

Real-time monitoring of organic carbon in the Sacramento River and California State Water Project Using Process Analyzers

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1. Introduction

Despite three decades of improvement, over 40% of rivers and streams in the United States still do not meet federal and state water quality standards. Impaired water bodies include over 20,000 individual river segments, lakes, and estuaries representing approximately 300,000 miles of rivers and shorelines and approximately 5 million acres of lakes (USEPA). Major pollution sources include sediments, excess nutrients, and pathogenic microorganisms. Section 303(d) of the 1972 Clean Water Act requires States to: 1) develop lists of water bodies that fail water quality standards, 2) determine priority rankings for waters on these lists and 3) develop total maximum daily loads (TMDLs) of pollutants for these water bodies. A TMDL stipulates the maximum amount of a pollutant that a water body can receive and still meet water quality standards, and allocates pollutant loadings among pollutant sources. While TMDLs have been required by the Clean Water Act since 1972, until recently few states have developed them. A major impediment to the development of TMDLs is the lack of high frequency, spatial distributed water quality data. Large spatial and temporal variations exist in pollution loads and surface water concentrations, particularly with respect to biologically labile compounds of C, N and P. This variability reduces the utility of routine grab-sample monitoring. In addition, water quality variability caused by rainfall patterns, catchment runoff responses and the timing and rates of agricultural and urban return waters makes it very difficult to accurately estimate pollutant loads with monthly to quarterly sampling.

Continuous monitoring of water quality at key points in a river or lake system could increase the accuracy of pollutant load calculations and aid the development of TMDL criteria for nitrate, total phosphorus and dissolved organic carbon (DOC).

However, due to the challenges of remote operation (biofouling of sensors, calibration stability etc.), continuous monitoring of water quality has been limited to relatively simple parameters such as temperature, pH, electrical conductance, and turbidity. Systems based on ion selective electrodes and colorimetric titration provide a limited means for measuring some nutrients and metals, but the detection limits for these methods are typically too high to be useful in making measurements in natural waters. While quantitative relationships can be developed between simple parameters and some pollutant loads (e.g., turbidity and sediment loads), in most situations it is difficult to accurately correlate biologically labile substances with water temperature, conductivity or pH, forcing resource managers to develop TMDLs on less frequent synoptic sampling of water bodies.

To overcome these data limitations, it would be ideal to bring the laboratory to the field and install laboratory grade water quality analyzers at remote locations and to telemeter the data back to a central database. Unfortunately laboratory instruments for example DOC analyzers, have limited ability to operate over long periods without direct human intervention (i.e., sample loading, calibration, maintenance etc.). The growing availability of semi-autonomous analyzers for industrial applications, however, has expanded the range of water quality parameters that can be monitored continuously. Process analyzers are now available to make continuous measurements of several drinking water contaminants including various anions and cations (via ion chromatography), total and dissolved organic carbon (via chemical and high temperature oxidation and spectral qualities) and disinfection byproducts such as bromate (by coupling liquid chromatography with an ICP-MS). For example, Volk et al. (2002), using

a portable TOC analyzer made daily measurements of TOC in raw and treated water at a drinking-water treatment facility over a 22 month period. The analyzer used in this study, a Sievers Model 800, provided real-time TOC data that plant operators could relate to precipitation and runoff events, and plant operating conditions. Overall the study demonstrated that TOC process analyzers were a robust and reliable method of monitoring TOC levels. Thus, expanded use of process analyzers in monitoring networks coupled with robust database systems could provide real-time access to high frequency water quality data. These data would be valuable for resource managers, utilities and researchers in the context of setting and monitoring pollutant TMDLs and for guiding treatment plant operations.

Organic C is the basic and essential precursor in the formation of potential cancer causing disinfection by-products (DBPs) in drinking water supplies. Oxidants, such as chlorine used in the disinfection of drinking water react with organic C to form trihalomethanes (THMs) and haloacetic acids (HAAs) and in the presence of bromide and free chlorine, organic C reacts to form brominated DBPs. (United States Environmental Protection Agency, 2001). Besides serving as a DBP precursor component, organic C increases the amount of chlorine and ozone needed to provide disinfection (CALFED Bay Delta Program, 2000). High organic C concentration can also increase the amount of coagulation, flocculation, and sedimentation required during water treatment, thereby raising costs. Water purveyors who use source waters with elevated levels of organic carbon may incur costs in the hundreds of million of dollars for plant upgrades to meet promulgated EPA criteria for DBPs in finished drinking water (Jung and Tran, 1999).

In this paper we describe a pilot program, conducted by the California Department of Water Resource's Municipal Water Quality Investigations Unit (DWR MWQI), to install and operate laboratory-grade TOC analyzers at key points in the Sacramento-San Joaquin Delta. To our knowledge this is the first use of these types of analyzers to make continuous measurements of TOC/DOC in natural waters in the United States and to publish them immediately to the Internet. The Sacramento-San Joaquin River system is the major source of water to the State of California, providing drinking water to two-thirds of Californians. Decades of agricultural use have lead to oxidation of peat soils and have caused rapid subsidence of Delta islands and tracts. Organic matter content in these soils is high and drain waters typically have TOC concentrations 30-50 mg L⁻¹ creating potential problems for users of Delta waters for urban supplies. Two different analyzers were formally tested in our pilot study and we present limited results from a third, optical system operated by DWR Operations and Maintenance: 1) Shimadzu model TOC-4100, 2) Sievers (Ionics) TOC 800 Series and 3) Tytronics FPA 1100 spectrophotometer. These analyzers represent the three most viable analytical methods for TOC determinations: 1) high temperature combustion, 2) chemical oxidation and 3) UV-254 absorbance, respectively. We will describe methodologies used in installing the analyzers, for providing a continuous sample stream (both unfiltered and filtered at 0.45 µm) and for telemetering data to a central database. We will present validation tests for the online measurements, including measurements of analytical precision and accuracy and tests of the water delivery system to demonstrate whether the online systems produced TOC and DOC data that is comparable to manual grab samples. A key component of the project was to assess the relative reliability of the different systems

over the three-year period of the study and these data will also be presented. Our overall objective is to demonstrate that specially designed, semi-autonomous analyzers are a viable means for forecasting water quality and for TMDL development.

2. Site Description

The Sacramento-San Joaquin Delta is the most critical junction for water in California. Two major rivers, the Sacramento and San Joaquin provide the majority of water inputs to the Delta from which two-thirds of Californians, approximately 22 million people, receive a portion of their drinking water. The Delta covers approximately 2300 km², and prior to 1850, was a vast freshwater-tidal estuary dominated by stands of great bulrush or tule (*Scirpus, lacustris*) and reeds (*Phragmites, communis*). By 1930, 1800 km² of the Delta estuary had been converted to agricultural use and only fragments of the native marsh still exist today. In the Sacramento-San Joaquin River Delta, high frequency dissolved and total organic carbon measurements (DOC and TOC) of surface waters are needed: 1) to compute daily to annual loads, 2) for forecasting source-water quality at municipal water-treatment plants, and 3) for research on C biogeochemistry in the Delta estuary. Understanding the sources, transformations and loads of organic carbon in this system is also critical to ongoing ecosystem restoration (CALFED Bay-Delta program) and for operation of the State Water Project. The TOC analyzers were installed at two existing water quality stations: at Hood Station (Hood) on the Sacramento River and at H.O. Banks Pumping Plant in the south Delta (Banks). The Sacramento River provides about 84% of the annual freshwater flow and real-time TOC/DOC monitoring at this location provides information on the majority of allochthonous inputs of OC. Banks Pumping Plant is the exit point for municipal source waters delivered to

Southern California and parts of Contra Costa County in the San Francisco Bay Area.

Real-time measurements of TOC/DOC concentrations and other water quality parameters at Banks provide critical information to water purveyors such as the Metropolitan Water District, helping guide water treatment operations.

3. Methods

3.1 Analyzer Systems

In selecting TOC analyzers for the pilot study we limited our choices to models designed specifically for semi-autonomous, remote operation. Laboratory analyzers are not designed to sample from a continuous sample stream and it would be difficult to modify them to do so. Process analyzers, on the other hand, have sample inlet systems specifically designed to sip from a moving stream of water. Furthermore, because of the high cost of operator time and travel, we chose systems that we believed could operate independently for up to two weeks and that had the capability to telemeter data via a datalogger back to a central computer database. Instrument price was limited to \$30,000 or less per analyzer, not including costs for the water delivery system, filtration and expendables such as reagents and dissolved gases.

The Shimadzu TOC 4100 is an on-line TOC analyzer using the established 680°C catalytic combustion and non-dispersive infrared detection method (NDIR detector; Table 1). The Shimadzu analyzers measured non-purgeable organic carbon (NPOC) after removal of inorganic carbon (IC) by acidification with 3N HCl and sparging with air (when supplied filtered water DOC is measured). Automatic calibration is incorporated using standard solutions stored on-board and was preformed daily (every three days over the past two years). The TOC 4100 has selectable analog output of 0-1VDC, 0-16mA or

4-20mA for interfacing with a datalogger. Contact closure inputs that can initiate or halt sample measurement and calibration start are also built in and allowed for limited remote control of the analyzer via a datalogger. Conditional alarms (high and low concentration limits) and event conditions (ready state, operating online, measuring, calibrating etc.) can also be recorded and telemetered providing data with which to judge measurement accuracy. A continuous supply of air was supplied to the TOC 4100 by a Domnick Hunter Nitrox Air Generator (Model No. UHPA301W 110v)

The Sievers model 800 TOC analyzer utilizes UV-persulfate along with patented membrane conductometric detection to measure DOC. The Sievers analyzer measures both total carbon (TC) and IC and computes TOC by difference; when supplied filtered water it measures DOC. Note: the Sievers TOC analyzer requires that samples be filtered to a porosity of 60 μm . To improve accuracy, inorganic carbon is reduced by vacuum degassing technique prior to IC measurement. Sample is introduced into the analyzer and first undergoes inorganic carbon measurement by acidification to pH 2 and transfer into the membrane conductometric detector. Next organic matter in unfiltered sample (TC) is chemically oxidized into CO_2 and ionic constituents in a sample reactor using UV light and persulfate. Oxidized sample is then passed into a transfer module where CO_2 diffuses across a semi-permeable membrane separating out interfering ions from CO_2 produced by oxidation. pH in the oxidized sample is adjusted so that CO_2 ionizes to HCO_3^- and H^+ which is then pumped into a conductivity cell. For both IC and TC, conductivity is proportional to concentration... Because of the stability of the conductivity detector instrument calibration is required only once per year. Data are stored on-board using PCMCIA cards when can be changed during field visits. In addition, the unit is connected

to a dot matrix printer to provide continuous printouts of the analytical results. The instrument also has analog outputs of 0-10V and 4-20 mA for interfacing with a datalogger.

The Tytronics FPA 1000 is an on-line spectrophotometer designed for process monitoring and control. UV Spectrophotometers relate sample absorbance at 254 nm to the concentration of DOC in the sample (note: only filtered water is supplied to the instrument hence the absorbance-concentration relationship can be developed only for DOC). This relationship must be periodically updated due to changes in lamp intensity and in the optical quality of DOC caused by changing sources. No reagents are added to the sample. Minimal maintenance is required because the flow through cell configuration provides a direct read measurement and does not require pumps or reagents. The analyzers have a single beam, dual wavelength optical configuration to correct for sample turbidity and light intensity changes. The system outputs are 0-5 VDC, 4-20 mA, RS 232 and Hi/Lo alarms which can all be recorded on a datalogger. Cross-calibration with laboratory instruments was accomplished using river samples and DOC values measured on an OI Analytical model 1010 TOC analyzer at least monthly (data not presented).

At the Banks station TOC and DOC were measured with Shimadzu and Tytronics analyzers; at Hood station, Shimadzu and Sievers analyzers were used to monitor DOC and TOC levels. The Shimadzu analyzers were installed in September 2001 and May 2002 at Banks and Hood respectively. While the Sievers and Tytronics instrument were installed earlier in 1999 and 2000, only data overlapping the period of September 2001 through September 2004 will be discussed in this report.

3.2 Water Systems

The Hood water quality station consists of a pier built over the river and a ~3 m x 3 m building situated at the end of the pier which houses all of the water quality instrumentation. Water is supplied to the TOC analyzers by a ½ HP submersible pump (Grundfos 16S05-5) and 1 inch ID Black, reinforced PVC hose (Ryan Herco PN 0514.110). Because the river elevation can change several meters over the course of the years, the hose is kept at a constant inlet depth of 1 meter using a hose reel and float system (Hannay Hose Reel, PN N818-25-26B). A constant depth is maintained by balancing the tension of the reel, the weight of the submersible pump and the buoyancy provided by a PVC-encased polyurethane float with a volume of approximately 0.25 m³. Water is lifted from 3 to 6 meters depending on river level. Flow rates range from 10 to 20 liters per minute depending on head. Through a series of Y-connectors and metering valves a by-pass stream is created for each of the TOC analyzers from which sample water can be sipped. When not sampling, all of the flow from the submersible pump is returned to the river via a drain (see <http://wetlands.ifas.ufl.edu/sickman/New%20system%20operational.JPG>) for photographs of the installation and plumbing). Per the manufacturer's recommendation we installed a Claris 60 µm nominal pore-size filter cartridge composed of melt-blown polypropylene fibers on the TOC stream to the Sievers analyzer to prevent sand entry.

The Banks water quality station is located in a 3.5 m x 3.5 m block building at the headgates of the California Aqueduct along the south side of the canal. Flow rates as high as 240 m³s⁻¹ can be produced by the 11 massive pumps as they lift water 75 meters from the Clifton Court Forebay below. The flow is extremely turbulent and precludes the use of a

float-system to maintain a constant sampling depth (earlier attempts to fashion such a system required high maintenance and were prone to failure and the design was abandoned). Instead we secured a dog-legged shaped metal bracket along the edge of the aqueduct to which we attached the inlet hose. The angle of the fitting was sufficient to place the inlet of the hose 1 meter away from the concrete side of the aqueduct and hold it at a depth of ca. 2 meters depending on flow in the aqueduct. Guy wires were attached to the bracket both upstream and downstream to help stabilize it and prevent motion that could weaken the metal. On shore a progressive cavity pump (Moyno PN 6230.352), with 316 stainless steel wetted components and nitrile stator (which was changed every 9 months), was used to lift water 2 to 3 meters into the instrument shelter located by the aqueduct. The lift pump required a heavy-walled tubing to prevent the collapse of the tubing due to the negative pressure of the lift action, therefore, 1 inch ID wire-reinforced PVC hose (Ryan Herco PN 0518-110) was used. Early on we attempted to use a Viton plastic stator but this material wore out in less than 4 months of continuous use. The water bypass system was very similar to the design of the system at the Hood station (see URL link above for photographs of the installation and plumbing).

3.3 Filtration System for DOC

The submersible pump at Hood is equipped with a coarse screen (10 mm) to prevent large detrital particles from damaging the pump; this water was used for TOC analyses. At Banks a coarse screen, 10 mm, was installed on a check-valve on the inlet line to prevent large particles from damaging the progressive cavity pump and this water was used for TOC analyses. For DOC samples a continuous stream of 0.45 μm water was required. Our first attempts focused on using a Collins model 9000 filtration system

equipped with two- 20 cm diameter filter heads and 0.45 μm Teflon filters. In this system magnetic coupled agitators run at 3000 RPM to provide turbulence for particle removal from the filter surface to prevent clogging. To further enhance the filter element cleaning process, a three-way solenoid valve operated by a cycle timer is used to alternately block the flow from the two filters. When flow is blocked, filter cleaning occurs because the differential pressure across the filter element is zero. Particles washed from the filter surface are removed from the Model 9000 in the bypass stream.

Owing to high turbidity and continuous operation, the Teflon filters typically clogged within 2 days lowering the effective filtration size to 0.1 -0.2 μm based on particle size scanning. Over-filtration led to a sharp decline in measured DOC levels that stabilized after about 2 days (Figure 1a). The result was a loss of DOC on the order of 20-50% depending on season due to removal of colloidal-sized DOC from the sample streams (Figure 1b). Approximately 70-80% of the TOC at Banks occurs in dissolved fractions less than 0.45 μm (Figure 1b). Of this DOC, about half is found in the size range of 0.1 to 0.45 μm and is likely composed of colloidal material. Recent work has shown that a significant fraction of riverine DOC is comprised of colloidal-size amino-sugars derived from lysed bacterial cell walls (Leenheer et al., 2000). These colloids have been identified in a variety of freshwater systems (Leenheer et al., 2004) and show gross similarities to colloidal organic matter isolated by ultrafiltration from the open ocean (Santschi et al., 1995). The ^{14}C content of these colloids are of modern abundance, consistent with them being residue of recent biological activity, and having a short lifetime in the water column (Leenheer et al., 2004).

In our next attempt, the Collins system was used as a 5 μm prefilter (stainless steel) to feed a 0.45 μm polysulfone pleated filter (Pall PN WFN0.45-10USM3314) installed in a polypropylene housing (US Filtration PN vp10-3/4-222). This system produce a consistent stream of 0.45 μm filtered water for DOC over at least a two week period even in the winter when turbidity exceeded 30-40 NTU. To save on costs, the stainless steel filters were cut using a custom-made die from large sheets of fabric, rather than purchasing pre-cut filters. In addition, the steel filters could be re-used several times after muffling at 500°C and acid rinsing or by using a sonicator cleaning bath. The polysulfone pleated filter was changed at least monthly or more often if we noted any signs of clogging such as reduced flow rate (currently filters are changed every two weeks).

3.4 Operation Procedures

Measurements can be made every ten minutes on the Shimadzu analyzers and every six minutes on the Sievers analyzer. The Tytronics analyzer continuously measures UV 254nm absorbance. Because the Shimadzu analyzers could not measure DOC and TOC simultaneously, we had them measure DOC during odd-numbered hours and TOC during even-numbered hours. For the Sievers analyzer a series of 5 readings were made every hour with the first two hourly readings discarded to allow for the internal sample delivery system to flush and to allow the conductivity detector to stabilize. Analyzer data were recorded on a Campbell CR10X datalogger and uploaded every two hours via phone modem to a centralized Access database in Sacramento. The Access database software screened the data for outliers and monitored the analyzers' performance. Screened data was sent by FTP to the California Data Exchange (CDEC), and then

uploaded to the CDEC website where it was available to the general public. Tytronics data were recorded as instantaneous readings every hour and uploaded to CDEC via an Access database every hour using a second Campbell datalogger system. All data were further screened by DWR personnel daily and outliers were removed from or flagged in the CDEC database.

3.5 Quality Control and Validation Procedures

Standard quality control/quality assurance methods were followed to validate the online analyzer systems. Precision is defined as the repeatability and reproducibility of multiple analysis of a homogeneous and well mixed sample. While the Shimadzu and Sievers analyzers made dozens of measurements per day, these were not truly replicate analyses since heterogeneity existed in the river or canal where the samples were withdrawn. Instead we used onsite replicated analyses of river or canal water collected using a 20 liter stainless steel bucket. This sample was subsampled into a 40 ml glass vial with a churn splitter (TOC) or filtered through a 0.45 μm membrane filter into a 40 ml glass vial (DOC). Triplicate analyses from these vials were performed on the Shimadzu and Sievers analyzers at both sites; measurements of precision began immediately after the analyzers were installed. Our target for analytical precision for TOC and DOC analyses was +/- 30% measured as relative standard deviation ($\text{RSD} = [\text{sample standard deviation} / \text{mean of replicate analyses}] \times 100$). No precision measurements were made for the Tytronics.

Accuracy is defined as the ability to produce results which are statistically the same as the true value. Accuracy was evaluated by the use of matrix spikes into deionized water and natural water samples (both filtered and unfiltered) and by inter

laboratory check samples. Spikes were made from National Institute of Standards and Technology (NIST)-traceable potassium hydrogen phthalate (KHP) using a high accuracy automatic pipettor and a volumetric flask. Deionized water, standards and ambient waters samples were spiked and measured onsite beginning in August 2003. Target values for this accuracy determination were 80-120% spike recovery.

An interlaboratory performance evaluation was also conducted during January 2003 and involved all of the DWR online analyzers, the oxidation and combustion analyzers at Bryte Laboratory (see below) and instruments housed at outside laboratories and universities. Standard reference materials (SRMs) were produced and certified by an outside quality control laboratory, Absolute Standards, a certified vendor in NIST's National Voluntary Lab Accreditation Program. The SRMs were prepared from KHP and caffeine and the upper and lower control limits were determined using EPA's guidance criteria; concentrations ranges from ca. 2-6 mg L⁻¹. The goal of this performance evaluation was to determine if the online analyzers could produce DOC measurements within the certified control limits.

Since the analyzers made measurements on sample streams pumped from the Sacramento River and California Aqueduct it was crucial that we insured that sample aliquots were representative of the bulk sample from which they were taken. The pumps, tubing and valves were constructed of inert plastics and metals, but it was still possible that small amounts of DOC could be lost or gained when water moved through the system due to microbial processes or by settling of larger particles in the case of TOC measurements. Beginning when the analyzers were installed we collected grab samples from the water delivery system at the following locations: 1) in the canal or river, 2) at

the inlet to the Collins Filter (TOC), 3) at the outlet to the Collins Filter (5 μm filtered), 4) at the TOC spigot (input point for unfiltered water delivery) and 5) at the DOC spigot (input point for 0.45 μm filtered water). All samples were collected into 40 ml glass vials and measured onsite with the process analyzers in triplicate. However, for the purpose of this report only data from the TOC and DOC spigots will be compared to the TOC and DOC samples collected from the canal and river. This comparison is the most informative since the spigot samples represent aliquots of natural samples that have passed through the entire water delivery system. If there is no difference between the DOC and TOC spigots samples and DOC and TOC grab samples from the river and aqueduct we can conclude that the water delivery systems produced aliquots that are representative of the bulk sample from which they were taken. The target value for representativeness was agreement between grab and online measurements of 80-120% on any day ($[\text{spigot value}/\text{canal or river value}] \times 100$) with no bias through time (i.e., no long periods where representativeness was consistently greater than or less than 100%).

Comparability determines whether analytical conditions are sufficiently uniform for each analytical run and between analytical runs to insure that all of the reported data will be consistent. In a laboratory setting, comparability would typically be measured by running standard reference materials or standards at the beginning and end of an analytical run and over several analytical runs. With our online instrumentation systems this was impractical since the analyzers were operated continuously and an operator only visited the sites every two weeks. We instead assessed comparability by comparing TOC and DOC levels in grab samples of the river or aqueduct measured both with the online analyzers and with a similar instrument at DWR's Bryte Laboratory in West Sacramento.

Filtration of DOC samples was done with a 142 mm filter holder and 0.45 μm cellulose acetate filters immediately after collection; the water that was filtered was drawn from a completely homogenized 20 liter samples of the river or aqueduct. TOC samples were drawn from a 20 liter churn splitter. Our method of subsampling the DOC and TOC samples insured that identical samples were measured on the laboratory and field instruments.

Assessment of comparability began immediately after the analyzers were installed. Comparability measures for the Shimadzu process analyzers were based on comparisons between onsite DOC/TOC results and DOC/TOC measurements made on a laboratory OI Model 1020 analyzer which utilizes an identical high temperature, catalyzed combustion/ NDIR detector methodology. For the Sievers analyzer we compared TOC measurements made onsite with laboratory assays made on an OI Model 1010 TOC analyzer which utilizes persulfate oxidation and NDIR detection. Despite the fact that the Sievers and OI analyzers utilize somewhat different methods for oxidizing organic matter (UV-persulfate vs high temperature-persulfate) and CO_2 detection (membrane conductometric detection vs NDIR) we feel that comparing these two instruments is more valid than comparing the Sievers to the laboratory Shimadzu. Comparability was computed relative to laboratory readings: $(\text{online analyzer value} / \text{laboratory analyzer value}) \times 100$.

Completeness is typically a measure of the percentage of data which is valid data, i.e., data obtained that meet all quality control criteria. There are currently no legal compliance uses for the DOC/TOC data for raw Delta waters and there is no fraction of the planned data that had to be collected in order to fulfill statistical criteria. For the

purposes of the feasibility study we have established the following goals for data completeness: (1) data capture of at least 50% during any one month and (2) data capture of at least 75% during any yearly period. For any day, 100% data capture was reached if three replicate measurements were made; this number of samples would be adequate to compute a mean daily load when combined with daily discharge (i.e., a TMDL). For each water year (2002, 2003 and 2004) we tallied the number of system breakdowns, their average length and an overall percent data capture.

4. Results and Discussion

4.1. Quality Assurance and Quality Control

4.1.1 Accuracy

Based on spike recoveries the Shimadzu and Sievers TOC analyzers generally produced accuracy within our target zone of 80-120% during 2003 and 2004 based on spike-recovery (Figures 2 and 3; note: accuracy by spike recovery was not assessed prior to August 2003). For the Shimadzu analyzers at Hood and Banks, accuracy was typically between 90-110% for spiked ambient samples and a little wider range was observed for spiked DI water. Overall accuracy for the Shimadzu analyzers at Hood and Banks was 103% and 102% respectively. Most of the out-of-range recoveries occurred with spiked DI water; these samples had typically lower concentrations ($3\text{-}5\text{ mg L}^{-1}$) which increased measurement variability. Paired t-tests indicate no significant differences in spike recovery between DI water and ambient waters demonstrating that there were no matrix effects in either the river or the aqueduct waters. At Hood, accuracy for the Sievers analyzer (mean 105%) always fell within the target zone, although nearly all values were greater than 100% indicating a slight bias towards over-recovery of spike (Figure 3).

However since there was no statistically significant differences (paired t-test) between spike recovery in DI water and ambient waters we conclude this over-recovery was not due to matrix effects.

The January 2003 interlaboratory comparison study was conducted by the Quality Control/Quality Assurance group within the MWQI unit. A total of eight separate analyzers were included in the study including all three of the process analyzers and the two TOC analyzers housed at Bryte Laboratory. Three SRM materials were created, each with a different mixture of dissolved carbon forms and concentrations. A $\sim 2 \text{ mg L}^{-1}$ KHP standard, acidified to pH 2.0 with phosphoric acid was the least difficult of the four SRMs to analyze since it contained an easily oxidized organic substrate and all inorganic carbon was removed by acidification. The second SRM was identical except that 65.1 mg L^{-1} of NaHCO_3 was added to test the ability of the analyzers to remove or compensate for inorganic carbon in the samples. Caffeine (ca. 6 mg L^{-1} and acidified to pH 2.0) was used in the remaining SRM and provided a more rigorous test of the oxidation/combustion ability of the analyzers.

The Shimadzu analyzer at Banks hit all SRM targets as did the Sievers analyzer for the KHP SRMs (Table 2). However, the Hood analyzers missed the SRM target range for all three SRMs, producing results that were about 1 mg L^{-1} too high in the case of the KHP SRM (Table 2). In contrast, the Sievers analyzer appeared to have trouble oxidizing the caffeine SRM, yielding measurements that were a slightly below the lower certified limit. Previous studies have shown that the persulfate oxidation method typically produces less than 100% recovery of difficult to oxidize compounds such as caffeine and dodecylbenzene sulfonic acid (Aiken et al. 2002). All three analyzers did very well in

removing or compensating for high inorganic carbon levels in the KHP+NaHCO₃ SRM with no bias detected.

The poor performance of the Hood Shimadzu is largely explained by the calibration method employed on the analyzer during January 2003 and high instrument background. The instrument was set up with a 2-point calibration using a 10 mg L⁻¹ standard and deionized water as a zero standard. To compensate for DOC background in the deionized water used for the calibration standards, Shimadzu TOC analyzers can shift the calibration curve obtained in a 2-point calibration downward to insure that the curve passes through the origin (Burns et al. 2005). This feature is useful when the TOC level in the deionized water used for the calibration is appreciable; ignoring high TOC levels in deionized water would yield sample concentrations that would be biased low. In actual use, however, this feature can produce measurements that are biased high when the instrument background is high, as when an exhausted CO₂ scrubber or air leak causes elevated peak area counts. In the shift-to-origin feature, the entire calibration curve is shifted downwards by the area count of the zero standard, however, since the correction is applied only to the calibration standards and not the samples, any additional blank introduced by instrument background will be added to the true concentration of the sample.

Since the process analyzers are operated continuously, it can be difficult to maintain a low instrument background. Ideally CO₂-free air would be supplied to the analyzer from a compressed air cylinder, however, since the analyzers are operated continuously in remote locations, an onsite air generator was the only practical method of air supply. Thus, the air supply contained CO₂ that had to be removed using soda lime

scrubbers. Under perfect conditions, i.e., new CO₂ scrubbers, new slider valve, new catalyst and halogen scrubber, Type-1 deionized water will produce an area count of approximately 500-1000. For comparison a 10 mg L⁻¹ standard produces an area of 20,000-35,000 counts. An area count of 1000 is typically small in relationship to a sample area count, however at Hood we routinely encounter DOC levels near 1 mg L⁻¹ which produce area counts ca. 5000. As the expendable components wear out, area counts for deionized water slowly climb to the range of 1000-1500, thus much of the blank being corrected for in the shift-to-origin feature is caused by instrument background and not organic carbon in the deionized water. When deionized water area counts climb above 2000, the high bias of samples starts to become appreciable. During routine operation, counts as high as 3000-7000 have been measured for deionized water and are an indication that a scrubber needs to be replaced or there is an air leak into the system. Under these conditions the high-bias becomes more severe and can result in overestimates of DOC concentration by a factor of 2. This is what occurred during the January 2003 performance evaluation at Hood.

Perhaps the major shortcoming of the process analyzers is their relatively simplistic calibration procedures. In contrast to laboratory analyzers where multi-level calibrations are routinely employed, process analyzers like the Shimadzu and Sievers analyzers are not capable of running calibrations with more than 2 standards. With the Shimadzu 4100 the decision of whether to use the shift-to-zero calibration correction is a trade-off and comes down to what type of error one wants to avoid, i.e., high or low bias. Given high purity deionized water with low TOC levels, our experience suggests that leaving the shift-to-zero feature off will produce excellent results for TOC values greater

than about 2 mg L⁻¹; at lower concentrations background contamination of the deionized water used for calibration can lead to mild to moderate low bias. With the shift-to-zero feature on operators must be vigilant to large increases in the zero standard area and should replace consumables and check seals at the earliest hint of upward drift in area counts, otherwise readings may become biased high.

4.1.2 Precision

A target precision level of 30%, measured as relative standard deviation (SD/mean), was established for both the Shimadzu and Sievers analyzers. With only two exceptions, this target level was met (Figures 4 and 5). The Sievers had significantly better precision ($p < 0.0001$; mean = 1.9%) than either of the Shimadzu analyzers. Similarly, the Shimadzu at Banks (mean 3.9%) had significantly better precision ($p < 0.001$) than the Hood Shimadzu (mean 8.8%); this finding is most likely due to the lower TOC/DOC levels at Hood compared to Banks. For the Shimadzu analyzers there was no significant difference between precision of TOC or DOC. Precision levels for all three analyzers remained steady during the three year study.

4.1.3 Representativeness

While our target levels for representativeness (80-120%) were generally met, several biases were noted for all three analyzers and indicate that the water delivery systems did not always supply water that was representative of the bulk sample from which it was taken (Figures 6 and 7). Biases were generally restricted to DOC sample streams for the Shimadzu analyzers and the TOC sample stream to the Sievers analyzer.

At Hood, the Shimadzu TOC sample stream had a mean agreement with grab samples of the river of 99.9% and paired t-tests ($p = 0.232$) showed there was no bias

through time. The TOC sample stream at Banks was also unbiased relative to aqueduct grab samples (mean agreement = 99.0%, $p=0.781$). In contrast the DOC sample streams at Hood and Banks showed significant low-bias. At Hood mean percent agreement was 87% between April 2003 and October 2004 and a paired t-test demonstrated a significant difference between spigot and river DOC levels ($p<0.0001$). The low-bias at Hood indicates that the DOC sample stream was possibly over-filtered resulting in the loss of colloidal DOC in size range of 0.2 to 0.45 μm . At Banks, bias between DOC in the sample stream and aqueduct grab samples was only detected from October 19, 2001 through January 29, 2002 (mean agreement = 72%) and was caused by clogging of the 0.45 μm Teflon filters installed in the Collins filter. This problem was largely corrected by using a combination of the 5 μm stainless steel filter in the Collins along with the 0.45 μm Pall cartridge filter. Mean percent agreement was 91.6% for DOC samples at Banks after January 2002. Overall, these results demonstrate the difficulty in supplying a stable stream of 0.45 μm filtered water to the TOC analyzers. Filter clogging is a constant problem and the degree of bias introduced by reduction in effective pore-size is likely to be most severe where ambient waters have substantial DOC in the 0.2 to 0.45 μm size range (colloidal). The fact that the bias at Hood was more severe than at Banks is most likely explained by difference in size distribution of DOC rather than how the filtration systems were operated; filter changes at both stations were done monthly or more frequently if reduced sample flow was observed).

Mean agreement between TOC measured in the Sievers sample stream and river grab samples was 89% and the differences in the measurements was significantly different ($p<0.0001$). There are two possible reasons for this bias. First, particulate

organic carbon (POC) may have settled out of the sample stream as river water was pumped to the analyzer. However, given that there was no bias in the TOC sample stream to the co-located Shimadzu analyzer, settling of POC is unlikely to be the cause of measurement bias. Instead, the sand filter used at the inlet of the Sievers analyzer probably became clogged with time and removed coarse POC or it could have harbored microbes that removed DOC from the stream (less likely). The sand filter was not changed as frequently at the Millipore filter (typically every 1-2 months) so more frequent replacement might help, however some filtration of POC would likely still occur resulting in a low-bias for the TOC stream.

4.1.4 Comparability

Of the four QA/QC procedures utilized in the feasibility study, comparability data between field and laboratory analyses are the most difficult to interpret. Differences in TOC/DOC values can be caused by errors in either the field or laboratory analyses and given the fact that the field analyzers are the equivalent of laboratory instruments it is not clear that laboratory results are anymore reliable than the field measurements. Therefore, in interpreting the comparability results we assumed that the data came from five equally-reliable laboratory instruments in a semi round-robin fashion (i.e., laboratory OI 1010 (oxidation), laboratory OI 1020 (combustion), Hood Shimadzu 4100, Hood Sievers, and Banks Shimadzu 4100). For example if TOC measured by laboratory combustion was lower than TOC measured with the two Shimadzu and the Sievers analyzers, we concluded that the laboratory measurements were inaccurate. In contrast, if the Hood TOC measurements (Shimadzu and Sievers) agreed with laboratory measurements, but Banks data did not, then we assumed that the Banks data were inaccurate.

In the comparability analysis we utilized comparisons between river grab samples which were split into subsamples (TOC and filtered DOC) and measured on both the online analyzers and the laboratory instruments at Bryte Laboratory. Duplicate measurements were made on additional samples collected from the water delivery systems as part of our tests for representativeness, but since these samples might have been influenced by the water delivery system they are less useful for comparability studies and were not included in the analysis.

From September 2001 until May 2002 agreement between TOC/DOC measurements on the laboratory and the Banks Shimadzu ranged from good to poor (Figure 8). For the early part of this period agreement was within our target range of 80-120%, however between January and May 2002, field measurements were between 40-80% of laboratory values. We suspect that the laboratory readings were too high because duplicate samples collected at Banks and measured on another Shimadzu 5050 analyzer by the Metropolitan Water District of Southern California (MWD) agreed very well with Banks Shimadzu values (Figure 9). From May 2002 through July 2003 agreement between the Banks and Bryte Shimadzu TOC/DOC measurements were generally between 80-120%, although several instances of high Banks values were noted between June 2002 and October 2002. Since no similar high bias was observed at Hood during this period we conclude that the values at Banks were too high. For most of 2002 and 2003 agreement between the Hood Shimadzu and Bryte laboratory fell between 80-120% although there was a slight low-bias to the Hood data (Figure 8).

Between July 2003 and June 2004, no comparability measures were made between the field and laboratory Shimadzu analyzers. From July 2004 through September

2004 both field analyzers produced values that were only 40-85% of laboratory measurements, thus it is possible that Bryte measurements were biased high during this period and that the field analyzers produced more accurate readings (Figure 9). However, when comparing Sievers data to values obtained by laboratory oxidation method, a high-bias was observed for the Sievers analyzer (Figure 9). Since we do not have any independent measurements of Sacramento River TOC/DOC for late 2004, it is somewhat hard to conclude why there was a lack of agreement among the five independent instruments, however, concentrations in both the Sacramento River and California Aqueduct were low ($1.5 - 4 \text{ mg L}^{-1}$) and absolute differences between laboratory and field readings were typically less than 1 mg L^{-1} (see Figure 9, triangles).

Our overall conclusion from comparing the laboratory and field instruments is 1:1 comparisons are of limited value since all of the analyzers had the capability to produce high quality measurements. Large absolute differences in TOC/DOC values were rare and occurred most frequently when errors could be identified in laboratory measurements. In general, the comparability data were of less value than measurements of accuracy, precision and representativeness due to their ambiguity. We believe that similar ambiguity would exist even when comparing among laboratories. Most round-robin style programs involve several dozen labs and “true” values for the reference samples are derived from the average of multiple measurements done on multiple systems.

4.2 Completeness of Online Measurements

Excluding the period immediately after the analyzers were installed, breakdowns were uncommon and could generally be resolved in a few days. Overall, water system

problems caused more lost data than problems with the analyzers themselves. For example, at Banks the water intake support broke at least once per year and the stator inside the progressive cavity pump wore out every 6-12 months. At both stations periodic power outages resulted in downtime and on occasion, water levels in the aqueduct fell below the inlet of the water system.

At Hood station the analyzer/water delivery system was down from 2 to 11 times per year with average breakdowns of 2-3 days (Table 3). Overall data capture for the Hood Shimadzu was 92-98% with slightly higher data capture for TOC vs. DOC. Except for water year 2002, the Sievers analyzer was about as reliable as the Shimadzu, with similar numbers of breakdowns and data capture of 97-98%. During water year 2002, the Sievers analyzer was down for several extended periods due to problems with instrument calibration, long waits for spare parts and breakdowns in the water delivery system. In addition, new construction on the building and time down for pump replacements also contributed to loss of data.

Water system problems along with delays in receiving replacement parts (NDIR detector) were the main reasons for extended downtime for the Banks Shimadzu analyzer (Table 4). For all of water year 2002 data capture was 80-83% with more than two dozen breakdowns of an average of 5-6 days. During water years 2003 and 2004 total breakdowns ranged from 5-14 incidences and average downtime was 1.4 to 2 days; data capture for these years ranged from 93-98% for both TOC and DOC. The Tytronics sensor experienced extended downtime in water year 2002 due to lamp failures and faulty replacement lamps. For water year 2002 total downtime was 118 days for a data capture efficiency of only 47%. In subsequent years lamp reliability was better and data capture

improved. During water years 2003 and 2004 breakdowns ranged from 4-8 per year, with an average downtime of 4.6 to 7.3 days; data capture for these years was 83% in 2003 and 92% in 2004.

4.3 Time Series Data

At both Hood and Banks there was good agreement in TOC/DOC patterns among the different analyzers (Figures 10 and 11). In the Sacramento River an annual pattern of high winter values (5-8 mg L⁻¹) and lower concentrations in the spring through autumn (~2 mg L⁻¹) was observed. As expected DOC concentrations at Hood were about 80% of TOC levels and generally exhibited less variability on hourly to daily time steps. Mean daily TOC/DOC concentrations captured most of the long-term concentration patterns, but missed transient events wherein concentration changed by several mg L⁻¹ (e.g., Hood TOC during April and May 2002). During 2004 all data from the Sievers analyzer were erroneously transferred to CDEC which explains the relatively large excursions in instantaneous TOC concentrations relative to mean daily values (Figure 10).

At Banks a similar, although less pronounced annual pattern of TOC/DOC and UVA absorbance was observed (Figures 11 and 12). Winter TOC/DOC at 6 to 10 mg L⁻¹ and reached minimum levels of 2-3 mg L⁻¹ during the late summer and early autumn. UVA absorbance peaks coincided with organic carbon maxima and were typically in the range of 0.02 to 0.025 cm⁻¹. Peaks in specific UVA (SUVA) absorbance typically occurred in winter, but the pattern was more muted (Figure 12). Typical SUVA values ranged from 0.02 to 0.05 cm⁻¹/mg L⁻¹ with the exception of water year 2004. During 2004 SUVA values increased sharply beginning in April 2004 and reached a peak of 0.1 cm⁻¹/mg L⁻¹ in mid June 2004.

4.4 High Frequency Events

One of the major advantages of real-time measurements is the ability to observe high frequency events that would normally be missed with less frequent synoptic sampling. Capturing these events will improve loading calculations and aid understanding of processes that control TOC concentrations in surface waters. As an illustration we have highlighted three such events in the Sacramento River and California Aqueduct that were identified in water year 2002 (Figure 13). Rainfall during February 2002 resulted in TOC spikes at Hood which were proportional to the rate of rainfall accumulation (Figure 13 a&c). These data suggest that runoff processes taking place in the upper Sacramento River basin exert substantial control on TOC loads in the river. During the spring and summer a diurnal pattern was detected at Hood which might be related to daily tidal cycles, upstream variations in wastewater inputs from Sacramento or photolytic degradation of TOC in the river channel (Figure 13d). Transient spikes in TOC were commonly observed at the Banks during winter months. Wind mixing in the shallow Clifton Court Forebay rapidly increased water turbidity in the California Aqueduct resulting in higher TOC concentrations (Figure 13 b&e). Making the connection between meteorology and water quality in the Aqueduct would be nearly impossible without real-time data.

4.5 Monthly Loads and VWM TOC: Daily vs Monthly Chemistry

In order to demonstrate the impact of real-time TOC monitoring on loading calculations and estimates of volume-weighted mean chemistry we compute these parameters during water year 2002 at both Banks and Hood based on: 1) high frequency chemistry and 2) monthly chemistry (Figure 14). TOC loads and concentration computed

with monthly grab samples differed by as much as 50% from estimates computed with TOC from the online Shimadzu analyzer. Differences in mean monthly chemistry differed by 1-2 mg L⁻¹. The high-frequency data proved most valuable during winter months with rapidly changing TOC concentrations and river discharge. Use of high frequency data not only produces more accurate loading and mean concentration data, the confidence limits around these estimates will be much smaller given that there is less sampling error when loads and concentrations are computed with real-time data.

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Table 1. Summary of TOC analyzer systems use in the pilot study. NPOC = non-purgeable organic carbon, TC = total carbon, IC = inorganic carbon.

	Shimadzu model 4100 (Banks and Hood Stations)	Sievers model 800 (Banks Station)	Tytronics model FPA 1000 (Banks Station)
Measurement Type	NPOC (IC removal by acidification and sparging)	TOC (TOC measured as the difference between TC and IC)	Absorbance at 254 nm with turbidity correction (DOC computed from regression between UVA 254 and laboratory DOC measurements)
Measurement Principle	Catalytically aided combustion with NDIR detection	UV/persulfate oxidation with membrane- conductivity detection	Single beam dual wavelength spectrophotometer
Range	0 - 1000 mg L ⁻¹	0.05 – 50,000 µg L ⁻¹	0 – 100 mg L ⁻¹
System Price	\$30,000	\$25,000	\$15,000

Table 2. Performance of the online analyzers during the January 2003 inter-laboratory comparison study. Average reading is the mean concentration from 3-5 replicate measurements of the SRM. Low and upper limits denote the control limits of the SRM material. Concentration units are mg L⁻¹.

Site	Analyzer	Method	SRM Code	Average Reading	Lower Limit	Upper Limit
Hood	Shimadzu	Combustion	1	3.3	1.7	2.4
Hood	Shimadzu	Combustion	2	3.4	1.7	2.5
Hood	Shimadzu	Combustion	3	6.8	5.5	6.8
Hood	Sievers	Oxidation	1	2.1	1.7	2.4
Hood	Sievers	Oxidation	2	2.1	1.7	2.5
Hood	Sievers	Oxidation	3	5.4	5.5	6.8
Banks	Shimadzu	Combustion	1	2.0	1.7	2.4
Banks	Shimadzu	Combustion	2	2.1	1.7	2.5
Banks	Shimadzu	Combustion	3	5.8	5.5	6.8
SRM Codes						
1 KHP with phosphoric acid						
2 KHP with 65.1 mg/L sodium bicarbonate--no acid						
3 Caffeine with phosphoric acid						

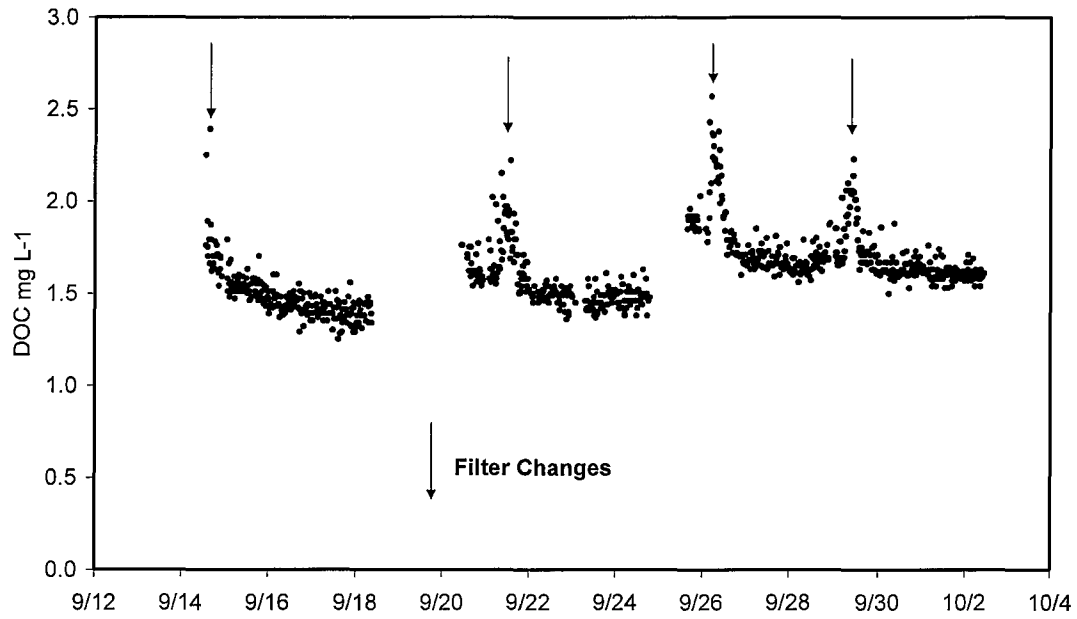
Table 3. Completeness of online analytical systems at Hood Station. Total breakdowns are the number of individual malfunctions of the analyzers of the water delivery system. Missed days are the total number of days where the number of measurements was less than three. Average downtime is the ratio total missed days to the total of breakdowns (days). Percent data capture is the number of days within the water year with 3 or more measurements divided the number of days in the year. Data for Hood TOC WY 2002 and Hood DOC WY 2003 were for a partial water year.

Site	Total Breakdowns	Total Days Missed	Average Downtime	Data Capture
Hood DOC				
WY 2002	Na	Na	NA	Na
WY 2003	7	17	2.4	92%
WY 2004	11	25	2.3	93%
Hood TOC				
WY 2002	2	4	2.0	98%
WY 2003	7	18	2.6	95%
WY 2004	8	15	1.9	96%
Sievers TOC				
WY 2002	14	107	7.6	71%
WY 2003	4	10	2.5	97%
WY 2004	6	9	1.5	98%

Table 4. Completeness of online analytical systems at Banks Station. Total breakdowns are the number of individual malfunctions of the analyzers of the water delivery system. Missed days are the total number of days where the number of measurements was less than three. Average downtime is the ratio total missed days to the total of breakdowns (days). Percent data capture is the number of days within the water year with 3 or more measurements divided the number of days in the year..

Site	Total Breakdowns	Total Days Missed	Average Downtime	Data Capture
Banks DOC				
WY 2002	14	74	5.3	80%
WY 2003	15	24	1.6	93%
WY 2004	6	12	2.0	97%
Banks TOC				
WY 2002	11	63	5.7	83%
WY 2003	14	20	1.4	95%
WY 2004	5	9	1.8	98%
Tytronics DOC				
WY 2002	8	118	14.8	47%
WY 2003	8	37	4.6	83%
WY 2004	4	29	7.3	92%

Banks Pumping Plant: 2001
Clogging of 0.45 μ m Collins Filters



Effect of Filtration Size on Organic Carbon
Banks PP December 11, 2001

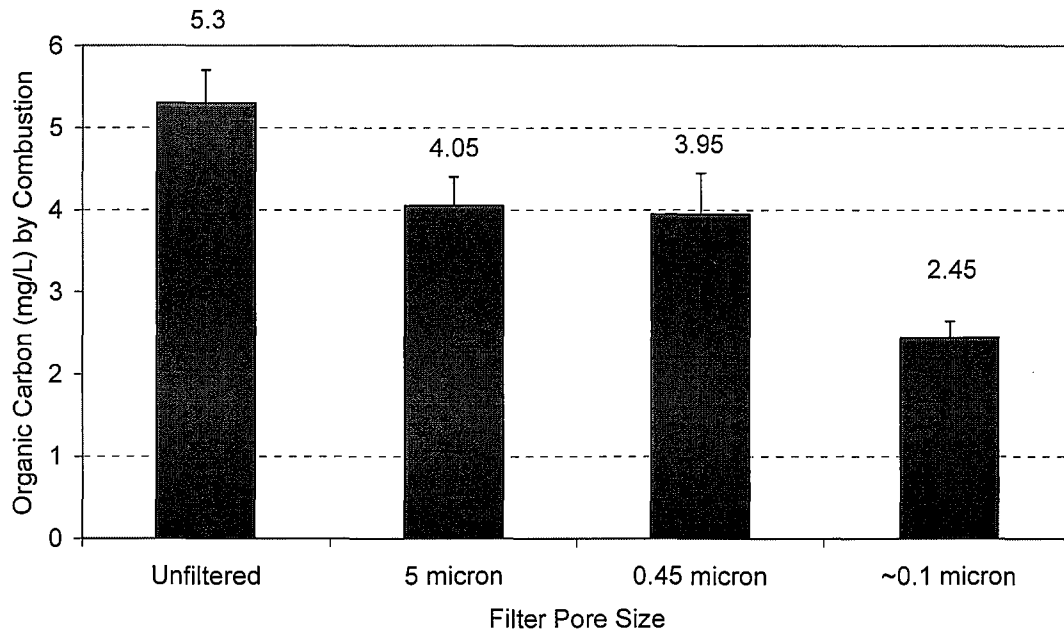


Figure 1

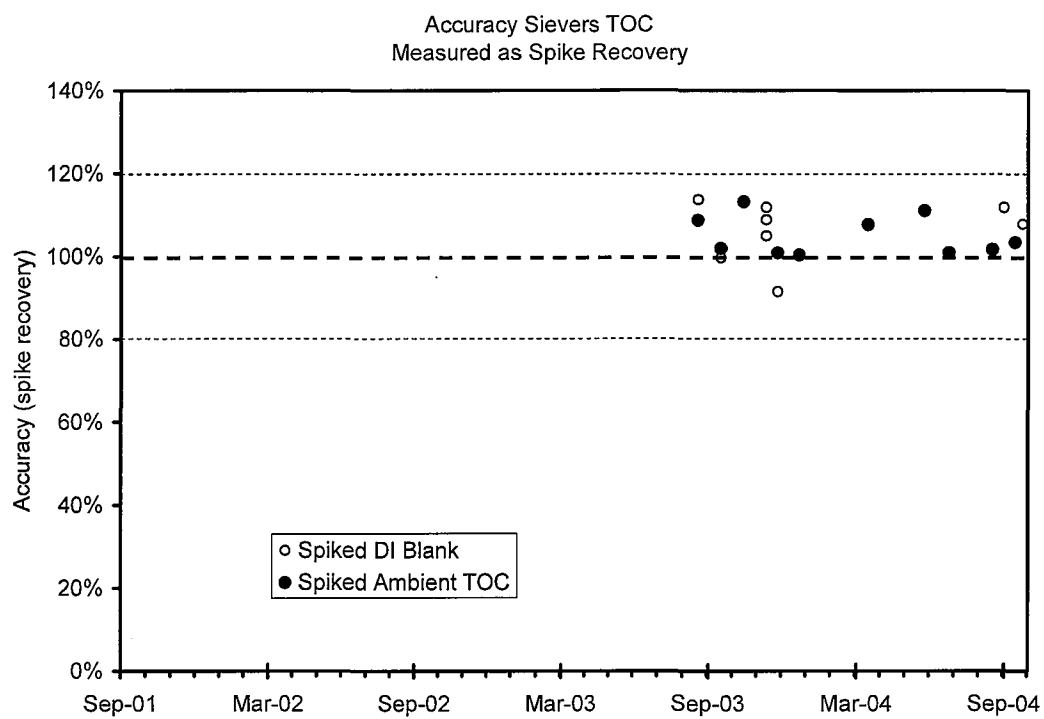
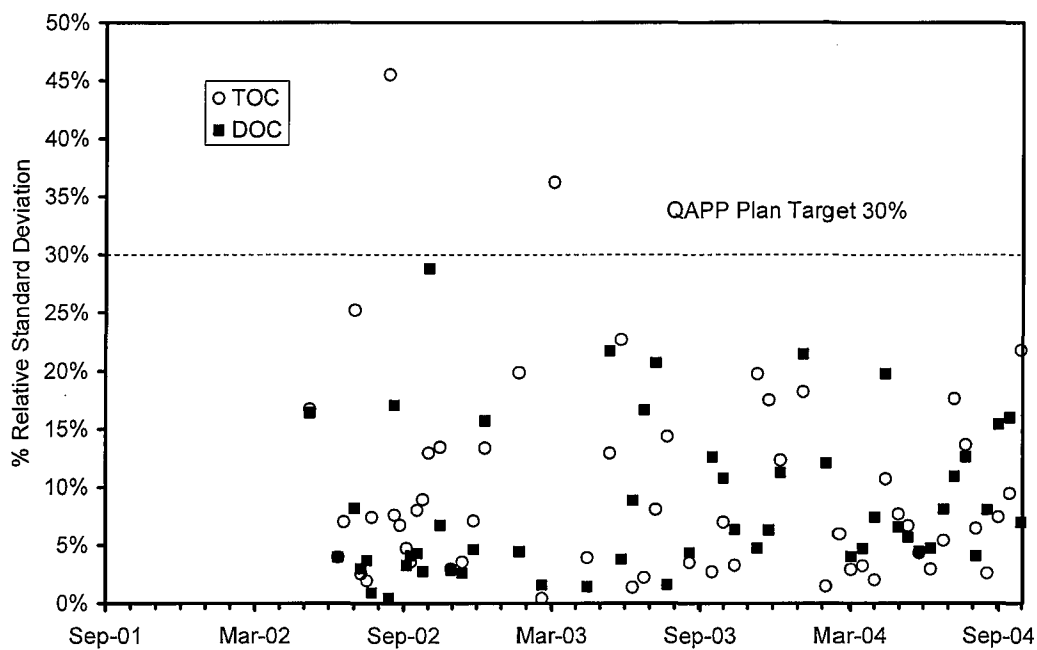


Figure 3

Hood Shimadzu Precision (TOC and DOC River)



Banks Shimadzu Precision (TOC and DOC River)

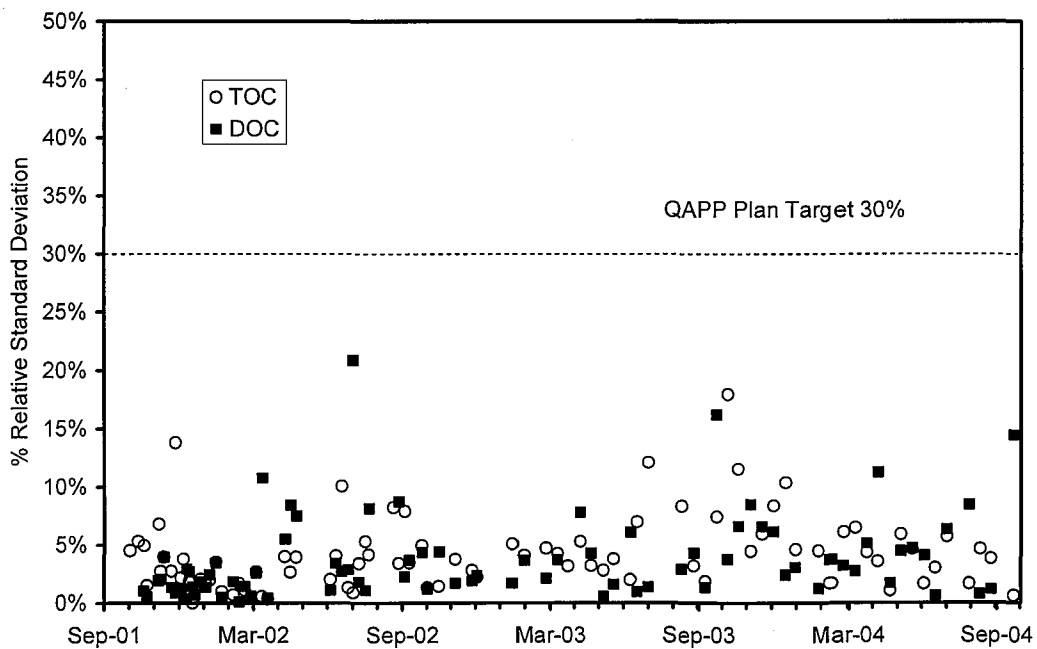


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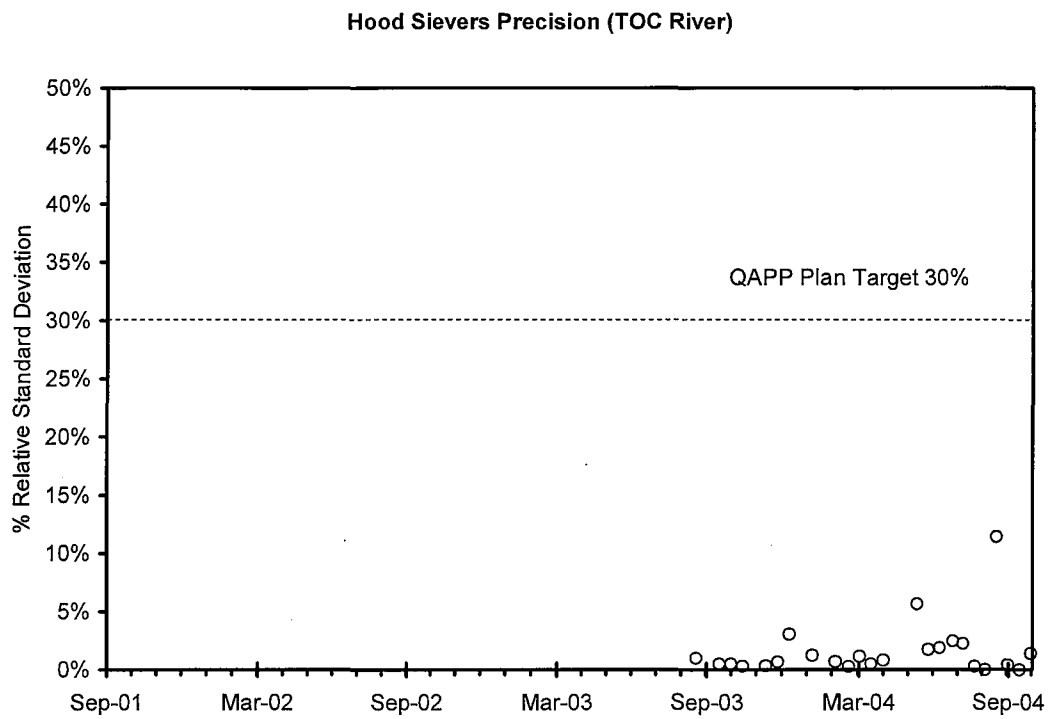


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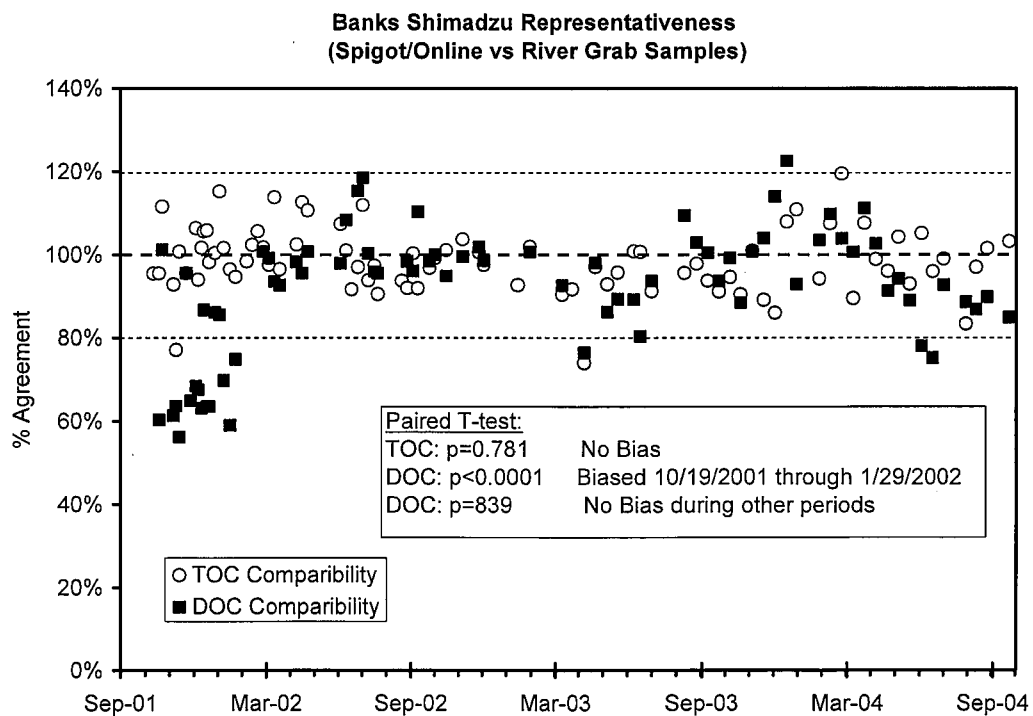
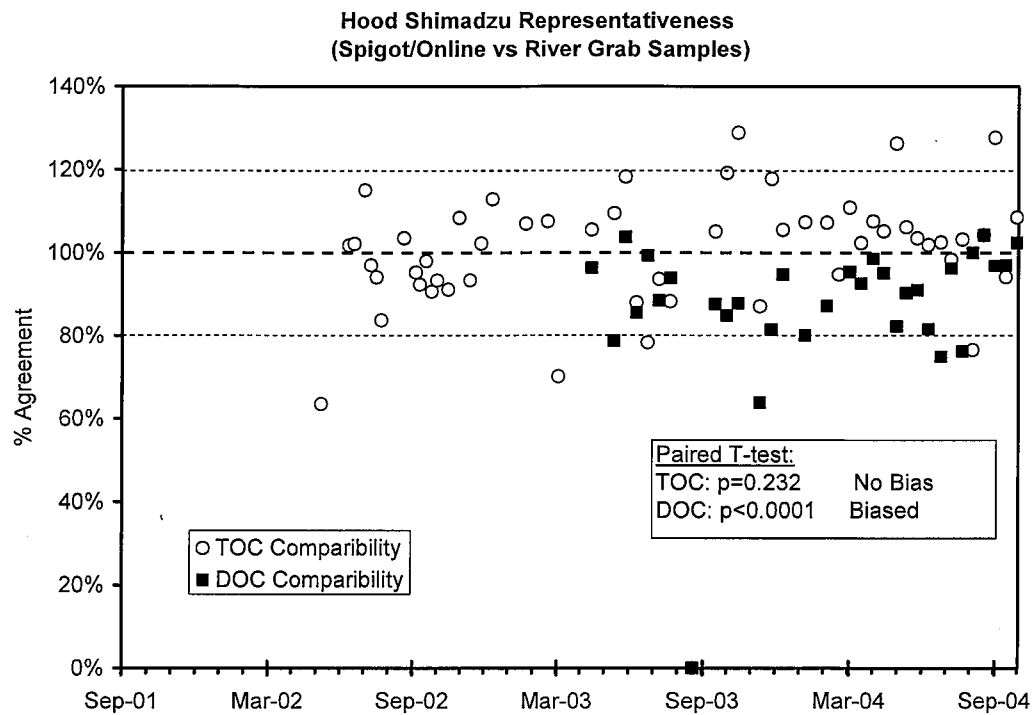


Figure 6

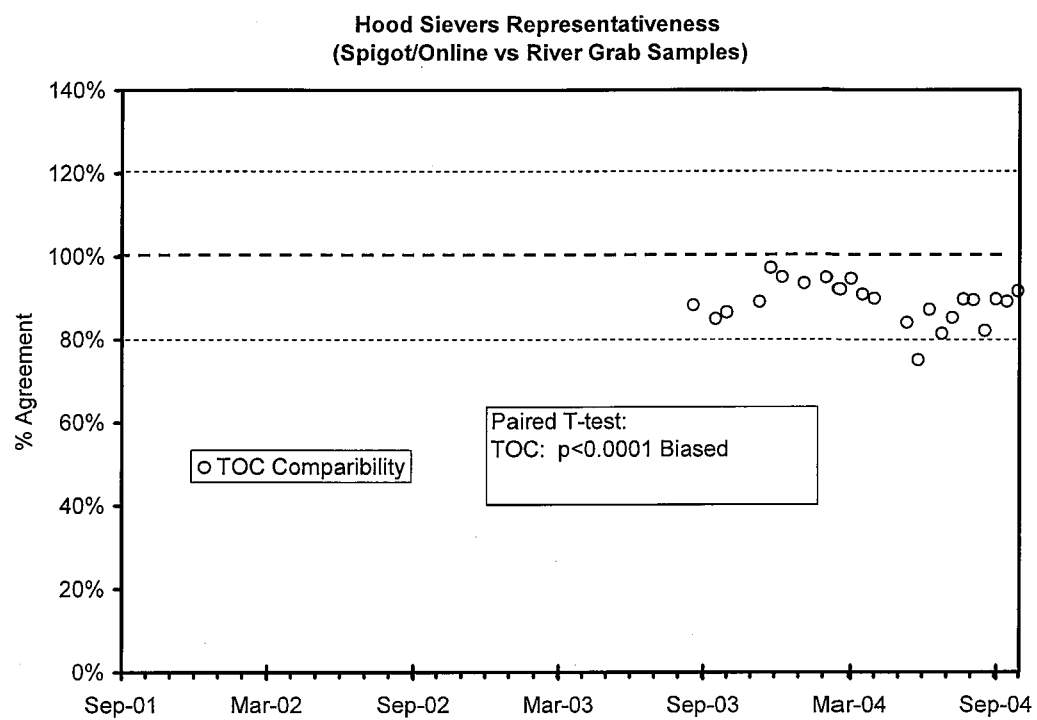


Figure 7

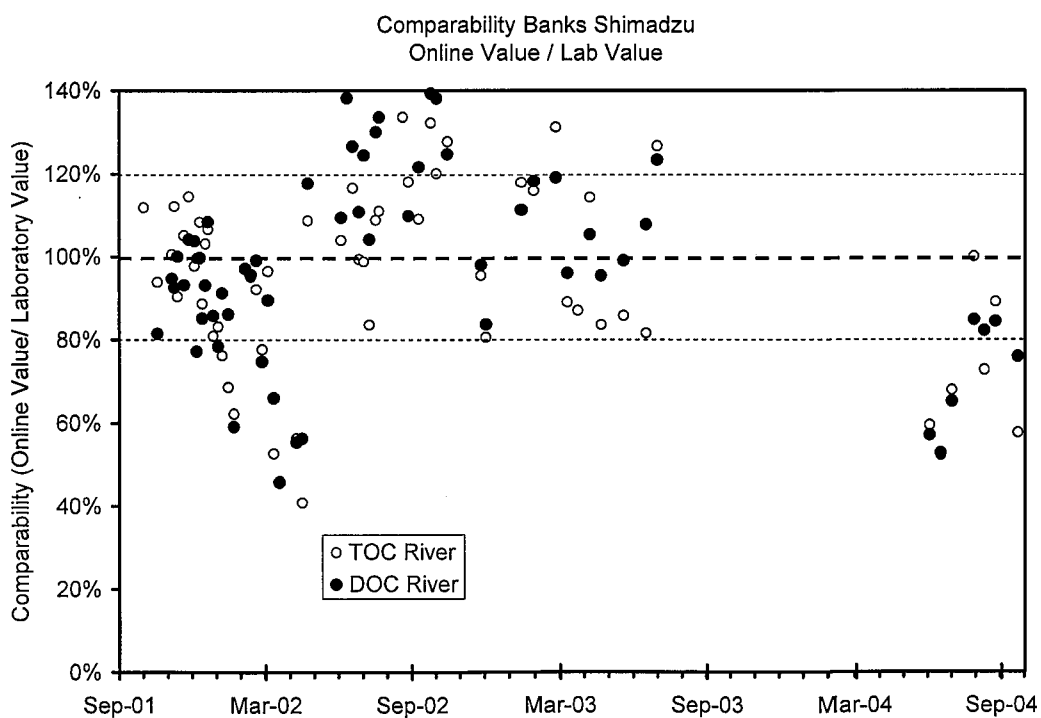
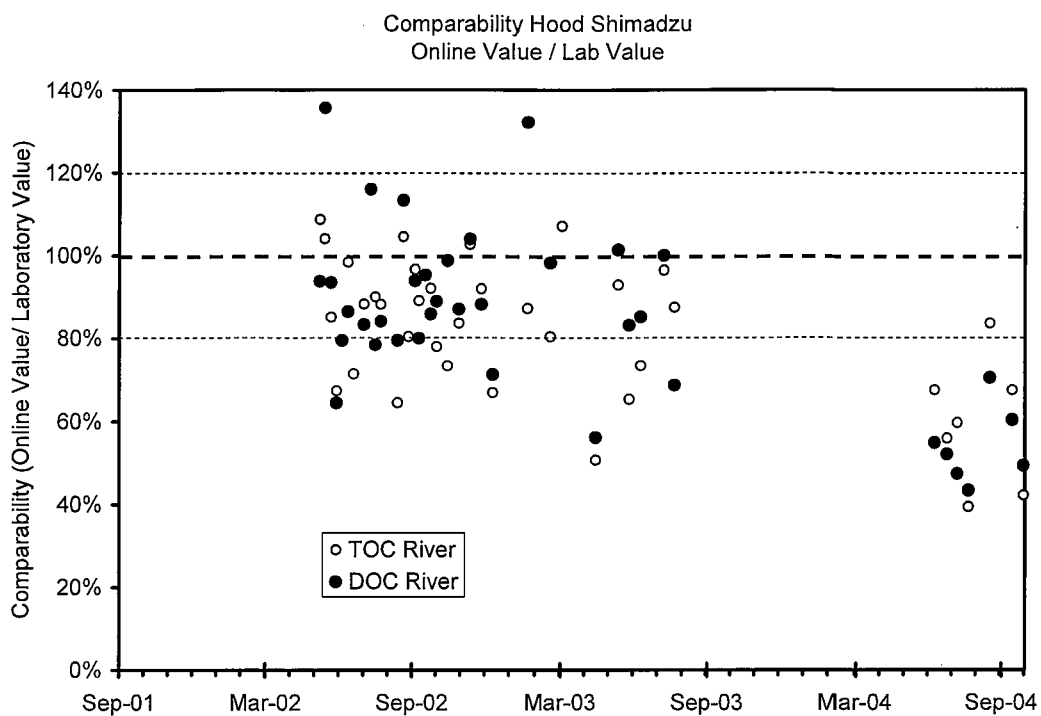
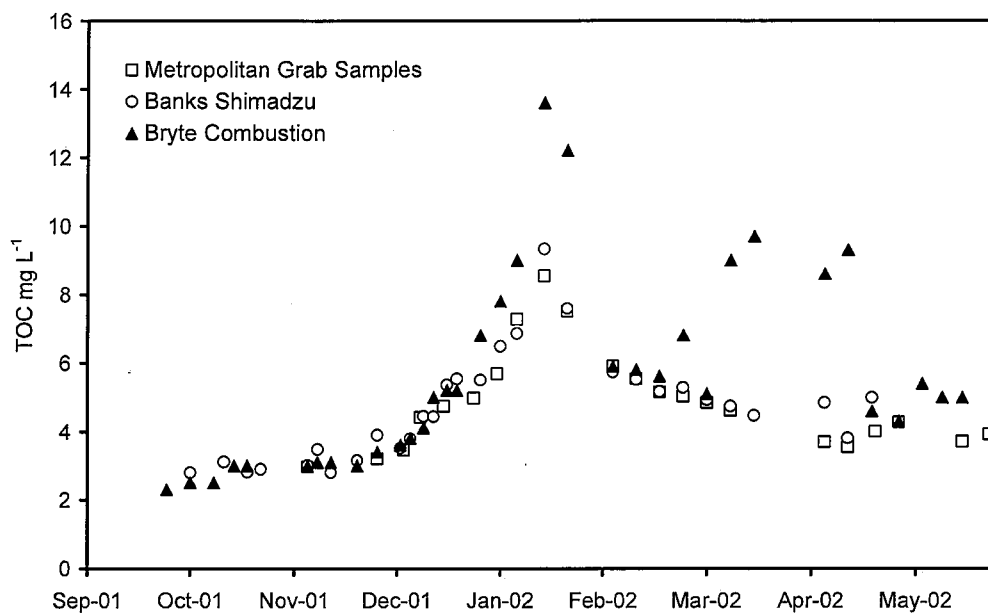


Figure 8

Inter-Instrument Comparison
MWD vs Banks vs Bryte Lab



Comparability Hood Sievers
Online Value versus Lab Chemical Oxidation or Combustion Value

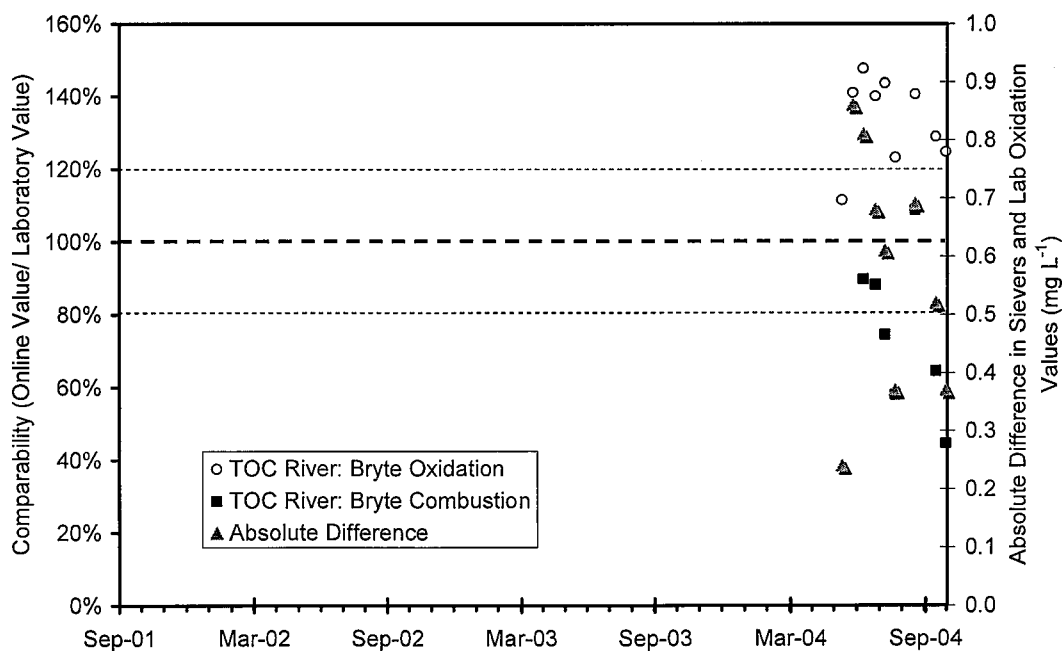


Figure 9

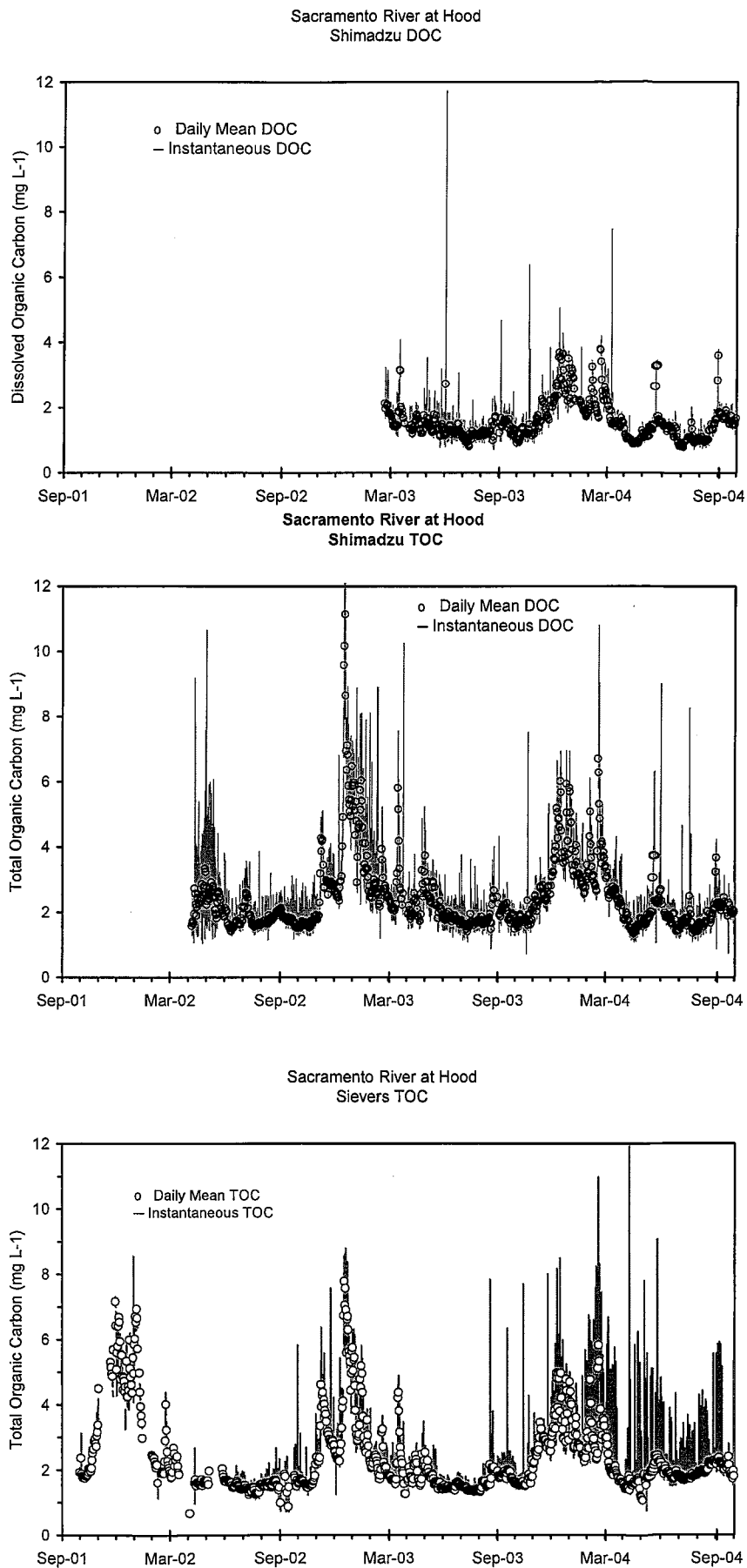
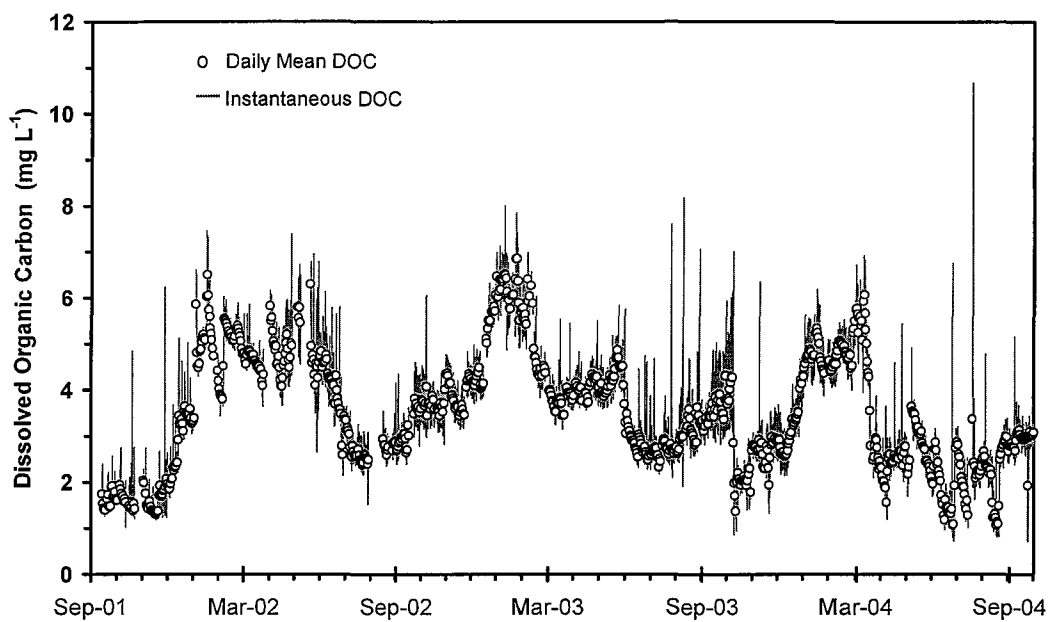


Figure 10

Banks Pumping Plant
Shimadzu DOC



Banks Pumping Plant
Shimadzu TOC

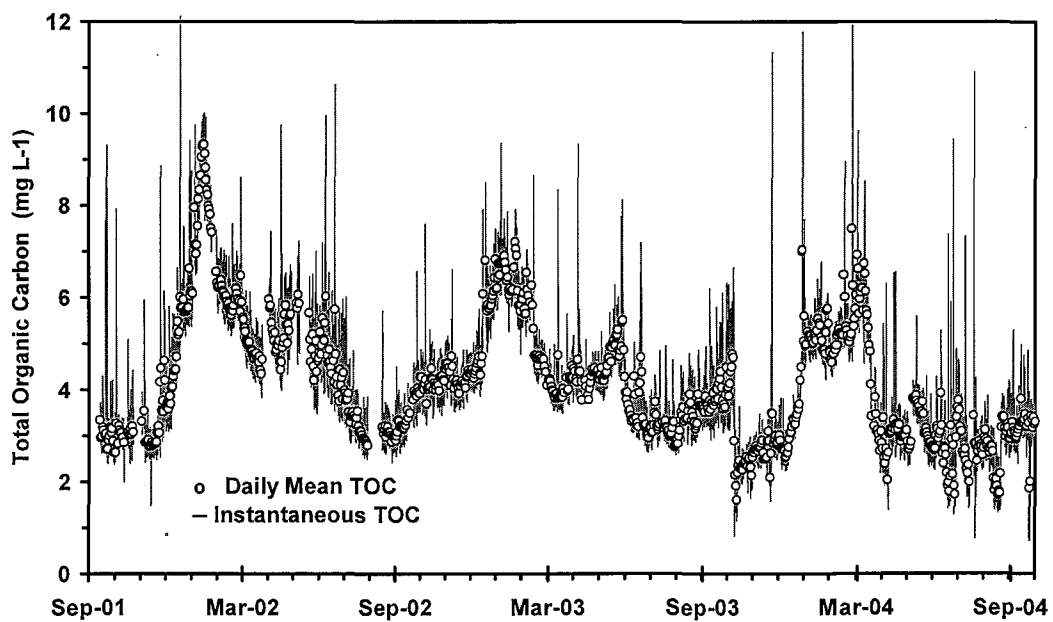
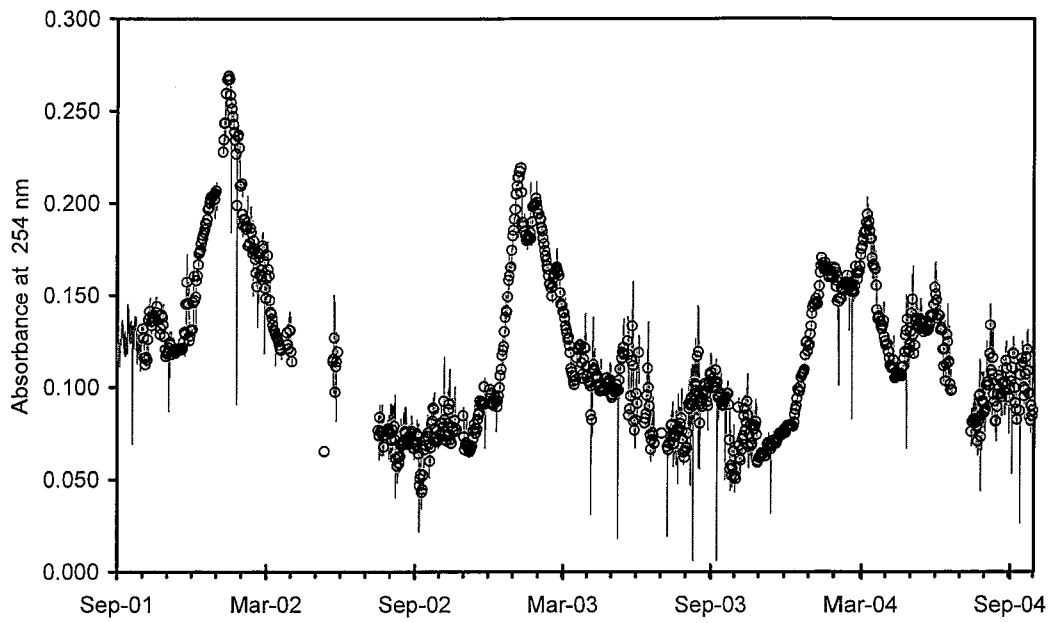


Figure 11

Banks Pumping Plant
Tytronics UVA 254 Sensor



Banks Pumping Plant
Tytronics UVA 254 Sensor

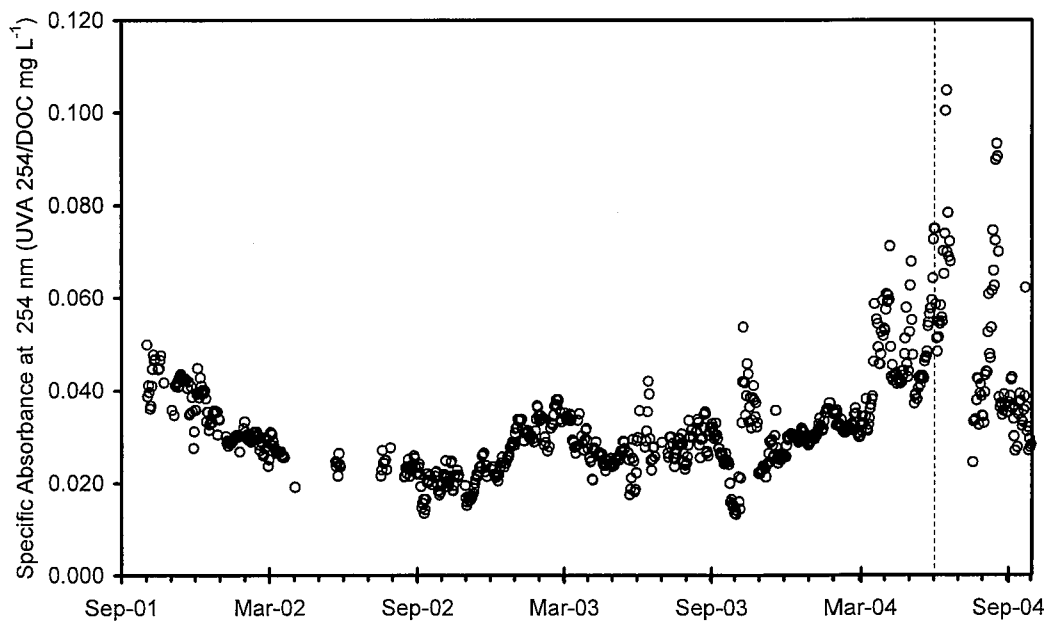


Figure 12

Annual Time-Series and High Frequency Events

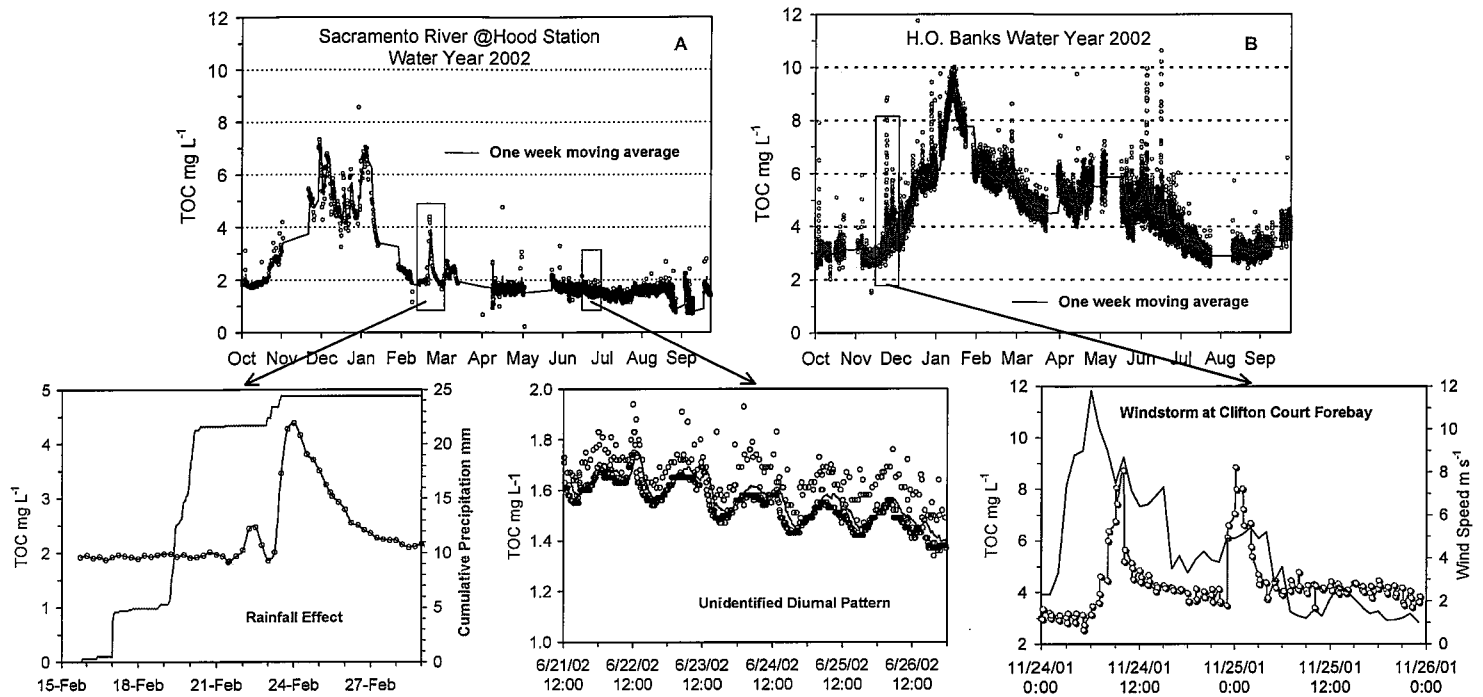


Figure 13

Monthly Carbon Flux and Mean TOC Concentrations: Daily vs. Monthly Samples

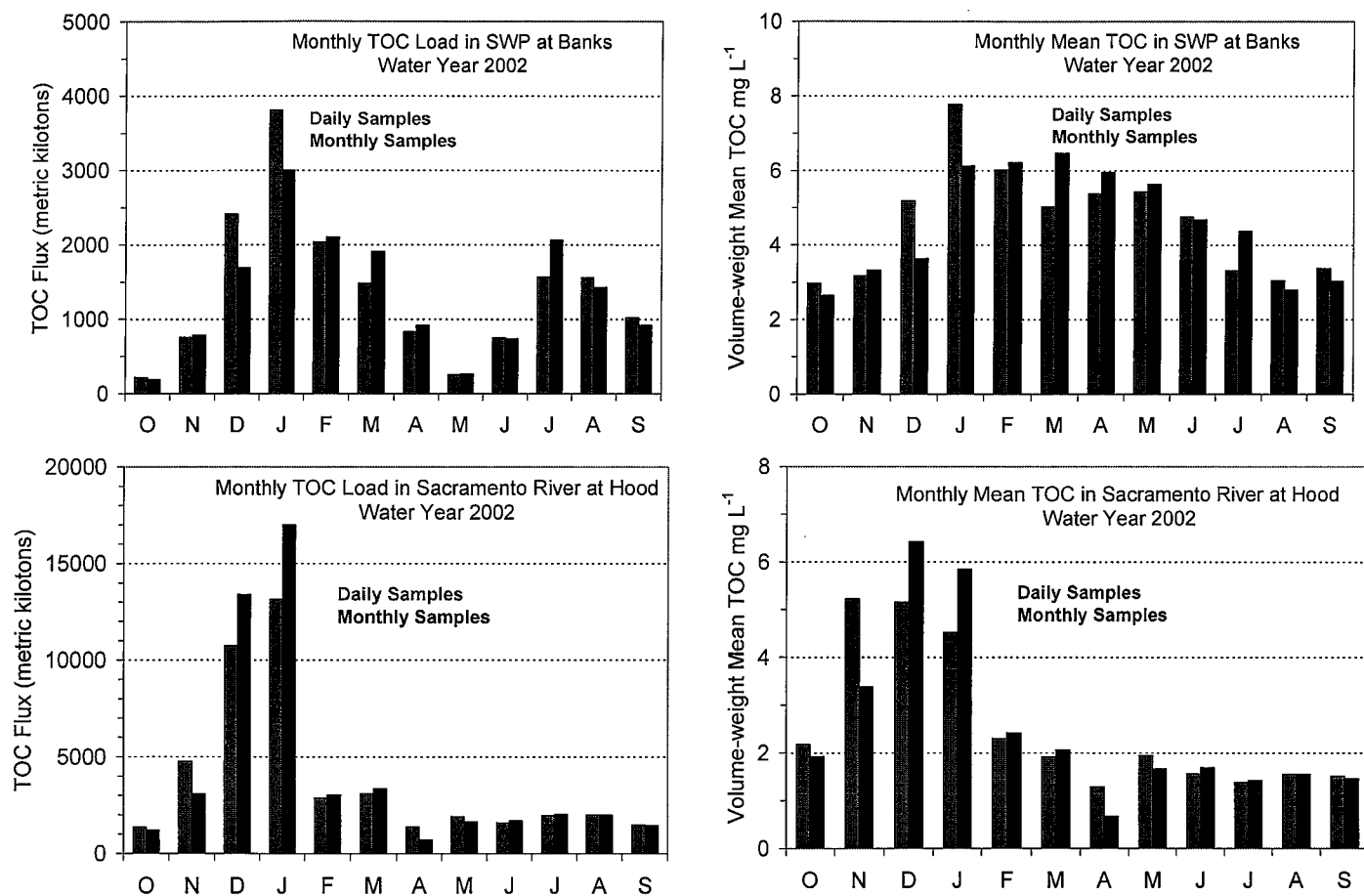


Figure 14