

Ionic Strength and DOC Determinations from Various Freshwater Sources to the San Francisco Bay

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Recent work in marine systems have indicated that high-temperature ($>400^{\circ}\text{C}$) catalytic oxidation techniques may be more effective than low-temperature ($<100^{\circ}\text{C}$) wet chemical methods in oxidizing dissolved organic carbon (DOC) to carbon dioxide, possibly because of the interference of chloride (Sharp 1973; Sugimura and Suzuki 1988; Williams and Druffel 1988). It was hypothesized that some organic carbon is resistant to complete oxidation by the persulfate in the high ionic strength (I) matrix of seawater. Sharp (1973) observed significant differences between low- and high-temperature techniques for total organic carbon measurements in samples taken from the central western North Atlantic Ocean. For example, a DOC concentration of 0.81 mg-C/L was determined using persulfate oxidation whereas 1.31 mg-C/L was measured using high-temperature combustion from samples taken at 150–400 m in depth. Samples taken below 400 m exhibited an average discrepancy between methods of 0.3 mg-C/L with persulfate oxidation consistently yielding lower values.

In the San Francisco Bay, there is a negative correlation between measured DOC and salinity indicating freshwater sources of DOC (Kuwabara et al. 1989; Ota et al. 1989). In addition, significant positive correlation between DOC and dissolved metals (Cu and Zn), and results of chemical speciation calculations indicate that chemical association between dissolved organic matter and trace metals can potentially control speciation and hence bioavailability of certain metals. An accurate determination of DOC within this salinity (or ionic strength) gradient is therefore important to better understand the extent to which DOC could affect metal speciation. This major, urbanized estuary offers an excellent opportunity to examine effects of ionic strength on DOC determination.

A low-temperature persulfate/oxygen/ultraviolet wet oxidation method was used for determination of DOC in samples that had been adjusted for ionic strength from major freshwater sources of the northern and southern reaches of San Francisco Bay. The ionic strength of samples was adjusted with a chemically defined seawater medium up to 0.7M (i.e., over the ionic strength range observed in the Bay). Therefore, modifications in the ionic strength of

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samples were directly proportional to the chloride ion concentration. Comparable experiments were also run using two chemically defined fulvic acid standards isolated from the Suwannee River.

The results of the low-temperature DOC determination method showed minimal effect of ionic strength (and hence chloride) on oxidation efficiency for DOC sources to the Bay over an ionic strength gradient of 0.0 to 0.7M. Similarly, no significant effects of ionic strength were observed for two Suwannee River fulvic acids. In all cases, observed effects related to ionic strength were smaller than differences observed in the marine environment between high- and low-temperature methods. Our results are discussed in terms of methodological differences.

MATERIALS AND METHODS

Water samples were obtained from six major freshwater sources draining into the northern and southern reaches of San Francisco Bay (Figure 1): the Sacramento River at Sacramento 97.5 river km up gradient from the eastern entrance to Suisun Bay; the Colusa Drain 38.3 km upstream of the Sacramento River site; the Guadalupe River in San Jose 19.8 km upstream from the South Bay; Coyote Creek 10.8 km upstream of the San Jose-Santa Clara Water Pollution Control Plant; and effluent from the Palo Alto Sewage Treatment Plant (PASTP) and the San Jose-Santa Clara Water Pollution Control Plant (SJWPCP). Treatment plant effluent constitutes a major freshwater point source to the South Bay especially during the typically dry summer and fall months and during drought conditions.

All glassware used for this procedure was initially soaked in a 1N HCl acid bath for at least 1 hr. They were then rinsed with low organic carbon laboratory water (< 0.1 mg-C/L), placed in a muffle furnace and baked at 450°C for at least 6 hr. Fluoroethylene polymer parts (e.g., filter holders and bottle caps) were washed in a chromic/sulfuric acid solution at 50°C for at least 1 hr then rinsed in low organic carbon water.

From the northern reach of San Francisco Bay, two replicate samples of 3L were taken from the Sacramento River (mid channel) at the Tower Bridge in Sacramento and from the Colusa Drain using an isokinetic fluoroethylene polymer sampler.

From the southern reach of San Francisco Bay, the water samples taken from the Coyote Creek and Guadalupe River were grab-sampled by submerging capped 1-L glass bottles. The caps were removed after the bottles were submerged, and replaced before the filled bottles resurfaced to avoid surface film contamination. Bottles were rinsed with ambient water before final samples were collected.

Samples from the Palo Alto Sewage Treatment Plant (PASTP) and the San Jose-Santa Clara Water Pollution Control Plant (SJWPCP) were obtained directly from effluent lines. Approximately 1L of water (2 replicates) was

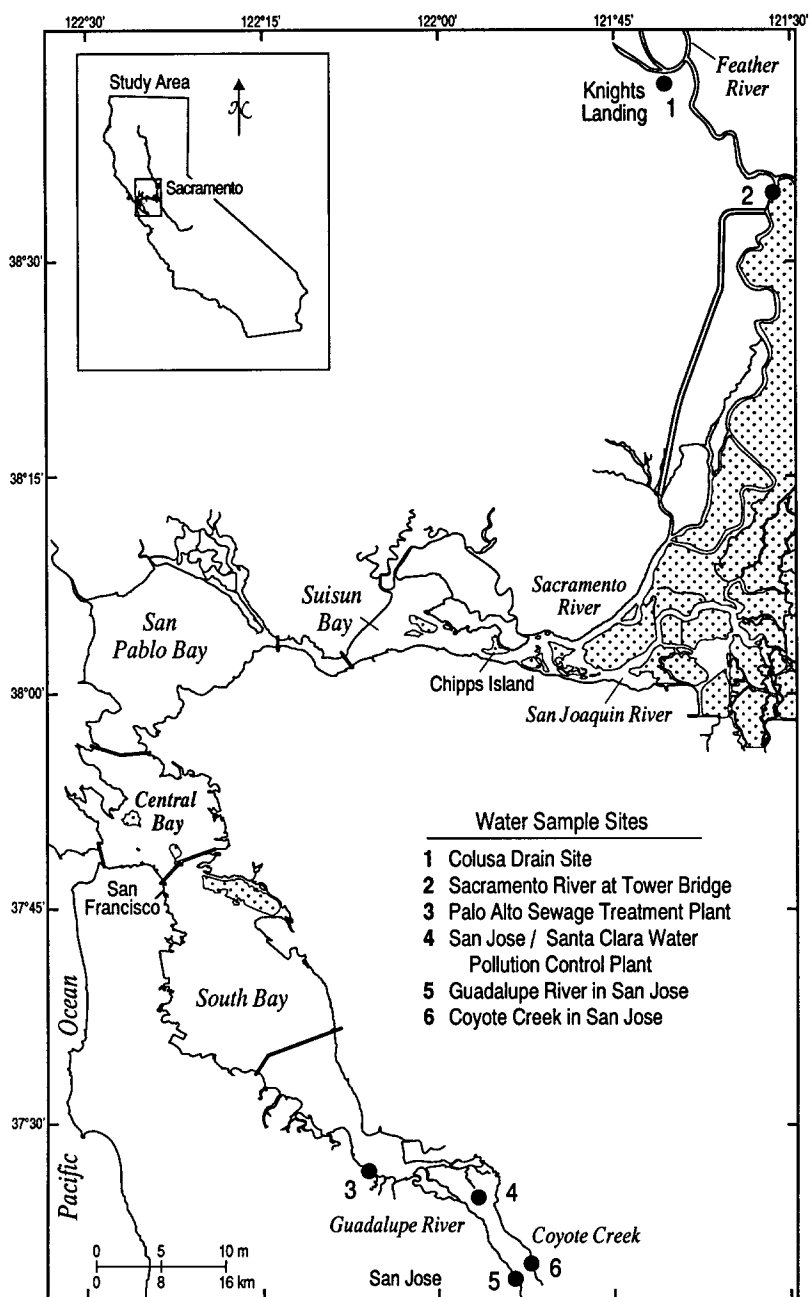


Figure 1. Sampling locations.

taken. Samples were vacuum filtered using 0.2 μm silver membranes (Poretics, 47mm, baked at 200°C for at least 1 hour), within one hour of sampling.

The ionic strength of water samples from each freshwater source was adjusted in increments of 0.1M up to 0.7M initially with a major salts solution twice the concentration of standard ocean water (2xSOW), prepared with the following salts: sodium chloride (NaCl), calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), potassium chloride (KCl), sodium sulfate (Na_2SO_4), sodium bicarbonate (Na_2HCO_3), and magnesium chloride ($\text{MgCl}_2 \cdot \text{H}_2\text{O}$). Using this chemically defined seawater matrix, changes in the sample ionic strength were directly proportional to changes in chloride ion concentration. Therefore, in the context of our experiments, subsequent references to "chloride effects" and "ionic strength effects" are used interchangeably. Efficiency of organic carbon oxidation was also determined using two Suwanee River fulvic acid standards (i.e., of defined elemental composition) over the same ionic strength range. One standard was filtered with a silver membrane (hereafter referred to as Suwanee/Silver; 54.2% carbon by weight) and the other was glass-fiber filtered for comparison (hereafter referred to as Suwanee/GF; 55.0% carbon by weight). Statistically, the effect of ionic strength was evaluated by least squares determination of the slope of the line generated by all measured DOC concentrations over the entire ionic strength range (i.e., only first-order effects were estimated). The 95% confidence interval was used to test for the significance of the slope.

DOC concentrations were determined by persulfate/oxygen/ultraviolet oxidation (Dohrmann DC-80 Total Carbon Analyzer). Unlike conventional ampoule methods, samples were injected into a reaction vessel containing an oxidizing reagent. The reagent was prepared according to the manufacturer's specifications for high ionic strength samples (30.0 mM reagent grade HgCl_2 , 28.0 mM reagent grade $\text{HgNO}_3 \cdot \text{H}_2\text{O}$, 74.0 mM reagent grade $\text{K}_2\text{S}_2\text{O}_8$, and 80 mM reagent grade HNO_3). The reagent was prepared in a 1-L batch on the morning of the analysis using low DOC laboratory water (Sybron/ Barnstead Organicpure, D3600; < 0.1 mg-C/L). Before analysis, samples were acidified to pH 2 and sparged with ultra-high-purity grade O_2 to remove dissolved inorganic carbon. Carbon dioxide produced by the DOC oxidation was measured by an Infrared gas detector (Horiba, model PIR 2000) using O_2 as the carrier gas.

The instrument was calibrated at least once daily using phthalic acid ($\text{C}_6\text{H}_4\text{-1,2-}(\text{CO}_2\text{H})_2$) standards to check for drift in instrument sensitivity. Baseline drift was also monitored between each sample injection. DOC measurements were recorded along with the amount of time required for sample digestion (instrument truncates the CO_2 signal after 7 min of sample digestion). Injection volumes of either 0.2 or 1.0 mL were typically used. Lower (0.2 mL) injection volumes and alternating injections of sample and water blanks were used in the case of high ionic strength samples in order to minimize the accumulation of salts in the reaction vessel. A blank test was done to determine if the instrument was significantly contributing to the measured DOC, as observed for instrument blanks in high-temperature catalytic devices. Injection volumes (0.2 to 1.0 mL) were also adjusted to keep measured DOC values within the linear range of the instrument.

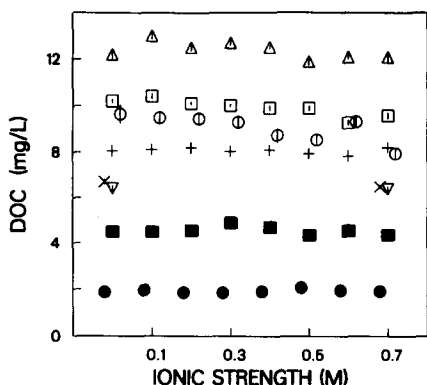


Figure 2. DOC concentrations ($n \geq 3$, with standard error bars) from all freshwater sources as a function of adjusted ionic strength. Symbols designating sampling locations are as follows: Guadalupe R. on July 22, 1991 (Δ), PASTP (\square), Coyote Cr. on July 25, 1991 (\circ), Coyote Cr. on July 6, 1992 ($+$), SJWPCP (\times), Guadalupe R. on July 25, 1991 (∇), Colusa Drain (\blacksquare), and Sacramento R. (\bullet).

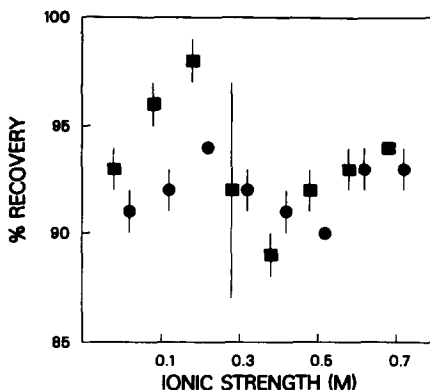


Figure 3. Measurements of DOC recovery with standard error bars relative to adjusted ionic strength using two fulvic acid standards. Closed square (\blacksquare) and circular (\bullet) symbols denote data for Suwanee/Silver and Suwanee/GF fulvic acids, respectively.

RESULTS AND DISCUSSION

DOC data from diverse freshwater sources to the bay indicated minimal ionic strength effects up to $I = 0.7M$ (Figure 2). Standard errors about the mean were typically about 0.10 mg-C/L at each ionic strength but as high as 0.4 mg-C/L for the 1991 Coyote Creek Sample at ambient ionic strength. At the 95% confidence level, $n \geq 24$, the decrease in measured DOC with increase in ionic strength was statistically significant for our initial sampling of Coyote Creek, Guadalupe River and the Palo Alto Sewage Treatment Plant (Table 1). The Guadalupe River was resampled on July 25, 1991 to confirm the results of July 22, 1991. The second Guadalupe River series showed no ionic strength effect (Figure 2) and a 50% drop in DOC concentration (approximately 12 down to 6 mg/L). The sampling dates were only three days apart, during a period of no rainfall. Therefore, one would not expect pronounced changes in stream discharge due to natural processes (e.g., runoff or ground water inflow). We attribute this variability in results to dilution effects resulting from an 8-fold increase in discharge (daily average of 0.0031 m^3/sec on July 22, 1991 to 0.0250 m^3/sec on July 25, 1991) at the site (Trujillo et al. 1991), that is affected by regulated flow from Lexington Reservoir, located 19 km upstream. Similarly, experiments repeated on water samples collected from the Coyote Creek site approximately one year after our initial sampling did not indicate an ionic strength effect at the 95% confidence interval. Unlike the Guadalupe River, flow of Coyote Creek near our sampling site is not monitored. Therefore, we

Table 1. Significance (95% confidence level) of effects due to ionic strength on DOC determinations for major carbon sources to the San Francisco Bay and two chemically defined fulvic acid standards.¹

SITE	DOC	Slope	Significance
GUADALUPE RIVER 7/22/91	12.2 ± 0.2	-0.83±0.74	yes
GUADALUPE RIVER 7/25/91	6.40 ± 0.14	*	no
COYOTE CREEK, 7/25/91	9.64 ± 0.40	-0.46±0.23	yes
COYOTE CREEK, 7/6/91	8.06 ± 0.12	-0.34±1.33	no
PASTP	10.2 ± 0.1	-1.24±0.46	yes
SJWPCP	6.20 ± 0.13	*	no
COLUSA DRAIN	4.50 ± 0.19	-0.12±0.45	no
SACRAMENTO RIVER	1.88 ± 0.07	0.13±0.21	no
SUWANEE/SILVER	5.06 ± 0.03	-0.15±0.41	no
SUWANEE/GF	4.28 ± 0.04	0.07±0.22	no

¹ DOC concentrations (mg-C/L, n=3) for freshwater samples at ambient ionic strength are also shown with standard errors. Symbol "*" indicates that replicate samples (n=3) were run at 0.0 and 0.7M ionic strengths only, and no significant difference between data at the two ionic strengths was determined by t-test (P<0.05).

can only speculate from these results that the composition of the dissolved organic matter varied between sampling dates.

Additional data were obtained from tests performed using phthalic acid standards at higher ionic strengths up to I= 4.8M. The increase in ionic strength, again, did not cause significant decrease in measured DOC. In fact, in initial determinations at the higher ionic strengths of I= 4.0M and I= 4.8M there was an apparent increase in DOC concentrations. As mentioned in the previous section, this "carry-over" effect with inefficient DOC digestion at the high ionic strengths was mitigated by reducing sample injections to 0.2 mL and alternating injections of low organic carbon water to dilute the ionic strength in the reaction vessel.

Experiments using fulvic acids isolated from the Suwanee River indicated that ionic strengths up to 0.7M had an insignificant effect on measured DOC (Figure 3). Organic carbon recovery for both standards were consistently high (typically > 90%).

Although in the initial results from Coyote Creek, Guadalupe River and Palo Alto Sewage Treatment Plant, DOC significantly decreased with an increase in

ionic strength, the effect was small (13%, 8% and 5% decrease, respectively for the sites over the 0.0 to 0.7M ionic strength range, Figure 2). By comparison Sharp (1973) observed a decrease in DOC of approximately 0.5 mg-C/L (i.e., a decrease of approximately 22%) when marine samples ($I=0.7M$) were analyzed by persulfate oxidation relative to high-temperature combustion, suggesting a much stronger chloride (ionic strength) interference for their oceanic samples using their analytical techniques. The results of our blank test indicated a relatively small amount of carbon being added by the low-temperature instrument (0.07 ± 0.04 mg-C/L at a 1-mL blank injection; corresponding to the maximum sample injection volume). In contrast to high-temperature catalytic methods, our measurements on blank injections did not significantly increase with injection volumes between 0.0 and 1.0 mL.

Samples analyzed here represent a high diversity in organic carbon sources (industrial, agricultural, and municipal). Although observed ionic strength effects were typically insignificant for this wide range of samples, exceptions (viz. the initial Coyote Creek and Guadalupe River samples and Palo Alto Sewage Treatment Plant effluent) indicate that certain organic compounds might have been incompletely oxidized by our low-temperature method. However, this effect is consistently small (< 13% decrease) over the ionic strength range.

Although the inconsistency between our results and those from previous marine studies could be due to differences between the composition of dissolved organic substances in the oceanic environment and the various sources to estuarine environments, we propose that a pronounced chloride interference was not observed in our experiments because of methodological differences. First, unlike low-temperature ampoule methods, our samples (0.2 to 1.0 mL) were injected into a reaction vessel (68 mL) containing the persulfate reactor reagent described above, exposed to UV radiation, and bubbled with ultra-high-purity grade O_2 to facilitate organic carbon oxidation. Chloride concentrations in high ionic strength samples were thereby diluted, presumably to a point below which interferences were manifest. Second, mercuric compounds were added to the reactor reagent to effectively complex with chloride in the sample and hence mitigate the effect. Future access to a high-temperature catalytic oxidation instrument planned within our organization will allow us to directly quantify methodological effects using estuarine and marine samples. Results presented herein indicate that these differences should not be pronounced if they are primarily generated by chloride interferences.

The biogeochemical implications of our results should be noted. Kuwabara et al. (1989) observed a strong correlation between measured DOC and dissolved copper and zinc. Using available thermodynamic data describing metal-humate complexation from other estuaries, chemical speciation calculations indicated that metal speciation (and hence bioavailability) was controlled by humate complexation for copper but not for zinc. Two explanations for this discrepancy between observed and modelled results for zinc have been proposed. First, we proposed that the thermodynamic data for humate complexation reported for other aquatic systems may not account for the

diversity of organic ligand inputs to San Francisco Bay (Kuwabara et al. 1989). Certain organic ligands present in the bay may have a higher affinity for zinc complexation than indicated by our thermodynamic data set. Association constants for zinc complexation with dissolved organic matter from San Francisco Bay are being directly determined by others using polarographic methods. Results from these studies will test our hypothesis. An alternative hypothesis is that our low-temperature analytical technique may have underestimated the DOC concentrations due to chloride (or ionic strength) interference, analogous to observations reported by others in marine studies. Hence, a higher concentration of organic ligands may have been available for zinc complexation. We now reject this hypothesis because the minimal ionic strength effects reported herein cannot account for a shift in chemical speciation control to zinc complexation with dissolved organics.

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