

Comparisons of Organic Carbon Analyzers and Related Importance to Water Quality Assessments

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ABSTRACT

This study tested whether analyzers using different methods were equally capable of measuring organic carbon in diverse environmental water samples from California's Sacramento/San Joaquin Delta and its watersheds. The study also evaluated whether the different instruments might provide differing organic carbon concentration measurements, which could in turn trigger (or not) a regulatory requirement for enhanced coagulation at a water treatment plant. In Phase 1, samples were collected in eight monthly events at five stations associated with California's State Water Project and analyzed using three high temperature combustion and three chemical oxidation instruments. Significant differences between instruments occurred in only 20% of the analyses. However, 80% of the observed differences were attributed to one combustion instrument that reported higher values compared to the other instruments. In Phase 2, four certified standards were analyzed with nine instruments. Results suggested that the main contributor of the observed differences was some instruments' inability to remove inorganic carbon, an important step in the analytical process. There were no significant differences in the frequen-

cies at which different instruments would have prescribed enhanced coagulation at a water treatment plant. We concluded that properly operating instruments using any of the standard methods were equally capable of analyzing the diverse concentration levels of organic carbon in the Delta.

KEYWORDS

organic carbon analysis, drinking water quality, disinfection byproducts, food chains

SUGGESTED CITATION

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INTRODUCTION

Organic carbon (OC) is an important water quality constituent. In aquatic food chains, particulate OC plays a part in energy transfers between trophic levels and is essential in ecosystem restorations (Jassby and Cloern 2000). On a larger scale, OC is of interest in the study of global carbon cycling and climate change (Morgans-Bell and Cohen 2004). OC can also increase the cost of disinfecting drinking water.

Chemical reaction between OC and chlorine disinfectant forms carcinogenic disinfection byproducts (DBPs), which are regulated under the Safe Drinking Water Act. In 1998, the US Environmental Protection Agency (EPA) established the Stage 1 Disinfectants and Disinfection Byproducts Rule (DBPR1) to reduce DBP formation. If OC concentration levels exceed limits prescribed by the rule, a water treatment plant (WTP) is required to use enhanced coagulation to reduce the OC levels. The rule allows exemptions from enhanced coagulation if a WTP meets alternative water quality conditions.

Analyzers (instruments) using three approved methods measure OC in drinking water (EPA 1998a): high temperature combustion (HTC), ultraviolet persulfate oxidation, and wet chemical oxidation. Standard Methods (SM) describes the analytical procedures as 5310B, 5310C and 5310D respectively (Eaton et al. 1995). Studies differ on whether data from these methods are comparable to each other. Some research indicates that the methods are comparable (Sharp 1997; Sharp et al. 1993); some report mixed results (Aiken et al. 2002); others indicate that HTC is more accurate in measuring dissolved organic carbon (Koprivnjak et al. 1995; Wenhao and Wangersky 1993); others indicate HTC is more accurate in measuring particulate OC (Najm et al. 2000). In an extensive review of the methods, Urbansky (2001) observed that obtaining accurate and precise OC analysis has been a challenge for at least the past 20 years. He concluded that, although standard methods are available, the protocols leave too much discretion in following the analyzer manufacturer's recommended operation procedures.

The Sacramento-San Joaquin Delta (the Delta) is a source of drinking water for approximately 70% of California's residents. The California Department of

Water Resources (DWR) operates the State Water Project (SWP) which delivers water from the Delta to 29 public water contractors (DWR 2002). DWR monitors OC in the Delta and the SWP using a mix of oxidation and HTC instruments in its own laboratory, field stations and commercial contract laboratories. DWR has been analyzing OC since 1986, and the data are used by many outside agencies for Delta ecological and drinking water quality studies.

Since DWR has been using different total organic carbon (TOC) analyzers, there have been the following concerns about comparability of the OC data: (1) HTC instruments are more efficient than oxidation at handling matrix variations between sampling stations, and will generate higher OC results than oxidation at sites with complex water matrices; (2) HTC instruments are more efficient than oxidation in analyzing particulates, and their data could therefore potentially prescribe TOC removal at a WTP more frequently; (3) HTC data are preferable to oxidation data in Delta ecosystem studies because the method will reveal more food chain-related particulate OC. We conducted this study to provide information that could resolve the above concerns.

METHODS

Study Scope

DWR quality assurance policy requires all departmental environmental sampling programs to follow standard operating procedures (DWR 1997; DWR 1998). We designed the study to acquire OC data in the manner in which instruments are normally operated in order to obtain a true evaluation of the quality of DWR's grab samples analyses. The instruments in Phase 1 were those that normally analyze DWR's samples and are located in the department's chemical laboratory, field stations, and commercial contract laboratories. Instruments in Phase 2 were DWR's, plus those of outside volunteer participants (Table 1).

Study Sites

We selected sampling sites from existing DWR monitoring stations based on historical surface water quality data, with stations selected to provide a wide range of

Table 1. Study participants included DWR chemical laboratory and field stations, commercial contract laboratories, and non-department volunteers.

| Instrument code | Analyzer model | Standard Method | Participant | Study phase |
|------------------|------------------------|-----------------------|----------------|-------------|
| 1 ^a | OIC 1020 | Combustion (SM 5310B) | DWR | 1, 2, |
| 2 | Shimadzu TOC 4100 | Combustion (SM 5310B) | DWR | 1, 2, |
| 3 | Shimadzu TOC 5000A | Combustion (SM 5310B) | Commercial lab | 1 |
| 4 ^a | OIC 1010 | Oxidation (SM 5310D) | DWR | 1, 2 |
| 5 ^a | Tekmar Dohrmann DC 180 | Oxidation (SM 5310C) | Commercial lab | 1 |
| 6 | Sievers 800 | Oxidation (SM 5310C) | DWR | 1, 2 |
| 10 | Shimadzu TOC-V CSH | Combustion (SM 5310B) | University | 2 |
| 90 ^a | Tekmar Dohrmann DC 180 | Oxidation (SM 5310C) | SWP contractor | 2 |
| 100 ^a | Sievers 800 | Oxidation (SM 5310C) | SWP contractor | 2 |
| 110 | Shimadzu TOC 5050A | Combustion (SM 5310B) | University | 2 |
| 120 | Shimadzu TOC 4100 | Combustion (SM 5310B) | DWR | 2 |

a. Instrument is in laboratory accredited by California Department of Health Services to perform drinking water analyses.

Table 2. Historical water quality at sampling stations. Sampling sites were selected from existing DWR monitoring stations based on historical surface water quality data and to provide a wide range of matrices.

| Station | TOC (mg C L ⁻¹) ^a | | | | | Turbidity (NTUs) ^a | | | | |
|----------|--|------|------|--------|-------|-------------------------------|-----|------|--------|-------|
| | Min | Max | Mean | Median | Count | Min | Max | Mean | Median | Count |
| Hood | 1.3 | 4.5 | 1.9 | 1.7 | 243 | 4 | 70 | 14 | 11 | 150 |
| Vernalis | 2.0 | 8.5 | 3.2 | 3.0 | 172 | 4 | 176 | 22 | 18 | 333 |
| Banks | 1.6 | 6.3 | 3.5 | 3.2 | 72 | 2 | 33 | 10 | 8 | 192 |
| CK13 | 2.5 | 4.1 | 3.1 | 2.9 | 11 | 3 | 14 | 5 | 4 | 12 |
| Barker | 2.3 | 22.9 | 8.4 | 6.9 | 166 | 9 | 256 | 45 | 27 | 180 |

a. except count, which is a frequency and not a chemical concentration.

matrices (Table 2). The stations were Hood (38.367°N, 121.519°W), Vernalis (37.667°N, 121.267°W), Banks (37.798°N, 121.623°W), CK13 (37.074°N, 121.015°W), and Barker (38.276°N, 121.788°W) (Figure 1).

Sampling Methods

In Phase 1, TOC samples were collected by DWR field crews in eight sampling events from December 2001 to October 2002. Samples were collected as follows. A clean 9.5 L stainless steel bucket attached to a stainless steel cable was lowered to about 1 m below the water surface and rinsed three times. (Bulk samples at CK13 were collected from a faucet attached to a pipe

originating 3 m below the water surface). At each station, the bulk sample was kept well mixed while filling 40-mL glass vials acidified with phosphoric acid (H₃PO₄) to pH < 2. All samples were stored in coolers with blue ice at 4°C for transportation to DWR field headquarters, where they were then shipped to study participants.

Phase 2 consisted of the analyses of four certified performance evaluation (PE) samples conducted in December 2002. The PE samples were formulated by Absolute Standards Inc. (Hamden, CT), using procedures outlined by EPA (EPA 1998b). Sample 1 was

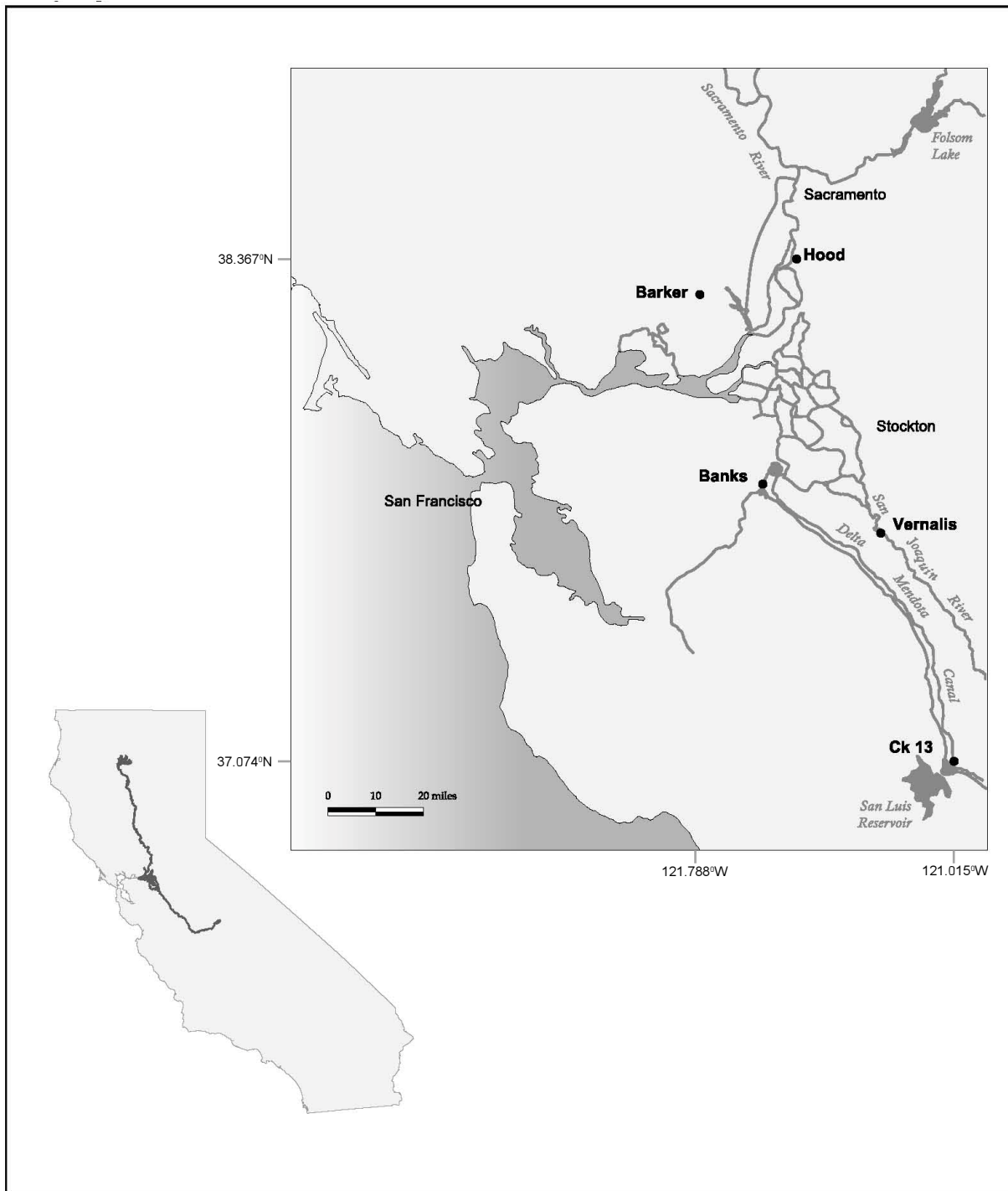


Figure 1. Location of sampling stations. Hood is on the Sacramento River bank above Delta tidal influences below a watershed approximately 69,930 km². Vernalis is on the San Joaquin River bank above Delta tidal influence below an agricultural watershed approximately 33,670 km². Banks is the transfer point from the Delta into the SWP. CK 13 on the SWP aqueduct is approximately 113 km downstream from the Delta. Barker is at the North Bay Aqueduct intake, but is not in the SWP main stem.

potassium hydrogen phthalate (KHP, concentration of 2.0 mg L⁻¹), a widely used calibration standard for OC analyzers. Spiking an aliquot of sample 1 with 30 mg L⁻¹ of 99% purity American Chemical Society-grade sodium bicarbonate (NaHCO₃) created sample 2 at 2.0 mg L⁻¹. Sample 3 was caffeine (6.0 mg L⁻¹). An aliquot of sample 3 was spiked with 30 mg L⁻¹ of 99% purity ACS grade NaHCO₃ to create sample 4 at 6.0 mg L⁻¹. All the samples except sample 2 were acidified with H₃PO₄ by the vendor to pH < 2 (sample 3 was acidified by mistake) as required by the method. Samples with inorganic carbon (IC) added posed a dilemma because acidification would have sparged the IC. All PE samples were analyzed blind by nine study participants (Table 1, Phase 2).

The KHP standard (sample 1) tested the laboratory's ability to analyze a simple sample in the low concentration range. The KHP amended with NaHCO₃ (sample 2) tested the laboratory's ability to remove IC, which can be a problem (Fair, EPA, pers. comm.; Potter and Wimsatt 2002). The IC spiking level was within the alkalinity range found in the SWP. Samples 3 and 4 (caffeine) were to test the instruments' ability to analyze a complex OC molecule at a higher concentration range.

Statistical Tests

We conducted all statistical analyses using Minitab Release 14 (Minitab Statistical Software, State College, PA). We compared different instrument TOC results between stations for matrix effects and against DBPR1 TOC removal criteria for potential impacts on WTP operations.

First, we used Kruskal-Wallis (K-W) test to detect whether there were significant differences between all instruments' TOC measurements at a station. The K-W test only showed that differences existed between instrument measurements. Second, we ran K-W multiple comparison pair-wise tests to determine which TOC measurements significantly differed from each other. Multiple pair-wise comparisons are widely used to determine significant differences among several treatments (Conover 1999; Helsel and Hirsch 2002, Zar 1996). K-W pair-wise tests used the Bonferroni method (Zar 1996) to control alpha inflation and keep the adjusted individual Bonferroni p-value at 0.013.

RESULTS

TOC Analysis (Phase 1)

As expected from DWR's historical water quality data (Table 2), Barker had the highest and Hood the lowest TOC values of sites sampled in the study. Boxplots indicated that TOC data from most instruments were skewed (Figure 2). The medians of TOC values from instrument 1 were distinctly higher and had wider scatter than the other instruments' data at all stations.

K-W tests indicated significant differences ($p < 0.05$) in TOC measurements of samples from all stations except at CK13 (Figure 3). The "z" standardized rank distance shows the limits outside which pairs of instruments' medians were significantly different ($p < 0.05$). Pair-wise comparisons showed that significant pair-wise differences occurred only in 20% (15 of 75) of the analyses. Instrument 1 accounted for 80% of the significant differences. Instrument 1's TOC measurements were significantly higher than all the other instruments at Hood and Vernalis. Instrument 1's TOC measurements were also significantly higher than instruments 4 and 6 (both oxidation) at Banks and Barker. The only other significant differences were between TOC measurements of instruments 3 (HTC) and 4 (oxidation) for samples from Hood and Banks, and instrument 3 and 6 (oxidation) for Barker samples.

We then categorized each instrument TOC result at each station into a DBPR1 enhanced coagulation interval assuming an alkalinity of < 60 mg L⁻¹ as calcium carbonate. An instrument's TOC result could only fall into one of the following 4 intervals. Interval 1 (no TOC removal): TOC result < 2 mg L⁻¹; Interval 2 (35% TOC removal): TOC result > 2 and ≤ 4 mg L⁻¹; Interval 3 (45% TOC removal): TOC result > 4 and ≤ 8 mg L⁻¹; Interval 4 (50% TOC removal): TOC result > 8 mg L⁻¹. The majority of the TOC results fell into Interval 2. We then tested the frequencies in each removal interval using K-W tests. Barker was the only site with significant differences in Intervals 1 and 2, where in 2 instances instrument 6 (oxidation) was significantly different ($p = 0.01$) than instruments 1 and 3 (both HTC). This was approximately 0.4% of all the TOC removal frequencies, and we deemed it to be of no practical importance to a WTP. The results therefore

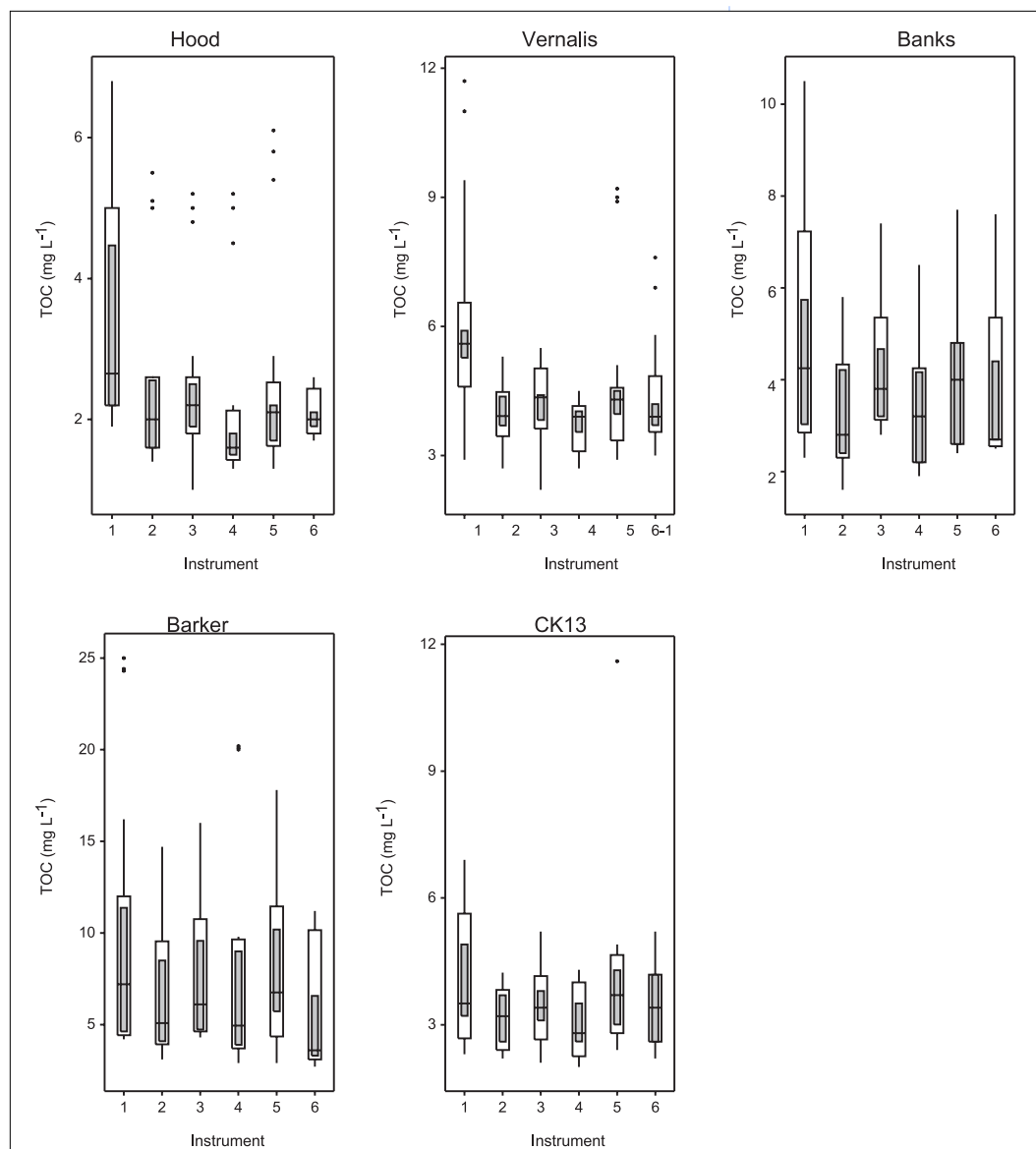


Figure 2. Boxplots of instrument TOC results by station. The boxplots include median (dash), confidence interval around the median (inner box), interquartile range (exterior box), whiskers and outside points (*), which are values between 1.5 and 3 times the interquartile range. The whiskers extend from the interquartile range to the highest and lowest outlying points.

indicated that HTC and oxidation instruments would both prescribe TOC removal at similar rates. We believe that these are important findings because, to our knowledge, no other study has been conducted to statistically test how varying OC analytical methodology would impact DBPR1-required enhanced coagula-

tion implementation across diverse water quality matrices.

PE Samples Analysis (Phase 2)

The PE samples results revealed several problems (Figure 4). HTC instruments 1 and 2 overestimated and HTC instrument 10 underestimated KHP (sample 1). This suggested that these instruments were not properly calibrated or had other problems as described by EPA (2005). The same HTC instruments, plus instrument 90 (oxidation) had problems with KHP + IC (sample 2). This indicated that, although both HTC and oxidation can have difficulties removing (sparging) IC, HTC instruments have more problems with this analytical step. All oxidation instruments had difficulty with caffeine (samples 3 and 4), and none was within the certified limits, suggesting that these instruments may have problems oxidizing and analyzing complex OC molecules. On the other hand, among HTC

instruments, only instrument 10 was outside the caffeine certified standard, indicating these instruments generally did not have a problem with this type of sample.

DISCUSSION

Instrument Comparisons

Significant differences ($p < 0.05$) between instruments' TOC measurements occurred in only 20% ($n=75$) of the pair-wise TOC comparisons of environmental samples. Most (80%) of these differences were

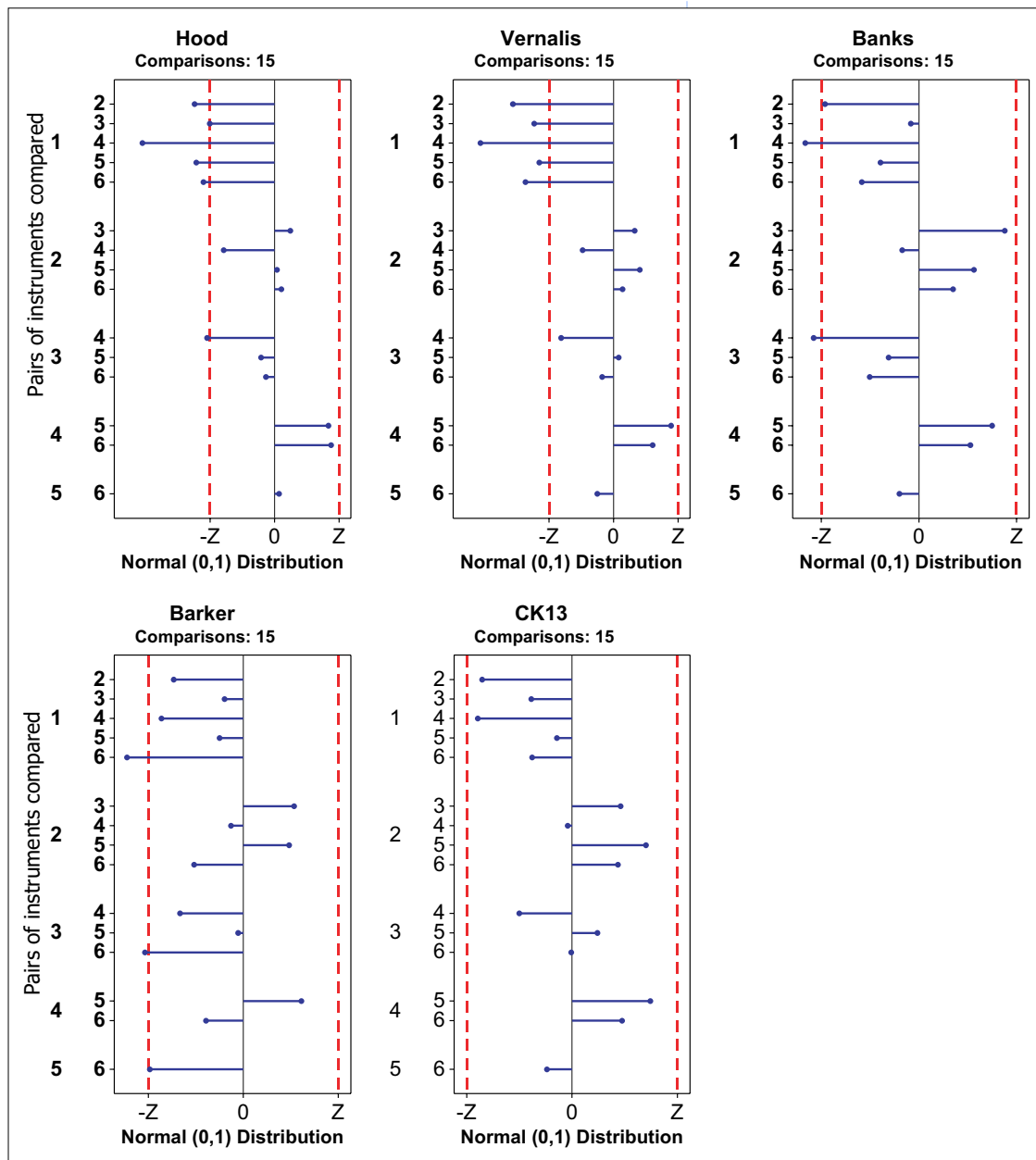


Figure 3. Kruskal-Wallis pair-wise instrument TOC comparisons. The “z” limits are equivalent to about 2 standard deviations. If the second instrument of a pair is outside the “z” limits, the instruments are different. The graph also indicates whether the result of the first instrument is higher (dot to the left of zero) or lower (dot to the right of zero) than the second instrument.

between instrument 1 and the others. Instrument 1 also inaccurately reported the certified KHP + IC standard in Phase 2, which suggested that this analyzer’s high TOC values in regular environmental samples

were probably due to problems with IC removal, and that this instrument was an outlier. Instrument 10 was below the control limits in all four PE samples while instruments 110 and 120 measured the samples accurately, showing that discrepancies can occur between HTC instruments’ measurements of simple as well as complex matrices. The other few discrepancies between instruments can be attributed to the normal between-laboratory differences that typically occur in interlaboratory comparisons, regardless of analytical method. These differences may result from operator errors, instrument design anomalies, etc. EPA has found IC removal problems and suggested possible reasons for OC analytical discrepancies between instruments (Fair, EPA, pers. comm.; Potter and Wimsatt 2002) as follows: (1) Combustion chambers

of HTC instruments that use internal sparge may retain carryover OC if sparged gas is not completely flushed; (2) Calculation errors may occur in instruments that calculate TOC as the difference between total carbon and IC; (3). The internal calibration curve for IC may not be high enough, thereby underestimating IC and overestimating OC. EPA has developed a new analytical method to resolve the IC removal problems (EPA 2005). This method was not available during this study.

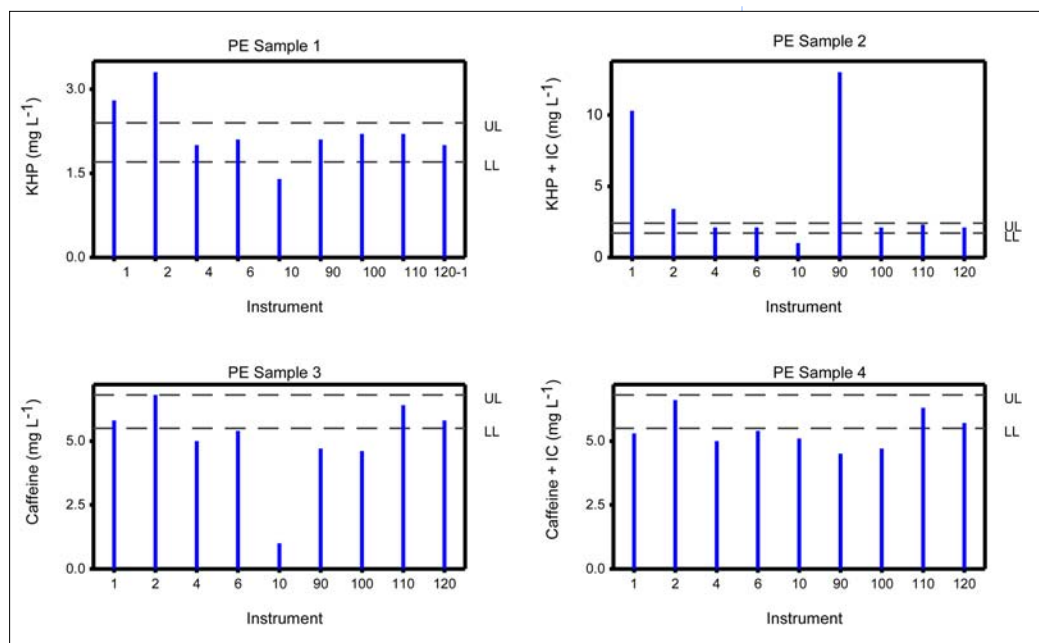


Figure 4. Results of performance evaluation sample analyses in Phase 2. Results were accurate if they were between the certified lower limit (LL) and upper limit (UL). All oxidation instruments had difficulty with caffeine, suggesting problems breaking down complex OC compounds.

In the PE analyses, overestimation of KHP + IC in sample 2 by instruments 1 and 90 showed the need for the new EPA 415.3 method in order to ensure complete IC removal before OC analysis. Underestimation of caffeine by oxidation instruments indicated a potential inability of that method to break down complex molecules, but the practical implication was unclear because the resemblance of caffeine to a WTP's source water is unknown. HTC instruments may be prone to errors due to accumulation of nonvolatile residues in the combustion chamber, which leads to false, continuously changing background carbon levels (blank contamination). Due to these design peculiarities, more variability is to be expected within HTC instruments and between HTC and oxidation instruments. Oxidation instruments were not significantly different to HTC in oxidizing any OC particulates that may have been present at the study stations, despite the wide spectrum of environmental matrices analyzed. This suggested that HTC data are not inherently superior to oxidation for ecological studies in the Delta, where particulate OC is of added interest.

Comparisons to DBPR1 TOC Removal Criteria

There were no significant differences in potentially prescribing WTP enhanced coagulation between instruments. The lack of differences can be explained by examining the DBPR1 TOC removal criteria, which have fairly wide intervals. Only Hood could consistently fall in the first interval (no TOC removal) at $< 2 \text{ mg L}^{-1}$ during the period sampled. The second interval (TOC > 2 and $\leq 4 \text{ mg L}^{-1}$) has a width of 2 mg L^{-1} . The third interval (TOC > 4 and $\leq 8 \text{ mg L}^{-1}$) is 4 mg L^{-1} wide. The fourth interval is

open-ended (TOC $> 8 \text{ mg L}^{-1}$). The width of these intervals mean that one instrument would have to report a very low TOC value and the second instrument a very high value for there to be a difference in the TOC removal prescribed by the pairs of instruments at a WTP. However, boxplots of TOC at the study stations show that, with the exception of instrument 1, most instrument distributions overlapped during the course of the year so that the results fell inside the same TOC removal intervals. This could explain the lack of significant differences between instruments in potentially prescribing TOC removal if the sampling sites were WTPs.

Study results agree with EPA that the analytical methods are comparable. The observed differences are likely due to IC removal problems for some instruments. The study did answer DWR's concerns regarding OC carbon instruments using different methods. The study disproved assumptions that HTC data are significantly superior to oxidation data for ecological or drinking water quality management uses in the Delta.

CONCLUSIONS

Our results do not indicate that HTC instruments produce significantly higher TOC results than oxidation at sites with more complex OC matrices in the Delta and

its watersheds. Also, there were no results that indicated HTC instruments would significantly increase the frequency of TOC removal at a WTP when compared to oxidation instruments. The study showed that when operating properly, both HTC and oxidation instruments are adequate at analyzing organic carbon as typically found in the SWP.

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