

1994

Ionic strength effects on dissolved organic carbon determinations from freshwater inputs to the San Francisco Bay

Yvonne Rivera
San Jose State University

Follow this and additional works at: https://scholarworks.sjsu.edu/etd_theses

Recommended Citation

Rivera, Yvonne, "Ionic strength effects on dissolved organic carbon determinations from freshwater inputs to the San Francisco Bay" (1994). *Master's Theses*. 949.
DOI: <https://doi.org/10.31979/etd.y2z7-wrn7>
https://scholarworks.sjsu.edu/etd_theses/949

This Thesis is brought to you for free and open access by the Master's Theses and Graduate Research at SJSU ScholarWorks. It has been accepted for inclusion in Master's Theses by an authorized administrator of SJSU ScholarWorks. For more information, please contact scholarworks@sjsu.edu.

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI

A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600

IONIC STRENGTH EFFECTS ON
DISSOLVED ORGANIC CARBON DETERMINATIONS FROM
FRESHWATER INPUTS TO THE SAN FRANCISCO BAY

A Thesis

Presented to

The Faculty of the Department of Geography
and Environmental Studies

San Jose State University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by

Yvonne Rivera

December, 1994

UMI Number: 1361208

Copyright 1994 by
Rivera, Yvonne
All rights reserved.

UMI Microform 1361208
Copyright 1995, by UMI Company. All rights reserved.

This microform edition is protected against unauthorized
copying under Title 17, United States Code.

UMI

300 North Zeeb Road
Ann Arbor, MI 48103

©1994
Yvonne Rivera
ALL RIGHTS RESERVED

APPROVED FOR THE DEPARTMENT OF
GEOGRAPHY AND ENVIRONMENTAL STUDIES

Lynne Trulio

Dr. Lynne Trulio, Assistant Professor of
Environmental Studies Committee Chairperson

Rhea L. Williamson

Dr. Rhea Williamson,
Professor of Civil Engineering

James S. Kuwabara

Dr. James Kuwabara, Hydrologist
U. S. Geological Survey

APPROVED FOR THE UNIVERSITY

M. Lon Lenczowski

ACKNOWLEDGEMENTS

I would like to thank Dr. J.S. Kuwabara at the U.S. Geological Survey for all his help, patience and advice throughout this study, and for allowing me the use of the appropriate resources that made this study possible. I would also like to thank Dr. Lynne Trulio and Dr. Rhea Williamson for their valuable suggestions and comments, without which this thesis would not be complete. In addition I would like to thank my father for the encouragement to attain a higher education, and my husband for supporting my decision to do so.

TABLE OF CONTENTS

ABSTRACT	iii
ACKNOWLEDGEMENTS	iv
LIST OF FIGURES	vi
LIST OF TABLES	vii
Chapters	
1. INTRODUCTION	1
Background regarding DOC and DOC methods	
Background regarding the San Francisco Bay	
Trace metals in the San Francisco Bay	
Purpose of Study	
2. STUDY AREA	16
North Bay	
South Bay	
3. MATERIALS AND METHODS	21
4. RESULTS	29
Results of Ionic Strength Experiments	
Results of International Intercalibration study	
5. DISCUSSION	41
Discussion related to this study	
Discussion of International Intercalibration Study	
6. CONCLUSION	47
LITERATURE CITED	49

LIST OF FIGURES

Figure	Page
1. Sites located in the Northern San Francisco Bay region indicating measured DOC concentrations and their measured salinity	9
2. Sampling locations of freshwater inputs to San Francisco Bay	17
3. DOC concentrations ($n \geq 3$, with standard bars) from all freshwater sources	30
4. DOC concentrations with standard error bars from three freshwater sources sampled in 1993	31
5. DOC concentrations measured for Coyote Creek sampled three consecutive years (1991, 1992, and 1993)	32
6. DOC concentrations for 8x SOW. DOC increase at $I=4.8M$ are believed to be caused by salt accumulation in the reaction vessel	34
7. Percent recovery of carbon for two Suwanee River fulvic acid standards (Silver and Balston)	36
8. DOC concentrations measured by HTO and LTWC methods. Marks between the two upper lines (approx. 30-40) depict analyses that fall within ± 7.5 percent of the expected DOC values for two samples, POW and SPOW. Analyst number for this thesis is 43	38
9. DOC concentrations measured by LTWC methods only. Marks between the upper lines (approx 80-90) and the two lower lines (approx 30-40), depict analyses that fall within ± 7.5 percent of the expected DOC values for two samples, POW and SPOW. Analyst number for this thesis is 43	40

LIST OF TABLES

Table	Page
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	19
2. Rainfall data for three North Bay sites and three South Bay sites, for three consecutive years (1991, 1992, and 1993)	22
3. Major salt solution concentrations for 2x SOW in 1 liter of solution	25

INTRODUCTION

The purpose of this study was to examine how dissolved organic carbon (DOC) measurements of freshwater samples from a variety of DOC sources to San Francisco Bay may be affected by changes in ionic strength. As a result of salinity changes, ionic strength changes are expected along a longitudinal gradient of the estuary.

This study is important because the analysis of DOC is believed to provide basic information in the understanding of the complex nature of organic compounds in aquatic systems. DOC concentrations must be accurately determined in order to understand the role and fate of DOC because of its potential ecological importance relative to carbon cycling and metal complexation (bioavailability).

There is presently some uncertainty within the scientific community regarding an appropriate means of measuring DOC. This is because there is believed to be a chloride interference which in high salinity (high ionic strength) samples causes incomplete oxidation of organic carbon into carbon dioxide. It has been asserted that low-temperature DOC procedures that employ persulfate oxidation are particularly susceptible to inefficient oxidation of organic compounds.

The various types of water which flow into the San Francisco Bay include municipal, industrial, agricultural, and fluvial sources (Hunter and Kuwabara, 1994). Because these sources are different in origin, they are potentially different in DOC composition. These differences provide an

excellent opportunity to determine if each source will be affected to a different extent by ionic strength changes typically observed between freshwater and seawater end members (i.e., fluvial and oceanic end points).

A low temperature technique using ultra violet (UV)/ oxygen (O₂)/ persulfate oxidation was used to determine the DOC concentrations of freshwater sources into the San Francisco Bay.

Background Regarding DOC and DOC Methods

Carbon is an important component of organic matter. It also represents a link between inorganic material and living organisms (Stumm and Morgan, 1981). Carbon serves as a macronutrient in all aquatic environments, and is critical for the survival, growth and productivity of organisms. In particular, DOC has been studied extensively because it can help to "...provide new explanations for the enigmas [e.g., carbon cycling, metal speciation, or bioavailability] associated with oceanic carbon..." (Suzuki et al., 1992, 186). On a global scale the ability to determine DOC concentrations in the oceans may help to better quantify carbon fluxes between the atmosphere and oceans (Peltzer et al., 1991). Also, this may enable scientists to better predict dangerous increases in the level of atmospheric carbon by use of global carbon models.

Many determinations of DOC concentrations in water have focused on the oceanic environment, where the ionic strength is approximately 0.7M (Motekaitis and Martell, 1987). These studies have been motivated by apparent methodological

problems associated with DOC determinations in the oceanic environment.

Sugimura and Suzuki (1988) suggested that there may be a much larger reservoir of carbon in the oceans that was not detected by low-temperature, wet chemistry (LTWC) methods. This has set off a globally organized attempt to determine accurate DOC values for high ionic strength samples, by means of method intercalibration (standard methods i.e., sample handling, blank determination and calibration of reference materials) (Wangersky, 1993).

Since Sugimura and Suzuki (1988) published their data, the lack of reproducibility has forced them to review their results and prior interpretations. They have since concluded that the previous work was incorrect and should not be used as a comparison for seawater DOC comparisons (Suzuki, 1993) even though some researchers have had success in reproducing Sugimura and Suzuki's elevated DOC concentrations (Hedges and Wangersky, 1993). This complicated situation has caused further confusion surrounding seawater analyses for DOC concentrations.

Previous work dealing with DOC in the San Francisco Bay water column has determined that there exists a negative correlation between DOC and salinity (i.e., DOC concentrations decline as salinity increases), suggesting freshwater sources of DOC (Kuwabara *et al.*, 1989; Kuwabara and Luther, 1993). This is because oceanic DOC concentrations are typically lower than in freshwater inputs to San Francisco Bay (Kuwabara and Luther, 1993). Using a low-temperature DOC method, a positive correlation between

DOC and dissolved metal concentrations was observed (as DOC increases so does metal concentrations) (Kuwabara et al., 1989). Results of chemical speciation calculations indicated that chemical associations between dissolved organic matter and trace metals can control chemical speciation and thus bioavailability of certain biologically reactive metals. The survival and growth of aquatic organisms maybe adversely affected by elevated concentrations of metals in biologically available forms (Kuwabara et al., 1989). DOC represents dissolved organic matter that has a high affinity to bind with the trace metals to form complexes which are less available for uptake from solution by benthic and planktonic organisms (Kuwabara et al., 1989). An accurate determination of DOC within the salinity gradient is therefore important in order to better understand to what extent DOC may affect the biological availability of trace inorganic contaminants.

The sources and sinks of organic carbon in the San Francisco Bay have been studied to determine the importance of DOC in the carbon cycle. Carbon sources in the San Francisco Bay (values differ between the North and South Bay) include two major sources: autochthonous (i.e., generated within the aquatic system) primary production by microalgae (phytoplankton) and fluvial inputs of allochthonous (i.e., generated externally) organic carbon (Jassby et al., 1993). Jassby et al., (1993) identified the primary sink for organic carbon in the South San Francisco Bay as the respiration of planktonic and benthic organisms. Organic carbon in the San Francisco Bay fluctuates from year to year and the biological and ecological implications of this variability are presently

unknown (Jassby et al., 1993). Analogously, on a global scale, it is very important that the carbon fluxes between the ocean, atmosphere and sediment be understood. Our limited understanding of these fluxes prohibits future predictions of current trends of increased anthropogenic pollution and its impacts on our environment (Brewer et al., 1986). Until these interactions and cycles are more completely understood, the effects of an increase or decrease of carbon into or out of aquatic systems may be difficult to relate to biological response. In addition, appropriate environmental regulations will be difficult to justify without accurate measurements of important variables such as DOC.

Although there are numerous analytical techniques for measuring DOC; methods can typically be classified into 2 major groups: high-temperature catalytic oxidation (HTCO) methods which use oxidizing temperatures greater than 400°C, and low-temperature wet chemistry (LTWC) methods which use temperatures less than 100°C. The disparate DOC values produced from these techniques have caused controversy within the scientific community (Williams and Druffel, 1988). Numerous researchers hypothesize that the discrepancy observed between these two methods is at least in part due to elevated chloride concentrations, i.e. high ionic strength, in marine samples (Peyton, 1993; Wangersky, 1993). A chloride interference observed with use of LTWC methods are believed to prohibit complete oxidation of organic carbon into carbon dioxide. Therefore, DOC determinations of high

ionic strength samples by all LTWC have been suspected to underestimate actual DOC concentrations.

Peyton (1993) described the processes that result in the chloride interference. The elevated chloride in seawater is believed to bind with sulfate radical anions (SRA) which are present in the persulfate reactor reagent. Chloride ions compete against oxygen for complexation with the SRA and consequently interfere with oxidation of the organic carbon. Organic carbon in the sample must be oxidized to carbon dioxide for accurate DOC measurement (typically by infrared detection of CO₂). If oxygen is out competed for SRA binding sites by chloride, then incomplete oxidation occurs and actual DOC levels are underestimated (Peyton, 1993).

This current hypothesis suggests that all LTWC methods for DOC analysis of high ionic strength samples are relatively inefficient as compared to HTCO methods (Sharp, 1973; Williams and Druffel, 1988; Suzuki *et al.*, 1992). This would also suggest that DOC concentrations determined by Kuwabara *et al.*, (1989) in San Francisco Bay were also underestimated because of their use of an LTWC method used over a longitudinal salinity gradient.

Past studies have indicated discrepancies between results obtained by LTWC and HTCO methods. Sharp (1973) observed differences in results of DOC concentrations obtained by the use of high and low temperature methods of analysis for samples taken in the central-western area of the North Atlantic Ocean. The values obtained by the use of a HTCO method were nearly two times the values determined by LTWC.

Williams (1975) reported that two teams of researchers doing studies on DOC (Menzel and Vaccaro, 1964; Gordon and Sutcliffe, 1973), both concluded in their DOC studies that the LTWC method gave lower seawater concentrations of DOC as compared to the HTCO method. Again, an interference by chloride was believed to be the cause of the deviation. Different methods of analysis for high ionic strength samples suggest that the interference of chloride may be mitigated with HTCO. Sugimura and Suzuki (1988) used a HTCO technique which they claimed yielded 100 percent recovery for many of the reference materials tested (three of four reference materials used). They did not observe a chloride interference in the oxidation of carbon using their HTCO method even when there was a deliberate addition of salts (chloride, sulfate and fluoride) to the seawater being tested.

Background Regarding the San Francisco Bay

The San Francisco Bay is a unique estuarine system because it is a hydrodynamically, chemically and biologically complex system and it is severely impacted by urbanization. The estuary is divided into three hydrodynamically distinct components: North Bay, Central Bay and South Bay (Smith and Flegal, 1993; Smith, 1987). In the North Bay, primary freshwater inflow is received from the Sacramento River and the San Joaquin River (Smith and Flegal, 1993; Smith, 1987; Jassby et al., 1993). These two sources have been consequently determined to be major influences in regulating the chemical composition of the northern component. The

South Bay on the other hand, has been determined to be minimally influenced by the small inputs of freshwater from local tributaries (Jassby et al., 1993) and is impacted to a greater extent by anthropogenic inputs from freshwater discharges (i.e., municipal and industrial discharges) (Smith and Flegal, 1993).

Although the North and South Bay have different sources of inputs and are found to vary in chemical and biological composition, certain trends in DOC concentration are similar. Kuwabara and Luther (1993) found that in the North Bay, DOC concentration significantly increased along the salinity gradient from saltwater to freshwater and declined with depth due to a vertical salinity gradient. In the shallow South Bay, DOC also increased with proximity to freshwater sources, but no concentration gradient with depth was observed (Kuwabara and Luther, 1993).

Other sources (e.g., oils and greases from oil refineries located in the North Bay and urban runoff) which may enter the Northern component of the Bay do not appear to significantly alter DOC concentrations. Kuwabara et al., (1994) studied the Northern component of the Bay and observed a linear relationship between salinity and DOC (Figure 1). If excess hydrocarbons (carbon) from oils and greases were added to the Bay, then the DOC-salinity trend would depart from linearity near the source areas.

The Central Bay is characterized by a deep narrow channel which connects the Northern and Southern components. Freshwater moves through this channel and is carried throughout the Bay and out to the Pacific Ocean (Russell et

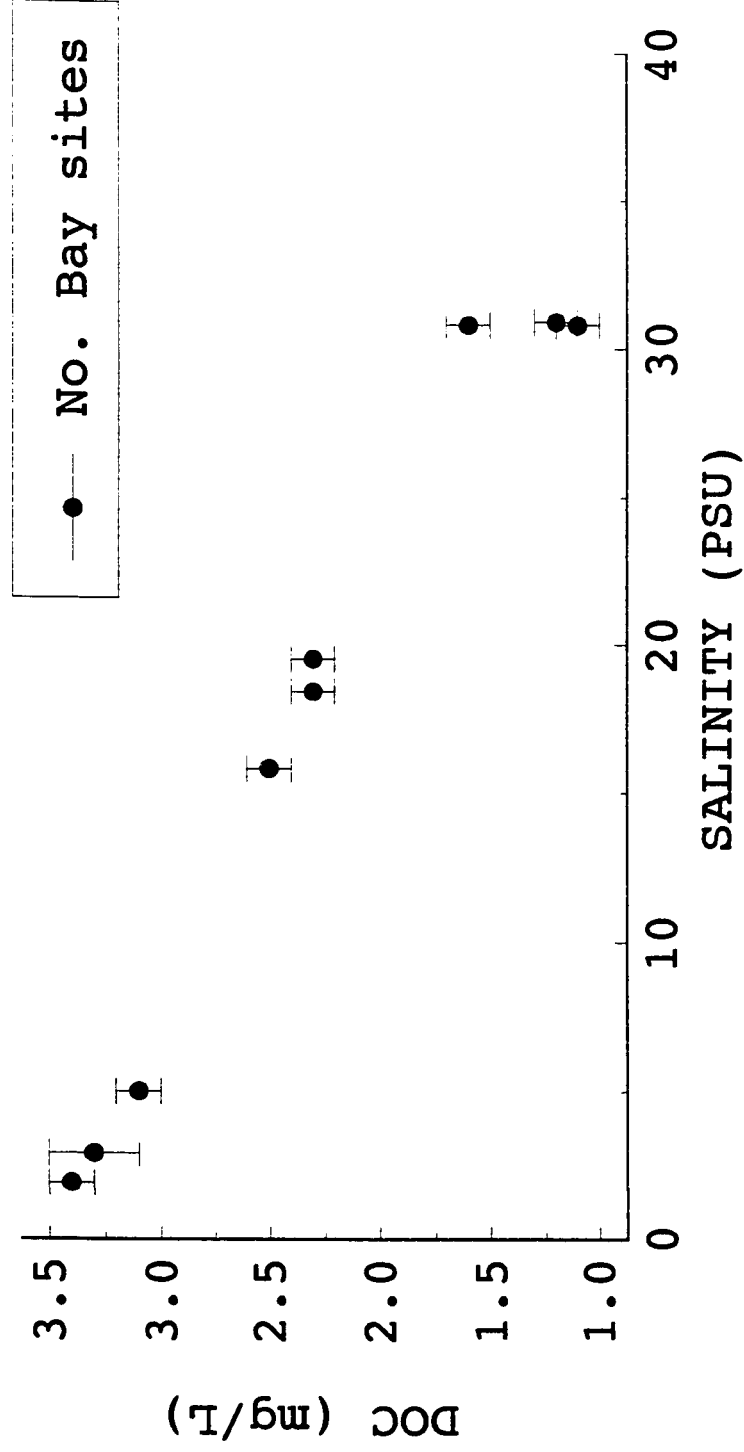


Figure 1. Sites located in the Northern San Francisco Bay region indicating measured DOC concentrations and their measured salinity. Source: Modified from Kuwabara et al., (1994).

al., 1982). The Central Bay can heavily influence the South Bay during times of low discharge from the Delta when, the South Bay can have salinities similar to the Central Bay (Smith, 1987). The Central Bay is important for flushing and mixing important components throughout this system, but not much is known about organic carbon sources and sinks (Jassby et al., 1993) and is not often studied. This study focused on freshwater sources to the Northern and Southern components where longitudinal salinity gradients are typical.

Trace Metals in the San Francisco Bay

As a result of an increase in anthropogenic activities (increase in population, expansion of industry and agriculture), the San Francisco Bay and the processes (hydrological, biological, chemical, etc.) which occur there are becoming so severely impacted that chemical and physical variables are being altered (Smith, 1987). The extent to which these variables are affected, and how they in turn affect the biota has been a difficult task for scientists to access. More information and a better understanding of these delicate and extremely important interactive processes are required.

In order for ecological implications to be predicted (modeled) and impacts possibly prevented, identification and quantification of the problems and relevant processes are necessary (Kuwabara et al., 1986). Trace metals are among many variables which are potentially problematic in the San Francisco Bay. Trace metals are involved in important

biological and chemical processes which occur in the Bay, some of which are necessary for growth of planktonic species. In suboptimal conditions, symptoms of deficiency may result. Conversely, trace metals in excess quantities (sometimes even at submicro molar concentrations) can cause toxic effects. Because of this, it is extremely important that processes regulating trace metal processes (dispersion, diffusion, complexation, nutrient uptake, etc...) (Kuwabara et al., 1986) are also understood. Trace metals may be one of several factors which regulate the growth of planktonic communities. The extent to which these metals (e.g., copper and zinc) affect plankton growth is important information for water quality management decisions. (For example, the U.S. EPA and San Francisco Regional Water Quality Control Board are presently involved in setting a site-specific copper standard for San Francisco Bay). In addition, it is absolutely crucial that we know how these metals enter the Bay, in what concentrations they are found, and in what forms they become available for biological uptake, because they may be detrimental to the aquatic organisms which live there.

Kuwabara et al., (1989) found that copper and zinc were indirectly correlated with salinity and directly correlated with DOC, suggesting that copper and zinc speciation is controlled by metal-humic material complexation in the South Bay. Results from their calculations (by use of a computer model) for metal speciation, led them to conclude that: 1) zinc did not behave as copper did in forming metal-humic complexes, and that 2) high metal ion activity may be a factor that controls growth of some planktonic species in the

South Bay. However, in light of their use of a LTWC technique, the implications of their results may need to be reconsidered if ionic strength effects are significant for their analytical method.

Purpose of Study

Numerous DOC studies suggest that DOC results will vary depending on the analytical method used. As discussed earlier, the methods used can be grouped into: high-temperature catalytic oxidation (HTCO) methods and the low-temperature wet chemistry (LTWC) methods. The DOC values resulting from these techniques have caused controversy within the scientific community (Williams and Druffel, 1988).

The scientific community has yet to come to an agreement on the most appropriate method to determine DOC concentrations in high salinity environments. Values obtained from HTCO were reportedly higher by 22 percent over those of LTWC values (Sharp, 1973), and 50 percent to 400 percent higher in other studies (Williams and Druffel, 1988). The inability to determine why there is such a wide range of differences, which values are correct, and which methods are more reliable is a complicated matter which must be resolved. On a global scale, this controversy must be resolved to make an accurate determination of the oceanic DOC pool and other reservoirs within the carbon budget (Williams et al., 1993).

Previous studies that concentrated on the oceanic environment (Sharp, 1973; Sugimura and Suzuki, 1988) have determined that there is a decrease in measured DOC with an increase in salinity. Accurate determinations of DOC

concentrations is important and may be done by taking the known salinity in the Bay over the salinity gradient, and determining if the salinity affects DOC measurements.

The results of this study will be applicable to questions such as: 1) how an essential macronutrient (DOC) is cycled within in an estuarine environment and 2) the chemical speciation of metals and the resultant bioavailability of these trace inorganic contaminants. Relevance of the results of this study to water quality standards set for the San Francisco Bay will be examined and discussed.

Given the assertion that all LTWC methods are susceptible to ionic interferences, the purpose of this thesis was to: 1) examine the effect of ionic strength on freshwater sources to the San Francisco Bay, 2) to shed light on the question of which methods provide acceptable accuracy and 3) to examine a variety of freshwater sources to the San Francisco Bay for their DOC concentrations. These results may be applicable to local regulatory issues as well as research into the global carbon budget.

This project focuses on DOC measurements for a diverse range of freshwater sources which flow into the North and South Bay. This project has four components: 1) collect freshwater samples representing major inputs into the San Francisco Bay (municipal/ industrial, agricultural and natural sources) 2) artificially impose an ionic strength gradient using these freshwater samples by the addition of a Standard Ocean Water (SOW) matrix, 3) statistically examine the data and give a quantitative description of the

significance of ionic strength effects on organic carbon oxidation and how this may affect the DOC concentration generated by the LTWC method, 4) examine the implication of these results on water quality issues and 5) examine the variability of results from the LTWC method used for this study relative to others participating in the International Intercalibration Study.

This study examines the DOC concentrations of six diverse freshwater inputs that flow into the San Francisco Bay. Two of the freshwater samples flow into the North Bay while the remaining four flow into the South Bay. Upon entering the estuary, the DOC from these freshwater sources mix and combine with oceanic waters to form a longitudinal salinity gradient that ranges between 0 and 35 psu (practical salinity units or 0.0M to 0.7M ionic strength). This study will attempt to answer the following questions:

- 1) Will increase ionic strength (over the range observed in San Francisco Bay) of freshwater samples cause a significant decline in the oxidation efficiency of the organic carbon to carbon dioxide using a LTWC technique?

- 2) What are the implications of observed ionic strength effects on interpretations of past DOC data for estuaries and other aquatic systems?

- 3) If there is a change in the oxidation efficiency relative to ionic strength, how do the changes compare to those observed in previous marine studies?

- 4) How do DOC values from the various types of freshwater inputs to the San Francisco Bay differ between a drought year and one which had above normal rainfall?

5) Does the HTCO methodologies give better results than those obtained from the LTWC method used for this study?

STUDY AREA

North Bay

Water samples were taken from two North Bay sites (Figure 2). These sites included the Sacramento River and the Colusa Drain. The Sacramento River was sampled at the Tower Bridge in Sacramento CA, which is located 97 km up-gradient from the eastern entrance to Suisun Bay. The Colusa Drain (an agricultural drain) was sampled at Knights Landing, and is located 38.3 km upstream of the Sacramento River site.

The Sacramento and San Joaquin rivers are the two major freshwater sources for the northern reach of the San Francisco Bay. Estimated total drainage volume of these rivers are approximately 8631 acre-feet (AF), 9698 AF, and 24,210 AF for three consecutive years 1991, 1992, and 1993 respectively (Markham et al., 1991; Anderson et al., 1992; Mullen et al., 1993). The amount of water which is delivered to the San Francisco Bay on a monthly basis varies especially between the wet winter and spring months and the dry summer and fall months.

The fluctuations in discharge from the Sacramento and San Joaquin Rivers cause concentration and transport variations of dissolved and particulate substances in the North Bay (Schemel et al., 1989). Fluctuations are caused mostly by river diversions and withdrawals by agriculture and other uses. The important diluting and flushing actions of the Sacramento River made this an ecologically important sampling site for this study.

The Colusa Drain is also a source of freshwater for the

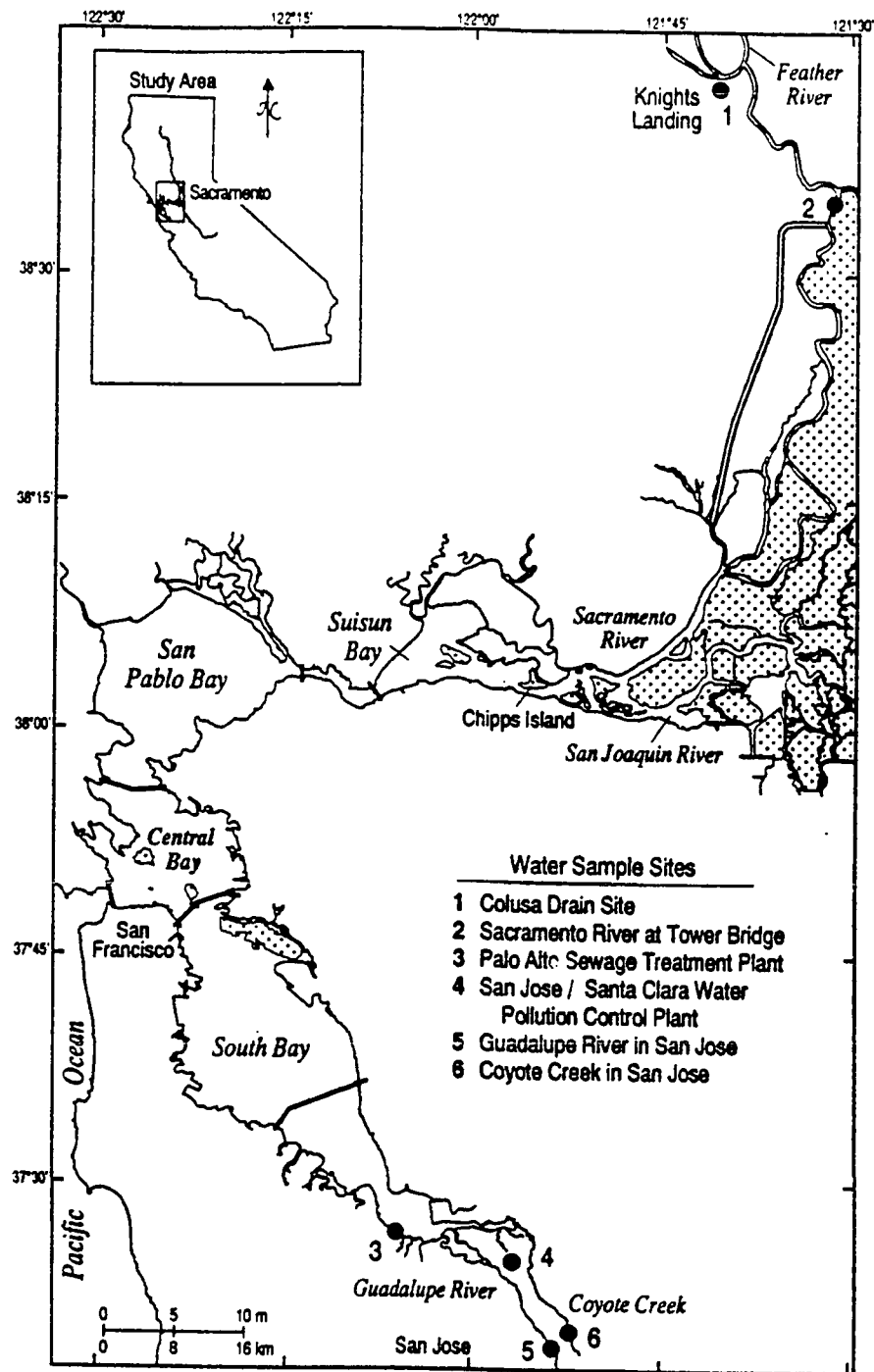


Figure 2. Sampling locations of freshwater inputs to San Francisco Bay.
 Source: Modified from Hunter and Kuwabara, (1994).

San Francisco Bay via the Sacramento River. It influences and supplies dissolved and particulate substances to the Sacramento River, and hence to the North Bay including pollutants from runoff of agricultural pesticides and herbicides (Schemel *et al.*, 1989).

South Bay

South San Francisco Bay is quite a contrast to the North Bay. It is, for example, more heavily impacted by anthropogenic inputs of municipal water treatment plants (Smith, 1993). The South Bay receives most of its freshwater from Coyote Creek and from municipal sewage treatment plants. Coyote Creek provides freshwater mostly during the wet winter months. The municipal sewage treatment plants discharge freshwater all year long and are the South Bay's primary freshwater source (Kuwabara *et al.*, 1989; Cutter *et al.*, 1990).

Coyote Creek was sampled in the summer of 1991, 1992, and 1993 (Table 1). The site location was located 10.8 km upstream of the San Jose-Santa Clara Water Pollution Control Plant. Three consecutive years of sampling were performed to compare DOC concentrations between two drought years and one year with almost normal rainfall (1993).

The Guadalupe River is a freshwater source to the South Bay. The location of the sample site was within the city of San Jose, about 19.8 km upstream from the South Bay. The U.S. Geological Survey maintains a discharge station at this site. It is used to represent the amount of water that passes a water-recharge zone and the amount of water that is

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. 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 ($P<0.05$).

SITE	DOC	Slope	Significance
Guadalupe River 7/22/91	12.2 \pm 0.20	-0.83 \pm 0.74	Yes
Guadalupe River 7/25/91	6.40 \pm 0.14	*	No
Coyote Creek 7/6/92	8.06 \pm 0.12	-0.34 \pm 1.33	No
Coyote Creek 7/25/91	9.64 \pm 0.4	-0.46 \pm 0.23	Yes
Coyote Creek 6/18/93	1.46 \pm 0.2	-0.01 \pm 0.09	No
PASTP 7/91	10.2 \pm 0.1	-1.24 \pm 0.46	Yes
PASTP 7/93	8.4 \pm 0.40	-0.08 \pm 0.24	No
SJWPCP	6.20 \pm 0.13	*	No
Colusa Drain 7/91	4.50 \pm 0.19	-0.12 \pm 0.45	No
Colusa Drain 7/93	4.7 \pm 0.20	0.03 \pm 0.28	No
Sacramento River 7/91	1.88 \pm 0.07	0.13 \pm 0.21	No
Suwanee/ Silver	5.06 \pm 0.03	-0.15 \pm 0.41	No
Suwanee/ Balston	4.28 \pm 0.04	0.07 \pm 0.22	No

Source: Modified from Hunter and Kuwabara (1994).

received as urban rainfall runoff from the San Jose area (Sylvester, 1986).

The Palo Alto Sewage Treatment Plant (PASTP) and the San Jose-Santa Clara Water Pollution Control Plant (SJWPCP) are the two municipal treatment plants that were sampled for this study. These treatment plants discharge effluent year round and constitute major freshwater point sources to the South Bay especially during the dry months in summer and fall and during drought conditions (Hunter and Kuwabara, 1994).

MATERIALS AND METHODS

Water samples for this study were obtained from six major freshwater sources which drain into the North and South Bay (Figure 2). All materials, equipment and laboratory space were provided by the U.S.G.S. in Menlo Park, CA.

A comparison of DOC from these six locations was performed using data collected over a period of three consecutive years. The first two years were years of less than normal rainfall (1991 and 1992) while the third year (1993) was a year of about normal rainfall (NOAA, 1991; NOAA, 1992; NOAA, 1993) (Table 2). The purpose of this comparison was to see if there was any significant change in DOC concentration from one extreme hydrologic condition to the next.

The fluvial samples from the South Bay (Coyote Creek and Guadalupe River) were grab-sampled by submerging 1 liter glass bottles and removing the caps while under water. The caps were then replaced on the filled bottles while still under water to reduce the possibility of contamination by the surface film (typically elevated in organic content). Bottles were conditioned with the native water before the samples were collected by rinsing 3 times to mitigate the effects of solute interaction with container walls.

Samples from the SJWPCP and the PASTP were sampled directly from their effluent lines. Two replicate samples of about one liter each were obtained from each site. The water was filtered within one hour of sampling in order to minimize potential changes in DOC concentration resulting from

Table 2. Rainfall data for three North Bay sites and three South Bay sites, for three consecutive years (1991, 1992, and 1993).

Site Location	Site Name	Year	Rainfall (in)
No. Bay	Martinez	1991	15.59
		1992	18.85
		1993	22.40
	Sacramento City	1991	15.87
		1992	20.91
		1993	22.02
	Sacramento Airport	1991	NA
		1992	16.51
		1993	20.49
So. Bay	Newark	1991	12.63
		1992	16.65
		1993	21.40
	Palo Alto	1991	12.56
		1992	15.80
		1993	19.21
	Redwood City	1991	16.80
		1992	19.62
		1993	21.93

Sources: Climatological Data Annual Summary, California 1991, vol. 95, no. 13 and California 1992, vol. 96, no. 13., National Oceanic and Atmospheric Administration. Climatological Data California 1993 vol. 97, nos. 1-12., National Oceanic and Atmospheric Administration.

microbial activities. A vacuum filtration device containing 0.2 μ m Silver membranes (Poretics 47mm) was used.

Northern region samples were taken from the Sacramento River at the Tower Bridge in Sacramento from mid-channel and from the Colusa Drain up gradient from the Tower Bridge (Hunter and Kuwabara, 1994). An isokinetic fluoroethylene polymer sampler was used to obtain two replicate depth-integrated samples of 3 liters.

Sampling differences were due to site differences. Variations in depth and width (spatial scales) determined the sampling procedures used. The Sacramento River and Colusa Drain were of the order of tens of meters in width and depth (i.e., probably not homogeneous in cross section) and were sampled from a bridge and overpass, respectively using depth-integrating techniques. Coyote Creek and Guadalupe River, in contrast, were both narrow and shallow (less than one meter in depth). Therefore, a depth integrated grab-sample was taken. The PASTP and SJWPCP are both point sources (discharge water directly from effluent lines), and were sampled directly from these sources.

All glassware for this project was initially soaked in an acid bath which consisted of 1N HCl for at least six hours. Glassware was then rinsed with a low organic carbon laboratory water (<0.1 mg-C/L), placed in a muffle furnace and baked at 450°C for at least 6 hours. The fluoroethylene polymer parts (i.e., filter holders and bottle caps) were washed in a chromic/ sulfuric acid solution at 50°C for at least 1 hour, allowed to slowly cool in the acid bath, and

rinsed in low organic carbon laboratory water. This was done to ensure all organic residue was removed to reduce the possibility of sample contamination. The low carbon laboratory water was obtained in steps, first by use of a deionization device (Millipore Milli-Q) which uses a series of three cartridges (1 activated carbon and 2 adsorbing resin) to remove excess ions in the water, producing a deionized water with a conductivity of 18M Ohms. This deionized water was used as feed water to an ultraviolet oxidation device (Sybron/ Barnstead Organicpure, D3600) that removed residual DOC.

In the laboratory, water samples collected from the various sample sites were adjusted for ionic strength in increments of 0.1M up to 0.7M using a major salt matrix which contained two times the concentration of standard ocean water (2x SOW). The 2x SOW solution was 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 ($\text{MgCl}_2 \cdot \text{H}_2\text{O}$) (Williams, 1975). Concentrations for the 2x SOW components are shown in Table 3.

In order to determine the accuracy of the methodology and instrument, tests on two Suwanee River fulvic acid standards were run using the same ionic strength adjustments. For these standards, the carbon content was known before analysis by NMR spectroscopy. Percent recovery was determined by comparing analysis data to the known carbon content.

Table 3. Major salt solution concentrations for 2x SOW in 1 liter of solution.

Salt	Grams used	Final Molarity
NaCl	98.12	.42
CaCl ₂ ·2H ₂ O	6.16	1.1x10 ⁻¹
KCl	2.80	9.4x10 ⁻³
Na ₂ SO ₄	16.36	2.9x10 ⁻²
NaHCO ₃	0.08	2.4x10 ⁻³
MgCl ₂ ·6H ₂ O	44.40	5.5x10 ⁻²

Source: Modified from J.P. Riley and G. Skirrow, eds., Chemical Oceanography (London: Academic Press, Inc., 1975) p. 559, table 3.

The two Suwanee River standards were obtained separately and filtered by two different means. One standard was filtered with a silver membrane (referred to as Suwanee/Silver, 54.2 percent carbon by weight) and the other was glass-fiber filtered (referred to as Suwanee/Balston, 55.0 percent carbon by weight).

A Dohrmann DC-80 Total Carbon Analyzer which uses persulfate/ oxygen/ ultra violet oxidation (a LTWC method) was used to determine the DOC concentration of all samples analyzed. This method uses a reactor reagent modified for high ionic strength samples which was prepared according to manufacturers specifications. The reagent included the following concentrations of reagent grade compounds: 30 mM mercuric chloride (HgCl_2), 28.0 mM mercuric nitrate ($\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$), 74.0 mM potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), and 5 mL of concentrated nitric acid (HNO_3). These reagents were mixed together and diluted with low organic carbon laboratory water to make a total of 1 liter of high ionic strength reactor reagent. Before analysis, samples were acidified to pH 2 with nitric acid and degassed with O_2 to remove the inorganic carbon present in the sample. The carbon dioxide which was produced by the DOC oxidation was measured by an infrared detector (Horiba PIR 2000).

The DOC instrument was calibrated each day before sample analysis. The use of a phthalic acid ($\text{C}_6\text{H}_4\text{-1,2-(CO}_2\text{H)}_2$) standard was used for drift detection in the instrument. The DOC values obtained from the instrument were recorded as were the times required for sample digestion (instrument detection

aborts after 7 minutes of sample digestion).

Sample volume injected into the analyzer varied with sample. In some cases injection volumes remained constant at either 0.2 mL, 0.5 mL or 1.0 mL. In other cases, the volumes decreased from high to low (1.0 mL to 0.5 mL or 0.2 mL) because there was a tendency for the salt from the sample to accumulate in the reaction vessel causing precision of the analysis to decline and time for sample digestion to increase beyond the limits of the instrument. Water blank injections of 1.0 mL were alternated with sample injections in order to minimize the accumulation of the salts in the reaction vessel. Injection volumes were also adjusted to keep the measured DOC values in the linear range of the instrument.

A blank test was performed to determine if the instrument was significantly adding to the measured DOC (sometimes referred to as a "machine or instrument blank"). This was necessary because the addition of measured DOC by the instrument had been observed to occur in HTO devices (Williams *et al.*, 1993).

Freshwater replicates were analyzed three times each day of analysis. Each ionic strength-adjusted sample was prepared in three separate test tubes; each test tube sample was injected into the instrument at least three times. This generated at least 9 DOC values for each ionic strength increment in order to quantify the reproducibility of data. The three separate sample tubes were used to compare the differences in samples from the same site this is also known as sample replication. The injections from each tube ($n \geq 3$) were used to determine variability in sample analysis,

referred to as "pseudoreplicates" (Hurlbert, 1984) or analytical replication. Replications of both types are necessary to determine sources of error (Underwood and Peterson, 1988).

To test whether DOC measurements would be affected by increases in salinity, an adjustment of the sample ionic strength was made by adding, in 0.1M increments, the standard ocean water (2x SOW) matrix, as described in detail earlier. The chemically defined solution was used in lieu of seawater (as a control substance) to minimize the potential for DOC contamination. This adjustment of ionic strength to the freshwater samples was done to represent the natural mixing processes within the estuary. The samples that were analyzed were done so in replicates of three to quantify the reproducibility of the data.

The resulting DOC data were analyzed to quantify ionic strength effects by use of linear regression analysis (Borland QUATTRO PRO version 5.0) and the standard t-test (Microsoft for Windows, EXCEL version 5.0).

RESULTS

The results of this study (1991 through 1993) indicate that generally, there is a minimal effect on measured DOC concentrations for the various freshwater sources when subjected to incremental increases of ionic strength from 0.1M up to 0.7M (Figures 3 and 4). Standard errors about the mean were typically about 0.15 mg-C/L at each ionic strength increment. Maximum standard errors of 0.40 mg-C/L for the 1991 Coyote Creek sample and the 1993 PASTP sample were measured at ambient ionic strength. At the 95 percent confidence level ($n \geq 24$) (this number was obtained using data from the three injections for each of the three replicate tubes at each of the 8 ionic strengths) ionic strength was statistically significant for the initial analysis of Coyote Creek, Guadalupe River and the Palo Alto Sewage Treatment Plant (Table 1). None of the other sampling sources for this study exhibited statistically significant ionic strength effects (Hunter and Kuwabara, 1994). Analyses were repeated on water samples collected from the Coyote Creek site in 1992 and 1993. Results did not indicate any ionic strength effect at the 95 percent confidence level.

The analysis of data for Coyote Creek indicated that for 1993 there was a 6.5-fold decrease in DOC concentrations compared to 1991, and a 5.5-fold decrease in 1993 compared to 1992 (Figure 5). A second sampling of the Guadalupe River on July 25, 1991 was performed to verify results of the samples taken on July 22, 1991. This second sampling showed no effect of ionic strength on DOC. However, there

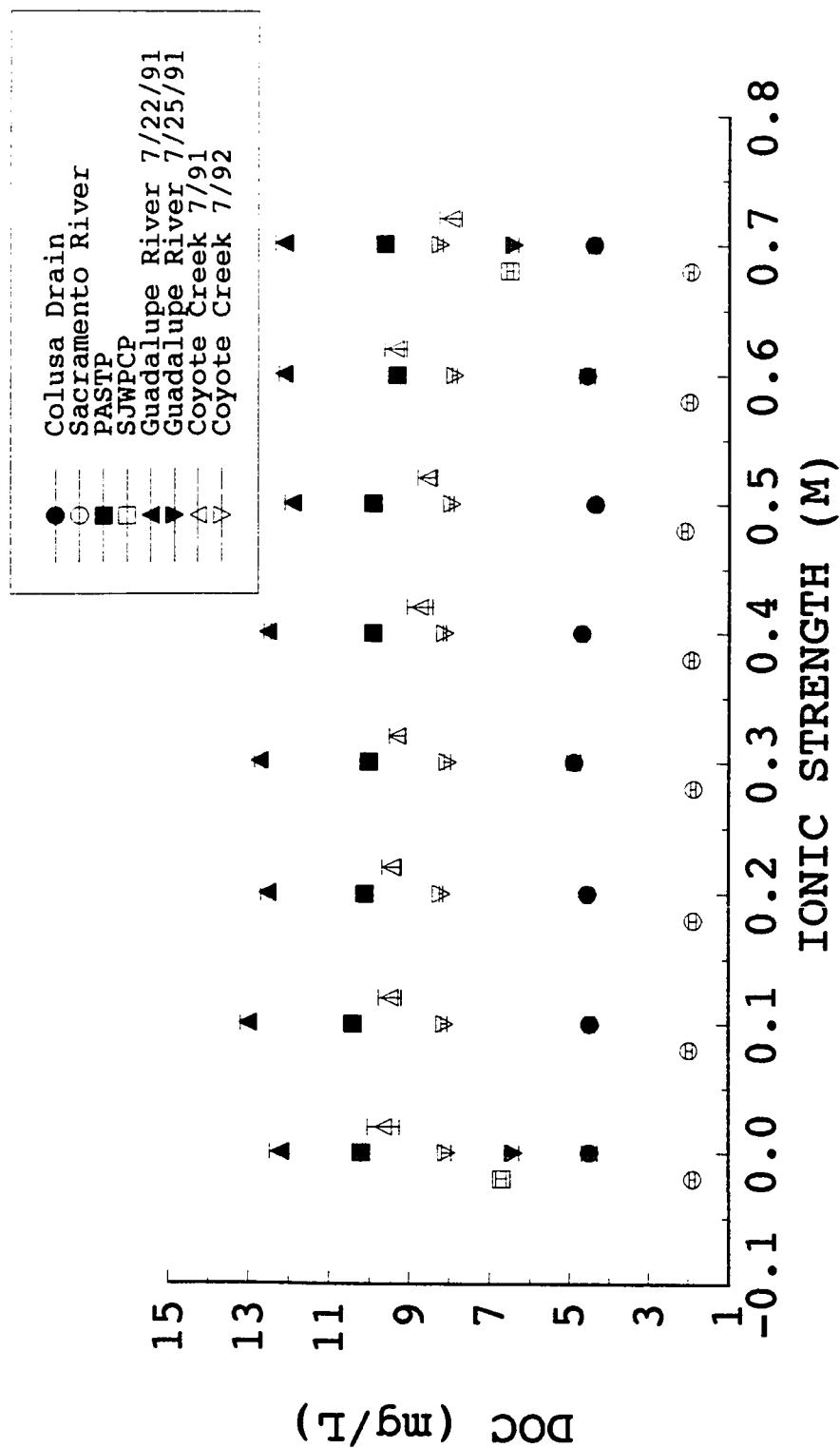


Figure 3. DOC concentrations ($n \geq 3$, with standard error bars) from all freshwater sources. Source: Hunter and Kuwabara, (1994).

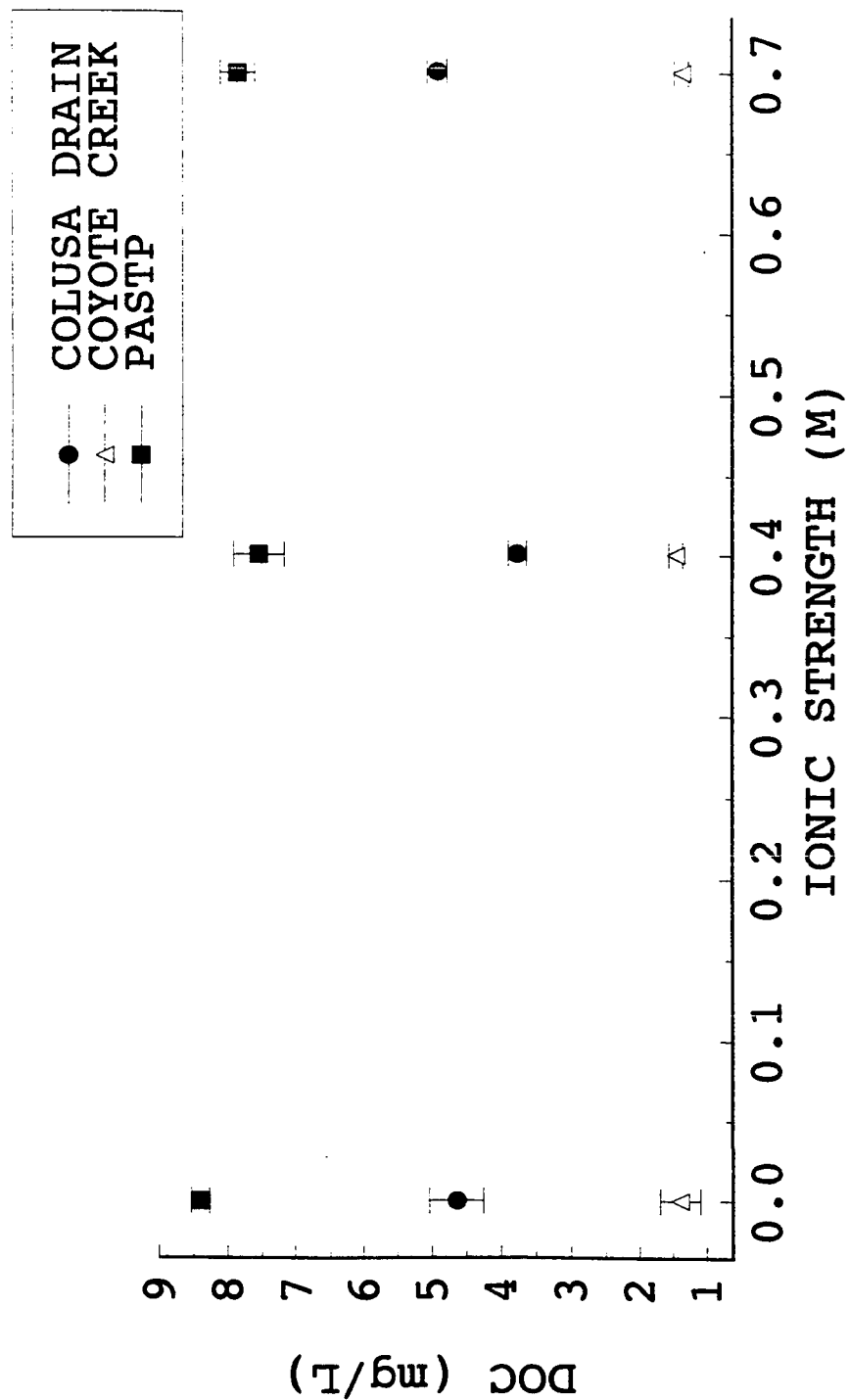


Figure 4. DOC concentrations with standard error bars from three freshwater sources sampled in 1993.

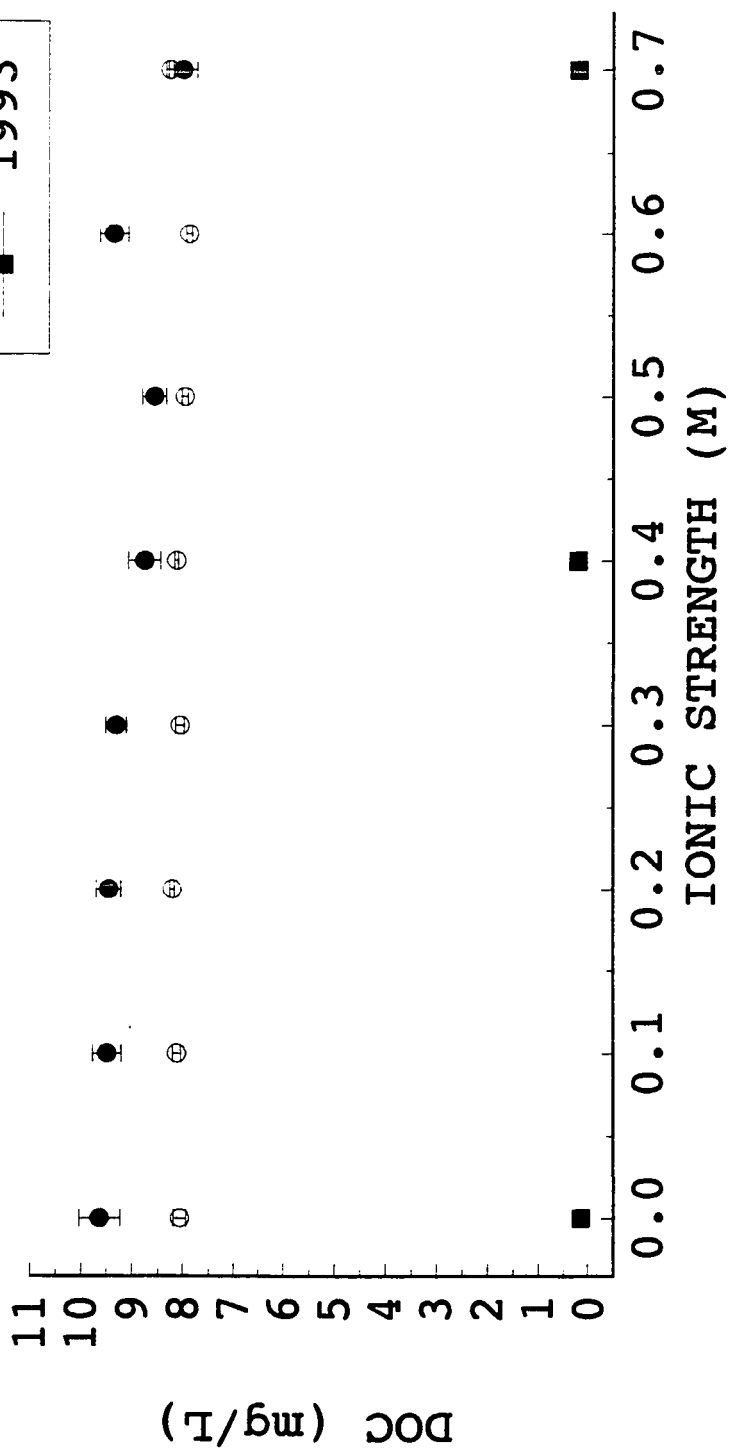


Figure 5. DOC concentrations measured for Coyote Creek sampled three consecutive years (1991, 1992, and 1993).

was a 50 percent drop in DOC concentration from the first to the second sampling date (Figure 3). Because sampling was done approximately 72 hours apart, a decline of this size in DOC was not expected. The observed decline in DOC concentrations may have been caused by an 8-fold increase in discharge (July 22, 1991 had a daily average of $0.0031 \text{ m}^3/\text{sec}$ and on July 25, 1991 had a daily average of $0.0250 \text{ m}^3/\text{sec}$) at the site (Trujillo *et al.*, 1991). Discharge of Coyote Creek is affected by regulated flow from the Lexington Reservoir, located 19 km upstream (Hunter and Kuwabara, 1994). Coyote Creek, unlike the Guadalupe River, is not gauged for stream flow. Therefore, it can only be speculated that the amounts of dissolved organic matter in the samples taken in the three sampling years would vary.

Initial data collected from the PASTP showed a significant effect of ionic strength on freshwater DOC. However, the observed decrease in DOC was relatively small (5 percent) compared to the decrease measured in the analyses of marine samples (approximately 22 percent) (Sharp, 1973).

Additional data were collected from tests which were performed using phthalic acid standards at higher ionic strengths up to $I=4.8\text{M}$ (approximately 7 times greater than maximum ionic strength in San Francisco Bay). The increase in ionic strength, again, did not decrease the measured DOC (Figure 6). In initial DOC determinations at the higher ionic strengths of $I=4.0\text{M}$ and $I=4.8\text{M}$ there was an apparent increase in DOC concentrations. This seemed to be caused by a "carry-over" of DOC from previous injections, which is

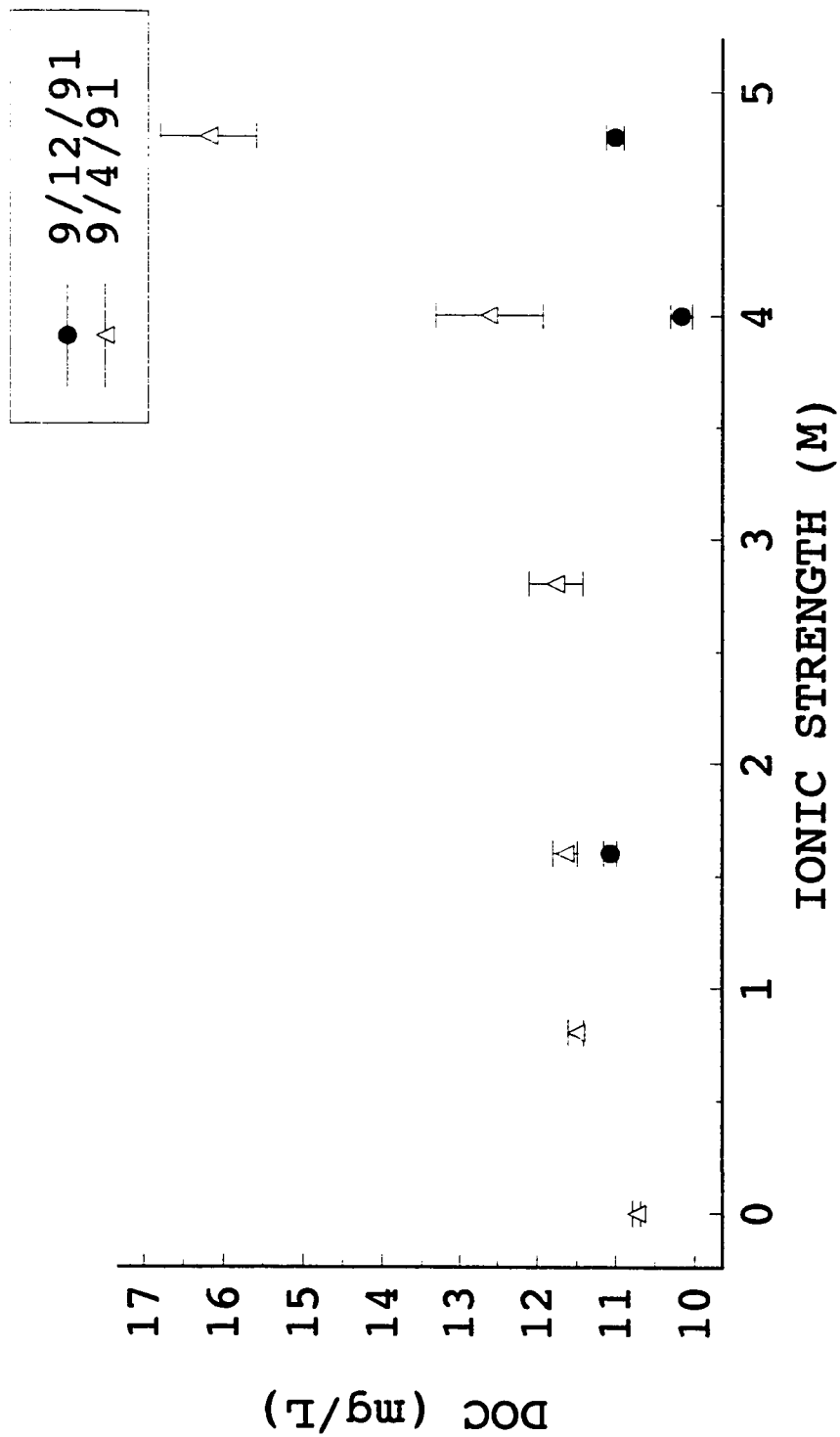


Figure 6. DOC concentrations for 8x SOW. DOC increase at $I=4.8M$ are believed to be caused by salt accumulation in the reaction vessel.

caused by salt accumulation in the reactor vessel. This was verified by the inconsistent values generated by the instrument as well as the amount of time it took for the analysis to be completed. Analyses which take more than 7 minutes to complete cause the instrument to stop analysis. Carbon analysis is incomplete and is carried over into the next analysis. This "carry-over" effect was reduced by decreasing sample volumes injected into the instrument from 1.0 mL to 0.2 mL (allowing ample time for digestion) and alternating injections of low organic carbon water to counteract the salt accumulation in the reaction vessel.

Experiments were done to determine the accuracy of this LTWC method. Fulvic acid standards, isolated from the Suwanee River were used to determine the percent of carbon recovered from the UV/ persulfate/ O₂ (LTWC) method of analysis used in this study. The first set of data generated was from the Suwanee/Silver fulvic acid which contained 54.2 percent carbon by weight and the second set of data was from the Suwanee/Balston fulvic acid, which contained 55.0 percent carbon by weight. Experiments on both fulvic acid standards indicated that ionic strengths up to 0.7M did not have a significant effect on the measured DOC concentration (Figure 7). Organic carbon recovery for both standards were typically greater than 90 percent indicating close agreement with NMR analyses.

An instrument blank test was performed to determine if the instrument was contributing carbon to the samples during analysis. Results indicated that 0.07 ± 0.04 mg-C/L was being added when using a 1 mL blank injection (corresponding

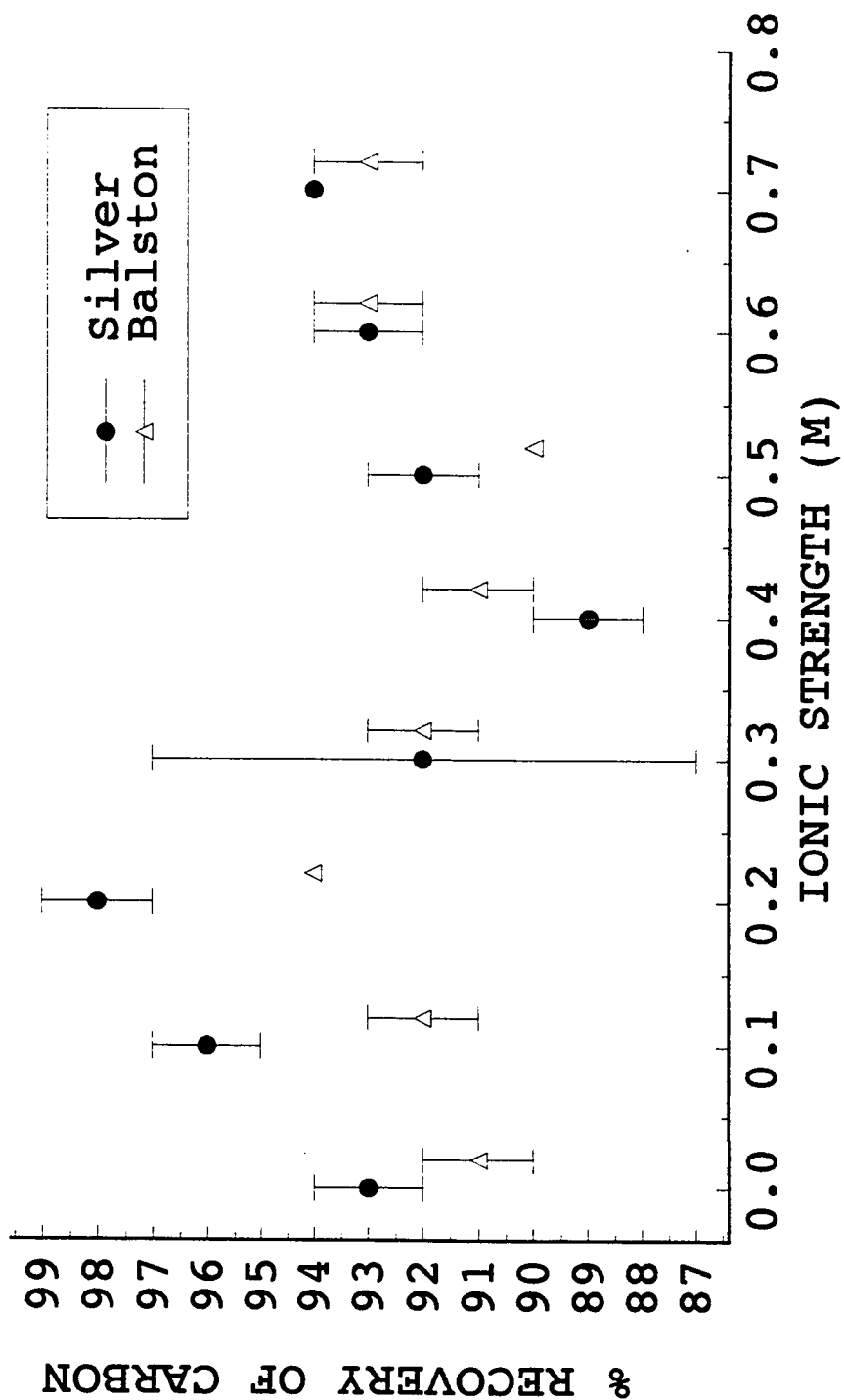


Figure 7. Percent recovery of two Suwanee River fulvic acid standards (Silver and Balston). Source: Hunter and Kuwabara, (1994).

to the maximum sample injection volume used in this study). In contrast to HTCO methods, this measurement of blank injection was small relative to DOC concentrations (less than 10 percent of mean values and smaller than confidence intervals), and did not significantly increase with injection volumes between 0.0 and 1.0 mL (Hunter and Kuwabara, 1994); a distinct advantage with the procedure used in this study.

Results from the International Intercalibration Study

The opportunity arose in November, 1993, to participate in a comparative study between DOC analytical methods used throughout the world. Professor Jonathan Sharp (College of Marine Studies, University of Delaware) organized the study as part of the Joint Global Oceanic Flux Study (JGOFS), in which participants from the United States and several other countries (e.g., Canada, Turkey, Sweden, and Germany) were given samples of water with a known DOC concentration. In the first phase of this study, participants were given samples to analyze by any method desired. The participants of the Sharp study used either HTCO or LTWC methods. The most popular method used was HTCO, which gave consistently good results. The data obtained from this study were determined to be very encouraging by Professor Sharp and his colleagues. After the completion of the first stage of this comparison, Dr. Sharp believes that the data obtained, by the many instruments and methods used, has not clearly shown that one method is better than the others (Sharp, personal communication, 1994) (Figure 8). This is in direct contrast to previous reports suggesting that the use of LTWC methods

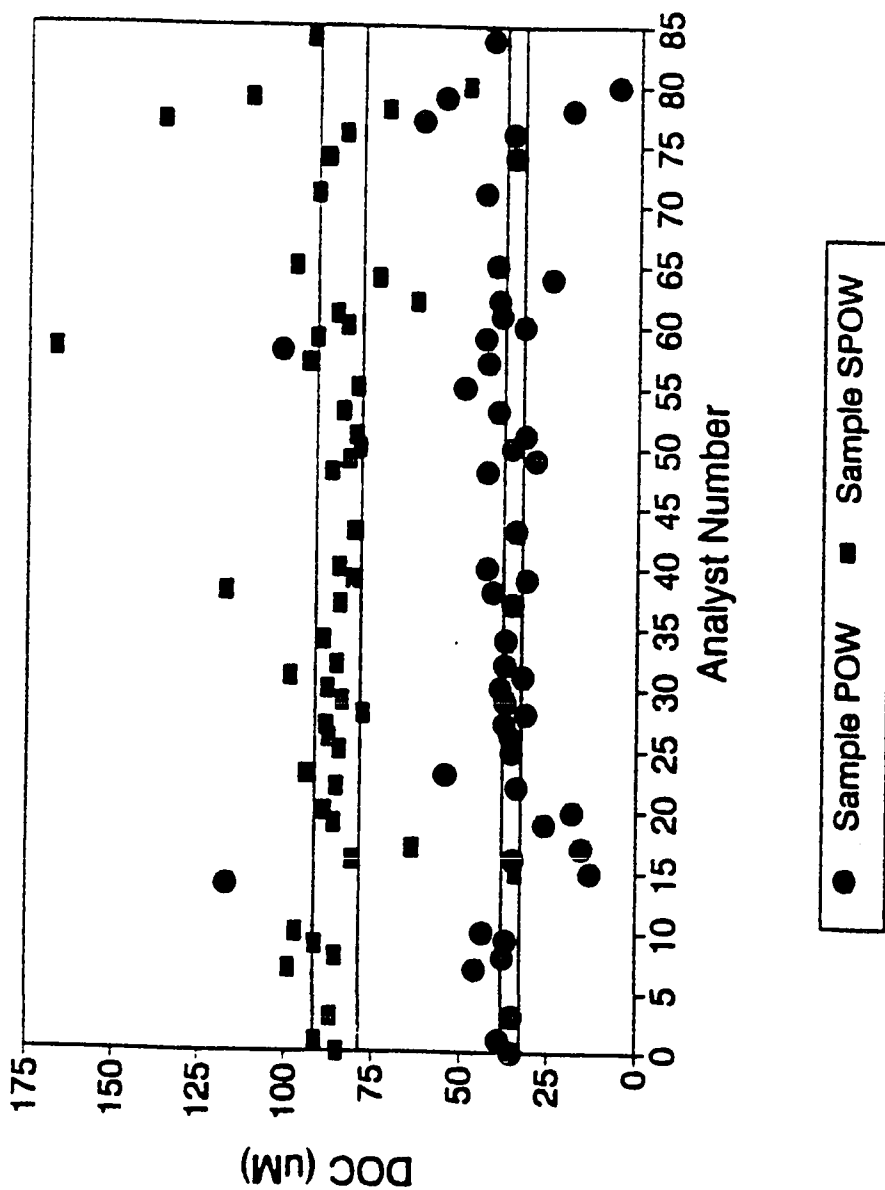


Figure 8. DOC concentrations measured by HTCO and LTWC methods. Marks between the two upper lines (approx. 80-90) and the two lower lines (approx. 30-40), depict analyses that fall within ± 7.5 percent of the expected DOC values for two samples, POW and SPOW. Analyst number for this thesis is 43. Reprinted by permission, from Dr. J. Sharp, University of Delaware.

were inappropriate for analysis of high ionic strength samples, and is consistent with the results presented herein. A protocol for sample handling and calibration was given to all participants. Participants were also provided with a set of numbers that represented the expected DOC values for each sample to be analyzed.

Raw data (from the analyzers) were returned to Professor Sharp for data analysis, interpretation, comparison, and graphical representation. Data obtained from analysis performed at the U.S.G.S. were determined by Professor Sharp to fall within ± 7.5 percent of the expected boundaries for this study (personal written communication, Sharp, 1994). Data results as compared to the overall results for this comparative study were determined to be "very good" by Professor Sharp (analyst number 43 in Figure 8). In comparison to results obtained by others using LTWC methods, data analyzed for this thesis were also described as "very good" (Figure 9).

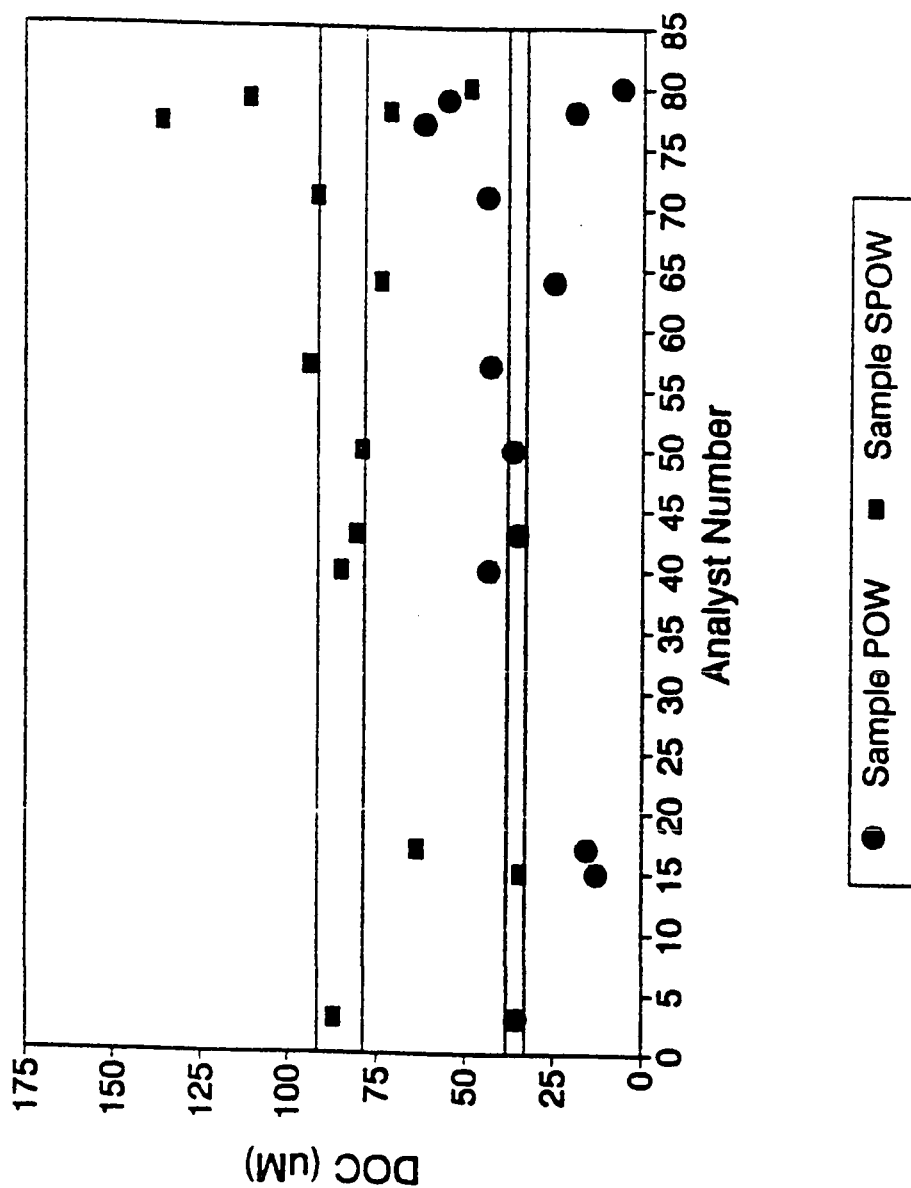


Figure 9. DOC concentrations measured by LTWC methods only. Marks between the upper lines (approx. 80-90) and the two lower lines (approx. 30-40), depict analyses that fall within ± 7.5 percent of the expected DOC values for two samples, POW and SPOW. Analyst number for this thesis is 43. Reprinted by permission, from Dr. J. Sharp, University of Delaware.

DISCUSSION

Although the initial results from the Coyote Creek, Guadalupe River and Palo Alto Sewage Treatment Plant, showed a significant decrease in DOC as ionic strength increased, the effect was small (13 percent, 8 percent, and 5 percent decrease, respectively for the sites over the 0.0 to 0.7M ionic strength range, Figures 3 and 5). For example, in comparing these results to deep sea studies, Sharp (1973) observed a more pronounced decrease in DOC in samples taken from the central western North Atlantic Ocean. The decrease observed was approximately 0.5 mg-C/L (about 22 percent in samples from depths greater than or equal to 400 m) at an ionic strength of 0.7M (marine samples), analyzed by LTWC methods relative to the HTCO method. This suggests that in these particular oceanic samples there was a much stronger chloride (ionic strength) interference using their analytical techniques. This may be due to analytical differences or specific elements found in marine samples (i.e. salts) that are more readily available to react with the chloride than those elements which are found in riverine samples and the 2x SOW matrix. It is suspected, however, that measures taken here to mitigate ionic strength effects account for differences in results.

HTCO methods have been known to add significant amounts of carbon during analyses resulting from catalyst contamination. Suzuki et al., (1992) reported that their blank values obtained by the HTCO method added from 0.18 mg-C to 0.36 mg-C, while the persulfate oxidation method added

from 0.036 mg-C to 0.06 mg-C. These data indicate about a six-fold difference between the two methods of analysis.

The addition of carbon comes from the reagents used, the water used, and from the instrument itself. One problem is that in many previously published papers, authors have often incompletely reported the methods used to assess these blanks and when they were reported they often widely varied (Williams *et al.*, 1993). Therefore the need exists to address the analytical blank. Blank analysis is very important and failure to account for it may result in an overestimation of DOC in the sample.

Samples analyzed for this study represent a wide variety of organic carbon sources (industrial, agricultural, and municipal). Although observed ionic strength effects were typically insignificant for these samples, exceptions (Coyote Creek, Guadalupe River and PASTP effluent) indicate that certain organic compounds might have been incompletely oxidized by the LTWC method used. However, if this is the case, the effect which was observed was consistently small (less than 13 percent decrease) over the ionic strength range which was used (Hunter and Kuwabara, 1994).

The results of this study as compared to marine studies that questioned all LTWC methods are inconsistent. This may be due to the dissolved organic substances in the oceanic environment as compared to those present in various sources to estuarine environments. A pronounced chloride interference was not induced by the addition of a seawater matrix to the wide variety of samples tested in this study. Possible explanations may be because of methodological

differences. Unlike some other LTWC methods, these samples were directly injected into a reaction vessel (68 mL) containing a persulfate reactor reagent which was exposed to UV radiation, and bubbled with an ultra-high-purity grade O₂ to aid organic carbon oxidation. Chloride concentrations in high ionic strength samples were diluted in this reaction vessel presumably to a point below which interferences were manifest. In addition, mercuric chloride compounds were added to the reactor reagent to effectively complex with chloride in the sample and hence mitigate the effect. This work: 1) tested a methodology thought to underestimate DOC values, and 2) verified that previously observed copper and zinc correlations with DOC are not significantly affected by the LTWC method.

These results indicate that differences in analytical concentrations generated by HTOC and by the LTWC method used for this study should not be pronounced if those differences are primarily generated by chloride (ionic strength) interferences and if mercuric chloride is used to complex chloride.

The implications of these results relative to metal speciation should be noted. Kuwabara et al., (1989) observed a strong correlation between measured DOC and dissolved copper and zinc. By the use of available thermodynamic data from other estuaries, chemical speciation calculations indicated that metal speciation (and hence bioavailability) was controlled by complexation with dissolved organic substances for copper but not for zinc. Two possible reasons for this discrepancy between the observed and modeled results

for zinc were proposed. First, their measured DOC values were possibly underestimated because of their LTWC analysis. Second, the zinc-humic matter complex, Zn-humate thermodynamic data were underestimated in their speciation calibration, hence leading to an underestimated Zn complexation. Results herein suggest that the first reason can be rejected, because the methods used here and by Kuwabara *et al.*, (1989) are identical.

The metal speciation for copper as determined by Kuwabara *et al.*, (1989) suggests that copper speciation is controlled by complexation with dissolved organic ligands. The findings of their study suggested that about 80 percent of the available copper can become organically complexed to humic material. Results from a later study performed by Donat *et al.*, (1994) support Kuwabara *et al.*, (1989) results. The results for copper as calculated by Donat (1994) indicate, that in the South San Francisco Bay, 80 to 92 percent of the total dissolved copper becomes complexed with humic material. This shows the importance of accurate determinations of DOC concentrations in order to appropriately determine the chemical speciation of biologically reactive elements such as copper.

Discussion of the International Intercalibration Study

A problem observed by Williams *et al.*, (1993) (a "DOC Subgroup" formed to study the current status of DOC analysis) is that in past studies, DOC procedures and sampling protocol had been different for each study conducted. This should be avoided if a program which examines DOC on a global scale is

to be successful (Williams et al., 1993). The current differences observed by both analytical and methodological processes must be resolved. Until there is an adopted standard for sample handling and data quality, then DOC analytic methodologies will continue to generate highly variable data.

The data generated for the comparison study was done per the LTWC method. Analyses for this study were determined by Dr. Sharp to agree well with the expected values. He concluded that there was no clear indication that there was one method that was better than the others.

The reasons which may have led to consistently good results for the Sharp comparison study may have been due to the fact that all of the participants of this study were given the same samples which had been handled (sampled and stored) the same way. Participants were also given a specific protocol for sample analyses and numerical calculations that included the correction for a sample blank. Standardization of a sampling protocol and data reduction may be the reason why Dr. Sharp's comparison study was successful in obtaining more consistent results than previous oceanic studies had reported.

Although data for this thesis was determined to be "very good" and consistent, commitment to participate in a future study has been made. The second stage of this study is "blind" (i.e., estimated values are not provided). It is hoped that participation in this second stage will further verify that the LTWC method used for this thesis is comparable to those of the HTCO methods.

Previous studies have demonstrated that if allowed to exist, elevated free metal ion activities can affect the community structure of phytoplankton, by inhibiting reproductive rates. Current water quality standards are not, however, based upon the determination of DOC. Although DOC may affect planktonic growth and metal speciation (e.g., for copper and zinc), it is difficult to regulate because DOC represents a range of organic compounds (Kuwabara personal communication, 1994). If DOC were to be used as a parameter for water quality standards and if these standards were based on DOC concentrations then a number of precautions should be noted. The HTCO method may work well, however results should be carefully analyzed so as to not overestimate DOC values because of the addition of carbon by instrument and sample blanks. Prior to recommendations for a standard based upon the HTCO data, the LTWC method could be used as a comparison and instrument blanks be carefully monitored. The sample and data analyses should be standardized. A methodological comparison would be useful because there still exists some uncertainty on which method, if any, provides the most accurate data.

For reasons discussed above, DOC results may have direct implications on the strategies by which the discharge of inorganic and organic contaminants may be regulated. With standardized methods of DOC analysis, and confirmation between comparative methods water quality standards may one day be more appropriately set to protect aquatic organisms, wildlife and human health.

CONCLUSIONS

Dissolved organic carbon data generated by use of the persulfate/ UV/ O₂ LTWC method for this study generally did not show a significant effect of ionic strength on various freshwater DOC sources to the San Francisco Bay. The chloride interference, which was observed in previous DOC studies that focused on the marine environment, was not a pronounced factor in this study.

The implications of these results with respect to metal speciation and water quality standards suggest that DOC concentrations by LTWC may one day be used to estimate quantities of humic (organic) material present in a body of water as a carbon food source. These DOC measurements may also be used to estimate the concentrations of metal forms that are available for biological uptake and determine at what concentrations these metals potentially may harm aquatic biota.

The results of this study suggest that, although DOC methodologies differ, any one method is not far better than another as long as sampling and sample processing is appropriate (standardized). Methodological and analytical variations still exist for each method and will continue to be used until sampling protocols and analytical data procedures are standardized, and blank determinations are routinely incorporated into sample analysis. Until a standard protocol is developed either H₂CO or LTWC methods may be used as long as preliminary tests indicated that comparable results are generated. Until standardization

occurs, the scientific community cannot confidently determine which DOC values may be applied to address fundamental problems dealing with carbon budgets, and the bioavailability and toxicity of trace metals to aquatic organisms.

Future research to chemically characterize DOC is needed before DOC concentrations may help define water quality standards and set limits on anthropogenically induced pollution to protect wildlife and maintain human health.

LITERATURE CITED

- Anderson, S.W., J.R. Mullen, M.F. Friebel, and K.L. Markham. 1992. Water Resources Data, California, Water Year 1992., vol.4. U.S. Geological Survey Water-Data Report, CA-29-4.
- Brewer, P.G., K.W. Bruland, R.W. Eppley and J.J. McCarthy. 1986. The global ocean flux study (GOFS): Status of the U.S. GOFS program. EOS., no. 44, 67(Nov 4):827-832.
- Cutter, G.A. and M.L.C. San Diego-McGlone. 1990. Temporal variability of selenium fluxes in San Francisco Bay, in The Science of the Environment., R.J. Allen, P.G.C. Campbell, U. Förster, K. Lum, eds., vol 97 & 98., Nov 1990, 235-250.
- Donat, J.R., K.A. Lao, and K.W. Bruland. 1994. Speciation of dissolved copper and nickel in South San Francisco Bay: A multi-method approach. Analytica Chimica Acta., 284:547-571.
- Hedges, John, C. Lee, P. Wangersky. 1993. Comments from the editors on the Suzuki statement. Marine Chemistry., 41:289-290.
- Hunter, Y.R., and J.S. Kuwabara. 1994. Ionic strength effects on DOC determinations from various freshwater sources to the San Francisco Bay. Bulletin of Environmental Contamination and Toxicology., 52:311-318.
- Hurlbert, Stuart, H. 1984. Pseudoreplication and the design of ecological field experiments. Ecological Monographs., 54(2):187-211.
- Jassby, A.D., J.E. Cloern, T.M. Powell. 1993. Organic carbon sources and sinks in San Francisco Bay: variability induced by river flow. Marine Ecology Progress Series., 9:39-54.
- Kuwabara, J.S., J.A. Davis, and C.C.Y. Chang. 1986. Algal growth response to particle-bound orthophosphate and zinc. Limnology and Oceanography., 3:503-511.
- Kuwabara, J.S., C.C.Y. Chang, J.E. Cloern, T.L. Fries, J.A. Davis, and S.N. Luoma. 1989. Trace metal association in the water column of South San Francisco Bay, California. Estuarine, Coastal and Shelf Science., 28:307-335.

- Kuwabara, J.S., G.W. Luther III. 1993. Dissolved sulfides in the oxic water column of San Francisco Bay, California. Estuaries., no. 3A, 16:567-573.
- Kuwabara, J.S., C.C.Y. Chang, A.I. Khechfe, and Y.R. Hunter. 1994. "Implications of dissolved sulfides and organic substances for the chemical speciation of trace contaminants in the water column of San Francisco Bay, California", in San Francisco Bay: The Ecosystem, Symposium papers from the Pacific Division 75th Annual Meeting, San Francisco State University. T.J. Hollibaugh, ed., In press.
- Markham, K.L., S.W. Anderson, J.R. Mullen, and M.F. Friebel. 1991. Water Resources Data, California, Water Year 1991., vol 4. U.S. Geological Survey Water-Data Report, CA-91-4.
- Mullen, J.R., M.F. Friebel, K.L. Markham, and S.W. Anderson. 1993. Water Resources Data, California, Water Year 1993., vol. 4. U.S. Geological Survey Water-Data Report CA-93-4.
- Motekaitis, R.J. and A.E. Martell. 1987. Speciation of metals in the oceans. I. Inorganic complexes in seawater, and influence of added chelating agents. Marine Chemistry., 21:101-116.
- National Oceanic and Atmospheric Administration. 1991. Climatological Data Annual Summary California 1991., vol. 95, no. 13. See U.S. Department of Commerce 1991.
- National Oceanic and Atmospheric Administration. 1992. Climatological Data Annual Summary California 1992., vol. 96, no. 13. See U.S. Department of Commerce 1992.
- National Oceanic and Atmospheric Administration. 1993. Climatological Data, January-December, 1993. vol. 97, nos. 1-12. See U.S. Department of Commerce 1993.
- Peltzer, E.T., P.G. Brewer, Y. Suzuki and Y. Sugimura. [1991]. Measurement of dissolved organic carbon in seawater by high temperature catalytic oxidation. Submitted to Journal of Marine Research., April 24, 1991.
- Peyton, Gary R. 1993. The free-radical chemistry of persulfate-based total organic carbon analyzers. Marine Chemistry., 41:91-103.

- Russell, P.P., T.A. Bursztynsky, L.A. Jackson, and E.Y. Leong. 1982. Water and waste inputs to San Francisco Estuary-An historical perspective. San Francisco Bay: Use and Protection. W.J. Kockelman, T.J. Conomos, and A.E. Leviton eds., San Francisco, CA., (June):127-136.
- Schemel, L.E., A.Y. Ota, S.W. Hager and A.M. Swithenbank. 1989. Sources of dissolved and particulate substances to the Sacramento River near Sacramento, California, Summer 1985. U.S. Geological Survey Open-File Report, 89-45.
- Sharp, Jonathan H. 1973. Total organic carbon in seawater - comparison of measurements using persulfate oxidation and high temperature combustion. Marine Chemistry., 1:211-229.
- Smith, G.J. and A.R. Flegal. 1993. Silver in San Francisco Bay estuarine waters, Estuaries., no. 3A, 16:547-558.
- Smith, Lawrence H. 1987. A review of circulation and mixing studies of San Francisco Bay, California. U.S. Geological Survey Open-file Report, 87-534.
- Stumm, Werner and J.J. Morgan. 1981. Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters., John Wiley & Sons, Inc., Toronto.
- Sugimura, Yukio and Yoshimi Suzuki. 1988. A high-temperature catalytic oxidation method for the determination of non-volatile dissolved organic carbon in sea water by direct injection of a liquid sample. Marine Chemistry., 24:105-131.
- Suzuki, Yoshimi. 1993. On the measurement of DOC and DON in seawater. Marine Chemistry., 41:287-288.
- Suzuki, Yoshimi, Eiichiro Tanoue, and Hiroshi Ito. 1992. A high-temperature catalytic oxidation for the determination of dissolved organic carbon in seawater: analysis and improvement. Deep Sea Research., 39:185-198.
- Sylvester, M.A. 1986. Water quality and flow of streams in Santa Clara Valley, Santa Clara County, California, 1979-81. U.S. Geological Survey Water-Resources Investigations Report, 84-4196.
- Trujillo, L.F., K.L. Markham, J.R. Palmer, and M.F. Friebe. 1991. Water Resources Data California Water Year 1991, vol 1. U.S. Geological Survey-Data Report CA-91-2., p. 315.

- Underwood, A.J. and C.H. Peterson. 1988. Towards an ecological framework for investigating pollution., B.L. Bayne, K.R. Clarke, and J.S. Gray, eds., Marine Ecology Progress Series., nos. 1-3, 46(June):227-234.
- U.S. Department of Commerce. 1991. Climatological Data Annual Summary California 1991., vol. 95, no. 13. See National Oceanic and Atmospheric Administration 1991.
- U.S. Department of Commerce. 1992. Climatological Data Annual Summary California 1992., vol. 96, no. 13. See National Oceanic and Atmospheric Administration 1992.
- U.S. Department of Commerce. 1993. Climatological Data California., January-December, 1993. vol. 97, nos. 1-12. See National Oceanic Atmospheric Administration 1993.
- Wangersky, P.J. 1993. Dissolved organic carbon methods: a critical review., Marine Chemistry., 41:61-74.
- Williams, P.J. le B. 1975. "Biological and chemical aspects of dissolved organic material in sea water", in Chemical Oceanography. J.P. Riley and G. Skirrow eds., vol 2., second edition. Academic Press, London. p.301-357.
- Williams, P.J. le B., J. Bauer, R. Benner, J. Jegeman, V. Ittekkot, A. Miller, B. Norrman, Y. Suzuki, P. Wangersky and M. McCarthy. 1993. DOC subgroup report. Marine Chemistry., 41:11-21.
- Williams, P.M. and E.R.M. Druffel. 1988. Dissolved organic matter in the ocean: comments on a controversy. Oceanography., 1:14-17.

Written Communication

- Sharp, Jonathan H., Professor, University of Delaware, College of Marine Sciences. Written communication, November 1993. DOC data pertaining to Intercalibration study, Lewes, Delaware.

Verbal Communication

- Kuwabara, James S., Hydrologist, U.S. Geological Survey. Verbal interview, July 1993. DOC uses and water quality standards. Menlo Park, CA.



COLLEGE OF MARINE STUDIES, LEWES, DE 19958-1298

JONATHAN H. SHARP, PROFESSOR
(302) 645-4259 (OFFICE), (302) 645-4007 (FACSIMILE)
TELEMAIL: J.SHARP
INTERNET: jsharp@brahms.udel.edu

November 17, 1993

Yvonne R. Hunter (Kuwabara)
U.S. Geological Survey
Water Resources Division
345 Middlefield Road, Mail Stop 465
Menlo Park, CA 94025

Dear Ms. Hunter:

For our two stage DOC methods comparison to be most effective, I am trying to respond to each analyst with comments and suggestions as results from the first stage are received. We have had an overwhelming interest in this DOC exercise and I have mailed over 75 sets of samples to individuals in the U.S. and 17 other countries. I continue to send samples and will do so as long as there is interest. However, our deadline of 30 November will hold in order for me to have time to summarize results to that date and give a summary feedback before the second stage samples are sent (probably in late January). Results from samples sent after then will not be included in the summary. The samples were designed for seawater analysts (very low DOC content and full salt content) and these are more difficult for fresh water analysts than for the marine workers who are more used to this type of sample. Therefore, analysts in the first stage of the comparison have produced varying results ranging from very successful to having difficulty with blanks and the low level carbon content. My response to you is intended to help to get better results on the second stage samples.

Your results look very good. However, I did some recalculations. The LCW may be lower than your than your blank water; it is supposed to be very clean. However, it still should be used as the absolute positive blank. The average peak measurement for the LCW should be subtracted from each sample peak measurement and the resultant number should be divided by the slope. Also, the average LCW peak measurement divided by the slope gives the absolute value of your instrument blank. I recalculated the data and then averaged your results for what I list as your response:

LCW = 12.1 μ M C
POW = 34.5 (\pm 1.7) μ M C
SPOW = 81.2 (\pm 1.6) μ M C
Difference (Spike) = 47 μ M C

The seawater samples agree well with the expected values and the replication is very good. I am delighted because your results are with a wet chemical method and the majority of the participants in this exercise are using HTC methods. You most certainly may mention any of this in your thesis. I will be providing a summary of the first stage results in January and that may be even more helpful. Good luck with your research.

Sincerely,


Jonathan H. Sharp

AN EQUAL OPPORTUNITY UNIVERSITY