievers Analyzer TOC mg/L	Bryte - Outlet TOC mg/L	Bryte - River TOC mg/L	Average TOC mg/L	ANOVA Variance	Point Estimate of 2 Std. Deviations mg/L	Spread of Std. Deviation
2/25/00	3.70	3.10	3.10	3.30	0.12	0.69	1.39
3/3/00	3.08	2.60	2.60	2.76	0.08	0.55	1.11
3/17/00	2.19	1.80	1.70	1.90	0.07	0.52	1.03
3/24/00	2.08	1.70	1.80	1.86	0.04	0.40	0.79
3/31/00	1.89	1.60	1.70	1.73	0.02	0.29	0.58
4/7/00	1.76	1.50	1.50	1.59	0.02	0.30	0.61
4/14/00	1.98	1.70	1.70	1.79	0.03	0.33	0.65
4/21/00	2.58	2.20	2.40	2.39	0.04	0.38	0.76
4/28/00	1.75	1.30	1.40	1.48	0.06	0.47	0.94
5/5/00	1.48	1.40	1.60	1.49	0.01	0.20	0.40
5/12/00	1.85	1.60	1.60	1.68	0.02	0.29	0.58
5/19/00	2.08	2.00	2.20	2.09	0.01	0.20	0.40
5/26/00	1.82	1.60	1.60	1.67	0.02	0.26	0.51
6/2/00	1.91	1.60	1.60	1.70	0.03	0.36	0.72
6/9/00	1.90	1.70	1.70	1.77	0.01	0.23	0.45
6/16/00	2.07	2.00	1.90	1.99	0.01	0.17	0.34
6/23/00	1.77	1.50	1.50	1.59	0.02	0.31	0.63
6/30/00	1.86	1.50	1.60	1.65	0.03	0.37	0.74

## **Quality Control Samples**

The series of Quality Control sample analyses in this study provided a high degree of assurance that the performance of the Sievers analyzer and the data it produces are of acceptable precision, accuracy, and quality.

## **Performance Evaluation Samples**

Results from the performance evaluation (PE) sample analysis provided insight into the analytical accuracy and precision of the Sievers analyzer. In both rounds of PE sample analysis, the results of the Sievers analyzer were within the established acceptable range of recovery for all samples analyzed. The results of these analyses are presented in Tables 11 and 12. These data show the close agreement in the results and the low standard deviation between the analyses. For both calibration checks, all the results were below the maximum acceptable 30 percent RPD level for precision between the Sievers analyzer and the Bryte Chemical Laboratory's O/I Analytical 1010 analyzer. The first calibration check was completed on June 18, 1999. The first check standards were made to concentrations of 1.25 mg/L of carbon and 1.0 mg/L of carbon. The 1.25 mg/L standard had a RPD of 11 percent and the 1.0 mg/L standard had a RPD of 10

**Table 11. Round 1 - Performance Evaluation TOC Sample  
Results between the Sievers Analyzer and the Bryte  
Chemical Laboratory O/I Analytical 1010 Analyzer**

11/22/99	PE Sample #1 (mg/L)	PE Sample #2 (mg/L)	PE Sample # 3 (mg/L)
Sievers 800	3.47	0.811	6.02
	3.46	0.797	6.04
	3.46	0.792	6.06
	3.46	0.789	6.07
<b>Mean/Avg</b>	<b>3.46</b>	<b>0.797</b>	<b>6.05</b>
Standard Deviation	0.005	0.009	0.022
11/22/99			
Bryte Lab O/I 1010	3.1	0.7	5.5
	3.1	0.7	5.6
	3	0.6	5.5
<b>Mean/Avg</b>	<b>3.07</b>	<b>0.67</b>	<b>5.53</b>
Standard Deviation	0.058	0.058	0.058
<b>ERA Certified Value</b>	<b>3.12</b>	<b>0.569</b>	<b>6.06</b>
<b>ERA Acceptance Range</b>	<b>2.34 - 3.91</b>	<b>0.427 - 0.714</b>	<b>4.27 - 7.11</b>

**Table 12. Round 2 - Performance Evaluation TOC Sample Results between the Sievers Analyzer and the Bryte Chemical Laboratory O/I Analytical 1010 Analyzer**

6/23/00	Matrix Spike Sample #1 (mg/L)			Matrix Spike Sample #2 (mg/L)		
Sievers 800	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
	5.0	4.8	4.8	6.2	6.2	6.2
	5.0	4.8	4.8	6.2	6.2	6.3
	5.0	4.8	4.8	6.2	6.9	6.3
<b>Mean/Avg</b>	<b>4.9</b>			<b>6.3</b>		
Standard Deviation	0.1			0.2		
6/23/00						
Bryte Lab O/I 1010						
	5.6	5.7	5.8	8.7	8.8	8.5
<b>Mean/Avg</b>	<b>5.7</b>			<b>8.7</b>		
Standard Deviation	0.1			0.2		
<b>ERA Certified Value</b>	<b>4.8</b>			<b>7.8</b>		
<b>ERA Acceptance Range</b>	<b>3.8 - 5.9</b>			<b>6.3 - 9.4</b>		

percent when analyzer results were compared. The second calibration check standard was completed on June 9, 2000. The second check standards were made to concentrations of 1.05 mg/L of carbon and 5.20 mg/L of carbon. The 1.05 mg/L standard produced a RPD of 21 percent and the 5.20 mg/L standard had a RPD of 6 percent when analyzer results were compared.

The three Sacramento River sets demonstrated a consistent difference between the sets of samples between the two analyzers. Three sets were collected at the Hood facility for three consecutive weeks in October and November 1999. The grab-sample sets from the Sacramento River analyzed by the Sievers instrument revealed RPDs of 20 percent, 18 percent, and 20 percent when compared to the samples analyzed by Bryte Chemical Laboratory.

Another sample set was collected from Barker Slough to evaluate the analyzer's performance with higher turbidity water. The turbidity of the Barker Slough sample analyzed by Bryte Chemical Laboratory and the Sievers analyzer was 41.9 NTU (compared to Sacramento River samples ranged from 15 NTU to 20 NTU). Barker Slough results had an RPD of 8 percent between the Sievers analyzer and Bryte Chemical Laboratory. Both analyzers demonstrated little variability within the results of each sample set collected and analyzed as turbidity increased.

The results of the replicate variability analysis from the O/I Analytical carbon analyzer at Bryte Chemical Laboratory produced precise measurements. The mean and the standard deviation of the mean of these analyses are shown in Table 13. These data showed little variability within each sample group. This set of samples supports the quality of the data collected by the Sievers analyzer and the grab samples analyzed by the O/I Analytical 1010 at the Bryte Chemical Laboratory.

## **CONCLUSIONS AND RECOMMENDATIONS**

The Sievers organic carbon analyzer has demonstrated the ability to operate consistently and reliably with the water from the Sacramento River at the Hood facility. The analyzer has provided data of acceptable precision and quality, although the analysis of raw surface water is outside the realm of normal application for this instrument. This study demonstrated that the amount of data a field-dedicated analyzer can economically generate exceeds any amount that field staff can obtain by collecting grab samples. The information gathered from the remote installation and operation of this analyzer provides credence to the proposal to establish a series of real-time TOC monitoring stations in the Sacramento-San Joaquin Delta. The Sievers analyzer has proven itself to be dependable and reliable. The instrument has not experienced any breakdowns or required major repairs outside of routine maintenance since it was put into service. The few problems observed were a result of the water delivery system modifications and not with the analyzer itself. The MWQI Program has



**Table 13. Bryte Chemical Laboratory Replicate Analysis  
Variability of DOC and TOC Samples**

Sample Type	Sample Purpose	Collection Date	TOC/DOC mg/l	
TOC	Unfiltered Blank Water	7/24/03	< 0.1	
TOC	Unfiltered Blank Water	7/24/03	< 0.1	
TOC	Unfiltered Blank Water	7/24/03	< 0.1	
TOC	Unfiltered Blank Water	7/24/03	< 0.1	
TOC	Unfiltered Blank Water	7/24/03	< 0.1	
TOC	Unfiltered Blank Water	7/24/03	< 0.1	
TOC	Unfiltered Blank Water	7/24/03	0.1	
TOC	Unfiltered Blank Water	7/24/03	< 0.1	
TOC	Unfiltered Blank Water	7/24/03	0.2	<b>Mean 0.04</b>
TOC	Unfiltered Blank Water	7/24/03	0.1	<b>Standard Deviation 0.07</b>
DOC	Filtered Blank Water	7/24/03	0.2	
DOC	Filtered Blank Water	7/24/03	0.2	
DOC	Filtered Blank Water	7/24/03	0.2	
DOC	Filtered Blank Water	7/24/03	0.1	
DOC	Filtered Blank Water	7/24/03	0.1	
DOC	Filtered Blank Water	7/24/03	0.2	
DOC	Filtered Blank Water	7/24/03	0.2	
DOC	Filtered Blank Water	7/24/03	0.2	
DOC	Filtered Blank Water	7/24/03	0.3	<b>Mean 0.2</b>
DOC	Filtered Blank Water	7/24/03	0.3	<b>Standard Deviation 0.067</b>
TOC	Unfiltered Matrix Water	7/24/03	1.4	
TOC	Unfiltered Matrix Water	7/24/03	1.4	
TOC	Unfiltered Matrix Water	7/24/03	1.5	
TOC	Unfiltered Matrix Water	7/24/03	1.5	
TOC	Unfiltered Matrix Water	7/24/03	1.5	
TOC	Unfiltered Matrix Water	7/24/03	1.5	
TOC	Unfiltered Matrix Water	7/24/03	1.5	
TOC	Unfiltered Matrix Water	7/24/03	1.5	
TOC	Unfiltered Matrix Water	7/24/03	1.4	<b>Mean 1.45</b>
TOC	Unfiltered Matrix Water	7/24/03	1.3	<b>Standard Deviation 0.071</b>
DOC	Filtered Matrix Water	7/24/03	1.3	
DOC	Filtered Matrix Water	7/24/03	1.4	
DOC	Filtered Matrix Water	7/24/03	1.4	
DOC	Filtered Matrix Water	7/24/03	1.5	
DOC	Filtered Matrix Water	7/24/03	1.5	
DOC	Filtered Matrix Water	7/24/03	1.5	
DOC	Filtered Matrix Water	7/24/03	1.5	
DOC	Filtered Matrix Water	7/24/03	1.4	
DOC	Filtered Matrix Water	7/24/03	1.8	<b>Mean 1.49</b>
DOC	Filtered Matrix Water	7/24/03	1.6	<b>Standard Deviation 0.137</b>

demonstrated that with an appropriate installation design, the autoanalyzer will operate satisfactorily under the conditions present at this field facility. One issue of the initial study plan that is still being developed is the telemetry component of having the Sievers analyzer data remotely accessible. It is planned to have the Sievers analyzer data collected by a datalogger that would feed the data to an on-line database like the California Data Exchange Center (CDEC). Work is progressing with this objective.

Another important aspect of this study was assessing and solving the field-related issues of how to install, operate, and maintain a field-dedicated instrument of this type. New sampling techniques and procedures were developed and refined to assure the quality of the sample collection process. Routine inspections and monitoring of the water delivery system were performed to detect problems or to initiate modifications to the system before problems developed.

Our understanding of the water delivery system and the review of grab sample data showed the importance of the filtration device in retaining organic matter dislodged from the water lines. If this extraneous matter had been allowed to enter the analyzer, it could have produced unrepresentative data or possibly have damaged the instrument. This issue resulted in design changes that will be incorporated into the water delivery system for the next phase of this study planned to start in early 2001.

The combined data collected for this study provided some unexpected information. When comparing data in the tables and graphs of the analyzer on-line results with the Bryte Chemical Laboratory grab sample results, the Sievers analyzer tended to produce values slightly higher than the corresponding Bryte Chemical Laboratory grab sample values. The difference in these values became more pronounced during the winter storm season when increased TOC levels and turbidities occur. After reviewing the data, the managers of the Bryte Chemical Laboratory concluded it was likely their analyzer was under reporting TOC in samples with turbidities over 100 NTU. Staff determined that the digestion method of analysis as employed by the lab might require some revision to provide better performance with samples of high turbidity. The limitations of the current analytical method in water with increased turbidity and matrix composition may have contributed to some of the differences between the Sievers and Bryte Chemical Laboratory data. Additional samples will be collected during the 2000/2001 storm season to evaluate the performance of the revised methodology.

While this study demonstrated the Sievers autoanalyzer's ability to perform satisfactorily with Sacramento River water, it is unknown how it will perform with water conditions at a different site. Other sites in the Delta under consideration for the installation of a TOC analyzer have water quality characteristics much different from those found at the Hood facility. Sites with severe water quality issues including high turbidity and suspended materials may be problematic for the Sievers analyzer. Because of this issue and other limitations of the Sievers unit, the MWQI staff investigated other types of TOC analyzers designed for field use. At the time the Sievers T-800 analyzer was purchased, it was determined to be the most applicable instrument on the market for our needs. In the

time since the Sievers unit was purchased, many developments in the technology of this field have occurred, and improved instrumentation might now be available.

After investigating new models of autoanalyzers and evaluating their respective operational components, a new model was selected for future use that has many new features not found on the Sievers T-800. The MWQI staff has chosen to field test a Shimadzu 4000 total combustion organic carbon autoanalyzer in conjunction with the Sievers analyzer. The total combustion method of analysis used by the Shimadzu is a more appropriate method for the TOC analysis of raw source water. The Shimadzu 4000 was chosen for the next phase of this study for its design, construction, and operational features that make it better suited for field operations. The Shimadzu unit can tolerate particle sizes up to 800.0  $\mu\text{m}$  without any configuration changes. It can be installed with two intake ports and can be configured to provide DOC analysis from one port and TOC analysis from the other. It can also be programmed to self-calibrate as well as store pre-programmed sampling scenarios which can be remotely initiated by computer command access.

A change in design for part of the Hood facility water delivery system is planned to limit the build-up of on-line sediments and algal growth and to accommodate the installation requirements of the Shimadzu analyzer. The fixed PVC water lines that currently connect the analyzer to the water delivery manifold will be replaced with Teflon lined tubing. The Teflon-lined tubing will be inserted into large PVC conduit to protect the tubing from light to minimize algal growth. If or when algal growth or sedimentation occurs in the tubing, the tubing can be disconnected, removed from the conduit and replaced with clean tubing.

The original concept of installing an organic carbon autoanalyzer in a field setting was conceived to monitor organic carbon in source waters for drinking water purposes. By installing an automated organic carbon analyzer at the Hood facility, the MWQI Program has demonstrated the potential for establishing TOC autoanalyzers at other critical water quality monitoring stations. The knowledge gained from the installation and daily operation of the Sievers autoanalyzer will provide valuable experience in testing new models of analyzers and equipping additional field stations with TOC autoanalyzers.

## **ACKNOWLEDGEMENTS**

This report was prepared by David Gonzalez and Chris Huitt of the MWQI Field Support Unit. David has been involved with this project from its beginning and supervised the implementation and operation of the project. Chris was responsible for the installation, operation and maintenance of the analyzer, sample collection, data collection, and other field activities required to complete this study.

The authors want to acknowledge our sincere appreciation to the many individuals and businesses who provided their valuable assistance and technological expertise in the development and execution of this study.

To Marvin Jung, private consultant to the Municipal Water Quality Investigations Program, we are especially grateful. He was instrumental in proposing the initial concept of this study and contributing much needed assistance in the early development and implementation of this project, and for his continued support throughout this study.

To the staff at Sievers Instruments who provided valuable input and guidance in the installation design and operation of the analyzer. They continue to provide the necessary support and materials that are critical to the successful operation of the analyzer.

To Bill Nickels and his staff at the Bryte Chemical Laboratory have who been extremely helpful in providing their expert services and assistance in designing and conducting the quality control evaluation components of the study and providing timely analysis of the samples.

A special thanks to Bruce Agee and Murage Ngatia of our Quality Assurance/Quality Control Program for the considerable work they did in developing and managing the database for this study.

Finally, to DWR's Environmental Services Office for providing access to the field facility for the installation and operation of the analyzer.

