

State of California  
The Resources Agency  
Department of Water Resources  
Division of Environmental Services

Municipal Water Quality Investigation Program

**Real-Time, Continuous Monitoring of  
Bromide and Nutrients at  
Harvey O. Banks Pumping Plant and  
San Joaquin River near Vernalis**

Final Report



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Arnold Schwarzenegger  
Governor  
State of California

Mike Chrisman  
Secretary for Resources  
The Resources Agency

Lester A. Snow  
Director  
Department of Water Resources

STATE OF CALIFORNIA  
**Arnold Schwarzenegger, Governor**

THE RESOURCES AGENCY  
**Mike Chrisman, Secretary for Resources**

DEPARTMENT OF WATER RESOURCES  
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Acting Chief Deputy Director

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Deputy Director

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Acting Deputy Director

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Deputy Director

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**Kasey Schimke**  
Asst. Director Legislative Affairs

**David Sandino**  
Chief Counsel

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**Barbara J. McDonnell, Chief**

Office of Water Quality  
**Stephen Ford, Chief**

Municipal Water Quality Program Branch  
**Danford J. Otis, Chief**

Municipal Water Quality Investigations Program  
**Cindy M. Messer, Chief**

Prepared under the direction of

**Danford J. Otis**

by

**Jaclyn Pimental, Project Leader**

**David Gonzalez**

**Steve San Julian**

**Editorial review, graphics, and report production**

**Gretchen Goettl**, Supervisor of Technical Publications

**Nikki Blomquist**, editor and page layout

**Joanne Pierce**, maps

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## Executive Summary

This paper describes a program conducted by the California Department of Water Resources' Municipal Water Quality Investigations Unit (MWQI) to install and operate laboratory-grade ion chromatography process anion analyzers at key points in the Sacramento- San Joaquin Delta. This paper describes how the analyzers were installed and operated, as well as the results from the Quality Assurance/Quality Control (QA/QC) procedures.

The anion analyzers collect continuous data on bromide, chloride, fluoride, sulfate and nitrate concentrations from waters of the Sacramento and San Joaquin rivers. Information collected on these constituents is utilized by water utilities which are strictly regulated with respect to the formation of disinfection by-products (total trihalomethanes [TTHM] and bromate) and who must also monitor and control for taste and odor issues associated with increased algal activity as a result of high nutrient levels in the water.

Overall, the anion analyzers were accurate when measuring certified standards from an outside source, certified laboratory. A target precision level of 30%, measured as relative standard deviation, was established for both anion analyzers. With only two exceptions, this target level was met. The target for representativeness was met using an equivalency test at 15%; therefore, from a practical standpoint, the delivery and filtration system did not impact the samples. Although not noticeably affecting day to day measurements, paired comparisons between samples analyzed on the field instruments versus a similar instrument in a laboratory did indicate a general tendency for the water delivery system on the field analyzer to affect samples.

The analyzers were also evaluated for reliability over the entire 2-year time period. The average data capture reliability for the Vernalis analyzer was 83% and 72% for the Banks analyzer. These analyzers worked well for this program because they were capable of producing a large amount of data at an acceptable level of quality. While the analyzers met the established targets for data quality, it took a significant amount of staff time and program resources to learn how to operate and maintain these analyzers in a remote setting. As a result of these difficulties, it is recommended that other analyzers that might require less maintenance be investigated for use in remote settings.

# 1. Introduction

The Sacramento-San Joaquin Delta (Delta) is the source of drinking water for approximately 23 million people in California. Fluctuating source water quality and more stringent regulatory requirements have made providing safe, reliable and affordable drinking water increasingly challenging for water utilities. These utilities must comply with strict regulations about the formation of disinfection by-products. The by-products of greatest concern for Delta water users are total trihalomethanes (TTHM) and bromate. Bromide concentrations in source water are a key factor in the formation of these compounds. CALFED recognized this when it established its target for providing safe, reliable, and affordable drinking water as either: (a) average concentrations of 50 µg/L for bromide and 3.0 mg/L total organic carbon (TOC) at Clifton Court and other southern and central drinking water intakes; or (b) an equivalent level of public health protection (ELPHP) using a cost-effective combination of alternative source waters, source control, and treatment technologies (CALFED 2000).

In order for utilities to meet this target it became apparent that data needed to be collected from Delta source water more frequently than the weekly or monthly grab samples that were the standard of the day. Simply increasing the number of grab samples collected, which would have been prohibitively time consuming and expensive, would still not provide the frequency of data needed to accurately describe the water quality at the intake pumps. Thanks to technological advances, the growing availability of semi-autonomous analyzers for industrial applications has expanded the range of water quality parameters that can be monitored continuously. Process analyzers are now available to make continuous measurements of bromide and other anions possible via ion chromatography. Having such instruments installed throughout a watershed would give water utilities the tools they need to help meet the CALFED bromide target. High bromide levels can be anticipated and mitigated through the use of continuous and real-time data, and operational changes—such as reducing pre-chlorination, reducing sedimentation basin contact times, or blending water sources—can be made to reduce the potential for TTHM formation during treatment.

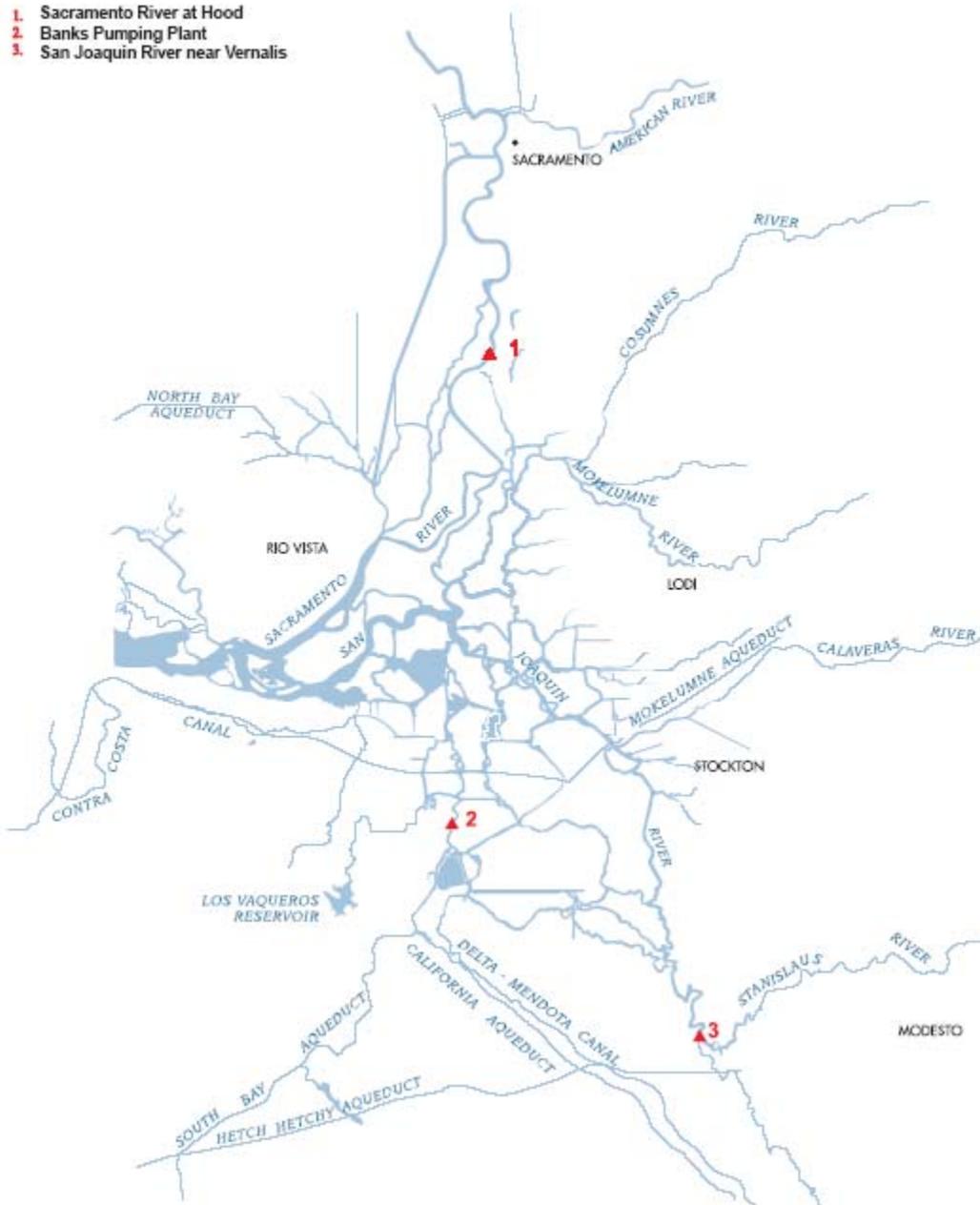
In 1999, the Municipal Water Quality Investigations Unit (MWQI) at the California Department of Water Resources (DWR) began a pilot program to install TOC instrumentation at remote field stations. After its initial success, the program was expanded and now encompasses three stations (Figure 1) that report real-time TOC and dissolved organic carbon (DOC) data. With TOC now adequately monitored at critical sites, MWQI turned its attention to increasing the frequency of data collected for bromide and other anions.

This paper describes a pilot program conducted by MWQI to install and operate laboratory-grade ion chromatography analyzers at key points in the Delta. To our knowledge this is the first use of these types of analyzers to take continuous measurements of bromide and other anions in waters in the United States and to publish the data immediately on the Internet.

This paper also describes the methods used for: (1) installing the analyzers in the field stations, (2) providing a continuous sample stream of filtered water to the analyzers, and (3) transferring data from the field to a centralized database for publication on the Internet. Validation tests were performed on the data; these tests measured the precision and accuracy with which the data was gathered and they compared the data measured by the analyzers with manual grab samples to determine whether the automatic (online) system produced anion data that was comparable. A key component of this project was the assessment of the relative reliability of the ion chromatography systems during the period of the study. The overall objective of this project was to demonstrate that specially designed, semi-autonomous analyzers used in a field setting are a

viable means of generating real-time water quality data for use in forecasting and for water utility operations.

**Figure 1. MWQI's real-time sampling stations**



## 2. Site Description

Delta waters serve millions of people living in the San Francisco Bay-Delta region and in Southern California. Therefore, maintaining good water quality is important to public health and to the economy of California. Two major rivers, the Sacramento and the San Joaquin, provide the majority of freshwater input to the Delta. To expand the range of water quality parameters being measured in real-time at critical points in the Delta, two anion analyzers were installed in key locations.

The sites were selected based on their relative contributions of bromide and other anions of interest to drinking water utilities. The two sites were (1) the Harvey O. Banks Pumping Plant (Banks P.P.) near Byron, and (2) a field station on the San Joaquin River near Vernalis (Vernalis) (Figure 1). The Banks P.P. site was selected because it is at the head of the State Water Project (SWP). Banks P.P. receives blended Delta water from the Sacramento and San Joaquin rivers and this water is representative of what water utilities south of the Delta receive through the SWP. Real-time measurements of bromide at Banks P.P. provide the State Water Contractors (SWC) with the information they need to better manage water quality and the costs associated with treating water for municipal purposes. Through the use of real-time data, high bromide levels can be anticipated and operational changes at treatment plants can be instituted in a timely manner.

The Vernalis site was selected because it represents the levels of bromide and nutrients from agricultural runoff in the San Joaquin River as it enters the Delta. In addition, continuous nitrate measurements on the San Joaquin River aids in understanding baseline nutrient loads. Nutrients such as nitrate can enlarge algal blooms that affect water filtration and cause taste and odor problems in finished drinking water. Real-time nutrient data can help water utilities anticipate algal blooms, as well as help resource managers monitor any water quality improvements from nutrient reduction projects or practices. Data on real-time anion concentrations at both locations can be used by the SWC as an aid to water treatment and blending activities.

## 3. Methods

### 3.1 Analyzer System

When selecting analyzers for this study, only models that could operate unattended and remotely were considered. Normal laboratory analyzers are not designed to run unattended for long periods or to take samples from a continuous stream of water. Process analyzers, however, are designed to run independently and have sample inlet systems specifically designed to take samples from a moving stream of water. Furthermore, because of the high cost of operator time and travel, the chosen analyzer needed to operate independently for up to two weeks, be accessible remotely via computer, and store data for transfer to a centralized computer database. The chosen analyzer was the Dionex DX-800 process analyzer (Dionex Corporation, Sunnyvale, CA). The DX-800 (Figure 2) is an ion chromatography analyzer capable of measuring bromide, chloride, nitrate, and phosphate in surface waters and running unattended for up to 2 weeks.

**Figure 2. Dionex DX-800 Analyzer**



## 3.2 Water Delivery Systems

### 3.2.1 Vernalis station

The Vernalis water quality station consists of a pier built over the river with an approximately 4 meter x 4 meter building on a platform at the end. This building houses all of the water quality instrumentation (Figure 3).

River water is delivered to the station by a ½ horsepower submersible pump (Grundfos 16S05-5) and 1-inch interior diameter black reinforced PVC hose (Ryan Herco, PN: 0514.110) (Figure 4). Because the river elevation can change several meters over the course of the year, the intake is kept at a constant depth of 1 meter below the river surface 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 m<sup>3</sup>.

Water is lifted from 3 to 6 meters depending on river level. Flow rates through the intake pump range from 40 to 70 liters per minute depending on head. A sample stream is directed to the analyzer through a series of Y-connectors and metering valves. When the analyzer is not sampling, all of the sample flow from the submersible pump is returned to the river via a drain.

**Figure 3. Field station on the San Joaquin River near Vernalis**



**Figure 4. Submersible pump at Vernalis field station**



### **3.2.2 Banks P.P. station**

The Banks P.P. water quality station is in a 2.4 meter x 3.7 meter building at the head of the California Aqueduct on the south side of the canal (Figure 5).

Flow rates as high  $240 \text{ m}^3\text{s}^{-1}$  can be produced by the 11 pumps that lift water 75 meters from the Clifton Court Forebay to the California Aqueduct. Unlike the Vernalis station, 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. The system was prone to failure and the design was abandoned. Instead, the inlet hose was attached to a dog-legged-shaped metal bracket secured along the edge of the Aqueduct (Figures 6 and 7). 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 2 meters depending on the stage 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) was used to lift water 2 to 3 meters into the instrument shelter by the Aqueduct. The lift pump required 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. The sample stream system was very similar to the design of the system at the Vernalis station.

**Figure 5. Field station at Banks Pumping Plant**



**Figure 6. Inlet hose attached to Aqueduct at Banks Pumping Plant**



### **3.3 Sample Delivery System**

A continuous flow of filtered sample water was provided to the analyzer by the station pump and water delivery system. The submersible pump at Vernalis was equipped with a coarse screen to prevent large particles from damaging the pump; this water was used for anion analysis. At Banks P.P., an intake foot-valve provided coarse screening (10 mm); it was installed to prevent large particles from damaging the rotor and stator within the progressive cavity pump. A continuous stream of 0.45  $\mu\text{m}$  filtered water was required for anion samples. At both stations, dissolved organic carbon (DOC) was already being measured, so the filtration apparatus was already in place; it was a straightforward process to split the stream of dissolved river water to also measure anions. This filtration system consists of two “prefilter” filter housings which pass water to a 10-inch filter housing that contains the 0.45 micron polysulfone pleated finishing filter (Pall, PN:

WFN0.45-10USM3314). Prefilters consisted of 1 micron (nominal) to 30 micron (nominal) Pall Claris series of melt-blown polypropylene filters (general part no.). The micron ratings of prefilters were selected based on sample water conditions with the intent of making adjustments to maximize the longevity of the 0.45 micron polysulfone pleated filter. Based on sample water conditions, the added demands on the filtration system made it necessary to adjust the service interval from every two weeks to more frequent filter changes.

## **3.4 Operation Procedures**

### **3.4.1 Sample analysis**

Every hour a sample from the continuous stream is bypassed into a 100  $\mu$ L loop and injected onto an AS-19 analytical column (Dionex Corporation, Sunnyvale, CA). Certain analytes are retained on the column longer than others. After the sample comes off the column, it goes through a suppressor, which lowers the background noise. The sample then flows to the conductivity detector where the analytes are detected. The result is shown on the computer screen as a chromatograph with each analyte having its own retention time and integrated peak that determines its concentration.

Each analysis consisted of one sample injection that measured each of the 5 analytes. Samples were run in sequences, with each sequence consisting of 14 samples and 1 check standard. The check standard was used to verify that the calibration was still valid. The Dionex DX-800 analyzer was manually calibrated as needed using a 5-point calibration with a stock standard mix of the 5 anions of interest. The stock contained 10,000 mg/L of chloride and sulfate, 1,000 mg/L of nitrate, 100 mg/L of fluoride, and 50 mg/L of bromide. The anion analyzer measured concentrations for each of these anions; however, because of their importance, this report focuses only on the results for bromide, chloride, nitrate, and sulfate. Stock solutions were prepared by the MWQI staff using NIST-Traceable Standard Reference Materials. Calibration results were recorded on the analyzer's computer and electronic copies were stored on computers at MWQI headquarters.

The analyzers were connected to computers with analyzer-specific software. The analyzer software created files containing results of each analysis, as well as all of the calibration data and sample date and time. The calibration data included standards identification, injection amount, and calculated coefficient value. The data files were initially kept on the analyzer's computer system and then transferred to a database at the MWQI office.

### **3.4.2 Data transfer and storage**

Because of the distance between the office and field stations, a reliable data transfer system was developed to manage the analyzers via a remote desktop connection. A frame relay connection was installed at both sites. The remote desktop system enabled staff to remotely start and stop sample analysis, run calibrations, and edit data. Remote access also allowed staff to transfer and store data on headquarter computers. The remote desktop connection was used for daily system and quality checks on the analyzer status and the sampling results. Data were obtained at headquarters by manually exporting and copying data to a shared network drive using the remote desktop connection.

After the quality of the data had been evaluated for the analyzers, these data were made available in a weekly report published by MWQI's Real Time Data and Forecasting Project (RTDF).

MWQI staff also created a database to store the anion data. Roughly every 50 minutes, data from the field instruments was sent via FTP connection to a DWR server. This server was then queried

from an internal production server at 25-minute intervals to obtain, compile, and import data into a database for further analysis. The entire process was completed using automated scripting techniques and scheduled tasks set up on a number of personal computers and servers. Once inside the database, the data were reviewed for accuracy. Data considered incorrect due to an error in peak integration or shifting retention times was corrected or flagged. The anion data was then transferred to the California Data Exchange Center (CDEC) website for public access (<http://cdec/selectQuery.html>, station ID hro or sjr) and also included in the weekly report sent out via email. All data published in the weekly report and stored on the CDEC website are considered preliminary data. These data are used by the SWC, DWR staff and other interested parties.

### 3.5 Quality Control and Validation Procedures

Standard quality control/quality assurance (QA/QC) methods were followed to validate the online analyzer systems. The term online implies the analyzer systems are operating automatically and taking samples from the continuous sample stream provided by the water delivery system. QA/QC measurements did not begin immediately after installation because the analyzers operated inconsistently after the initial setup. During the first year after installation (2005), there were frequent periods of non-operation (for part replacement and method adjustments) that required MWQI and Dionex staff to visit the sites. Problems with reliability combined with the amount of time it took for staff to become familiar with instrument operation resulted in an extended evaluation period. The analyzers were also not easily configured to run in a grab sample mode. Although different approaches were tried and reviewed for consistency, there was no reliable method to obtain grab samples in a partially automated way.

The MWQI staff decided on a manual injection method for grab samples. The manual injection method required filling a 3 mL syringe with the sample and injecting it into the sample loop tubing while the analyzer was in the sample loading mode and the online sample flow was bypassed. Each sample took approximately 45 minutes to analyze; therefore, running multiple grab samples required a significant amount of staff time. Because of the time it took staff to perfect the grab sample technique and the analytical method, there was limited useable grab sample data to use to evaluate the analyzer. Grab samples included river or canal samples, as well as standards. A large number of samples was also collected throughout the study period and submitted to DWR's Bryte Laboratory.

Lab and grab sample data, as well as online data, were used in the QA/QC discussion of this report. All statistical comparisons were conducted using Minitab 14. Definitions of the different types of samples collected are given in Table 1. Table 2 lists the types of comparisons that were made for QA/QC purposes; they are described in more detail below.

**Table 1. Description of sample types for QA/QC**

Type of sample	Description	# of samples: Banks	# of samples: Vernalis
(Water delivery) system sample	Collected after the 0.45 µm filter, measured at Bryte Lab	75	85
Grab sample	Collected from the river or canal, measured at Bryte Lab	75	85
Field analyzer grab sample	Collected from the river or canal, measured on the field analyzer	10	15
Field analyzer online sample	Measured online by the field analyzers	75	85

**Table 2. QA/QC methods**

Quality control procedure	Method	Description
Accuracy	Standard reference materials	Measured the analyzers ability to reproduce results within certified limits.
Precision	Relative standard deviation	The repeatability and reproducibility of multiple analysis
Representativeness	1) Field analyzer grab sample vs. field analyzer online; 2) water delivery system sample vs. grab sample	Measured whether the analyzer samples were representative of the bulk sample from which they were taken (that is, river or canal)
Comparability	Field analyzer vs. Bryte Lab analyzer (field analyzer grab sample vs. grab sample)	Measured how well field instrument data compares to other instruments.
Completeness	Amount of valid data/amount expected (Days of complete data/# of days in month)	Shows the amount of valid data obtained compared to the amount expected.

### 3.5.1 Accuracy

Accuracy is defined as the ability to produce results that are (within certified limits) statistically the same as the true value (DWR 2006).

The analyzers' accuracy was evaluated by analyzing certified standards from an outside source, quality control laboratory (Wibby Environmental, Golden, CO). The standards were prepared as a mix of chloride, bromide, nitrate, and sulfate. The standards mix was prepared at two different concentrations: 40 ppm and 100 ppm. This allowed accuracy to be evaluated at different points along the calibration curve. Both concentrations of standards were measured by the anion analyzers in triplicate and the mean of the results was compared to the acceptance limits.

The certified acceptance limits were calculated using National Environmental Laboratory Accreditation Conference criteria and the certified value. The goal for this analysis was to determine if the online analyzers could produce anion measurements within the certified limits. These standards were also analyzed in triplicate at DWR's Bryte Laboratory using a similar Dionex analyzer.

### 3.5.2 Precision

Precision is defined as the repeatability and reproducibility of multiple analyses of a homogeneous and well mixed sample (DWR 2006).

Although the Dionex analyzers made 15 to 30 measurements per day, these were not truly replicate analyses because heterogeneity existed in the river or canal where the samples were drawn. For this report, precision was assessed by analyzing replicate samples of standards. The certified standards were from an outside source laboratory (Wibby Environmental, Golden, CO) and were analyzed 6 times during the study period starting in 2007. Triplicate or duplicate analyses from these standards were performed on the Dionex analyzers at both sites. The target for analytical precision for anion analyses was +/- 30% measured as relative standard deviation ( $RSD = [\text{sample standard deviation} / \text{mean of replicate analyses}] \times 100$ ).

### 3.5.3 Representativeness

Because the analyzers measured sample streams pumped from the San Joaquin River and the California Aqueduct, it was crucial that sample aliquots were representative of the bulk sample from which they were taken. The pumps, tubing, and valves of the water delivery system were constructed of inert plastics and metals, but due to microbial processes, it was still possible that anions could be lost or gained when water moved through the system. Grab samples were collected from the sample water delivery system at the sample inlet line to the analyzer (after the 0.45 µm filter, Figure 7).

**Figure 7. Sample delivery system**



Grab samples were collected from the river or canal to allow a comparison with the water delivery system samples. Samples were collected in clean 1 pint polypropylene bottles and sent to Bryte Lab for analysis. Initially, data from the samples measured at Bryte Lab were used as a check for the water delivery system, but, after seeing differences between system and grab sample results, the water delivery system was evaluated further.

To more effectively evaluate the water delivery system, grab samples were collected from the river or canal and measured on site using the anion analyzer. Grab samples were compared to online samples from the analyzer that were run on the same day. The online sample represented aliquots of samples that have passed through the entire water delivery system. If there was no significant difference between the field analyzer online samples and the field analyzer grab samples from the river or canal, then the water delivery systems did not influence final anion concentrations. Equivalency tests conducted at 15% were used to evaluate the differences in this data. With this test, if the differences are within 15%, then the samples are considered equivalent. Paired comparison test were also used to compare the online samples and grab samples measured on the analyzer. The assumption for this test was no difference between the grab and online samples.

### **3.5.4 Comparability**

Comparability expresses the confidence with which the data set can be compared to other data sets measuring the same properties (DWR 2006).

Comparability was assessed by measuring grab samples from the river or canal using the field analyzers and a similar instrument at Bryte Laboratory. Samples were filtered immediately after collection with a 142 mm filter holder and a 0.45  $\mu\text{m}$  cellulose acetate filter; the water that was

filtered was drawn from a completely homogenized 20-liter sample from the river or Aqueduct. The samples sent to the lab were collected in 1 pint polypropylene bottles. Sub-samples (approximately 3 ml) from the 1 pint bottle were measured at the sampling stations using the online analyzers. Sub-sampling ensured that identical samples were measured on the laboratory and field instruments.

As mentioned previously, there was a limited amount of grab sample data run on the field analyzers. To assess their comparability with a larger data set, online analyzer samples were also compared to samples analyzed at the Bryte Lab. The samples measured at Bryte Lab were collected from the delivery system at the sample inlet line to the analyzer (after the 0.45  $\mu\text{m}$  filter). Therefore both laboratory and field analyzed samples passed through the water delivery system prior to analysis. Bryte Laboratory samples were collected from the water delivery system close to the time that the online samples were measured.

Equivalency tests were used to evaluate comparability. The equivalency test assumed the samples were equivalent if the differences were within 15%. A difference of 15% was considered reasonable because the field analyzer is not expected to perform exactly the same as the lab analyzer because it is in a remote setting and does not get the immediate operator response and interaction as an analyzer does in a laboratory setting. A paired comparison test was also used to evaluate the data.

### **3.5.5 Completeness**

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount expected to be obtained under normal conditions (DWR 2006). The following goals were established for data completeness for this study: data capture of at least 50% during any one month and data capture of at least 75% during any yearly period. In addition, for any day, 100% data capture was reached if 10 measurements were made. For each monthly and annual period, the number of system breakdowns (days with no data or less than 10 measurements) were tallied and percent data capture was calculated.

## **4. Results and Discussion**

### **4.1 Quality Assurance and Quality Control**

#### **4.1.1 Accuracy**

At the Vernalis station, all anions fell within the acceptance limits at both concentrations (40 ppm and 100 ppm) (Table 3). At the Banks P.P. station, bromide was outside the acceptance limits on two occasions, once with the 40 ppm standard and once with the 100 ppm standard (Table 4). In both cases there was one outlier in the replicates that influenced the calculation of the mean. This could be due to an error in the method used to inject the standard or incorrect integration of the bromide peak by the analyzer. Overall, the anion analyzers proved to be accurate when measuring certified standards from an outside source certified laboratory.

#### **4.1.2 Precision**

A target precision level of 30%, measured as relative standard deviation, was established for both anion analyzers. This target level was met with only two exceptions. Bromide at the Banks P.P. station exceeded the 30% target for precision on two different dates. Overall, the precision for the analyzer at Banks was well under the target level (Table 5). The analyzer at the Vernalis station never exceeded the target level for precision. The analyzers' precision for bromide and nitrate was well under 30% (Table 6).

**Table 3. Accuracy for Vernalis field analyzer**

	<b>Certified Value</b>	<b>Acceptance Limit</b>	<b>8/7/2007</b>	<b>8/20/2007</b>	<b>2/5/2005</b>	<b>3/12/2008</b>	<b>4/21/2008</b>
Chloride	100	85.9 - 114	93.2	94.2	101.2	98.9	99.5
Bromide	0.5	0.375 - 0.625	0.5	0.5	0.5	0.5	0.5
Nitrate	10	7.20 - 12.8	9.3	9.4	9.0	9.0	10.0
Sulfate	100	84.5 - 116	93.3	95.1	100.5	98.2	99.0
Chloride	40	33.7 - 47.0	39.7	39.2	42.3	40.7	41.0
Bromide	0.2	0.150 - 0.250	0.2	0.2	0.2	0.2	0.2
Nitrate	4	2.05 - 5.95	4.0	3.9	4.0	3.9	4.1
Sulfate	40	33.0 - 47.0	39.8	39.2	42.5	41.6	41.9

**Table 4. Accuracy for Banks field analyzer**

	<b>Certified Value</b>	<b>Acceptance Limit</b>	<b>08/18/07</b>	<b>09/19/07</b>	<b>02/06/08</b>	<b>03/11/08</b>
Chloride	100	85.9 - 114	94.6	101.0	99.6	96.9
Bromide	0.5	0.375 - 0.625	0.5	0.6	1.4	0.5
Nitrate	10	7.20 - 12.8	9.7	10.2	9.1	8.5
Sulfate	100	84.5 - 116	94.4	102.7	111.6	96.1
Chloride	40	33.7 - 47.0	41.1	39.9	40.4	40.3
Bromide	0.2	0.150 - 0.250	0.7	0.2	0.2	0.2
Nitrate	4	2.05 - 5.95	4.3	4.1	3.6	3.9
Sulfate	40	33.0 - 47.0	47.2	46.6	41.6	40.5

**Table 5. Precision for Banks Field Analyzer**

<b>Sampling Date</b>	<b>Banks RSD 40 ppm</b>				<b>Banks RSD 100 ppm</b>			
	<b>Chloride</b>	<b>Bromide</b>	<b>Nitrate</b>	<b>Sulfate</b>	<b>Chloride</b>	<b>Bromide</b>	<b>Nitrate</b>	<b>Sulfate</b>
08/18/07	0.47	111.67	1.09	21.65	0.15	0.39	0.17	0.65
09/19/07	1.27	2.47	0.40	16.88	0.35	19.66	0.25	1.25
02/06/08	0.14	5.00	6.50	7.70	2.43	109.94	14.51	18.93
03/11/08	0.79	2.67	3.91	1.31	0.16	0.15	0.14	0.10

\* RSD limit = 30%

**Table 6. Precision for Vernalis Field Analyzer**

<b>Sampling Date</b>	<b>Vernalis RSD 40 ppm</b>				<b>Vernalis RSD 100 ppm</b>			
	<b>Chloride</b>	<b>Bromide</b>	<b>Nitrate</b>	<b>Sulfate</b>	<b>Chloride</b>	<b>Bromide</b>	<b>Nitrate</b>	<b>Sulfate</b>
02/05/05	0.85	2.66	0.33	0.14	0.36	1.08	0.00	0.00
03/12/08	0.40	2.93	0.25	0.18	0.23	0.08	0.08	0.11
04/21/08	0.41	1.33	0.49	0.30	0.05	0.09	0.46	0.36
08/07/07	0.36	0.58	0.36	0.19	0.09	0.16	0.21	0.23
08/20/07	0.32	0.72	0.00	0.13	0.05	0.03	0.06	0.31

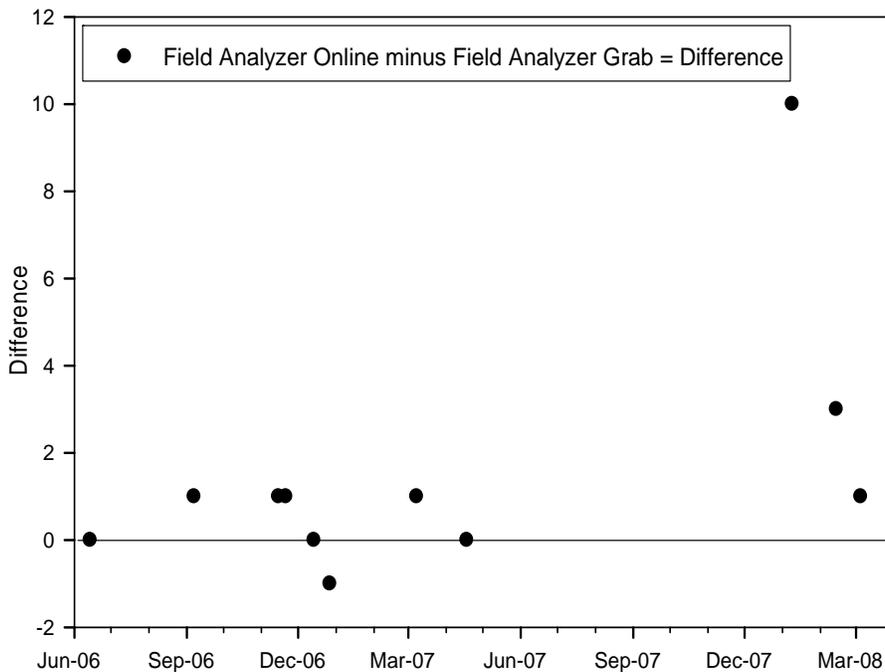
### 4.1.3 Representativeness

The target for representativeness was met using the equivalency test at 15%; therefore, from a practical standpoint, the delivery and filtration system did not impact the samples. Although not noticeably affecting day to day measurements, paired comparisons did indicate some general tendencies associated with the instruments water delivery or filtration system. For example, at both sites there were significant differences for nitrate and chloride ( $p=0.05$ ,  $0.03$  for chloride at Banks and Vernalis, respectively;  $p=0.008$ ,  $0.001$  for nitrate at Banks and Vernalis, respectively). There were no significant differences for the other anions.

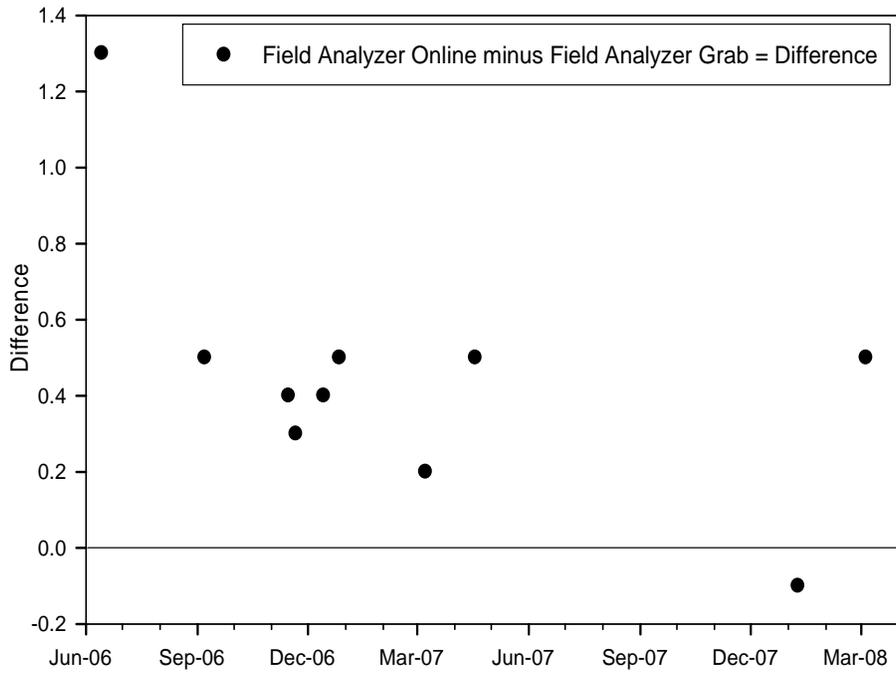
As shown in figures 8 through 11, the difference between the field analyzer online samples and the field analyzer grab samples indicated a bias towards the field analyzer online samples. This was true for both nitrate and chloride, indicating that the water delivery system added nitrate and chloride to the online samples. A difference in nitrate concentrations was also noticed in the samples measured at Bryte Lab ( $p=0.00$  for nitrate at Banks and Vernalis). As shown in figures 12 and 13, nitrate concentrations in the water delivery system samples were consistently higher than nitrate concentrations in the grab samples, indicating that the water delivery system added nitrate to the samples.

One potential cause for these biases was the age of the filter when these comparisons were run. The online samples were collected at the end of the two-week maintenance interval, when the filters had been in use the longest. It is possible that the age of the filter affected the online sample by contributing more nitrate and chloride to the samples. These results suggest that while sample results, according to the established target, were not compromised, further studies examining filter age might improve operator understanding of potential long-term biases that could influence the system over time.

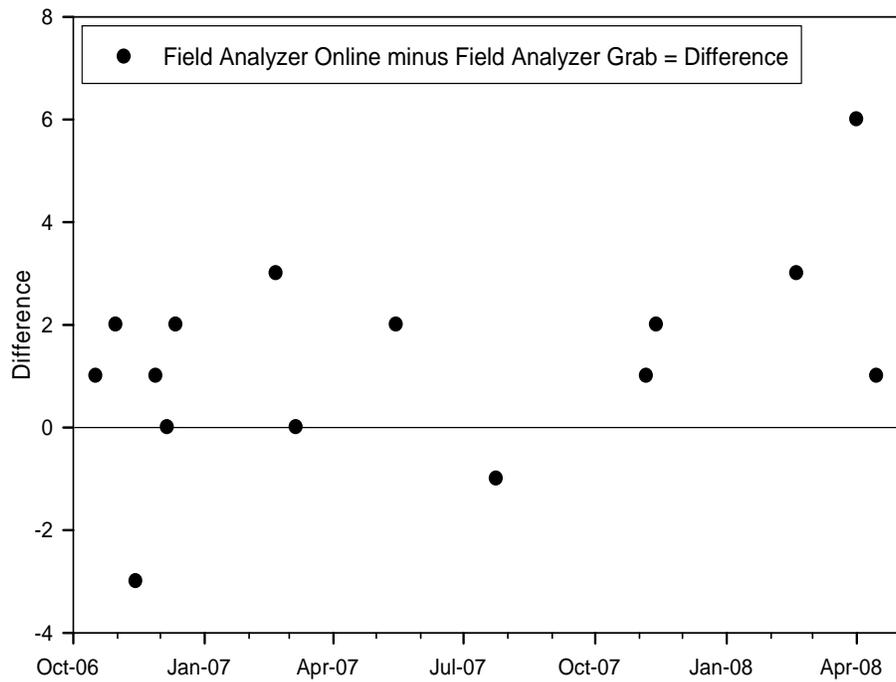
**Figure 8. Difference between chloride measurements at Banks**



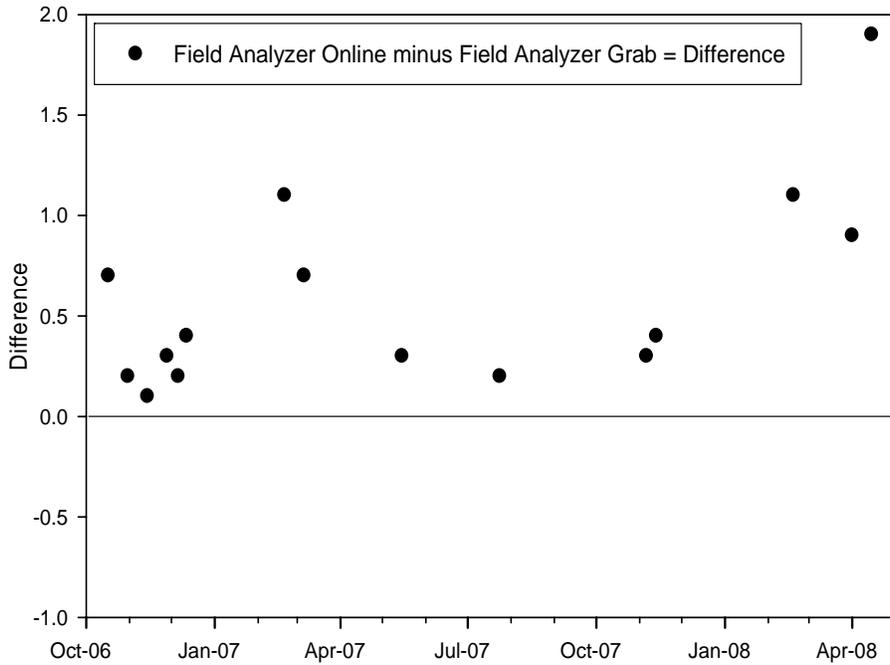
**Figure 9. Difference between nitrate measurements at Banks**



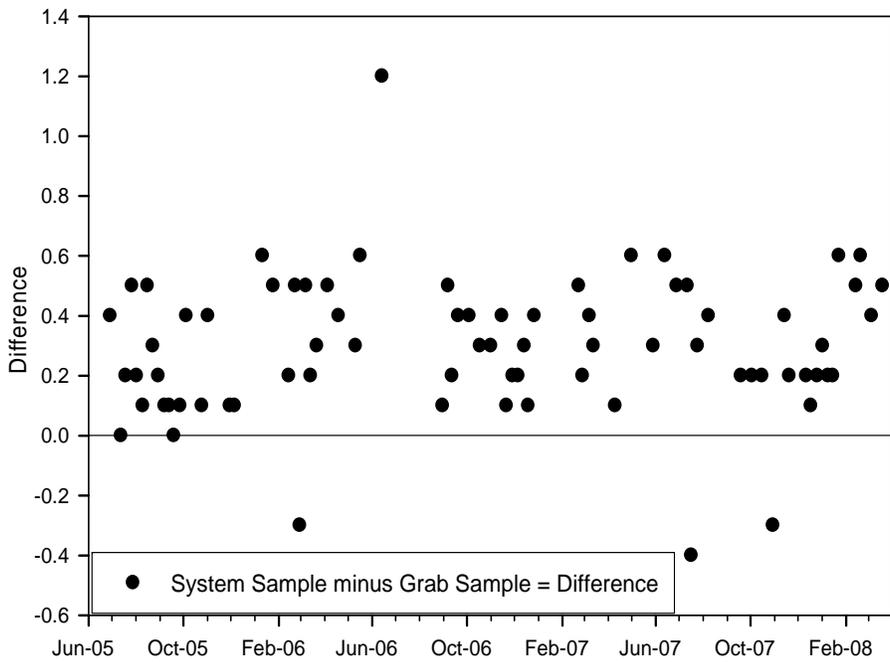
**Figure 10. Difference between chloride measurements at Vernalis**



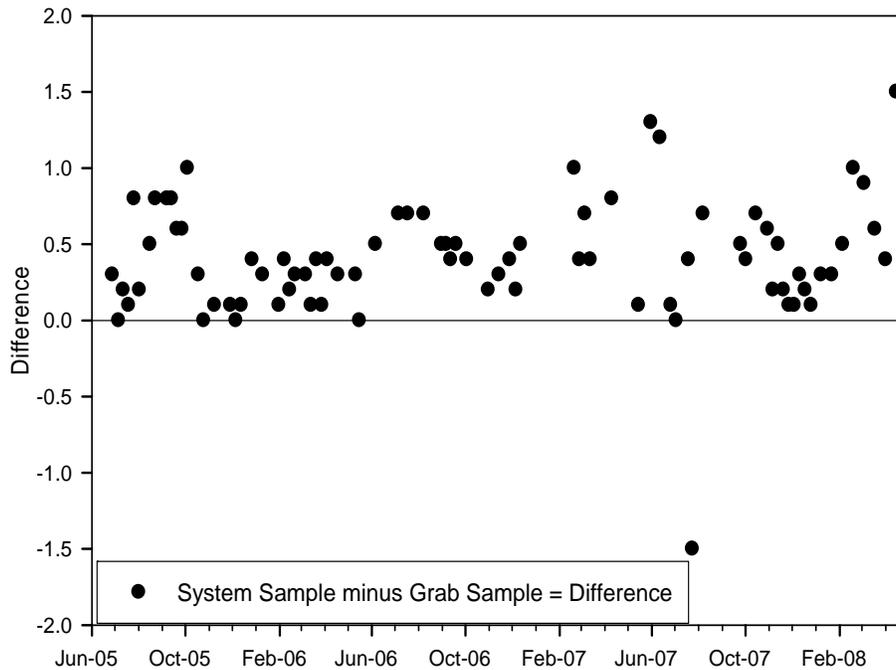
**Figure 11. Difference between nitrate measurements at Vernalis**



**Figure 12. Difference in nitrate measurements between water delivery system's samples and grab samples from the Banks station as measured at Bryte Lab**



**Figure 13. Difference in nitrate measurements between water delivery system's samples and grab samples from the Vernalis station as measured at Bryte Lab**



#### 4.1.4 Comparability

Comparability data between field and laboratory analyses was the most difficult to interpret. Differences in anion values can be caused by operator error in the field or the lab. The difference in how and where the analyzers are operated can also cause some differences in the results. Even if the field analyzers can be considered equivalent to the lab analyzer, it cannot be clearly determined that laboratory results are any more reliable than the field measurements.

An equivalency test at 15% was used to compare the two analyzers. River and canal grab samples were measured on both the field analyzers and the laboratory analyzer at Bryte Lab and the results were used to assess comparability. Both stations fell within the target of equivalency at 15%. Data was also analyzed using a paired comparison test. Grab sample data was not significantly different between the Banks station analyzer and the Bryte Lab analyzer. At the Vernalis station there were significant differences between the field and lab analyzers for chloride and sulfate as shown in figures 14 and 15. ( $p=0.046$ ,  $0.012$  for chloride and sulfate, respectively). However since both field analyzers and the Bryte Lab analyzer fell well within the acceptance limits of the certified standards and the equivalency test, these instruments were considered to be operating within a normal range of variability.

Because only a limited number of grab samples were measured by the field analyzers, online field analyzer samples were also compared to water delivery system samples measured at Bryte Lab. The samples measured at Bryte Lab were collected from the inlet line to the analyzer so that both laboratory and field samples passed through the water delivery system prior to analysis. Data was collected approximately every two weeks from 2005 to 2008. These comparisons were of limited value because the analyzers were not measuring the exact same sample of water; however, this data also met the target of 15% equivalency at both stations and there were rarely large absolute differences between laboratory and field readings.

Overall one-to-one comparisons of the laboratory and field analyzers were of limited value because both analyzers had the capability to produce high quality measurements. In general, the comparability data were of less value than measurements of accuracy, precision, and representativeness.

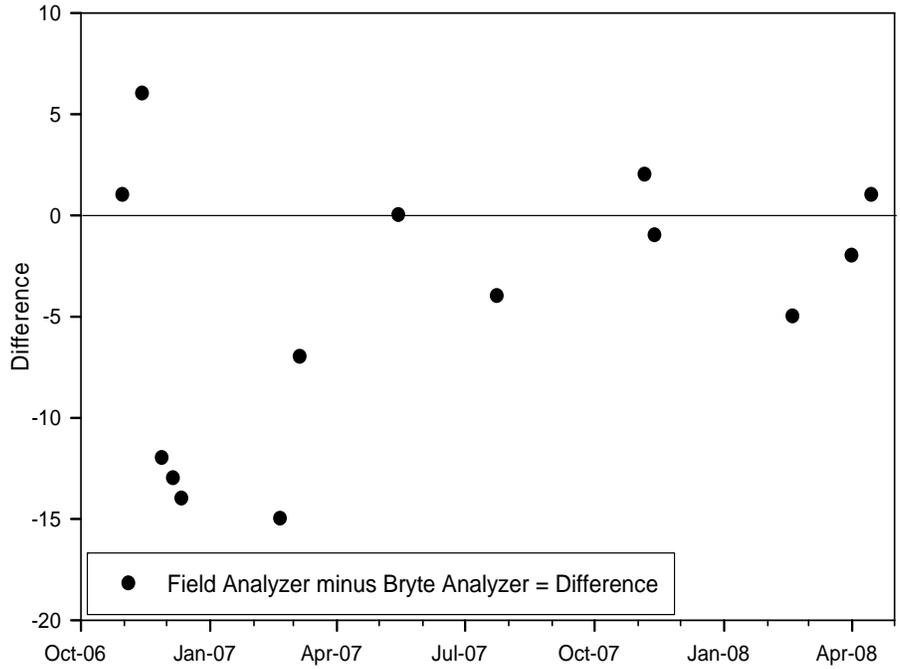
#### **4.1.5 Completeness of Online Measurements**

An assessment of data completeness was not conducted until after the instruments had been in operation for a year and a half. The first year after installation of the analyzer was considered a trial operational period. A considerable amount of time was spent learning operation and maintenance techniques and adjusting the method and calibration settings. Breakdowns were common during the first year and a half of operation. Initially, parts that needed repair and replacement caused most of the downtime. Some of the downtime was also due to periodic power outages, air compressor breakdowns, and software problems.

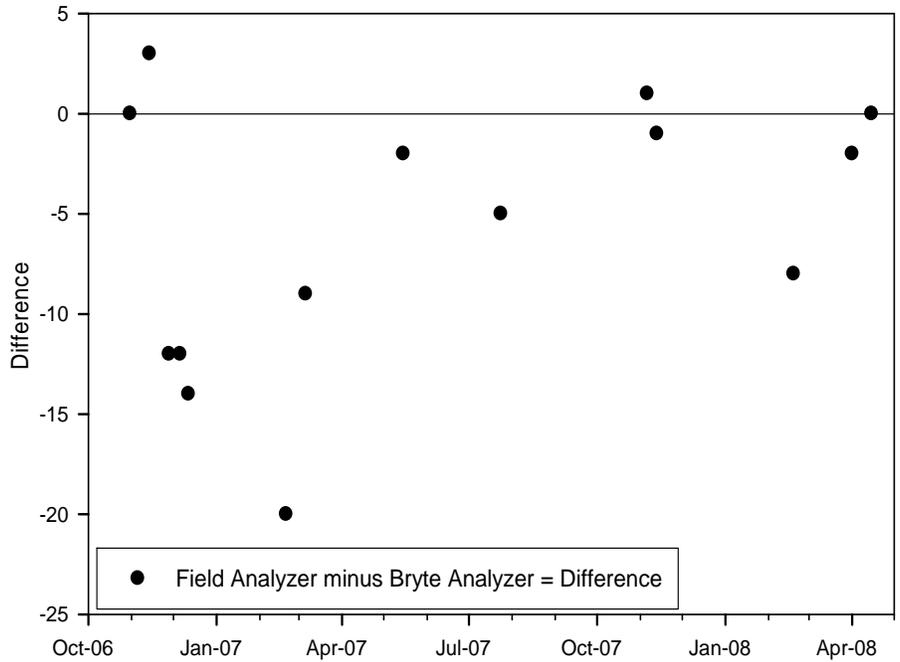
At the Banks P.P. station, data completeness was reviewed for 2006 to 2007. The months after installation were not included because of data gaps due to installation and training; this data was not included in the database. Between 2006 and 2007, the analyzer at the Banks P.P. station was down an average of 1 to 3 times per month. The percent data capture is shown in Table 7. The Banks P.P. analyzer had 72% data capture for 2006 and 73% for 2007. There was an extended period of downtime for January and February 2007 due to loading pump malfunction and to installation and testing of updated software. The analyzer did not meet the completeness criteria of 75% for a yearly period; however, during the last 6 months of 2007, data capture averaged 82% at the Banks P.P.

The Vernalis station analyzer had fewer missed days per month than the Banks P.P. analyzer and met the completeness criteria for a yearly period. Even though there were fewer missed days on average, there were only 5 months during the 2-year period (2006-2007) that had 100% data capture (Table 8). For 2006, data capture was 85% on average and for 2007 it was 82%. The month with the most missed days was January 2007. During that month, the analytical pump on the analyzer became non-operational and needed to be replaced. Over the entire 2-year period, the average data capture was 83% for the Vernalis analyzer and 72% for the Banks analyzer.

**Figure 14. Chloride difference between field analyzers and Bryte Lab analyzers at Vernalis**



**Figure 15. Sulfate difference between field analyzers and Bryte Lab analyzers at Vernalis**



**Table 7. Banks Completeness**

Month	Days Missed	% Data Capture
<b>2006</b>		
Jan-06	10	68
Feb-06	0	100
Mar-06	5	84
Apr-06	19	37
May-06	9	71
Jun-06	13	57
Jul-06	13	58
Aug-06	23	26
Sep-06	3	90
Oct-06	8	74
Nov-06	0	100
Dec-06	0	100
<b>Total %</b>		<b>72</b>
<b>2007</b>		
Jan-07	23	26
Feb-07	19	32
Mar-07	0	100
Apr-07	0	100
May-07	17	45
Jun-07	7	77
Jul-07	2	94
Aug-07	5	84
Sep-07	20	33
Oct-07	4	87
Nov-07	0	100
Dec-07	2	94
<b>Total %</b>		<b>73</b>

**Table 8. Vernalis completeness**

Month	Days Missed	% Data Capture
<b>2006</b>		
Jan-06	11	65
Feb-06	3	89
Mar-06	0	100
Apr-06	6	80
May-06	3	90
Jun-06	1	97
Jul-06	1	97
Aug-06	15	52
Sep-06	3	90
Oct-06	4	87
Nov-06	0	100
Dec-06	9	71
<b>Total %</b>		<b>85</b>
<b>2007</b>		
Jan-07	28	10
Feb-07	3	89
Mar-07	0	100
Apr-07	2	93
May-07	0	100
Jun-07	12	60
Jul-07	0	100
Aug-07	1	97
Sep-07	12	60
Oct-07	6	81
Nov-07	0	100
Dec-07	2	94
<b>Total %</b>		<b>82</b>

## 5. Conclusion and Recommendations

Overall, these analyzers worked well for the MWQI Program because they were capable of producing a large amount of data at an acceptable level of quality. Based on the significant amount of staff time required to learn how to operate and maintain these analyzers in a remote setting, it is recommended that other analyzers that require less maintenance be reviewed for use in remote settings.

For the continued use of the anion analyzers described in this paper, it is recommended that certified standards continue to be measured once a month on the field analyzers to further evaluate their accuracy. This data should also be used to produce control charts, which are valuable tools for quality control and identifying trends. The frequency of grab samples should increase to once a week; this data helped identify issues with the water delivery system and was valuable for comparison with other analyzers.

### Literature Cited

CALFED Bay-Delta Program. 2000. *Programmatic Record of Decision*.

Department of Water Resources. 2006. *Bryte Chemical Laboratory Quality Assurance Manual*. Quality Assurance Technical Document 8. ([http://www.wq.water.ca.gov/docs/bryte\\_pubs/Bryte\\_QA\\_Manual\\_2006.pdf](http://www.wq.water.ca.gov/docs/bryte_pubs/Bryte_QA_Manual_2006.pdf); Accessed June 2008)