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ONLINE PHOTOCHEMICAL OXIDATION AND FLOW INJECTION CONDUCTIVITY DETERMINATION OF DISSOLVED ORGANIC CARBON IN ESTUARINE AND COASTAL WATERS

By

Melchior Mataki
Department of Chemistry
School of Pure and Applied Science

A thesis submitted in partial fulfillment for the degree of
Master of Science at

The University of the South Pacific

November 1999

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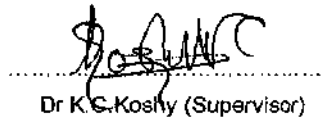
DEDICATION

This thesis is dedicated to my parents for their consistent love and support throughout academic endeavors.

DECLARATION

I declare that this thesis is a result of my own work, except for those sections expli acknowledged herein. The main content of this thesis has not been previously subm for a higher degree at any other university.

Melchior.Mataki



Dr K.C.Koshy (Supervisor)

ACKNOWLEDGEMENT

This thesis is a culmination of a project that involved the modification of an FIA method and its subsequent application for the measurement of DOC in estuarine and marine samples. The two parts of the project involved numerous tasks that have been achieved through the advice, assistance and cooperation of a number of people.

It is an honor to acknowledge and to give my heart felt thanks to my one and only Supervisor, Dr K.C.Koshy whose great effort and encouragement has made this project a success.

I am also indebted to thank my Sponsors, the Solomon Island Government and the British USP scholarship for their financial assistance in terms of tuition fees, maintenance and research allowances. Furthermore, I would like to thank the USP Chemistry Department for the extension of my Graduate Assistant tenure. Am also thankful for the assistance and brilliant ideas from the following in the course of the project.

- The Technical staff of the USP Chemistry Department: William Peter, Vas Deo, Kamlesh, Sese, Viilikesa, Shareena, Thomas, Tala and Eva and the Technical staff of the USP Marine Studies Programme.

- Dr Culwick Togamana, for his suggestions regarding the format of the thesis and words of encouragement as a *"wantok"*.

- Dr K.Osei, for the assistance rendered on the statistical analysis of the DOC data obtained in this project.

- Br Varaghese of Monfort Boys Town, for allowing me to use their HTCO Shimadzu 2000-UV unit for my DOC comparative work.

- Ernest Siota, for his unrelenting work on the graphics used in this thesis.

Lastly, but not the least I would like to express my sincere love and gratitude to "*MEDTS*" and my "*Wantok*" friends from the Solomon Islands and my Postgraduate colleagues for their support and friendship through out the course of my studies.

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LIST OF ABBREVIATIONS

1. mg C/L……*milligram carbon per liter (ppm)*
2. mg/L……milligram per liter
3. L……Equivalent to decimeter cube (dm^3)
4. $\%Cl_{ox}$……Percentage chloride oxidized (A measure of chloride interference)
5. DDW……Distilled deionized water
6. $35^0/_{00}$ NaCl solution….35g of NaCl salt dissolved in one liter
7. DOC……Dissolved organic carbon
8. KHP……Potassium hydrogen phthalate
9. FIA……Flow injection analysis
10. IC……*Inorganic carbon*
11. µm……Micrometer
12. TC_m……Total carbon measured in a natural water sample
13. IC_m……Inorganic carbon measured in a natural water sample
14. SD……Standard deviation
15. MS……millisiemens
16. UV……Ultra violet
17. HTCO……High temperature catalytic oxidation
18. WCO……Wet chemical oxidation
19. *n*……Number of experimental trials
20. mm……millimeter
21. R^2……Correlation coefficient
22. ANOVA……Analysis of variance
23. M……Moles per Liter

ABSTRACT

The determination of dissolved organic carbon (DOC) using flow injection analysis (FIA) was initially achieved through an FIA method described by (Koshy *et al.,* 1992). Their method involved the photochemical oxidation of DOC using persulfate and the gas diffusion of the carbon dioxide which was measured spectrophotometrically. The above method was reported to suffer from chloride interference when saline samples were analyzed.

This thesis presents the results of a research into the interference by chloride on the measurement of DOC using a modified FIA method based on the one described by (Koshy *et al.,* 1992). The work began in the middle of 1997 after considering the importance of DOC as a water quality parameter and the lack of a cheap and reliable method for DOC determination in the South Pacific. Furthermore, it became apparent that there was a need for a baseline study of DOC in the Suva lagoon given the input of organic substances from land based sources via the rivers streams, creeks, storm water outlets and the Kinoya sewage outfall into the lagoon.

By preparing corresponding concentrations of inorganic carbon (IC) in distilled deionized water (DDW) and in the $35^0/_{00}$ NaCl solution (to simulate seawater) and analyzing them on the modified FIA method, it was established that chloride interfered with the measurement of DOC even with the modified FIA method. The interference by chloride ($\%Cl_{ox}$) was found to be masked by IC to levels as low as 1% in the presence of IC concentrations greater than 8mg/L. The masking effect of IC on chloride interference was

facilitated by the rapid decrease in the ratio of chloride to IC as the concentration of IC increased. Because of the generally high levels of IC (near 20mg/L) in estuarine and coastal waters (Manahan, 1994), the masking effect of IC on chloride interference was incorporated to the modified FIA method.

With respect to the specific objectives of this project, attempts were made to eliminate or minimize chloride interference using a reduced oxidant (50% oxidant strength solution) boosted with a catalyst (TiO_2), a reducing agent ($NH_2OH.HCl$: Hydroxylaminehydrochloride) and a micro-porous tubing (Accurel PP Type S6/2 0.2μm pore size; Enka). When the catalyst was used with the reduced oxidant (50% oxidant strength solution) it raised the DOC recovery back to 100%. Unfortunately, the interference by chloride was also increased in the range of 12% to 51% greater than the levels of chloride interference observed with the 100% oxidant strength solution alone. $NH_2OH.HCl$ reduced the chloride signal by 81±3% on its own. In the presence of carbon (IC or DOC), the interference by chloride was reduced in the range of 80% to 98%. On the other hand, chloride interference was reduced by the micro-porous tubing by an average of 95%. It was apparent that the masking effect of IC on chloride interference was comparable to the minimization capacities of the reducing agent and the micro-porous tubing. Furthermore, the choice to utilize the masking effect of IC in the determination of DOC in estuarine and coastal waters did not alter the configuration of the modified FIA method.

The FIA method was found suitable for the determination of DOC in estuarine and coastal waters because it has a reasonably high carbon recovery of 98±9%, sample throughput of 60 samples per hour and a method detection limit (MDL) of 0.8mg/L (DOC). The carbon recovery of the modified FIA method described in this work was comparable to the carbon recoveries of a similar FIA method for DOC determination and a Beckman high temperature combustion instrument reported by (Koshy *et al.*, 1992). The MDL (0.8mg/L) of this modified FIA method made it suitable for the measurement of DOC in most estuarine and coastal waters because of the organic input from the land and the level of productivity in these types of waters. Moreover the interference by chloride on the measurement of DOC could be controlled in the FIA method described in this work.

The baseline study of DOC indicated that the organic discharge from the greater Suva land mass through the rivers, creeks, storm water outlets and the Kinoya sewage outfall significantly contributed to the DOC present in the Suva lagoon. The assertion was substantiated by the wide variation of DOC in each site on each day of sampling. The detectable DOC levels in the Suva lagoon in the period of study varied from 0.8mg/L to 35mg/L. The trend observed in the short period of study was that the levels of DOC in the sites monitored could be doubled or tripled when the Suva area experienced an average rainfall as low as 0.1mm in the three days prior to sampling. The modified FIA method described in this work could be used for the long term monitoring of DOC in the Suva lagoon and predictions could be made on the lagoon's DOC budget.

CHAPTER 1

INTRODUCTION

1.1 Dissolved Organic Carbon (DOC)

Carbon is the *link* between the inorganic environment and the *living* organisms. The carbon cycle basically illustrates the interchange of carbon between the atmosphere, hydrosphere, biosphere and the lithosphere (Stumm & Morgan, 1981). The focus of this thesis is the dissolved organic carbon (DOC) in natural waters, specifically marine and estuarine waters. In natural waters, the total organic carbon (TOC) is composed of particulate organic carbon (POC) and DOC. In most of these waters, the concentration of DOC is greater than the concentration of POC. For example, in the sea, the concentration of DOC surpasses POC by a factor of 50-100% (Robards *et al.,* 1994).

DOC in natural waters is usually made up of fatty acids, carbohydrates, amino acids, hydrocarbons, hydrophilic acids, fulvic acids, humic acids, viruses and clay-humic-metal complexes (Thurman, 1985, Libes, 1992 and Robards *et al.,* 1994). DOC is operationally defined by most analysts as the organic fraction that passes through a 0.45μm Millipore filter (Thurman, 1985) although DOC had been argued by (Jackson, 1988) to include POC. In this work, DOC would refer to the organic fraction that passes through a

0.45μm Millipore filter. The above argument probably arose from the difficulty in establishing the difference between particulate and dissolved organic carbon.

About 10% of DOC in most natural waters is made up of colloids. These colloids are basically large assemblages of humic acids with very large molecular weights of the order of 2,000 –100,000 (Thurman, 1985 and Chen & Wangersky, 1993). The colloids can be separated from water by cross-flow ultrafiltration or other methods resulting in a number of sizes and molecular weights (Guo *et al.*, 1995).

In fresh water bodies, DOC levels can be a few mg/L or occasionally in bogs and swamps, it could be as high as 50mg/L (Stumm & Morgan, 1981). In oceanic waters, DOC levels vary around 0.5mg/L, but can also be as high as 20mg/L in coastal waters and at the continental shelf (Riley & Chester, 1971 and Stumm & Morgan, 1981). The thin layer at the interface of seawater and the air (microlayer, <1μm in thickness) has a concentration range of DOC from 1.4 to 18mg/L. The DOC in the microlayer results from the high level of biological activity prevalent in it and the microlayer behaves like a polysaccharine – protein complex (Cauwet, 1976 and Ogura, 1976).

The actual concentration of DOC in an aquatic body will depend on the net productivity in terms of phytoplankton exudation and lysis, animal excretion and anthropogenic imports (rivers, industrial effluents, sewage outfalls etc.)

over outflow factors like uptake by organisms, biodegradation and sedimentation (Stumm & Morgan, 1981 and Libes, 1992). On the other hand, current movements and geochemical processes like sorption/partition, precipitation, volatilization, oxidation/reduction (both chemical and biochemical) and complexation within a water body will also affect the DOC concentration at a particular site (Thurman, 1985).

1.2 DOC in the Ocean

The total DOC in seawater is estimated at 10^{18}g, which is equivalent to a concentration of 0.7mg C/L (Riley & Skirrow, 1975) and is a major reservoir of organic carbon (Robards *et al.,* 1994 and Strom *et al.,* 1997). In coastal waters, because of increased phytoplankton activity and the input from land, DOC values can be as high as 20mg/L (Riley & Chester 1971). However, in estuaries, the concentration of DOC is about 10mg/L in the absence of any obvious input from the land (Head, 1976).

Terrestrial DOC can be transported to the ocean by wind, rivers or sediment pore run off and surface run off via storm water outlets and creeks. Rivers are by far the most prolific channels of DOC to the ocean, albeit the argument that the majority of DOC in the ocean is produced *in situ* (Thurman, 1985 and Libes, 1992). The above argument was based on the observation that rivers generally have low average annual DOC fluxes of 1.1×10^{8}g C/year with DOC levels in the range of 1-20mg/L (Libes, 1992). However, in areas of tropical climate where black water rivers are found, DOC concentrations may

range from 10 to 30mg/L. Furthermore, the DOC concentrations of rivers are not significantly affected by changing river discharges (Thurman, 1985).

The *in situ* production of DOC is led by the phytoplanktons via exudation and cell lysis (Lancelot, 1984, Lee & Wakeham, 1988, Libes, 1992 and Lee & Henrichs, 1993). The role of phytoplanktons in DOC production is also important in other natural water bodies like lakes, where such release is of ecological significance because the DOC released provides a source of energy to heterotrophic consumers and decomposers (Stumm & Morgan, 1981). The release of DOC by phytoplanktons is also considered to be a functional response of individual cells to changes in environmental conditions (Sundh, 1991). In addition to phytoplanktons, planktonic grazers like copepods and protist grazers also contribute to DOC production via excretion (Strom *et al.*, 1997). Other marine organisms also excrete DOC via their wastes and the decomposition of their dead bodies by microorganisms like bacteria and fungi (Lee & Wakeham, 1988, Lee & Henrichs, 1993 and Jaffes *et al.*, 1996).

1.2.1 Anthropogenic sources of DOC in the ocean

DOC may be derived from degradation products of terrestrial plants and animals, alternatively from sewage and industrial effluent, and are generally transported to the ocean via rivers, streams, ocean sewage outfalls and sediment pore waters (Robards *et al.*, 1994). Sewage input is by far one of the major contributors of the organic load to coastal seawaters. Sewage

effluents will usually contain wastes from domestic, commercial and food processing sources (Manahan, 1994). The concentration of TOC in marine waters receiving domestic and industrial sewage wastes occasionally exceed 100mg/L (Kennish, 1997). This is an alarming concentration because normal marine waters will generally have low DOC concentrations of a few milligrams per litre (Stumm & Morgan, 1981).

The amount of DOC transported via rivers to the ocean will depend on the activities in the rivers and on their banks, for example, agriculture, raw sewage dumping, logging, soil erosion and dredging. The transport of the DOC originating from such activities to the sea can be accelerated by rain *(Clair & Ehrman, 1996). Consequently, DOC from these anthropogenic* sources can offset the natural balance resulting in a host of problems to the water body *(see section 1.2.8)*.

1.2.2 The major components of DOC

Molecular weight distribution studies had shown that DOC has a number of different fractions (Guo *et al.*, 1995). However, not all the components/fractions of DOC can be identified and quantified easily in a routine laboratory procedure. The analytical difficulties associated with DOC identification and quantification in the sea are consequences of low DOC levels, interference by salt ions, complexities of some of the DOC components and their inherent chemical inertness (Libes, 1992). Because of the analytical difficulties associated with the measurement of individual

dissolved organic substances, bulk fractions like DOC and POC have been defined and measured. Humic acids, carbohydrates and hydrophilic acids have been identified as the major constituents of DOC (Stumm & Morgan, 1981, Thurman, 1985 and Rashid, 1985).

1.2.3 Humic substances

Humic substances account for 40-60% of the total DOC in seawater (Stumm & Morgan, 1981 and Thurman, 1985). Humic substances have been operationally identified as the colored polyelectrolytic organic acids, with carboxylic, hydroxyl and phenolic functional groups, which can be separated from water on XAD resins (nonionic macroporous resins) (Thurman, 1985 and Robards *et al.*, 1994). A similar distribution of DOC occurs in black stream waters and the major components of DOC identified are humic and fulvic acids, (Leff & Meyer, 1991). Figure 1 shows the typical structure of fulvic acid. The humic fraction consists of fulvic, humic and humin acids that can be separated at different pH levels. In aquatic bodies the humin fraction is insignificant compared to the fulvic and humic fractions. The humic acids can be precipitated from natural water samples by acidification to pH levels less than two (Stumm & Morgan, 1981 and Robards *et al.*, 1994). The remaining water after acidification should have the fulvic fraction.

Humic acids have very little carboxylic groups compared to fulvic acids and this is the main reason for the low solubility of humic acids (hydrophobic) in seawater. Furthermore, humic acid molecules are two to ten times larger

than fulvic acids and also have long chains of fatty acids ($C_{12} - C_{18}$) and these factors also contribute to the hydrophobic nature of humic acids. On the other hand, fulvic acids generally have abundant hydroxyl and phenolic groups (Thurman, 1985), which make them more soluble (hydrophilic) in seawater.

The aliphatic content of marine humic substances is greater than that of terrestrial humic substances and marine fulvic acids have very little or no phenolic hydroxyl functional groups, (Thurman, 1985 and Rashid, 1985). The aliphatic nature of marine humic substances make them less susceptible to coagulation than terrestrial humic substances. The coagulation of terrestrial humic substances is facilitated by the aromatic groups which have been said to be susceptible to flocculation when exposed to high concentration of electrolytes especially at a salinity range of 15 to 20psu (practical salinity unit) (Thurman, 1985 and Libes 1992).

Terrestrial humic substances also contribute indirectly to the formation of marine humic substances by biologically conditioning the seawater, which can result in the high production of phytoplanktons (Prakash *et al.,* 1973). Quinones, the aromatic constituents of terrestrial humic substances are responsible for the growth of phytoplankton (Prakash *et al.,* 1973). Researches by a number of workers have confirmed the positive effect of terrestrial humic substances on the productivity/growth of coastal phytoplankton communities (Fernandez, 1968, Lee & Bartlett, 1976 and Carlsson, 1999). Consequently, a larger number of phytoplankton will

increase the amount of DOC they release to the surrounding water. Unfortunately increased productivity by phytoplankton can sometimes result in red tide blooms (Carlsson, 1999).

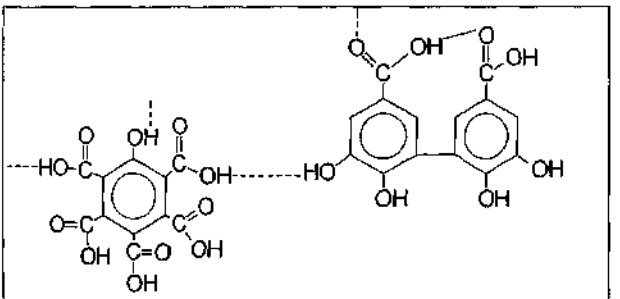


Figure 1 Structure of a fulvic acid, (Sturm & Morgan, 1981)

Apart from the DOC exuded by phytoplankton and from the decomposition of organic matter by microorganisms, humic substances are also produced from organic compounds by polymerization resulting from photochemical reactions of the marine DOC (Moran & Zepp 1997). The UV radiation absorbed by the chromophores present in the organic compounds assist in the polymerization reactions (Morris & Hagreaves 1997). The organic compounds involved in the polymerization reactions have been confirmed through chemical and isotopic studies to be degradation products of phytoplanktons (Nissenbaum & Kaplan, 1972 and Libes 1992). Photochemical reactions also result in the production of low molecular weight DOC and inorganic products like inorganic carbon (IC) and carbon monoxide (Zepp *et al.,* 1995). Humic substances are resistant to oxidation by bacteria.

1.2.4 Carbohydrates

Carbohydrates account for 5-10% of the DOC, in seawater (Thurman, 1985). All forms of planktonic cells (phytoplankton and zooplankton) consist of 10-70% carbohydrate and the DOC they release to the water column has a 30% component as carbohydrate (Hellebust, 1965, Burney *et al.*, 1981, Ittekot *et al.*, 1981, Mopper *et al.*, 1995 and Strom *et al.*, 1997). The contribution by carbohydrates to DOC has not been considered significant in the past because of the insensitive analytical techniques used for their measurement. The carbohydrates identified were predominantly polysaccharides (Thurman, 1985 and Strom *et al.*, 1997). Carbohydrates are highly reactive substrates and they support heterotrophic metabolism (Skoog & Benner, 1997).

1.2.5 Hydrophilic acids

Apart from fulvic and humic acids, there is another subclass of humic substances known as hydrophilic acids. Hydrophilic acids are organic acids that cannot be retained by the XAD resins at pH 2 (Thurman, 1985). The hydrophilic acid component of humic substances is a mixture of simple and complex acids. The range of acids could be from simple fatty acids to complex polyelectrolytic acids with numerous hydroxyl and carboxyl functional groups (Thurman, 1985). In seawater hydrophilic acids, constitute 50% of the DOC (Thurman, 1985). However, since the hydrophilic acids have been isolated only recently, very little is known about their structures and chemistry.

1.2.6 Other components of DOC in the ocean

The metabolic activities of marine organisms also results in the production of a range of biomolecules that form part of DOC in the ocean. These compounds (biomolecules) include, hydrocarbons, lipids, carboxylic acids and amino acids (Thurman, 1985, Stumm & Morgan, 1981, Rashid, 1985 and Libes, 1992). These compounds usually constitute 10 to 20% of the total DOC in most natural water bodies (Thurman, 1985 and Stumm & Morgan, 1981). The quantification and identification of these biomolecules are quite difficult because of their very low concentrations in seawater. These biomolecules can undergo biochemical and chemical condensation reactions to form complex assemblages and eventually polymerize to form humic substances (Rashid, 1985). Apart from these, there are other trace compounds like aldehydes, sterols, organic bases, organic sulfur compounds, alcohols, ketones, ethers, chlorophyll and other pigments, and organic contaminants (Thurman, 1985) that are present as DOC in estuarine and marine coastal waters.

1.2.7 The ecological role of DOC in estuarine and marine waters

DOC plays an important role in the biogeochemistry of any aquatic system because it is a component of the total carbon which is cycled through organisms, the water body, sediments and plants (Stumm & Morgan, 1981). Therefore the bulk analysis of water for DOC is essential for the overall

understanding of the production-decomposition cycle and the spatial temporal variability of DOC in an aquatic system (Robards *et al.*, 1994).

The tissue of all the plants and animals in the marine and estuarine waters have significant amounts of carbon. The carbon is taken in by the organisms primarily in the dissolved state. In other words, DOC in aquatic ecosystems provides energy and carbon for the metabolism of heterotrophic bacteria plus some species of phytoplankton which can subsist heterotrophically on dissolved organic substrates (Riley & Chester, 1971 and Volk *et al.*, 1997). Marine organisms also release DOC compounds to control some aspects of their environment. The released compounds can function as toxins to repel predators and competitors, neutralize toxins and to function as attractants for mating (Sundh, 1991 and Libes, 1992).

DOC in the form of humic substances have phenolic, hydroxyl and carboxylic groups that can chelate with toxic metal ions like Hg^{2+}, Al^{3+} and Pb^{2+} (Manahan, 1994). When toxic metals bind to DOC, their toxicity is reduced. This is because dissolved metal ions (free metal ions) are more toxic compared to their complexed form (Barber & Ryther, 1969, Campbell & Meadows, 1988 and Chin & Benoit, 1997). For example, it has been shown that the molecular weight, functional group chemistry and the lability of organic compounds have a controlling effect on the mercury cycling processes such as methylation and volatilization (Chin & Benoit, 1997). In aquatic systems, the complexation processes of metal ions by DOC also results in the transport of the metal ions through the up take of the

complexed DOC by organisms and the aggregation of DOC on particulate matter which eventually sink to the ocean bed (Stumm & Morgan, 1981).

The chelation of essential ions like Mg^{2+}, Ca^{2+} and Fe^{2+} is another important role of humic substances with respect to living systems in aquatic bodies like the sea. In the chelated form, the essential ions can be taken in by living organisms and furthermore, chelation prevents the essential ions from precipitating.

DOC, primarily in the form of humic and fulvic acids, binds organic pollutants such as phthalates and pesticides as in the case of heavy metals (Stumm & Morgan, 1981). Humic acids have a greater affinity for hydrophobic compounds than fulvic acids. In addition, unlike fulvic acids, humic acid's binding ability is not affected by large changes in pH. This is because fulvic acids are soluble throughout the entire pH range; therefore they are available for binding with suitable metal centers and organic pollutants (Fabrizo & Jussi, 1997). The storage of DOC by marine plants also assist in moderating the atmospheric concentration of the greenhouse gas carbon dioxide, because DOC acts as a sink for carbon dioxide (Hansell, 1995). Thus the longer the ocean retains CO_2 in terms of DOC the better it is for minimizing the greenhouse effect.

1.2.8 The negative effects of DOC

The ultimate fate of DOC in an aquatic system is its oxidation to carbon dioxide by bacteria, fungi, protozoan and animals present in water (Libes, 1992). Consequently, an excess of DOC might impose considerable demand on the oxygen budget of the water bodies (Jackson, 1988 and Robards *et al.*, 1994), seriously affecting water quality.

At 25^0C and 1 atmosphere pressure, a water body will have an oxygen content of 8.32mg/L, and this can be consumed by 7.8mg of organic matter (Manahan, 1994). The above estimates are based on this equation, $CH_2O + O_2 \rightarrow CO_2 + H_2O$, which is a representation of the DOC degradation (Manahan, 1994). DOC concentration correlates positively with apparent oxygen utilization (Hung & Chang, 1992), further reiterating the detrimental effect an excessive amount of DOC can have on the oxygen budget in any aquatic system.

Oxygen depletion is also related to eutrophication (the enrichment of aquatic bodies with nutrients like phosphate (PO_4^{3-}), nitrite (NO_2^-) and nitrate (NO_3^-)) (Manahan, 1994 and Kennish, 1997). Apart from the inorganic forms of the nutrients, the dissolved organic forms of the nutrients in marine waters may also be valuable sources for autotrophic growth (Kennish, 1997). The input of nutrients to estuaries and coastal waters tend to accelerate primary production (in phytoplanktons), when one of the nutrients become limited, the

phytoplankton (essentially DOC) perish and their decomposition can lead to extensive oxygen consumption as a result of increased rates of animal respiration and the decomposition activity of microorganisms (Blackmore *et al., 1987* and Clark, 1992). However, at the initial stages of eutrophication oxygen is also produced by the phytoplankton through photosynthesis (Kennish, 1997). Anoxic (lack of oxygen) conditions initiated through eutrophication have been reported in a number of coastal marine waters (Pokryfki & Randall, 1987, Portnoy, 1991, Doi & Nitta, 1991, Seiki *et al.*, 1991 and D' Avanzo & Kremer, 1994).

1.3 DOC measurement: Current Methods

The accurate measurement of DOC has not received much attention for most of the past two decades (Sharp *et al.*, 1993b) mostly because of the difficulties associated with experimental DOC determination (Hung & Chang, 1992). Renewed interest in DOC measurement was prompted by its importance in global ocean fluxes (Legendre & Gosselin, 1989) and in the microbial cycles (Kirchman *et al.*, 1991).

DOC in natural waters is normally measured by high temperature catalytic oxidation (HTCO) or wet chemical oxidation (WCO) methods. The two methods have different variations depending on the instrument specification. The basis of all the methods of measuring DOC has been the oxidation of DOC, followed by separation and the measurement of the resultant carbon dioxide (Wangersky, 1993 and Robards *et al.*, 1994). Neither HTCO nor

WCO is perfect, yet most analysts consider the HTCO techniques to be more reliable, since complete combustion of DOC is usually achieved during oxidation (Mackinon, 1978 and Hung & Chang, 1992).

1.3.1 HTCO methods for DOC analysis

The HTCO techniques employ high temperatures of the order of 600^{0}C or more for the oxidation of DOC to carbon dioxide (Perdue *et al.*, 1993). The quantification of the carbon dioxide can be achieved through a variety of procedures like gas chromatography, capacitance manometry and non-dispersive infra red spectrometry (Aleprin & Martens, 1993 and Robards *et al.*, 1994). Suitable catalysts like platinum, silica and alumina also assist the oxidation process. There are various commercial HTCO units available in the market along with their locally built or modified versions. In Table 1 are given examples of such commercially available HTCO instruments for the routine DOC determination in seawater. The major setbacks of HTCO methods are contamination and poor reproducibility (Hung & Chang, 1992).

All the instruments in Table 1 have detection limits, which can range from one part per billion to several parts per million. The instruments also have their own limitations that can be specific to a particular instrument or generic to a range of instruments especially when the mode of detection of carbon dioxide is the same. The limitations are usually associated with the interference from chloride that is present in large amounts in seawater,

although most of these instruments have halogen scrubbers to eliminate chloride interference.

Table 1

Some of the commercial and custom built HTCO instruments

Type of Instrument	Reference	year
Shimadzu TOC 500	Sharp *et al.*	1993b
Shimadzu TOC 5000	Sharp *et al.*	1993b
Dohrman DC-190	Sharp *et al.*	1993b
Sumigraph TOC 90	Hedges *et al.*	1993
Beckman 915-C analyzer	Koshy *et al.*	1992
Ionics TC-TOC 555	Sharp *et al.*	1993b
Mackinon HTCO unit	Mackinon	1978
Columetrics 5020-TC	Hedges *et al.*	1993
Sugimura &Suzuki HTCO unit	Sugimura & Suzuki	1988

1.3.2 WCO methods for DOC analysis

WCO methods utilize oxidants like persulfate and mercury (II) chloride to oxidize DOC to carbon dioxide. WCO methods and instruments are usually operated at temperatures in the range of 50^0C to 120^0C (Aleprin & Martens, 1993 and Hedges *et al.*, 1993). WCO methods can also be used in combination with an UV source and a catalyst. A strong UV source on its own

can be used as an oxidant to oxidize DOC (Robards *et al.*, 1994). Nowadays, UV sources and oxidants have been combined for enhanced oxidation and these combined units are more popular than the other conventional methods, see table 2. The combined units have been classified here as the WCO methods.

Table 2

Selected WCO instruments/methods

Instrument/Method	Reference	Year
Duursma-WCO	Duursma	1961
UV-Persulfate (Technicon Instrument)		1976
UV-Photo-oxidation	Gershey *et al.*	1979
Technicon A11-UV-Persulfate	Hedges *et al.*	1993
HM Automatic- UV-Persulfate	"	"
01 700-TOC Persulfate	"	"
UV-Persulfate	Mantoura & Woodward	1983
UV-Persulfate	Williams & Druffell	1988
Ampoulated UV-Persulafe	Sharp *et al.*	1993c

Different analysts sometimes use their own variations of the commercially available WCO instruments. Some of the instruments listed in table 2 were custom built.

1.3.3 Comparative work on DOC via HTCO and WCO

Comparative studies between HTCO and WCO methods have been done by a number of workers (Gershey *et al.*, 1979, Riley & Skirrow, 1975, Sugimura & Suzuki, 1988, Wangersky, 1993, Tugrul, 1993, Hedges *et al.*, 1993, Chen & Wangersky, 1993, Miller *et al.*, 1993, Sharp *et al.*, 1993b&c and Tupas *et al.*, 1994). In all such studies it was found that the DOC values obtained from HTCO methods were generally higher than the DOC data for the same seawater samples obtained from WCO methods. The comparative work by Sugimura and Suzuki in 1988 recorded the largest difference between HTCO and WCO. On the other hand, attempts to reproduce the work by Sugimura and Suzuki have not been successful (Chen & Wangersky, 1993, Sharp *et al.*, 1993b). Nevertheless that did not diminish the concern for the disparity between WCO and HTCO methods. It was also reported in other works that seawater samples initially oxidized by WCO methods and subsequently re-oxidized by HTCO methods recorded a significant amount of residual DOC (Druffel *et al.*, 1989 and Suzuki & Tanoue, 1991). Furthermore, the amount of residual DOC was equivalent to the difference in the DOC values obtained from WCO and HTCO methods (William *et al.*, 1993).

Table 3

Comparison of DOC values for HTCO and WCO methods

Authors	% Difference [HTCO – WCO] x [100/WCO]
(Riley and Skirrow, 1975)	50-60
(Gershey *et al.*, 1979)	5-10
(Wangersky, 1993)	10
(*Tugrul*, 1993)	32-33
(Hedges *et al.*, 1993)	2-4
(Sugimura and Suzuki, 1988)	50-400
(Sharp *et al.*, 1993b)	10-15
(Chen & Wangersky, 1993)	5-60
(Miller *et al.*, 1993)	50

Note: The above sources did not indicate the levels of uncertainty

In some comparative studies, differences between HTCO and WCO have been statistically found to be insignificant (Hedges *et al.*, 1993, DeBaar *et al.*, 1993, Kaplan, 1992 and *Aleprin* & Martens, 1993). *It is apparent from the* debate for and against the significant difference between HTCO and WCO data, that there is still a controversy over the methods for the accurate measurement of DOC (Tupas *et al.*, 1994). A compromise between HTCO and WCO methods is out of reach at the moment, because there is no comprehensive description of the DOC pool in seawater and none of the

methods available at the moment fulfil all the criteria set for accuracy (William *et al.,* 1993).

1.3.4 The reasons for the disparities between HTCO and WCO methods

The reported differences between HTCO and WCO methods discussed previously and reported elsewhere compelled DOC analysts to search for possible explanations to account for the differences. Generally, the HTCO methods were elucidating DOC values greater than the DOC values registered by the classical WCO methods for the same estuarine and marine samples. The generally higher DOC data obtained through HTCO methods undermined the fact that most model organic compounds and known DOC substances in seawater were oxidized efficiently by WCO methods (Perdue *et al.,* 1993 and Chen & Wangersky, 1993). Furthermore, the WCO methods have at that stage been accepted as standard techniques and the new data via HTCO had put into question the established data on marine DOC via WCO methods (Sugimura & Suzuki, 1988 and Lee & Henrichs, 1993).

1.3.4.1 Analytical blanks

The under estimation or total disregard of the analytical blank of DOC analysis with HTCO methods was one of the major factors (Miller *et al.,* 1993, Chen & Wangersky, 1993, Sharp *et al.,* 1993b, Hedges *et al.,* 1993 and Cauwet, 1994) for the high DOC values reported. For example, a rigorous assessment of DOC data obtained from twenty different WCO and HTCO

instruments/methods showed that the variability in the DOC data was caused by unaccounted blanks (Hedges *et al.,* 1993).

HTCO methods will have a reagent, water and system blanks. The blanks associated with HTCO methods arise from the possible DOC contributions from the chemicals used to prepare the reagents, the water used to prepare the reagents and from spurious signals inherent with that particular instrument. The reagent and water blanks can be controlled, because reagents of high purity (carbon free) can be obtained as well as low carbon water (William *et al.,* 1993). However, the system blank is difficult to establish, despite it being dependent on the type of catalyst, the support system and the carbon carried over from the previous injection (Perdue *et al.,* 1993). In most cases the system blanks DOC contributions will be less than the detection limits of the instruments (Miller *et al.,* 1993).

1.3.4.2 Incomplete Oxidation

Since WCO methods recorded the lower DOC values it is appropriate to consider the possibility of incomplete oxidation in this context. The oxidation of DOC via WCO methods can produce organic intermediates that are more refractory than the starting material (Peyton, 1993). As a consequence these organic intermediates would not contribute to the total DOC recorded. Humic substances and proteins are major components of DOC in marine waters. These substances are capable of reacting with chloride in sea water to produce organochlorines which have been demonstrated to be amongst the

most refractory substances to WCO and HTCO methods (Rook, 1977 and Lee & Henrichs, 1993). Furthermore, incomplete oxidation can also be caused by decreased availability of hydroxyl radicals as a consequence of chloride scavenging, (Peyton, 1993). The reaction between the persulfate radical and chloride ion is illustrated by the following equation.

$SO_4^{\cdot-} + Cl^- \rightarrow SO_4^{2-} + Cl$ (Minisci *et al.*, 1983).

Algal species, phytoplankton and bacteria are capable of releasing high molecular weight DOC fractions, especially at the surface of the sea and at estuaries. The high molecular weight DOC fractions have been speculated to be colloidal and can only be measured by HTCO methods (Sugimura & Suzuki, 1988 and Lee & Henrichs, 1993). Furthermore, these macromolecules could also contain sulfur and other constituents that inhibit oxidation (Lee & Henrichs, 1993).

The matching of the differences in the DOC data obtained through HTCO and WCO methods is still debatable, although factors like unaccounted blanks, refractory intermediates and colloidal DOC have been identified as the basis for the differences. Consequently, it is appropriate at this stage that both methods (HTCO and WCO) are used for DOC determination until a compromise is reached. Furthermore, as discussed earlier on, in some comparative studies the differences between HTCO and WCO methods in terms of the DOC determined for the same seawater samples were not significantly different.

1.4 Flow injection analysis (FIA)

In this project, we have used FIA principles for the modification of a method to measure DOC in estuarine and coastal waters. The Danish scientists Ruzicka and Hansen first proposed FIA in 1974. It involves the injection of a liquid sample into a moving non- segmented carrier solution coupled with suitable reagents, whereby a reaction or a series of reactions take place. The injected sample forms a reaction zone which is then transported toward a detector that continuously measures an appropriate physical parameter like absorbance or conductance as a function of time (Ruzicka & Hansen 1981 and Koshy *et al.*, 1992). It has application in diverse areas such as oceanography, clinical chemistry, agricultural, pharmaceutical and environmental analysis (Ruzicka & Hansen, 1975). Flow injection instrumentation for small systems are simple to construct. As of 1996, 6000 papers have been published concerning flow injection mainly in the field of instrumental analysis (Ruzicka *et al.*, 1996).

Flow injection was developed, with a view to automate serial assays. In the mid 1970s Ruzicka and Hansen began experimenting with their model FIA system to determine methyl orange, using spectrometry for detection. The methyl orange was selected because of its red color change and it was chosen to investigate their FIA system's ability to reproduce data and maximize sample throughput (Rucizka & Hansen, 1975). The determination of ammonia was by potentiometry, where an ion-selective electrode was used as the detector and this was to illustrate the versatility of FIA to any

form of detector. It was obvious that FIA at its infant stages has already shown versatility as an analytical tool.

In figure 2 is a generalized schematic of a FIA system. The common propelling unit is a peristaltic pump that comes in a number of models on the market. The pressure mounted between a set of rolling pins and the pump tubes facilitates the pumping action. The pumping can be achieved in both directions by means of a switch. The draw back of peristaltic pumps is the fact that they cannot be completely pulse free (Ruzicka & Hansen, 1981).

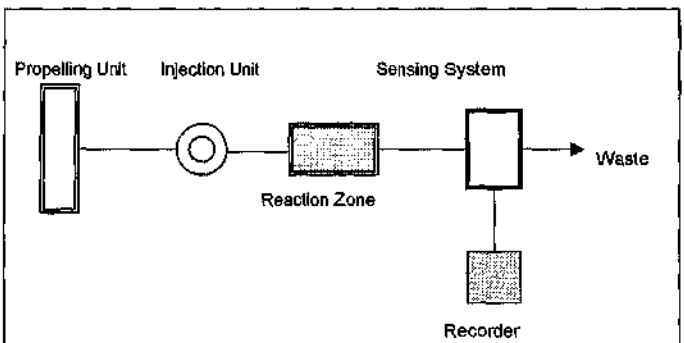


Figure 2 Generalized FIA system

The sample can be injected using a hypodermic syringe or as in modern instruments through the use of valve systems. The valves will have an injection and loading position and a switch is used to change from one to the other. The reaction zone is basically a certain length of Teflon tubing in which the desired reaction(s) take(s) place. The length of the tubing is dependent

on the kinetics of the reaction; a fast reaction will need a shorter tube than a slower reaction.

The sensing system depends on the physical parameter being measured which is (e.g. conductivity, absorbance, and pH) proportional to the concentration of the analyte of interest. The detectors that have been used include, conductivity detector, spectrophotometer (UV, IR and FTIR) and ion selective electrodes. For example, in the FIA determination of chloride, the detector used is a spectrophotometer (Ruzicka & Hansen, 1981). The monitor can be a simple flat bed chart recorder, an integrator or a computer.

FIA is a continuous flow method. The only difference it has with other flow methods like chromatography which aims at high resolution obtained through megarepetitive interactions by modulating the migration velocities of analytes through the system is that it exploits chemical reactions to transform analytes into species that can be selectively quantified by a detector (Ruzicka, 1992). FIA also allows for a dramatic reduction of reagents and solvents used. Since its development a series of reactors and detectors have been designed to accommodate solvent extraction, gas diffusion, photodegradation, colorimetric reagent regeneration, immobilized enzyme and ion exchange to name a few.

In any flow injection instrument, two processes explain the mechanism of analysis and detection that take place. First, the sample zone disperses within the carrier line and second the reaction(s) which occur(s) between the

analyte and the appropriate reagent(s). Initially the sample zone in the carrier stream form a rectangular concentration profile as shown in figure 3a. As it moves toward the detector, band broadening or dispersion via convection and diffusion occurs (Ruzicka & Hansen 1981 and Skoog *et al.*, 1998). Convection results from laminar flow, in which the center of the sample zone moves faster than the liquid adjacent to the walls of the tube, see figure 3b. Dispersion via diffusion occurs by radial mixing and not axial mixing because of the narrow tubes used in FIA. The combined effects of convection and diffusion result in the attainment of the sample concentration profiles shown in figures 3c and 3d.

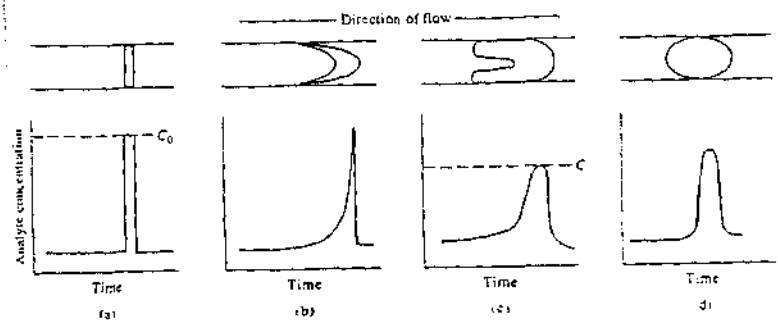


Figure 3 Effect of diffusion and convection on the sample zone as it moves toward the detector, (Skoog *et al.*, 1998)

1.4.1 Optimization of an FIA system

The optimization of FIA parameters is crucial for the improvement of sensitivity and the maximization of sample throughput. The parameters that can be optimized are flow rates, lengths and diameters of tubes, injection volumes, operating temperature and reagent composition. Optimization is achieved by trying different flow rates, lengths and diameters of tubes and injection volumes until the optimum results are obtained. However, a more

systematic way would be to use numerical methods like Powel and Simplex, which can enhance the optimization process (Ribeiro *et al.*, 1993). The point to note here is that different FIA systems will have different optimum conditions. Thus, it is the duty of the analyst to check and test for the best operating conditions despite its tedious nature. For example, two groups of investigators were only able to fix the length of the reaction coil after a series of optimization exercises for the measurement of iron and titanium (Andrade *et al.*, 1992 and Castanares & Mundo, 1995).

Interference with signal output, from species other than the analyte can affect the sensitivity, accuracy and precision of the output. Thus, the optimization of an FIA system is also necessary to minimize interference. It might also be possible to have incompatible optimum conditions for the different variables; as such a compromise has to be reached.

1.4.2 Methods developed from the original FIA system

The main consideration behind the first generation of flow injection systems was the speed at which sample solutions should be processed. FIA had evolved into other forms of systems, like stopped flow technique, reverse flow and sequential injection because of the need to enhance performance and achieve kinetic discrimination, titration ability and for its introduction to industrial applications.

The stopped flow technique exploits a concentration gradient from a dispersed sample zone. Methods based on stopped flow can eliminate background signals, provide kinetic discrimination and increase sensitivity (Christian & Ruzicka, 1992). The method itself is conservative in terms of reagent usage. However, this method has not found much application apart from its application in enzymatic measurement for monitoring bio-processes, enzyme reactions on solid surfaces and the determination of rate constants.

Sequential injection evolved from stopped flow injection. The sample and the reagent zones are stacked in tubular conduit, merged by means of flow reversal of the carrier stream and then transported into the detector (Ivaska & Rucizka, 1993). Sequential injection is applicable in process lines given its rapid and robust methodology. Sequential systems are preferred over FIA systems due to fewer requirements for maintenance in process environments (Ruis *et al.*, 1997).

Reverse flow injection has resemblance to stopped flow and sequential injection methodologies. Generally, the reagent is injected into a sample stream or a monitor was formed in the bolus (the segment of the injected sample in the carrier stream) by the dispersion of a concentration-limiting reagent contained in the carrier stream (Fogg *et al.*, 1990). In normal FIA the product is formed in the extremities of the sample bolus whilst in this method the product is formed at the center of the bolus. Any further dispersion will result in the dilution of the product. Reverse flow injection can allow a variable amount of mixing between the sample and carrier stream, increase

the efficiency of solvent extraction, leading to multiple detection capabilities and allow sampling and preconcentration of gaseous analytes (Clark *et al.*, 1991). The ability of this method for variable mixing allows for the construction of a capillary-based titration system. The above method has also found wide application in the determination of cations and anions (Esmadi *et al.*, 1990). The principles of reverse flow injection have been applied in reverse dual phase gas diffusion in which a liquid donor stream is coupled to a gas acceptor stream for the determination of metal hydrides (Smith & Pacey, 1993).

1.5 Determination of DOC using FIA

An innovative WCO method involving FIA for the determination of DOC was described by (Koshy *et al.*, 1992). The manifold used in this method is shown in figure 4 where, the organic carbon was oxidized by an alkaline solution of peroxoydisulfate (persulfate) under UV and the resulting carbonate was acidified and heated for conversion to carbon dioxide. The CO_2 generated is allowed to diffuse across a Teflon membrane into a weakly buffered (pH 9.75) phenolphthalein acceptor stream. The acceptor stream was directed to a flow through cell and the absorbance was measured by using a spectrophotometer (Hitachi U-2000). This method has an average recovery of 98% with a sample throughput of 45 samples/hour and a detection limit of 0.5mg C/L. From an analytical point of view, the FIA technique for DOC determination is of considerable practical value as it is efficient, fast and

above all considerably cheaper, making it suitable for laboratories in developing countries.

However, the above method suffers from chloride interference. A similar wet chemical method by Sakamoto & Miyasaka, for the determination of total organic carbon, showed considerable interference by chloride at concentrations greater than 250mg/L because of the simultaneous oxidation of chloride to chlorine gas (Sakamoto & Miyasaka, 1987). FIA is not the first flow method for the measurement of DOC. A similar flow method was developed by Schreurs to measure DOC in seawater. The organic materials were oxidized photochemically to carbon dioxide. The method had a linear range of 0.1-10mg/L DOC (Schreurs, 1978). However, the method has also suffered from chloride interference. Consequently, hydroxylaminehydro-chloride was used to reduce the chlorine back to chloride. Generally, the oxidation of chloride to chlorine (Schreurs, 1978, Sakamota & Miyasaka, 1987, Koshy *et al.,* 1992, and Peyton, 1993) has been identified as the major interfering process to the determination of DOC in estuarine and coastal waters.

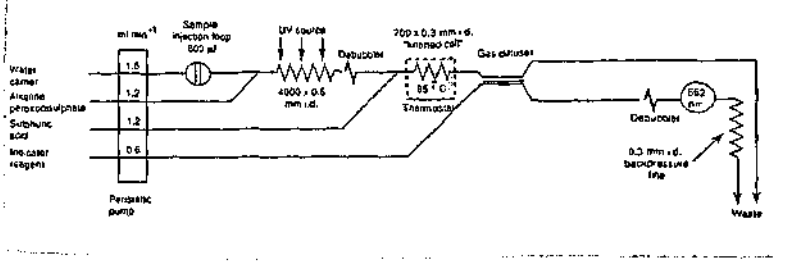


Figure 4 The FIA manifold used by (Koshy *et al.*, 1992)

1.6 The background of the project

DOC is an important determinant of organic matter in aquatic bodies apart from the chemical oxygen demand (COD) and the biochemical oxygen demand (BOD). The latter parameters estimate the quantity of oxidant required for the oxidation of organic constituents and measure the oxygen uptake in the microbiological mediated oxidation of organic matter respectively (Kennish, 1997). However, BOD and COD do not indicate the total dissolved organic matter in estuarine and seawater (Stumm & Morgan, 1981). Consequently, parameters like TOC and DOC are preferred over BOD and COD as indicators of organic matter.

DOC is also an indicator of water quality. Excess DOC could result in the depletion of oxygen, when DOC oxidizes and the water body is not able to replenish itself with oxygen. Consequently, the quantification of DOC in estuarine and marine coastal waters is important because in the Pacific Island countries the wastes generated are predominantly organic in nature and in most cases the wastes are not treated, but are directly discharged into the estuaries and coastal waters.

Automated instruments are favored for most types of analytical work these days. Most of these automated instruments are expensive to buy and maintain in the context of laboratories in developing countries. With the added emphasis on environmental monitoring throughout the world, the demand for cheaper field instruments and inexpensive methods of

automation are constantly increasing. Against this background FIA seems to be making a promising break through because the methodology is cheap, robust and portable (Koshy, 1989).

The main problem with the FIA method for DOC developed by (Koshy *et al.*, 1992) was the enhancement of the measured DOC levels in saline natural water samples by chlorine. Consequently, both carbon dioxide and chlorine diffuse across the Teflon membrane to the acceptor stream and changed the pH of the acceptor stream since both gases were acidic. Therefore, the interference by chlorine must be eliminated or minimized so that estuarine and seawater samples can also be analyzed for their DOC levels using the above FIA method. Moreover, in the modified FIA method used in this work a custom built conductivity detector was used instead of the spectrophotometer. The change of the detector to the custom built conductivity detector was necessary, given the high cost of buying and maintaining a UV-spectrophotometer in the South Pacific.

1.7 Research Objectives of this Project

The main objective of this project was to investigate the involvement of chloride in the determination of DOC using a modified FIA method developed from the FIA method described by (Koshy *et al.*, 1992). The minor objective was to use the modified method to do a baseline study of DOC in the Suva lagoon and correlate the DOC values with the possible terrestrial sources of organic matter in the landmass of Suva. To this effect, the following specific objectives were established.

- Quantify the chloride interference on carbon signals
- Reduce the power of the persulfate/borax oxidant and enhance it with titanium dioxide, so that chloride does not get oxidized.
- Use hydroxylaminehydrochloride ($NH_2OH.HCl$) to keep chlorine in the chloride form by means of reduction.
- To use a micro-porous tubing (Accurel PP Type S6/2, 0.2μm, Enka) after the UV chamber to remove gases formed in the UV chamber which included chlorine.
- To use the modified method to measure DOC on selected sites around Suva harbor and Laucala bay.

CHAPTER 2

EXPERIMENTAL

2.1 Chemicals

The major chemicals used in this work are listed below:

Borax (UNIVAR, Ajax Chemicals), Potassium persulfate (UNIVAR, Ajax Chemicals), Anhydrous sodium bicarbonate (UNIVAR, Ajax Chemicals) Concentrated Sulfuric acid (UNIVAR, Ajax Chemicals), Anatase titanium dioxide, Potassium hydrogen phthalate (UNIVAR, Ajax Chemicals), Citric acid (UNIVAR, Ajax Chemicals), Nicotinic acid (UNIVAR, Ajax Chemicals), Urea (UNIVAR, Ajax Chemicals), Thiourea (UNIVAR, Ajax Chemicals), Sodium acetate (UNIVAR, Ajax Chemicals), D-Glucose (UNIVAR, Ajax Chemicals), Sodium chloride (UNIVAR, Ajax Chemicals). The purities of these chemicals as stated by the manufacturers varied from 99% to 99.9% with the exception of the Sulfuric acid (UNIVAR, Ajax Chemicals) and Phosphoric acid (UNIVAR, Ajax Chemicals) which were of 98% and 84% purity respectively. The consideration of the above chemicals with 99% and 99.9% purity levels as having 100% purity did not cause significant changes to the concentrations of the solutions prepared from the chemicals.

2.2 Reagents

2.2.1 Preparation of distilled deionised water (DDW) and the $35^0/_{00}$ NaCl solution

DDW is distilled water that has been passed through four columns of universal ion exchanger (Cole-Palmer Instrument Company). These four columns removed all ionic substances. DDW has a low carbon content. DDW was used as the final rinsing solvent for all glassware.

The $35^0/_{00}$ NaCl solution was prepared by dissolving 35g of NaCl in 1 liter of DDW. Aleprin and Martens (1993) also used the above solution as a substitute for synthetic seawater on a similar work on DOC determination. Moreover, Hung and Chang (1992) used 3% NaCl solution as a substitute for synthetic seawater. The other major components of seawater like $MgCO_3$, $MgCl_2$ and Na_2SO_4 were not included because, the Mg^{+2} combined with the carbonate ions of the inorganic carbon standards to form a precipitate. Furthermore, the effect of chloride on carbon signals has to be isolated.

2.2.2 Preparation of carbon stock solution

The inorganic carbonate (IC) carbon stock solution of 1000mg C/L was prepared by dissolving 7.0008g of $NaHCO_3$ in 1litre of DDW. Depending on the range of standards required a working stock solution of 100mg/L or 500mg/L were prepared from the original stock solution. The pH of the IC

standards prepared in DDW was pH 7.8 and the IC standards prepared in the $35^0/_{00}$ NaCl solution had similar pH as those standards prepared in DDW. On the other hand, the KHP standards (DOC) prepared in both DDW and the $35^0/_{00}$ NaCl solution registered pH of 4. The slight acidity in the DOC standards is attributed to the acidic nature of KHP with a pKa of 5.4 (Aylward & Findlay, 1974). Preliminary work on the effect of the DOC standards on the pH of the oxidant showed that the acidic nature of the DOC standards did not change the pH of the oxidant (pH 9) consequently, the photochemical oxidation of DOC was not affected.

An accurately weighed amount of each organic model compound equivalent to 0.5000g carbon was dissolved in 1 liter of DDW (500mg/L). A 5mg C/L standard for each model compound was prepared from the respective stock solutions for the recovery analysis of carbon.

2.2.3 Preparation of 1M Sulfuric acid

The 1M H_2SO_4 was prepared by diluting 56ml of concentrated H_2SO_4 with DDW to one liter. The diluted acid was used for the acidification of the carbonate (from DOC oxidation) produced in the alkaline oxidation chamber. Furthermore, it was used to evolve the measured inorganic carbon in natural water samples and IC standards.

2.2.4 Preparation of the Oxidant

The oxidant was prepared by dissolving accurately weighed amounts of borax (17g) and potassium persulfate (20g) in 500ml DDW. This solution was freshly prepared each day for analysis and will be henceforth referred to as *100% oxidant strength*. The borax was added to buffer the oxidant at pH 9. The alkaline pH was necessary for the efficient oxidation of DOC.

2.3 Instrumentation

2.3.1 Glassware

All glassware used in the project were soaked in 30% Nitric acid overnight and then washed with distilled water and rinsed twice with DDW.

2.3.2 *FIA manifold*

The flow injection system used here consisted of the following components. The schematic representation of the manifold is given in figure 5 and plate 1.

- *Two Peristaltic pumps (model: Ismatec 5A)*
- Reodyne six port valve
- PTFE tubes with 0.3mm internal diameter used throughout the FIA system except the pump tubes (0.60mm internal diameter)
- Custom built conductivity detector
- Conductance meter (YSI Model 32)
- UV lamp at 360nm
- Gas diffusion manifold
- Hot water bath regulated at 58^{0}C
- Micro-porous tubing (Accurel PP Type S6/2, 0.2μm pore size; Enka)
- Hewlett Packard HP3395 Integrator

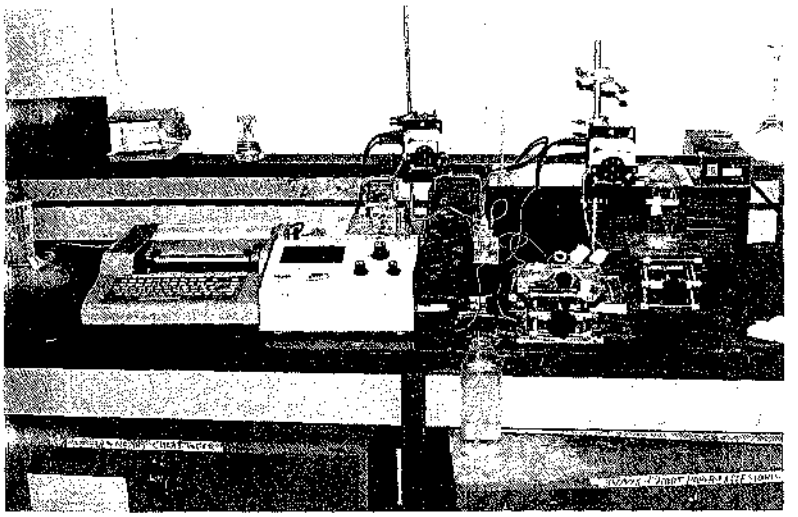


Plate 1 The FIA manifold used in this project

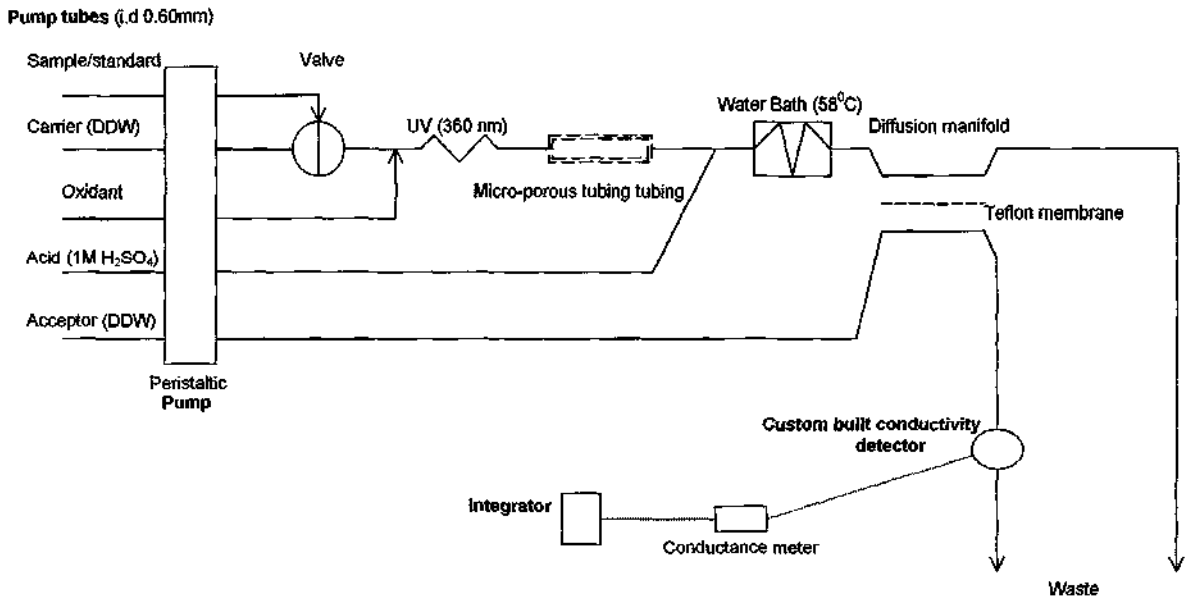


Figure 5 The schematic of the FIA system used in this work

Type of line	Flow rate (ml/minutes)
Carrier (DDW)	1.0
Sample	1.0
Oxidant (Alkaline Persulfate)	1.0
Sulfuric acid (1M H_2SO_4)	1.1
Acceptor (DDW)	1.1

2.3.2.1 The major components of the FIA manifold

Peristaltic pump: The pump consisted of two Ismatec 5A commercial models from EXTECH EQUIPMENT PTY Ltd. The pumping is facilitated by the pressure made by the pump gadgets on the pump tubes and eight rolling pins, (see figure 6).

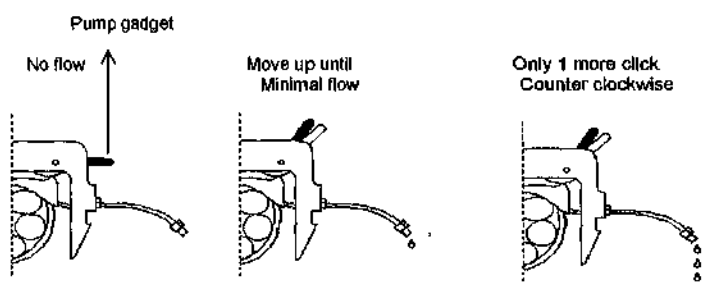


Figure 6 Peristaltic Pump

The pumping unit of this FIA system consisted of two Ismatec pumps, where as in the original method by Koshy and his co-workers, a Gilson Minipuls 2 pump

was utilized. The change in the type of pump used resulted in the use of larger pump tubes with internal diameters of 0.6mm. The change in pump tubes (0.3mm internal diameter) and pumping rates eased the problem of leaks that were prevalent when the pump tubes and rates specified by Koshy and his co-workers were used in the early stages. The pump rates for the FIA system developed by Koshy and his co-workers are given in figure 4.

Reodyne six way valve: This is a six port valve that changes in configuration when the switch is toggled between the load and inject positions, (see figure 7). At the load position, the sample line flows to fill a loop with a volume of 600μL. At the same time the carrier line is pumped continuously through the manifold. At the inject position, the internal configurations are changed and the carrier line is connected to the loop and it takes the sample for analysis.

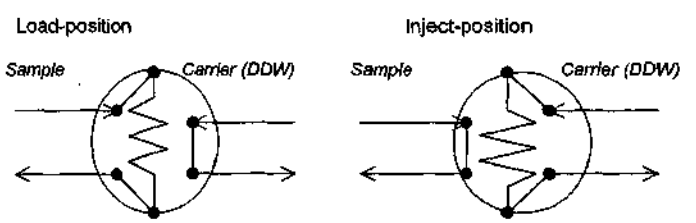


Figure 7 Reodyne six way valve

Reaction Zone: The major reaction zone was a 2-metre PTFE tube (0.3mm internal diameter) wound in a figure of eight around the UV lamp (360nm).

Water Bath: This is an ordinary laboratory water bath from Grants Instruments (Cambridge) Ltd. The temperature of the water bath was maintained at 58^0C. This temperature was sufficient to enhance the acidification of bicarbonate to carbon dioxide.

Micro-porous tubing: This is a micro-porous tubing (Acurell PP Type S6/2, 0.2µm pore size; Enka). It was placed immediately after the reaction zone (UV chamber) when it was used. The purpose of this accurel was to eliminate gaseous substances like chlorine and oxygen formed in the UV chamber.

Diffusion manifold: Gas diffusion was achieved using a Tecator chemifold V with a TBA permatite GT gas plumbing tape (membrane, thickness 0.2mm). The membrane was replaced twice a week. Figure 8 is a lateral cross section of the chemifold, also see plate 2.

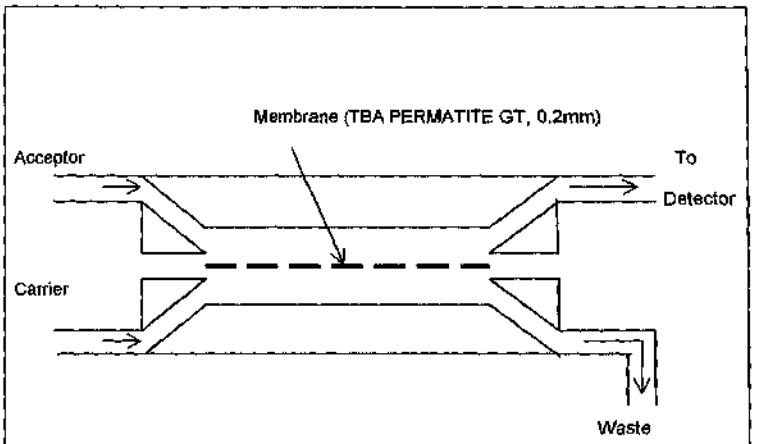


Figure 8 Diffusion manifold

Conductivity detector: The detector was custom built and it consisted of two square perspex blocks, separated by a Teflon separator, see figure 9 and plate 3. Each of the blocks had two cylindrical platinum electrodes. The two sets of electrodes detected the change in conductivity as the acceptor solution passed between them.

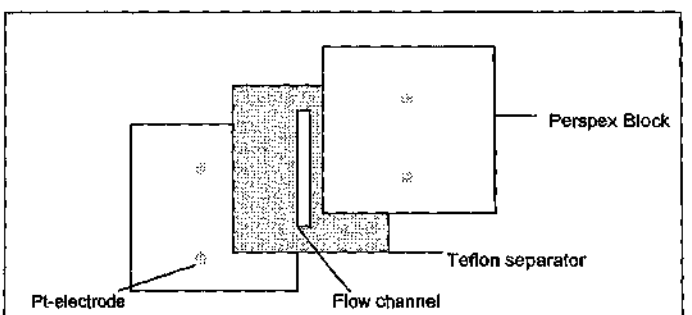


Figure 9 Conductivity detector

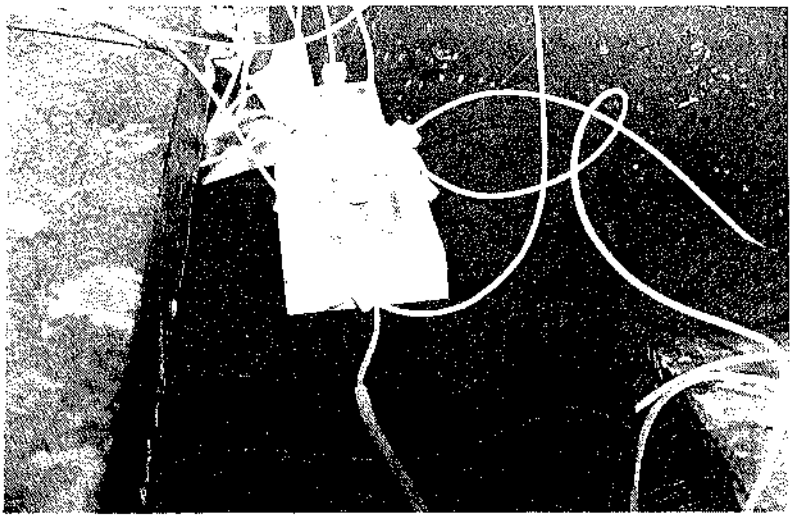


Plate 2 Diffusion manifold

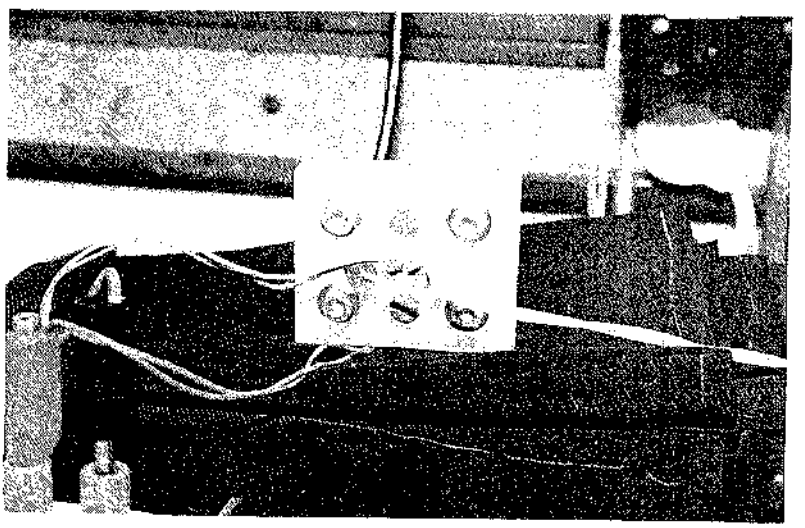


Plate 3 Conductivity Detector

Recorder: The change in conductivity was displayed digitally by a conductivity meter. This meter was connected to an integrator that transformed the change in conductivity to a graphical representation in the form of a peak. The integrator calculates the peak areas. In the initial work on this project, a flat bed potentiometric recorder was used to give the graphical representation of the change in conductivity of the acceptor stream.

2.4 Preliminary work on the FIA manifold

2.4.1 A typical run

All the lines of the FIA manifold (see figure 5) were pumping on any typical run. The sample loop (600μL) that was attached to the valve was filled by turning the knob on the valve to the loading mode. After 30 seconds, the knob was switched to the injection mode and the sample was subsequently introduced to the carrier stream, which was already flowing. The oxidant line was merged with the carrier and the carrier line passed through the UV chamber. At the UV chamber the DOC was oxidized to carbon dioxide. However, because of the alkaline condition in the UV chamber, carbon dioxide exists as carbonate and hydrogen-carbonate (Koshy *et al.*, 1992). The carrier line emerged from the UV chamber and the acid line merged with it to convert carbonate and hydrogen-carbonate to carbon dioxide. The heat provided by the water bath as the carrier line passed through it facilitated the conversion of carbonate to carbon dioxide. The carbon dioxide in the carrier stream passed through the semi-permeable

membrane and changed the conductivity of the acceptor stream, which was DDW. The acceptor stream flowed through the custom-built conductivity detector and the change in conductivity was measured. A single run took approximately 40 to 45 seconds to complete.

2.4.2 Effect of temperature on FIA signals

The following carbon (IC) standards 2, 4 and 6mg/L were prepared in the $35^0/_{00}$ NaCl solution and DDW. The standards were analyzed at 58^0C and 70^0C. The purpose of this exercise was to elucidate the effect of temperature on chloride interference (see section 3.1 and table 5 for the results).

2.4.3 Carbon recovery from model organic compounds

A 5mg C/L standard of the following organic compounds, Potassium hydrogen phthalate (KHP), Citric acid, Nicotinic acid, Urea, Thiourea, Sodium acetate and D-Glucose were prepared in DDW. In addition, a (IC) carbon standard of the same concentration was prepared and the recoveries of the organic compounds were compared with the recovery of the 5mg/L (IC) standard in terms of peak area (see section 3.2.1 and tables 6 and 7 for the results). The model organic compounds used are amongst the standard organic substances used for carbon recovery experiments of methods/instruments used to determine DOC (Koshy *et al.*, 1992).

The recoveries of the above compounds using this FIA manifold were compared with their recoveries utilizing the FIA manifold described by Koshy and his co-workers in 1992 because their method was similar to the one used in this work. Furthermore, the FIA method described by Koshy and others in 1992 is a recognized method for DOC determination using FIA (Robards *et al.,* 1994). The recovery experiment was necessary to establish the credibility of this method to measure DOC.

2.4.4 "Ghost peak"

It has been observed incidentally with seawater samples that peaks were obtained under no oxidant and acid conditions. Theoretically, these peaks were not expected. To investigate their cause and their nature, the following set of experiments were carried out. The peaks were termed as *ghost peaks (GP)* to differentiate them from the normal peaks obtained under photochemical oxidation and acidification. Initially, the "ghost peaks" were speculated to be caused by dissolved gases in the natural water samples. As a consequence, the samples were analyzed for *GP* before (Untreated) and after nitrogen bubbling and boiling. Nitrogen bubbling and boiling of the samples was aimed at eliminating any dissolved gases present in the samples. Furthermore, the effect of the UV source on *GP* was investigated, since it has the capacity to oxidize DOC on its own (Robards *et al.,* 1994). The independence of the donor stream from the acceptor stream was investigated in terms of its pH. DDW was also injected as a sample because of the need to eliminate the possibility of it, contributing to *GP* (see section 3.3 and table 8 for the results).

Attempts to Isolate and quantify GP

- 3 x 50ml samples from the following sites, Tamavua river, Nabukalou creek, and Lighthouse were analyzed under no oxidant and no acid conditions in the following manner.
- The first 50ml portion (untreated) was injected directly.
- The second 50ml sample was bubbled with Ultra- pure N_2 for 15 minutes; then injected.
- The third 50ml sample was bubbled with Ultra- pure N_2 for 15 minutes + boiled and then injected.
- Untreated 50ml samples were also injected when the UV was on and off.
- The pH of the donor line of the FIA manifold was also tested.
- DDW was also injected as a sample

2.4.5 Detection Limits

The instrument detection limit (IDL) was determined by repeatedly injecting DDW over a period of three days. From the instrument detection limit, the method detection limit (MDL) was calculated (see section 3.5 for the calculation of IDL and MDL). The above procedure of determining the detection limits was based on the procedure specified by Skoog and others in 1998.

The objective of this part of the procedure was to elucidate the ability of the FIA manifold to differentiate between a carbon signal and the instrument noise.

2.4.6 Calibration standards

On each day of analysis for DOC in seawater and estuarine samples and for the carbon recoveries of model organic compounds, calibration standards in the range of 1mg C/L to 25mg C/L were prepared in DDW or in the 35$^0/_{00}$ NaCl solution (see section 3.4, tables 9 and 10, figure 13 and the appendix 2 for the typical FIA plots for calibration standards). The (IC) standards in the range of 8-25mg/L were prepared from a 1000mg/L stock solution and the standards below the above range were prepared from stock solution of 100mg/L (this method of standard preparation minimized the dilution of the 35$^0/_{00}$ NaCl solution). The standards were prepared in 100ml volumetric flasks. The pH of the IC standards prepared in DDW and the 35$^0/_{00}$ NaCl solution was pH 7.8. The seawater samples exhibited a range of pH from pH 7.0 to pH 8.2. Therefore, the pH of the IC standards was close to median of the pH range of the seawater samples. In other words there is a strong correlation between the pH of the IC standards and the estuarine and seawater samples.

From these calibration standards, a calibration curve was obtained and a regression equation calculated (table 9, figure 13). Furthermore, the sensitivity of the FIA system was investigated in terms of its analytical sensitivity with respect to the standards prepared (see table 10).

2.4.7 Sample Collection and conditioning for analysis

The seawater and estuarine samples were collected from the sites (see figure 10) monitored in 750ml PVC containers that were acid washed and rinsed a day before sampling. Sample collection usually lasted 1-2 hours and the samples were conditioned for analysis soon afterwards in the following way.

On arrival at the laboratory, the samples were immediately filtered using sterilized 0.45μm Millipore (Type HA) ashless filter papers via suction filtration. The samples were analyzed on the same day or frozen for analysis the next day. The samples were not acid preserved because freezing was recommended to be sufficient (Peltzer & Brewer, 1993).

2.5 Sites monitored for the determination of DOC levels

The main area of study is the Suva lagoon, which is composed of the Suva harbor and Laucala bay. It is located on the southeastern portion of Viti-levu and forms the coastal sea adjacent to Suva City. Suva City is one of the largest populated cities in the South Pacific. The influx of people to Suva and the subsequent growth of industries might possibly increase the level of organic input into the lagoon, because organic input to coastal waters have been found to be partially influenced by the growth of population and industrialization (Stumm & Morgan, 1981). The major sources of freshwater input (usually has terrestrial organic input) to the Suva lagoon are the rivers, Navesi, Tamavua,

Vatuwaqa, Rewa and other smaller tributaries that open up to the lagoon. There were also sources like the Kinoya sewage outfall, the medium sized industrial sites along the coast, the Suva City sewer lines and in the older Suva area the direct sewage input into the Nabukalou creek.

The sites selected either receive direct organic discharge (rivers and a sewage outfall) or are located close to discharge points like storm water outlets and creeks. The site at Nukulau passage was the furthest site from the landmass of Suva and it was taken as the control site. The first sub group composed of sites at the interface of the land (coastal) and the sea. These included Tradewinds (11), Vugalei (10), Tamavua river (9), Nabukalou creek (8), Nasese (5), Lighthouse (13), and Suva point (4). The other sub group consisted of sites further out into the lagoon (offshore). A transect was taken from the Kinoya outfall (1), 200m from the outfall (2) and the Nukulau passage (3) which has a constant interchange with the ocean. The other sites were situated approximately 200m from the Centra (6), 200m from Nabukalou creek (7) and near Mosquito Island (12). The locations of the sites are on the map in figure 10.

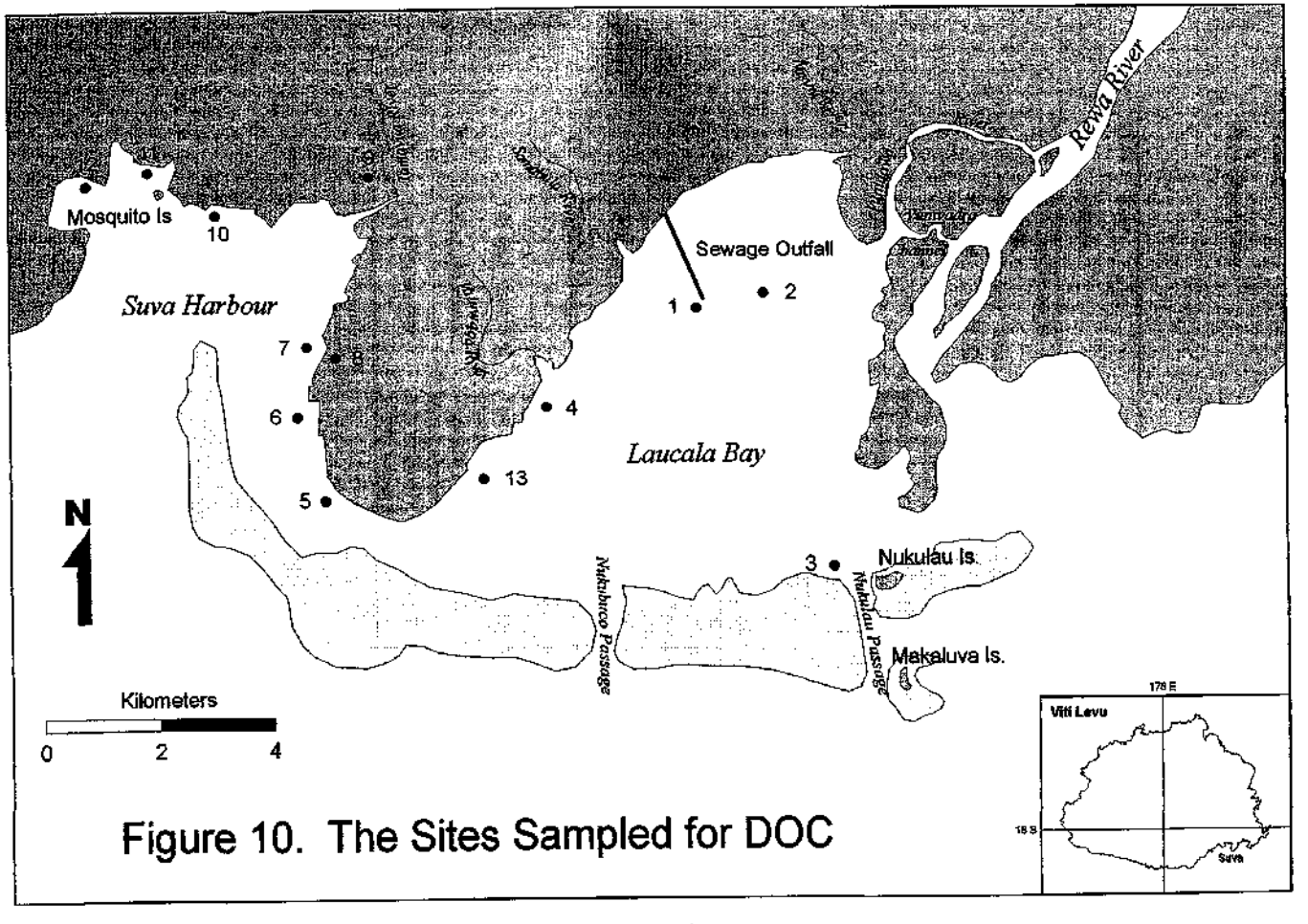


Figure 10. The Sites Sampled for DOC

Table 4

Sites Descriptions

Sites #	Sites Names	Description
1	Kinoya Sewage outfall	The area in which the sewage outfall is situated.
2	200m away from Kinoya Sewage outfall	The site is 200m away from the outlet and it is in front of the Vunivadra tributary.
3	Nukulau Passage	This is the furthest site from the Viti-Levu landmass and it is on an opening of the Laucala harbor to the ocean.
4	Suva Point	It is adjacent to a playground and two-storm water outlets that discharge into the area.
5	Nasese	The seafront of a residential area and two-storm water outlets discharge into the area.
6	Centra Hotel	The site is situated about 150m out in the sea from the hotel.
7	200m Nabukalou Creek	It is 200m from the Nabukalou opening to the sea and adjacent to the Suva Kings wharf.
8	Nabukalou Creek	The creek is in the Suva business center with numerous sewage lines discharging into it. It is always murky and emits foul smell.
9	Tamavua River	The site is located at about 60m from the Suva municipal dump and is in the Tamavua river.
10	Vugalei Bridge	The site is under this bridge that runs over a creek. There is a constant exchange between the fresh and seawater.
11	Tradewinds Hotel	The site is about 20m from the hotel and is adjacent to an opening of a creek inland to the sea.
12	Mosquito Island	The site is within the bay of islands close to the Mosquito island.
13	Lighthouse Bar	It is adjacent to a restaurant and 10m away from a storm water outlet.

2.5.1 The elimination/measurement of inorganic carbon (IC) from natural water samples

Part 1 A 25mg C/L standard was prepared in DDW. A 40ml aliquot required 0.04ml of 84% phosphoric acid for the complete evolvement of IC. The amount of acid added was calculated on the basis of the amount of IC present in the standard. Phosphoric acid is a common acid used to eliminate IC from natural water samples (Koshy *et al.,* 1992, DeBaar *et al.,* 1993 and Robards *et al.,* 1994). The 40ml aliquot of the standard plus the acid was vigorously stirred and moderately heated to evolve all the carbon dioxide. Another standard (IC) with a carbon concentration of 25mg/L was prepared in the $35^0/_{00}$ NaCl solution. A 40ml aliquot of the standard was acidified with 0.04ml of 84% phosphoric acid, bubbled with nitrogen gas for five minutes and sonicated for a further five minutes. Two sets of analyses were done with the two types of standards before and after acidification, (see section 3.6 and table 11 for the results).

This was necessary since it would elucidate the approximate amount of acid needed to evolve all the IC in the water samples.

Part 2 Natural seawater and estuarine samples were collected from three selected sites Suva point (4), Nukulau passage (3), and Nabukalou creek (7), (see figure 10 and table 11). The samples (40ml) were filtered (see section 2.4.7) and analyzed for their measured inorganic carbon (IC_m). The determination of IC_m was achieved by pumping all lines of the FIA system with their respective solutions (see figure 5) except for the oxidant line which had

DDW instead of the oxidant. The above procedure is an acidification process [Note: IC_m is not equivalent to the total IC (Alkalinity in the water sample)]. After that, the same samples (40ml) were acidified with 0.04ml of 84% phosphoric acid and nitrogen gas was bubbled through them for 5-6 minutes, the samples were then sonicated for a further 5 minutes before they were analyzed for their IC levels.

2.6 Quantification of Chloride Interference

A series of (IC) carbon standards (1, 1.2, 1.8, 2, 3, 4, 6, 8,16, 24mg/L) were prepared in DDW and the $35^0/_{00}$ NaCl solution. The DDW standards were analyzed first to avoid contamination from the $35^0/_{00}$ NaCl solution. Before switching to the $35^0/_{00}$ NaCl solution standards, the whole FIA system was flushed for 5 minutes with DDW.

The purpose of this part of procedure was to quantify the nature of chloride interference in the signals produced by the carbon in the standards prepared in the $35^0/_{00}$ NaCl solution. (see section 3.7 and table 12 for the results). The series of standards mentioned in paragraph 1 were analyzed 5 times on different occasions for their carbon and chloride signals. The differences in the corresponding pairs of standards prepared in DDW and the $35^0/_{00}$ NaCl solution were calculated as percentages ($\%Cl_{ox}$: percentage of chloride oxidized) of the respective standards prepared in DDW. The $\%Cl_{ox}$ was equivalent to the amount of chloride interference on each of the IC standards prepared in the $35^0/_{00}$ NaCl solution.

2.7. Attempts to eliminate/minimize Chloride interference

The following sub sections describe investigations relating to ways of eliminating or minimizing chloride interference on DOC measurements. This included reducing oxidant strength by 50% and adding a catalyst on the assumption that a reduced oxidant would not oxidize chloride, using $NH_2OH.HCl$ to reduce the chlorine formed in the UV chamber and the placement of micro-porous tubing after the UV chamber to eliminate the gaseous chlorine.

2.7.1 Reduction of the oxidant strength

A 5mg C/L potassium hydrogen phthalate (KHP) standard, prepared in DDW was arbitrarily chosen as the base concentration, to demonstrate the effect of reducing the oxidant strength on carbon recovery. To this end, the *100% oxidant solution* was diluted to 90, 70, 60, 50, 30, 10% oxidant strength solutions. The 5mg C/L KHP was oxidized using the diluted oxidants. The recoveries of the standard using the diluted oxidant solutions were compared with its recovery using the100% oxidant strength solution.

The objective of this part of the procedure was to reduce the power of the oxidant to a level that was low but would still be able to carry out oxidation (see section 3.8.1 and table 13 for the results). Prior to this, there was an uncertainty over the choice of the diluted oxidant to be used with the catalyst.

2.7.2 50% oxidant strength solution plus catalyst (TiO_2)

From the previous trials, the 50% oxidant strength solution was selected as the optimum for oxidation. The following carbon standards 2, 5, 15, 25mg C/L of KHP were prepared in DDW and subjected to DOC determination using the 50% oxidant strength solution and the 50% oxidant strength solution plus the catalyst. About 0.0048g TiO_2 was used as higher amounts were found to clog the FIA manifold (see section 3.8.1.1 and table 14 for the results). The carbon recoveries of the carbon standards using the "new" oxidant were compared with their carbon recoveries with 100% oxidant strength solution.

The objective of this part of the procedure was to elucidate the effect of the catalyst on carbon recovery.

2.7.3 The Effect of 50% Oxidant strength solution + 0.0048g TiO_2 on the Chloride signal

The following standards 2, 4, 16, 24mg C/L (IC) were prepared in the 35$^0/_{00}$ NaCl solution. The standards were analyzed and their peak areas were compared to corresponding standards made in DDW. The data obtained were further compared with corresponding data of the same standards prepared in the 35$^0/_{00}$ NaCl solution, but had been oxidized using the 100% oxidant solution.

The aim was to see if this "new" oxidant has any negative or positive effect on the chloride signal (see section 3.8.1.2 and tables 15 and 16 for the results). Although, TiO_2 had been used to catalyze the oxidation of DOC (Matthews *et al.,* 1990), the possible effects of the catalyst on the chloride present in estuarine and coastal water samples had not been fully investigated.

2.7.4 Effect of Hydroxylaminehydrochloride ($NH_2OH.HCl$) on the chloride signal

The first part of this section was carried out before the integrator was used, as a consequence peak heights were measured instead of peak areas. $NH_2OH.HCl$ has been demonstrated by Schreurs (1978) to be a viable suppressor of chloride interference effect, by reducing the chlorine gas formed in the UV chamber to chloride, (see section 3.8.2 and tables 17,18 & 19 for the results).

This part of the procedure was designed to determine the amount of $NH_2OH.HCl$ required to reduce the chlorine produced by the oxidation of chloride in the $35^0/_{00}$ NaCl solution and to use the optimized amount of $NH_2OH.HCl$ to reduce chloride interference on carbon signals.

Part 1. The following concentrations of the reducing agent 100, 300, 900, 1000, 3000, 12,000, 15,000 and 21,000mg/L were prepared in the $35^0/_{00}$ NaCl solution. The work by Schreurs (1978) did not indicate the amount of the reducing agent to be used, consequently, a large range of the reducing agent was tested. A stock solution was prepared by dissolving 250g ($NH_2OH.HCl$) in

250ml DDW in a volumetric flask. The concentrated stock solution alleviated the dilution of the 35$^0/_{00}$ NaCl solution because small volumes of the stock solution were used to prepare the $NH_2OH.HCl$ in the 35$^0/_{00}$ NaCl solution in 100ml volumetric flasks.

Part 2. The optimized amount of the reducing agent (3000mg/L) was placed with the **1M** sulfuric acid as recommended by Schreurs (1978).

The effect of the reducing agent was tested on the following standards 5,10,15,20 and 25mg C/L (IC & KHP) prepared in the 35$^0/_{00}$ NaCl solution (see section 3.8.2 and tables 18 and 19 for the results)

2.7.5 The effect of a micro-porous tubing (Accurel PP type S6/2, 0.2μm pore size; Enka) on chloride interference

The micro-porous tubing allow gases to permeate as they pass through it. In this project this micro-porous tubing (20cm) was fitted immediately after the UV chamber to eliminate any chlorine and oxygen gases that might be formed during photo-oxidation (see figure 4). To test its effect on chloride interference, the following standards 5, 10 and 15mg C/L were prepared in the 35$^0/_{00}$ NaCl solution and analyzed under *100% oxidant strength solution* with and without the micro-porous tubing (see section 3.8.3 and table 20 for the results). For comparative purposes, a similar range of standards was also prepared in DDW and analyzed under the same conditions.

2.8 DOC analysis for the offshore and coastal sites

The samples were prepared for DOC analysis as specified in section 2.4.7. The analysis for DOC was based on a numerical method whereby components like the IC, chloride interference effect and ghost peak (peak areas) were subtracted from sample peak area with the analysis carried out with the 100% oxidant strength solution, UV on and the acid line on (see sections 3.10.1 and 3.10.2).

- The carbon signals were measured in terms of peak areas
- The samples were injected 4 times without any oxidant, but with the acid line on. This gave peak areas, proportional to the measured inorganic carbon (IC_m) in the water sample (Note: it is not equivalent to the total IC in the sample)
- Another 4 injections of the samples were made with the acid and oxidant lines on. The UV source was switched on as well.

  Total Carbon measured: $[TC_m] = IC_m + DOC$
- Based on the level of IC_m, a correction for the chloride interference ($\%Cl_{ox}$) was calculated from the equation in figure 14 and subtracted from the average peak area of TC_m to give a corrected peak area for the total measured carbon ($TC_{m\ corr}$)
- The IC_m and TC_{mcorr} concentrations were calculated from calibration equations generated from IC standards prepared in the 35‰ NaCl solution, typical equations are given in table 9.
- **$[DOC] = [TC_{m\ corr}] - [IC_m]$**

CHAPTER 3

RESULTS & DISCUSSION

3.1 Effect of temperature on the Carbon and the Chloride signal

A set of standards (IC) with the following concentrations 2, 4, 6mg C/L were prepared in DDW and the 35$^0/_{00}$ NaCl solution and were analyzed using the 100% oxidant strength solution. For this purpose two temperatures, 58^{0}C and 70^{0}C were used.

Table 5

Comparison of carbon signals in terms of peak area and chloride interference at 58^{0}C and 70^{0}C
(Peak area x 10^7)

[C] mg/L	DDW (±1SD) n=4	35$^0/_{00}$ NaCl solution (±1SD) n=4	%Cl_{ox} 58^{0}C (±1SD)	DDW (±1SD) n=4	35$^0/_{00}$ NaCl solution (±1SD) n=4	%Cl_{ox} 70^{0}C (±1SD)
		58^{0}C			70^{0}C	
Regression equations	Y=0.3x +0.4 R^2=0.97	Y=0.3x+0.9 R^2=0.82		Y=0.3x +0.4 R^2=0.99	Y=0.4x + 1.9 R^2=0.99	
2	0.96(0.02)	1.36(0.04)	**42(4)**	1.1(0.2)	2.7(0.2)	**145(44)**
4	1.78(0.08)	2.38(0.05)	**33(5)**	1.8(0.2)	3.6(0.1)	**112(17)**
6	2.23(0.08)	2.49(0.05)	**11(3)**	2.4(0.1)	4.3 (0.2)	**79(9)**

% Cl_{ox} = % chloride oxidized
= [(35$^0/_{00}$ NaCl solution – DDW)] X [100/DDW]
≈ A measure of chloride interference

The operating temperature of the water bath used throughout the project was 58^{0}C. The above temperature was chosen as the optimum because it was the optimum temperature used by Hansen and Lausten (1995) with a similar FIA method. The carbon recoveries of the DDW standards were quantitatively close to 100% irrespective of the operating temperature of the water bath, because the DDW standards exhibited similar regression equations with correlation coefficients of 0.97 and 0.99 at 58^{0}C and 70^{0}C respectively. The 35$^0/_{00}$ NaCl solution standards at both temperatures were also quantitatively exhibiting 100% carbon recovery, although the interference by chloride was present. The chloride signal was added to the carbon signal and the peak areas tabulated for the 35$^0/_{00}$ NaCl solution standards were a combination of the carbon and chloride signals.

The interference by chloride on the carbon signals was more pronounced at 70^{0}C than at 58^{0}C (see figure 11) with each of the IC standard. The above result indicated that it would not be a positive option to use a higher temperature than 58^{0}C because such increase would lead to the enhancement of chloride interference. Furthermore, the interference by chloride was more varied given the larger standard deviations calculated for the %Cl_{ox} at 70^{0}C. The carrier stream registered 39^{0}C just before diffusion when the water bath was operated at 58^{0}C. By changing the temperature of the water bath to 70^{0}C, the carrier stream registered a temperature of 43^{0}C just before diffusion. The increase of temperature to 70^{0}C resulted in a warmer (43^{0}C) carrier stream arriving at the membrane, consequently both carbon dioxide and chlorine diffused but the chlorine diffused to a greater extent than previously when the

water bath was operated at 58^{0}C. Consequently, the level of chloride interference on the carbon signal in each standard increased. Diffusion was expected to increase when the temperature of the carrier stream was elevated to 70^{0}C (Schulze *et al.,* 1988). On the other hand, the standards prepared in DDW did not indicate significant changes to their carbon recoveries when the temperature was increased to 70^{0}C (see table 5) implying that 39^{0}C was sufficient for the complete diffusion of carbon dioxide. The sensitivity of the instrument (slope of the regression equations) remained fairly constant despite the change in temperature of the carrier stream (just before diffusion) from 39^{0}C to 43^{0}C. It was vital to understand that the sensitivity of the FIA system was not necessarily improved by increasing the temperature at which diffusion took place, although Su and others (1998) alluded to the possible increase in sensitivity when the temperature of the donor stream was increased.

The interference by chloride decreased as the ratio of chloride to inorganic carbon ([Cl]/[IC]) decreased and this was evident from the rapid decrease in chloride interference as the inorganic carbon level increased to 6mg/L (see section 3.7). The ratio of chloride to inorganic carbon decreased because the amount of inorganic carbon increased but the amount of chloride remained fairly constant in the standards although the disparity in the concentration of chloride and inorganic carbon in each standard was substantial. The oxidation of chloride to chlorine (Schreurs, 1978 and Koshy *et al.,* 1992) was not enhanced at 70^{0}C, but rather the increase in the diffusion of chlorine to the acceptor stream was responsible for the subsequent increase in chloride interference.

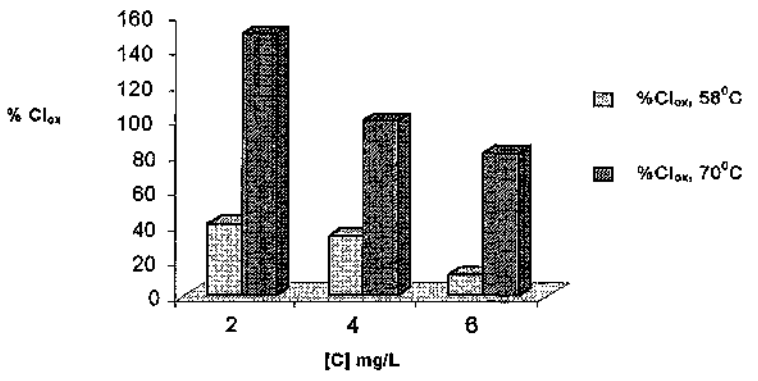


Figure 11 %Cl_{ox} at 58°C and 70°C versus carbon concentration

3.2 Recovery experiments

3.2.1 Model organic compounds

The efficiency of the 100% oxidant solution or the FIA system (manifold) as a whole was tested on seven model organic compounds to illustrate its ability to oxidize organic substances. The average carbon recovery was 98(±9)%, see table 6. The recoveries were estimated by comparing the carbon recoveries of 5mg C/L of each organic compound with the recovery of a 5mg C/L inorganic carbon standard. Complete conversion of inorganic carbonate to carbon dioxide after acidification was assumed for the IC standard because when this standard was acidified with 1M H_2SO_4 and reanalyzed, it did not register any carbon signal implying that all the IC in the standard had been evolved after the addition of the acid.

Table 6

Carbon recoveries of model organic compounds (5mg C/L)

(Peak area x 10^7)

Model Organic Compounds 5mg/L	Peak area (±1SD) n=8	%Recovery, FIA manifold, this work (±1SD) n=8	%Recovery FIA, (Koshy *et al.*, 1992) (±1SD) n=5	% Recovery Beckman HTCO (Koshy *et al.*, 1992) (±1SD) n=7
Citric acid	1.9(0.2)	105(12)	106.0(4.1)	108.0(1.0)
Thiourea	1.9(0.1)	100(5)	101.0(0.9)	100.0(0.8)
Sodium acetate	1.8(0.1)	95(5)	102.0(2.8)	106.0(1.0)
KHP	2.0(0.1)	105(3)	103.0(1.4)	
Urea	2.0(0.1)	105(8)	104.0(0.4)	102.0(1.6)
D-Glucose	1.8(0.1)	95(7)	96.0(1.8)	102.0(0.3)
Nicotinic acid	1.5(0.2)	79(11)	92.0(2.6)	100.0(0.8)
5mg/L (IC)	1.9(0.1)	100		
Average		98(9)	100.6(4.9)	103(3.3)

The oxidation efficiency of the FIA manifold used in this project was comparable to the oxidation efficiencies of the FIA manifold and the Beckman HTCO unit used by (Koshy *et al.*, 1992). This was substantiated by a statistical F test (95% confidence interval, F_{test} value = 3.4, $F_{critical}$ 6,6 =4.2, see appendix 6) performed on the recoveries of the model compounds using the FIA manifold used in this work and the FIA manifold described by (Koshy *et al.*, 1992). The above test showed an insignificant difference in the two sets of carbon recoveries. Unlike the recovery experiments by Chen & Wangersky (1993) with another WCO method, the nitrogen and sulfur containing compounds (Nicotinic acid, Thiourea, Urea and Citric acid) tested with this FIA manifold did not show complete refractory behavior. The oxidation capacity of this FIA manifold was also

comparable to a similar photo-oxidation method that had an average recovery of the model compounds in excess of 98% (Collins & Williams, 1977). In another measurement of DOC in lake water via photochemical oxidation, the average oxidation efficiency was 97% (Brooksbank & Goulden, 1975). The recovery exercise on the model compounds was deemed sufficient to demonstrate the oxidation capacity of the FIA system described in this work. The DOC data obtained in this project through the FIA system was compared with corresponding DOC data obtained from a HTCO Shimadzu 2000-UV carbon analyzer, (see section 3.10.1). The comparison would further substantiate the oxidation capacity of the FIA system described in this work.

Citric acid, Potassium hydrogen phthalate (KHP) and Urea recorded carbon recoveries slightly greater than 100% (see table 6). Though these compounds have recoveries above 100% they were still within an error of one standard deviation of their average recoveries. All the other compounds had recoveries equal to or greater than 90% with the exception of Nicotinic acid which had a low carbon recovery of 79%. Nicotinic acid was one of the most resistant materials to persulfate UV oxidation because of the slow degradation of the nitrogen components of the organic substances to the inorganic forms like nitrate and ammonia (Goulden & Anthony, 1978, Chen & Wangersky, 1993 and Guardia *et al.,* 1995). This compound seemed to be the only refractory compound among the range of model compounds analyzed. However, the situation might not be the same in a marine water body, given the complexity of the substances present. The FIA system described in this work generally had a high average carbon recovery (98±9%). However, the variation in terms of the

standard deviation (9%) alluded to the fact that like all other WCO and HTCO methods complete oxidation of DOC in seawater is not always possible. This is a reality analysts have to bear in mind when obtaining results from instruments, be it from complex instruments or laboratory constructed instruments like this FIA system.

3.2.2 Organic carbon recovery in the presence of high and low levels of inorganic carbon

Table 7

Carbon recoveries at a high and low levels of inorganic carbon (IC)

(Peak area x 10^7)

#	Sample	Peak area	% Recovery (±1SD)
1	4mg C/L (KHP, DDW)	1.8(0.1)	100
2	20mg C/L (IC, 35$^0/_{00}$ NaCl solution)	9.0(0.1)	
3	20mg C/L + 4mg C/L (IC + KHP, 35$^0/_{00}$ NaCl solution)	10.8(0.1)	100(8)
4	4mg C/L (IC, 35$^0/_{00}$ NaCl solution)	2.4(0.1)	
5	4mg C/L + 4mg C/L (IC + KHP, 35$^0/_{00}$ NaCl solution)	4.1(0.1)	94(9)

Note: The 4mg C/L (KHP) had a 100% carbon recovery.

The oxidation efficiency of the 100% oxidant strength solution did not appear to be affected by the presence of high or low levels of IC. This was evident from the results of samples 3 and 5 which were made in the 35$^0/_{00}$ NaCl solution to simulate the situation in the natural marine and estuarine environment (see table 7). When the 4mg/L DOC (KHP) was placed with 20mg C/L (IC in 35$^0/_{00}$ NaCl solution), the 4mg C/L (KHP) standard's carbon recovery was 100%, with

the 4mg C/L (IC in $35^0/_{00}$ NaCl solution), the 4mg C/L KHP standard had a recovery of 94%. However, the 94% carbon recovery of the organic standard in the low level of IC was within the interval (98±9%) provided for by the average recovery for the model compounds. The above results had also demonstrated the additive nature of the carbon signals. For example, the signal in terms of peak area of sample 3 was equivalent to the sum of samples 1 and 2.

3.3 "Ghost Peak" (GP) Analysis

Natural marine water samples were capable of producing peaks without the presence of the acid and the oxidant (see table 8). These peaks have been operationally defined as ghost peaks, because theoretically these peaks should not have appeared (see appendix 4.0).

Table 8

Representation of Ghost peaks from selected sites, under UV on & off as well as Treatment with and without ultrapure Nitrogen gas + boiling

(Peak area x 10^5)

Sample/standard	Untreated Peak area (±1SD) n=16	N_2-bubbled Peak area (±1SD) n=16	N_2-bubbled + boiled Peak area (±1SD) n=16
	UV OFF		
Light house	4.3(0.4)	4.6(0.4)	1.6(0.2)
Tamavua River	3.8(0.2)	4.4(0.3)	2.1(0.2)
Nabukalou	7.0(0.3)	4.2(0.4)	2.6(0.2)
	UV ON		
Light house	3.7(0.4)	4.1(0.4)	2.2(0.3)
Tamavua River	3.8(0.2)	4.2(0.2)	2.3(0.5)
Nabukalou	4.4(0.4)	4.1(0.1)	3.4(0.5)
1mg C/L (IC)	3.8(0.3)		

Note: Untreated: Samples were analyzed without degassing or boiling

N_2-bubbled: Samples were degassed with Ultra pure nitrogen gas for 15 minutes

N_2-bubbled + boiled: The samples were degassed then boiled

We speculated that dissolved gases caused the ghost peaks. To investigate further the above speculation, a selected number of sites were repeatedly analyzed for their GP and their magnitude in terms of peak areas were comparable to that of a 1mg/L (IC) standard prepared in DDW (see table 8). When the samples were degassed with ultra pure nitrogen gas for 15 minutes and subjected to the analyses, there were no major changes observed in the GP. Generally speaking, the peak areas of the degassed samples were greater than their peak areas before degassing, see table 8 and figure 12. This result suggests that dissolved gases were not responsible for the GP. The influence of

the UV source on the GP was also investigated but found to be generally insignificant for the degassed and untreated seawater samples. Further treatment such as degassing and boiling the samples were carried out and moderate reductions were observed in the GP. However, there would be technical problems if this approach was taken. First there is a great tendency that volatile organic materials will be lost in the boiling process. Secondly the boiling of the samples can increase the salt concentration which might increase chloride interference. When DDW and the 35$^0/_{00}$ NaCl solution were injected without the oxidant no GP signals were visible recorded indicating that the amount of possible carbon impurities in the DDW and the 35$^0/_{00}$ NaCl solution were not sufficient to cause the GP.

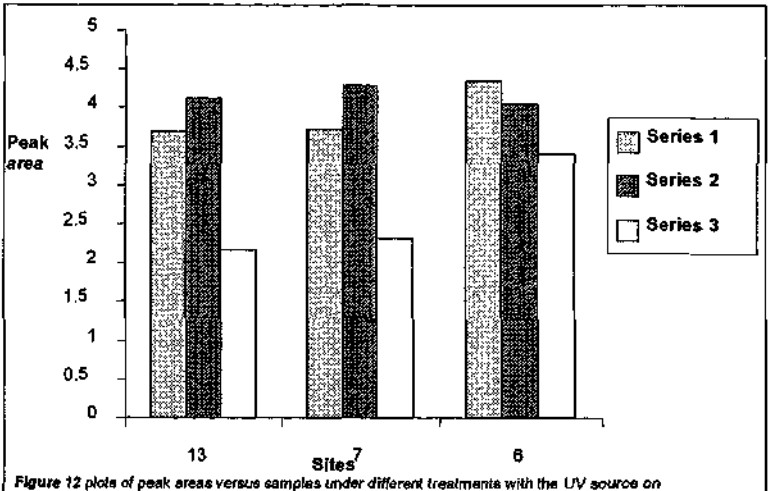


Figure 12 plots of peak areas versus samples under different treatments with the UV source on

Note: Refer to figure 10 and table 5 for the locations indicated by the numbers.
Series 1: Untreated
Series 2: N_2-bubbled
Series 3: N_2-bubbled + boiled

There were suggestions that the GP phenomena might be eliminated if all reagents were degassed, but as evident from figure 12 the degassed samples registered "ghost peaks" with areas greater than their counterparts that were untreated. It is recommended that the reagent bottles (containing the reagents pumped through the FIA system) be covered with parafilms to minimize the possible dissolution of gases in the reagents. Air bubbles have been observed in the FIA system described in this work to cause spurious changes to the conductivity of the acceptor stream (DDW) when air bubbles diffused across the semi permeable membrane. The effectiveness of the membrane in keeping the donor stream separate from the acceptor stream was also studied. This was investigated in terms of the pH of donor line (acidic) and the acceptor line (neutral). The pH of the donor line was 3 and the pH of the acceptor line prior diffusion varied between 6.5 and 7.0. The results were observed to be consistent with theoretical expectations. In other words, the change in conductivity in the acceptor stream resulting in the GP was not caused by the seepage of the carrier stream through the membrane.

The ghost peak data for the untreated sub samples required special attention, since the samples analyzed were not degassed. The ghost peaks under such conditions, had average peak areas of 5.0 $x10^6$ (untreated, UV off) and 3.9 $x10^6$ (untreated UV on) respectively, see table 8. The data showed that the GP could nearly doubled in some cases when the UV was off. This was not a problem in this project since the analyses for DOC was carried out with the UV source on. Nevertheless GP's will still be present. Their effect will be crucial when considering the measured inorganic carbon (IC_m) levels for the different

samples. Consequently, the average "ghost peak" area was subtracted from the IC_m peak areas before the $\%Cl_{ox}$ was calculated. A mean peak area for the GP (3.9×10^6) was subtracted from the IC_m peak areas of the seawater samples.

The ghost peak phenomenon has not been addressed in the literature therefore it is difficult at this stage to fully establish its cause. However, GP could have been caused by semi-volatile substances (DOC) that diffused across the semi permeable membrane under the pressure initiated by the flow in the thin (0.3mm, i.d) tubes. The preceding assertion was based on the facts that degassing the seawater samples could not remove the GP and more vigorous treatment like boiling resulted in a slight reduction in the GP. Dissolved gases were not responsible for the GP because the standard procedures of degassing with nitrogen gas and sonication have failed to eliminate GP. The GP phenomenon should be investigated in detail in any future work involving this FIA system.

3.4 Calibration curves

In analytical work unknown parameters are derived from a standard curve or a calibration curve. A calibration curve has an important impact on the accuracy and reliability of the data on the unknown parameter. In this project, calibration standards were freshly prepared on the day of analysis for DOC. The carbon standards were prepared from anhydrous sodium bicarbonate in DDW as well as in the $35^0/_{00}$ NaCl solution. Table 9 below gives the equations for typical calibration curves for standards prepared in DDW and the $35^0/_{00}$ NaCl solution

over a period of time (see appendix 2 for the FIA peaks of a typical set of calibration standards prepared in DDW).

Table 9

Typical calibration equations (equation for a straight line) used in the project

(Peak area x 10^7)

Date	[C] range mg/L	Slope Peak area	Y-intercept Peak area	R^2
8/8/97(DDW)	1-24	0.4	0.2	0.99
9/8/97(35$^0/_{00}$ NaCl solution)	1-24	0.3	0.9	0.99
7/7/98(DDW)	5-25	0.4	0.3	0.99
7/7/98(35$^0/_{00}$ NaCl solution)	5-25	0.3	1.9	0.99
8/7/98(DDW)	5-25	0.4	0.5	0.99
8/7/98(35$^0/_{00}$ NaCl solution)	5-25	0.4	1.5	0.99

The mean slope or calibration sensitivity was 0.4(±0.1). The slope varied slightly irrespective of the solvent (DDW and 35$^0/_{00}$ NaCl solution), used to prepare the standards (see table 9). The slight variation in the calibration sensitivity could have been caused by the variations in the conductivity of the acceptor stream (DDW) (Koshy *et al.*, 1992 and Kuban & Dasgupta, 1993) since the acceptor stream was not buffered. On the other hand, buffering the acceptor stream will increase its baseline conductivity and such increase will further reduce the calibration sensitivity of the FIA system used in this work (Koshy *et al.*, 1992). The variations in the calibration sensitivity of the standards (both in DDW and the 35$^0/_{00}$ NaCl solution) tabulated in table 9 were not significantly different in contrast to the work by DeBaar and others (1993) that recorded large

over a period of time (see appendix 2 for the FIA peaks of a typical set of calibration standards prepared in DDW).

Table 9

Typical calibration equations (equation for a straight line) used in the project

(Peak area x 10^7)

Date	[C] range mg/L	Slope Peak area	Y-Intercept Peak area	R^2
8/8/97(DDW)	1-24	0.4	0.2	0.99
9/8/97(35$^0/_{00}$ NaCl solution)	1-24	0.3	0.9	0.99
7/7/98(DDW)	5-25	0.4	0.3	0.99
7/7/98(35$^0/_{00}$ NaCl solution)	5-25	0.3	1.9	0.99
8/7/98(DDW)	5-25	0.4	0.5	0.99
8/7/98(35$^0/_{00}$ NaCl solution)	5-25	0.4	1.5	0.99

The mean slope or calibration sensitivity was 0.4(±0.1). The slope varied slightly irrespective of the solvent (DDW and 35$^0/_{00}$ NaCl solution), used to prepare the standards (see table 9). The slight variation in the calibration sensitivity could have been caused by the variations in the conductivity of the acceptor stream (DDW) (Koshy *et al.*, 1992 and Kuban & Dasgupta, 1993) since the acceptor stream was not buffered. On the other hand, buffering the acceptor stream will increase its baseline conductivity and such increase will further reduce the calibration sensitivity of the FIA system used in this work (Koshy *et al.*, 1992). The variations in the calibration sensitivity of the standards (both in DDW and the 35$^0/_{00}$ NaCl solution) tabulated in table 9 were not significantly different in contrast to the work by DeBaar and others (1993) that recorded large

differences in the calibration sensitivities of standards made in distilled water and synthetic seawater.

The FIA system used in this work has a 40% sensitivity of the most sensitive method/instrument for DOC determination, because the most sensitive method/instrument will have calibration sensitivity close to 1 (Skoog & Leary, 1992). The low calibration sensitivity of this FIA system was also reflected in the detection limit of this FIA method (see section 3.5) which was generally lower than other WCO methods like the method described by Koshy and others (1992). However, this method could be applied to estuarine and coastal waters that generally have DOC levels in the range of 1-20mg/L (Riley & Chester, 1971 and Head, 1976).

The Y-intercepts varied with the media of standard preparation, but not so much within calibration standards made from the same solvent. The calibration curves made from $35^0/_{00}$ NaCl solution standards showed higher values for the Y-intercept than the curves from standards prepared in DDW. The Y-intercept is the instrumental signal for a blank. The high instrumental signal for a blank in the $35^0/_{00}$ NaCl solution was a result of the oxidation of chloride to chlorine gas (Schreurs, 1978, Koshy *et al.*, 1992 and Perdue *et al.*, 1993). The average peak area equivalent to the mean Y intercept for the $35^0/_{00}$ NaCl solution calibration standard curves in table 9 was 1.4 ±0.6. When the $35^0/_{00}$ NaCl solution was injected as a sample, an average peak area of 1.3 units was recorded, this was 93% of the mean peak area of the Y-intercept for the standards prepared in the

$35^0/_{00}$ NaCl solution. The difference of 7% was probably caused by carbon impurities in the DDW and NaCl salt used, albeit the use of analytical grade NaCl. The mean Y-intercept for the DDW standards was 0.3±0.1. When DDW was injected as a sample, the "bumps" it caused could not be distinguished from the instrument noise implying that the DDW might have carbon residues less than the detection limit (see section 3.5) of the FIA system used in this work. Thus the intercept for the standards prepared in DDW could be caused by the presence of carbon residues in the solvent (DDW) or contributions from carbon from the previous injections and the contamination of the glassware although the DDW used did not register recognizable signals when injected and the glassware were soaked in 30% nitric acid.

The calibration curves registered correlation coefficients (R^2) of one. The high R^2 values indicated a strong association between the peak areas and the standard's concentrations. As a consequence the calibration curves were reliable and were elucidating quantitative carbon contents of the samples.

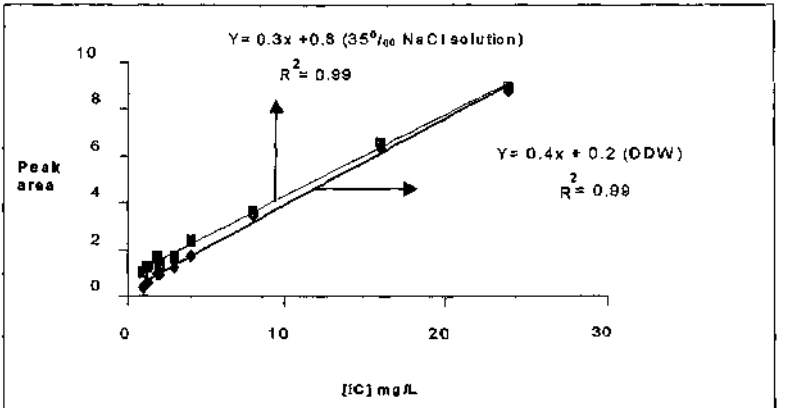


Figure 13 The calibration curves for the standards (DDW & 35‰ NaCl solution) prepared on 8/8/97 & 9/8/97

Since, the calibration sensitivity does not consider the precision of an individual datum in the calibration curves, the analytical sensitivity [(slope/standard deviation) at each point of the curve] was devised (Skoog & Leary, 1992). It was thought to be appropriate to include the precision of the data into sensitivity measurements. Table 10 exhibits the analytical sensitivity for a number of carbon concentrations. The analytical sensitivity was high at the low levels of carbon concentration. It decreased rapidly as the carbon concentration approached 5mg/L irrespective of the media of standard preparation. The analytical sensitivity observed for this method at the concentrations studied were consistent with those observed by (Koshy *et al.,* 1992). The only difference was that they considered carbon concentrations below 1mg/L. Analytical sensitivity is not subjective to data amplification and units of measurements (Skoog & Leary, 1992). It is however, dependent on the concentration of the standards as observed in table 10. The decrease in

analytical sensitivity was caused by low precision usually inherent with high concentrations and the departure from linearity as the concentrations of the standards increased.

Table 10

Analytical sensitivities (slope/standard deviation) for a range of carbon concentrations

[C] mg/L	Analytical Sensitivity 8/8/97 (DDW)	Analytical Sensitivity 9/8/97 (SSW)	Analytical Sensitivity 7/7/98 (DDW)	Analytical Sensitivity 7/7/98 (SSW)	Analytical Sensitivity 8/7/98 (DDW)	Analytical Sensitivity 8/7/98 (SSW)
1	16	17	2	2	4	3
2	9	4	-	-	-	-
3	6	7	-	-	-	-
5	-	-	2	2	4	3
10	-	-	0.5	2	0.7	2
15	-	-	0.6	0.6	0.8	0.5

In general, FIA methods usually have lower sensitivities than their manual and air segmented counterparts, because the measurements in FIA are performed under non-steady conditions. Sensitivity can be enhanced by on line pre-concentration and the introduction of solid interfaces to the system (Esmadi *et al.*, 1990 and Luque De Castro & Tena, 1993).

3.5 Detection Limits

Detection limits discern the ability of an instrument or method to differentiate between small amounts of the analyte of interest and the noise due to the instrument and other substances present in the solution. We are concerned with the instrument detection limit (IDL) and the method detection limit (MDL). The former limit gives the minimum distinguishable analytical signal (S_m) and is based on the sum of the mean blank value (S_{bl}) and three times the standard deviation of the blank value (SD_{bl}) (Skoog & Leary, 1992 and Skoog *et al.,* 1998). The MDL is the constituent concentration when processed through the complete method produces a signal with 99% probability that it is different from the blank. It can be calculated by taking the difference between IDL and SD_{bl} and divide it by the slope of the calibration curve.

In this project, the IDL was experimentally determined by repeated injection of DDW as the sample over a period of three days. In the process of injecting DDW, the other reagents were continuously pumped thus were simultaneously injected. It had a magnitude of 0.3 peak area units. The method detection limit was calculated based on the mean calibration curve of the DDW standards in table 9, MDL had a magnitude of 0.8mg/L or approximately 1part per million. In the method described by (Koshy *et al.,* 1992), the detection limit was 0.1mg/L, it was a better method in that sense. The difference could have been a result of the difference in modes of detection and the nature of the acceptor stream. Furthermore, the operating temperature of the water bath was different in both cases. In this project, the operating temperature was 58^0C, this was essential,

as increasing the temperature to 98^{0}C as in the original method by (Koshy *et al.*, 1992) would also result in enhanced chloride interference (see section 3.1).

IDL and MDL calculation

IDL= Σmean blank (S_{bl}) + 3(standard deviation of blank, SD_{bl})

= 0.3 + 3(0.1)

=0.6 peak area units

MEAN DDW EQUATION FROM TABLE 10: Y = 0.4X + 0.3

X = [C]= (0.6 – 0.3)/0.4

= 0.75mg C/L

=0.8mg C/L

MDL = 0.8mg C/L

Detection limits depend on the replicability of the baseline reading. Thus to achieve a low detection limit, the baseline has to be constant. The FIA system used in this work had a baseline conductivity that varied from 1 to 4 μS/cm. An increase in baseline conductivity has been observed to increase the carbon signal for that particular standard or sample in terms of peak area; the same was true for a decrease in baseline conductivity reading. The baseline in this method was based on the conductivity of DDW. It was not buffered and so it was subjected to variations caused by carry over effects, solutes adsorbed on the PTFE tubes, surface of the Pt - electrodes and possible slow diffusion of the previous injection caused by transfer kinetics at the membrane interface (Su *et al.*, 1998). The set back was that conductimetry is a non-selective method of

detection thus a high and variable baseline conductivity could cause unacceptable noise (Su *et al.,* 1998). If the DDW was buffered to avoid variations in the baseline, it could have been possible to achieve a better detection limit than that observed for this method. Although the flow of the acceptor stream was observed not to be obstructed by the detector, the retention of the DDW with ions cannot be disregarded. This was substantiated by the fact that when the detector was opened and washed with DDW, the baseline dropped. A change in the DDW passing through as the acceptor can also bring the baseline down. If the DDW was buffered it could have been possible to achieve a better detection limit than 0.8mg/L.

3.6 Attempts to eliminate/measure Inorganic carbon (IC)

3.6.1 Synthetically Prepared IC standards (25mg/L)

The acidification of the standards and samples was done without the presence of the oxidant. In the development of the FIA method used in this project, IC elimination was also considered despite the positive contribution it has on dealing with chloride interference, see section 3.7. IC elimination depended on a number of factors like pH, sample volume, the operating temperature and the rate of degassing with nitrogen or oxygen (Sharp *et al.,* 1993b).

IC removal was initially tested with a 25mg C/L standard made in DDW. From numerical calculations based on the amount of carbonate in 40ml of the standard, 0.04ml of 84% phosphoric acid was added for the complete removal

of IC. The average peak area for the standard before acidification was 13.1 peak area units, after acidification plus moderate heating and vigorous stirring, the same standard had a peak area of 1.1 units, see table 11. Since a concentrated solution of the acid was used, further addition of the acid to remove all IC in the standards will dilute the standard subsequently requiring the readjustment of the pH of the standard or sample for that matter with 1M NaOH to neutrality (pH 7). The readjustment of the pH of the standard or sample with 1M NaOH would further dilute the standard or sample. Nitrogen bubbling was not initially undertaken, in view of the fact that IC removal should utilize materials and options that are readily available in developing laboratories. The preceding reason might seem to be trivial in modern and developed laboratories, the same cannot be said for laboratories in third world countries. The significant reduction in peak area justified the above procedure. Furthermore, the 25mg C/L standard (DDW) which was vigorously stirred without degassing had almost the same recovery of IC after acidification as the standard that was degassed with nitrogen (see table 11).

Table 11

The peak areas of 25mg C/L standard (DDW and 35$^0/_{00}$ NaCl solution) and three seawater samples before and after acidification plus N_2 bubbling and sonication
(Peak area x10^7)

Type of sample	Prior Acidification (±1 SD) n=4	After Acidification (±1 SD) n=4	% reduction (±1 SD)
25mg C/L (DDW)*	13.1(0.1)	1.1(0.2)	92(9)
25mg C/L (35$^0/_{00}$ NaCl solution)	15.4(0.1)	1.4(0.1)	91(7)
Nabukalou creek	6.3(0.1)	0.4(0.1)	93.9(6)
Nukulau passage	4.8(0.6)	1.4(0.1)	71(7)
Suva point	6.7(0.2)	2.2(0.2)	67(7)

Note: * This standard was only moderately heated and vigorously stirred
Another 25mg C/L (IC) standard was prepared in 35$^0/_{00}$ NaCl solution and was analyzed as the previous standard but with nitrogen bubbling and sonication.

The carbon signal for the 25mg/L standard prepared in the 35$^0/_{00}$ NaCl solution (peak area) was reduced by 91%, (see table 11) after acidification, and the subsequent nitrogen bubbling and sonication. The high percentage reductions of the IC signal in both types of standards mean that the amount of acid added was not completely adequate. However, we are not concerned with eliminating all the IC in the seawater samples but to just measure the portion (IC_m) that can be determined by the FIA system described in this work. In circumstances where nitrogen gas and a sonicator are not available, vigorous stirring and moderate heating could be undertaken.

The measured inorganic carbon (IC_m) in the seawater samples was not equivalent to the total inorganic carbon in the seawater samples (Alkalinity: buffering capacity of the seawater sample). This stemmed from the comparison of the peak areas of the 25mg/L (IC) DDW standard and the seawater samples before acidification in which the seawater samples registered about 50% of the peak area of the standard.

3.6.2 Removal of IC from seawater samples

Natural water samples from three selected sites (Suva point, Nukulau passage and Nabukalou creek) were collected and filtered before analyses as in section 2.4.7. To each 40ml of the different seawater samples 0.04ml of phosphoric acid was added. The water samples were analyzed for their IC levels before and after acidification. The peak areas of the marine water samples after acidification plus nitrogen bubbling and sonication were smaller in magnitude than their peak areas prior to acidification. Complete removal of IC was not possible with the amount of acid added. The IC in these three samples was reduced by 67, 71 and 94% respectively after acidification. The immediate point to note here is that the standard procedure of adding a fixed amount of acid to seawater samples and purging with nitrogen or oxygen gas to eliminate all IC will not be successful in all cases. This is because different water samples will tend to require different amounts of acid for the complete removal of IC. The residual IC signals in all the samples after acidification were contributions from unconverted IC and from the individual GP in each water sample.

The complete removal of IC was not pursued any further because it has the ability to mask chloride interference (see section 3.7). Furthermore, acidification of seawater samples had been observed to change the composition of the DOC present in the seawater samples, as demonstrated by fluorescence studies of their spectra after acidification (Sharp *et al.*, 1993a). Another scenario of sample acidification is the fact that, acidification and the subsequent purging of the water samples can result in the removal of acid volatile DOC (Perdue *et al.*, 1993). It was not the intention of this work that the inorganic carbon in the seawater and coastal samples was to be completely measured. The preceding notion stemmed from the method of determining DOC in this FIA system which was by taking the difference between the IC_m and the IC_m plus the IC (TC_m) resulting from the oxidation of DOC (see section 2.8). Consequently, a high IC_m will obstruct the FIA system to elucidate the small differences to its value with the addition of IC from the oxidation of DOC (Aleprin & Martens, 1993). In the overall assessment of IC removal, it should be appreciated that complete removal of IC is not easy. Furthermore, the method of DOC determination utilized in this work did not require the measurement of the total IC in the sample.

3.7 The interference by Chloride on carbon measurement

The enhancement of carbon signals by chlorine gas has been observed with saline samples (Koshy *et al.*, 1992). In this part of the project, the interference by chloride had been quantified and shown to be present, see the following table and appendix 1 for the actual plots of selected standards prepared in DDW and the 35$^0/_{00}$ NaCl solution.

Table 12

The Interference by Chloride on the measurement of carbon (IC) standards

(Peak area X 10^7)

[C] mg/L	DDW Peak area (±1SD) n=10	35$^0/_{00}$ NaCl solution Peak area (±1SD) n=10	$\%Cl_{ox}$ (±2SD)	[Cl]/[IC] x10^3
0		1.30(0.01)		
1	0.38(0.03)	1.02(0.04)	168(16)	21
1.2	0.59(0.02)	1.21(0.01)	105(5)	18
1.8	0.95(0.03)	1.64(0.02)	73(8)	12
2	0.96(0.02)	1.36(0.02)	42(3)	10
3	1.27(0.04)	1.70(0.08)	34(7)	7
4	1.78(0.07)	2.38(0.05)	34(7)	5
8	3.46(0.02)	3.63(0.06)	5(2)	3
16	6.32(0.09)	6.60(0.03)	4(1)	1
24	8.84(0.09)	8.94(0.01)	1 (1)	1

Note: $\%Cl_{ox}$ =% difference in carbon signal caused by chloride
= [(35$^0/_{00}$ NaCl solution – DDW)] x (DDW /100)
= A measure of chloride interference
[Cl]/[IC] = The concentration ratio between chloride and inorganic carbon in a standard

Significant enhancements of the carbon signals occur at the low levels of inorganic carbon (IC) (<8mg/L). The overall differences caused by the chloride

in the 35$^0/_{00}$ NaCl solution standards were significant according to a ANOVA test (see appendix 6.0) on the data in table 12. However, as the concentration of IC increased, the level of interference by chloride decreased rapidly (see figure 14). A natural coastal marine water sample with an IC level as low as 8mg/L, would show approximately 5% chloride interference (%Cl_{ox}).

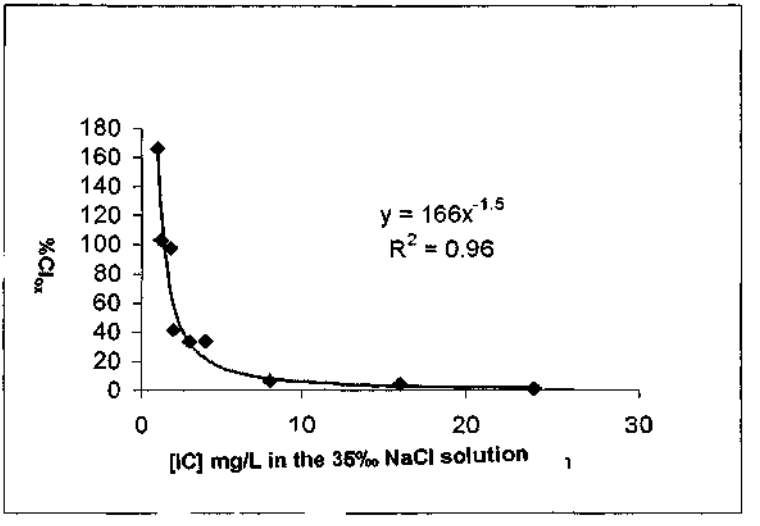


Figure 14 %Cl_{ox} versus inorganic carbon concentration in the 35$^0/_{00}$ NaCl solution

The decrease in chloride interference is a result of the rapid decrease in the ratio of chloride to inorganic carbon as the level of IC increased. The amount of chloride in each sample remained constant (35$^0/_{00}$) relative to the increasing IC in each consecutive standard. Carbon dioxide is a larger molecule than chlorine gas consequently, at the surface of the semi-permeable membrane carbon dioxide could have prevented the diffusion of chlorine. The prevention mode of

carbon dioxide on chlorine diffusion must have been more prominent as the level of IC increased (implying more carbon dioxide). The minimum amount of chloride in all the standards prepared in the $35^0/_{00}$ NaCl solution was $33^0/_{00}$. The doubling of carbon signals observed by Koshy and others (1992) must have been a consequence of the removal of IC prior to DOC determination.

On the other hand, the amount of chloride oxidized per standard was not equivalent to the amount of chloride oxidized when the $35^0/_{00}$ NaCl solution was injected as a sample without IC (see table 12, row **1**). To assume that chloride was oxidized consistently on all the standards prepared in the $35^0/_{00}$ NaCl solution would be contradictory to the above results. For example, the 1mg C/L standard ($35^0/_{00}$ NaCl solution) had a peak area that was not equivalent to the sum of the oxidized chloride in the $35^0/_{00}$ NaCl solution (1.30×10^7 peak area unit) and the 1mg C/L DDW standard (0.38×10^7 peak area unit). The rest of the standards ($35^0/_{00}$ NaCl solution) exhibited similar results as the above example. The preceding results alluded to the possible suppression of the oxidation of chloride by the inorganic carbon (Miller *et al.*, 1993) present in the standard.

3.7.1 The outcomes of Chloride Quantification

This part of the work had strongly demonstrated that the IC present in a sample could be used to the advantage of this method of DOC determination. The major objective of the project was to affirm the applicability of the flow injection method developed by Koshy and his co-workers in 1992 for the measurement

of DOC in marine and estuarine samples. From this chloride interference quantification exercise, one would realize that DOC from such sites could be quantified without too much interference from chloride. This is because natural marine waters have IC concentrations near 20mg C/L (Manahan, 1994), and for such levels of IC, the $\%Cl_{ox}$ will be quantitatively small when calculated from the equation in figure 14 ($Y=166X^{-1.5}$, $Y= \%Cl_{ox}$, $X= IC_m$). There need not be concern about whether all seawater or estuarine water samples will have an IC level near 20mg/L as an IC level as low as 8mg/L would only register chloride interference near 5%. Such low levels of chloride interference could be easily accounted for in the determination of DOC (see section 2.8).

Brackish and estuarine samples can have their IC_m quantified or enhanced with synthetically prepared IC and necessary numerical corrections can be made for any residual chloride interference using the above equation. The numerical approach for correcting the chloride effect is appropriate for this system since we do not want to introduce any more chemicals that may change the pH of the reaction media in any chemical method used for the elimination of chloride. In addition, the system should be kept as simple as possible for ease of operation, while at the same time provide accurate results.

3.8 Attempts to eliminate/minimize Chloride interference

3.8.1 Reduction of Oxidant power

One of the approaches suggested in the objectives of the project was to reduce the power of the oxidant with the hope of not oxidizing chloride. The amount of oxidant used in this work was based on the amount of oxidant used by (Koshy *et al.*, 1992) and it was initially thought to be excessive (Personal comm., Koshy). Therefore, reducing the oxidant strength could have reduced the possibility of oxidizing chloride given its high positive reduction potential at 25^{0}C (Alyward & Findlay, 1974). Consequently, the interference by chloride on the DOC signal will be eliminated or minimized. The proposed oxidation scheme for organic compounds by persulfate is given below. The oxidation ability of the persulfate is a result of its ability to produce hydroxyl radicals upon photodecomposition. The radicals are highly oxidizing in nature, most forms of organic carbon are converted to carbon dioxide (Koshy *et al.*, 1992).

Oxidation scheme of organic carbon by persulfate (Stumm & Morgan, 1981 and Minisci *et al.*, 1983)

$S_2O_8^{2-} \rightarrow 2SO_4^{\cdot-}$ (O-O bond scission)

$SO_4^{\cdot-} + H_2O \rightarrow HSO_4^{-} + OH^{\cdot}$ (hydroxyl radical production)

$2OH^{\cdot} + DOC + 1/2O_2 \rightarrow CO_2 + H_2O$ (oxidation of DOC)

$2OH^{\cdot} \rightarrow H_2O + 1/2O_2$ (removal of the hydroxyl radicals)

The objective behind this part of the work was to reduce the oxidant strength to a level that would have a carbon recovery near 80% with a view to boost carbon recovery to 100% using TiO_2 catalyst. The data in table 13 clearly demonstrated

the reduction in the oxidation efficiencies of the diluted oxidants compared with the oxidation efficiency of the 100% oxidant strength solution. The recovery of the standard did not drop below 80% even with 50% reduction of the oxidant strength. The results tabulated in table 13 confirmed the assertion by Koshy and his co-workers that the oxidant used in their work was excessive (Koshy *et al.*, 1992).

Table 13

The carbon recovery of a 5mg C/L (DDW, KHP) standard using different oxidant strength solutions

% Oxidant level	% Carbon recovery (±1SD) n=4
100	100
90	93(2)
70	87(4)
60	86(5)
50	86(3)
30	72(1)
10	62 (4)

As evident from the table above, the recovery of the 5mg C/L standard (KHP) using the different oxidant levels ranged from 62% to 93%. Even with substantial reduction of the oxidant strength the recoveries were still above 50%. Because of the moderate carbon recovery with the 50% oxidant solution, it was decided at that stage that this diluted oxidant solution would be used with a heterogeneous catalyst to compensate for the loss of oxidant strength. The carbon recovery of the 5mg C/L (KHP) standard at 50% oxidant strength level was 86%, which was reasonably high.

3.8.1.1 The use of the catalyst: Titanium dioxide

In section 3.8.1, the 50% oxidant strength solution was chosen as the new oxidant to be used in conjunction with the catalyst. The photocatalytic activity of titanium dioxide is well known especially amongst those in the paint industry, where it causes the problem of flaking. The catalyst has been found to oxidize most organic compounds including methane gas (Matthews *et al.,* 1990). TiO_2 has been widely used in the decontamination of effluents from industries and laboratories containing substances like dyes, nitroamines and other organic substances (Heller, 1995, Yu-Chuanming & Jiang, 1995, Harada, 1994, Martin *et al.,* 1995, Guittonneau *et al.,* 1995, Rao & Sangeeta, 1995, Tang & Huren, 1995, Tabata *et al.,* 1995 and Giglio *et al.,* 1995). The OH radicals were produced from titanium dioxide in the following sequence (Pramauro *et al.,* 1995)

$TiO_2 + h\nu \{E \geq E_{bg} \rightarrow e^-_{(CB)}\} + h^+$.....(i)

$O_{2(adsorbed)} + e^-_{(CB)} \rightarrow O_2^{\cdot -}{}_{(adsorbed)}$.....(ii)

$Ti^{IV}\text{-}OH^- + h^+ \rightarrow Ti^{IV}/.OH$.....(iii)

$Ti^{IV}\text{-}OH_2 + h^+ \rightarrow Ti^{IV}/.OH + H^+$.....(iv)

CB - Conduction band, E_{bg} - Band gap energy, h^+ - Valence band holes, $h\nu$ - UV

Note: The production of hydroxyl radicals occur at the surface of the catalyst particles

On the incident of about 3% UV radiation the TiO_2 particles absorb the radiation and promote electrons to the conduction band leaving corresponding valence band holes. The charge carriers (holes) can be lost through recombination or rapidly migrate to the surface of the particles to get trapped as radicals (holes:

$[Ti^{IV}\text{-}O^{\cdot}\text{-}Ti^{IV}]\text{-}OH^{\cdot}$). At the surface of the TiO_2 particles the surface radicals (holes) give rise to reactions (iii) and (iv).

The catalyst could be utilized as a suspension or it can be embedded on glass, without affecting its catalytic activity. The catalyst was used in this project as a suspension because of its simplicity in application.

Organic carbon standards (KHP) used in the recovery experiments were of the following concentrations: 2, 5, 15 and 25mg C/L (see table 14). The FIA system described by (Guardia *et al.*, 1995) required a specific amount of TiO_2 (0.5g/L) to be used for oxidation. However, the recommended amount was not applicable to the FIA system described in this work because Guardia and others (1995) used reaction tubes with larger internal diameters (0.8mm). Unfortunately, reaction tubes with internal diameters of 0.8mm were not available. Consequently, new amounts of the catalyst had to be tried on this FIA system and it was established that 0.0048g of titanium dioxide was the optimum amount required per 40ml of the standard. The suspension was made with the mixture of 50% oxidant solution and the catalyst by using a magnetic stirrer. This was to avoid the oxidant pump tube from taking in the large granules of the catalyst.

The information in table 14 was obtained using the 50% oxidant strength solution on KHP standards with and without the catalyst. With the 50% oxidant

strength solution alone, the carbon standard registered carbon recoveries that ranged from 81% to 92%.

Table 14

Recovery tests of 50% oxidant and 50% oxidant + catalyst on varying organic carbon levels represented by KHP (DDW) standards

[C] KHP mg/L	Recovery with 50% Oxidant (±1SD) n=4	Recovery with 50% Oxidant + catalyst (±1SD) n=4	Quantity of catalyst/g
25	92(2)	96 (2)	0.0048
15	81(2)	70(2)	0.0109
15	84(2)	87(2)	0.0048
5	89 (2)	103(2)	0.0048
2	89(2)	102(2)	0.0048

When 0.0048g TiO_2 was added to the 50% oxidant solution, the 2 and 5mg C/L standards registered recoveries just above 100%. The above result indicated that the amount of catalyst used was sufficient to compensate for the reduction in oxidant strength. The recoveries were 102% and 103% for the 2 and 5mg C/L standards respectively. However, the higher levels of DOC, 15mg C/L and 25mg C/L exhibited carbon recoveries less than 100%, at 87% and 96% respectively. The registration of lower recoveries by the 15mg/L and 25mg/L standards suggests that the amount of catalyst used was not sufficient to effectively compensate the reduction in oxidant strength. The next step taken was to increase the amount of catalyst for the high range of DOC, and so the 15mg C/L was analyzed with the 50% oxidant level plus 0.0110g of the catalyst.

The carbon recovery for this standard was less than its recovery with the 50% oxidant strength solution alone. The low carbon recovery for the 15mg C/L standard was the consequence of the irregular flow of the oxidant to the oxidation chamber. In the preceding experiment with the 15mg C/L standard and the 50% oxidant strength solution plus 0.0110g of titanium dioxide, leaks caused by blockages were frequent. To further substantiate the observation (blockage/leakage) that increasing the amount of catalyst was detrimental to the operation of the FIA system, a 2mg C/L and 15mg C/L (KHP) standards were oxidized with 50% oxidant strength solution plus 0.1000g TiO_2. The standards did not register any carbon signal at all because severe blockage of the tubes by TiO_2 made the FIA system operations very difficult.

Another possibility is to have this catalyst immobilized on the inside wall of the tube wounded around the UV source as was used by (Matthews *et al.*, 1990). However, this approach was not feasible for this method since the tubes are very small and the packing of the catalyst will mean that FIA parameters like pumping tubes and pumping rates etc., will have to be optimized again.

3.8.1.2 The effect of 50% oxidant+0.0048g catalyst on chloride interference

The "new" oxidant combination (50% oxidant strength solution + catalyst) was tested for its effect on chloride interference. The following standards, 2, 4, 16 and 24mg C/L (IC) were made in DDW and the $35^0/_{00}$ NaCl solution and subjected to the "new" oxidant. The data showed a positive enhancement of the chloride signal (see tables 15 & 16). The use of IC standards instead of organic

standards was purposely done to check for the possible enhancement of the carbon signal brought by the catalysis of the oxidation of chloride. It is an established fact that TiO_2 can quantitatively oxidize DOC to carbon dioxide (Matthews *et al.*, 1990). On the other hand TiO_2 is also a known oxidizing agent for compounds containing halogens like chlorine (Minisci *et al.*, 1983). Consequently, the objective of this part of the work was to elucidate the positive or negative effect of the catalyst on the oxidation of chloride before the new oxidant combination could be accepted for the oxidation of DOC in estuarine and coastal waters.

Table 15

Effect of 50% Oxidant + 0.0048g TiO_2 on Chloride interference

(Peak area x 10^7)

[C] mg/L	DDW (±1SD) n=4	35‰ NaCl solution (±1SD) n=4	$\%Cl_{ox}$ (±1SD)
2	1.0(0.1)	1.6(0.1)	60(4)
4	1.8(0.1)	2.8 (0.1)	56(2)
16	6.3(0.1)	9.2(0.1)	46(1)
24	8.9(0.1)	10.1 (0.1)	13(1)

The results of this set of experiment were similar to the results in table 12. That is, as the concentration of IC increased the level of chloride interference decreased. However, the percentage difference in carbon signals caused by chloride in this set of data were larger than the corresponding $\%Cl_{ox}$ obtained in section 3.7, see table 16 and figure 15.

Table 16

$\%Cl_{ox}$ obtained via two different oxidants

[C] mg/L	$\%Cl_{ox}$ (100% oxidant) (±1SD) n=4	$\%Cl_{ox}$ (50% oxidant + catalyst) (±1SD) n=4	Increase in $\%Cl_{ox}$ (±1SD)
2	42(3)	60(4)	18(5)
4	34(7)	56(3)	22(8)
16	5(2)	56(1)	51(3)
24	1(1)	13(1)	12(1)

Note: increase in $\%Cl_{ox}$ = $\%Cl_{ox}$ (50% oxidant + catalyst) - $\%Cl_{ox}$ (100% oxidant)

The enhancement of the oxidizing power of the 50% oxidant solution with the catalyst did not alleviate the interference by chloride. This could be a consequence of the fact that the catalytic property of TiO_2 is based on its ability to produce hydroxyl radicals which are also the oxidizing species in persulfate (Matthews *et al.*, 1990 and Praumauro *et al.*, 1995). The work on the catalyst was tried albeit its catalytic similarity to persulfate oxidation because the catalyst has an internal mechanism of removing excess OH radicals (Praumauro *et al.*, 1995). Another setback regarding the catalyst is that there is a possibility of it clogging the oxidant line. Effectively, there is little control on the blockage since the catalyst was used as a suspension. Clogging of the tubes will not be easy to deal with since the lines are very thin and long, thus purging them would be very difficult. On the other hand, fresh water samples with DOC levels ranging from 1-5mg C/L could be analyzed with this "new" oxidant combination.

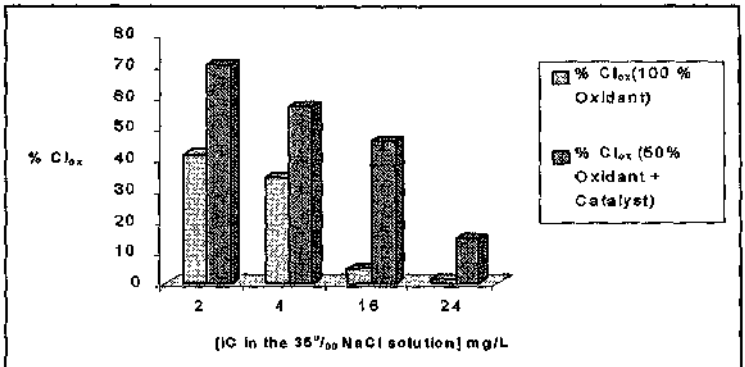


Figure 16 %Cl_{ox} using 100% oxidant & 50% oxidant + catalyst

3.8.2 The effect of Hydroxylaminehydrochloride ($NH_2OH.HCl$) on the chloride signal

$NH_2OH.HCl$ had been suggested to suppress the signal caused by chloride (Schreurs, 1978 and Tugrul, 1993) by reducing the chlorine gas produced in the oxidation chamber back to chloride ions. However, the appropriate concentration of the reducing agent to be used was not specified in the above articles. Consequently, various amounts of the reducing agent were added to the 35‰ NaCl solution and analyzed for the effect of the reducing agent on chlorine. The result is presented in Table 17. The dilution of the 35‰ NaCl solution was taken care of by using a concentrated stock solution of the reducing agent (see section 2.7.4), consequently small volumes of the reducing agent were added to the 35‰ NaCl solution in 100ml volumetric flasks.

Table 17

The effect of varying concentrations of Hydroxylaminehydrochloride ($NH_2OH.HCl$) on the chloride signal under 100% oxidant strength solution

35‰ NaCl solution + $NH_2OH.HCl$ [mg/L]	Peak height /mm (±1SD) n=3
35‰ NaCl solution	200(1)
35‰ NaCl solution+21,000	37(1)
35‰ NaCl solution+15,000	37(1)
35‰ NaCl solution+12,000	36(1)
35‰ NaCl solution+9,000	39(1)
35‰ NaCl solution+3,000	33(1)
35‰ NaCl solution+900	41(1)
35‰ NaCl solution+1000	36(1)
35‰ NaCl solution+300	46(1)
35‰ NaCl solution+100	41(1)
Mean peak height	38(3)

Note: Peak heights were measured instead of peak areas because a flat bed chart recorder was used instead of an integrator

The 35‰ NaCl solution with 3000mg/L $NH_2OH.HCl$ had the maximum suppressing effect on the chloride signal. On average, the chloride signal was reduced by 81±3% upon the addition of the reducing agent. The ability of the different concentrations of $NH_2OH.HCl$ to reduce chlorine was relatively constant, despite the large changes in their concentrations. However, the reducing agent was not able to completely eliminate the chloride signal. $NH_2OH.HCl$ has been suggested to work as reductant or oxidant (Sharp, 1990).

Since the $NH_2OH.HCl$ was placed in the $35^0/_{00}$ NaCl solution, in the oxidation chamber there was an oxidant and a reducing agent present simultaneously. However, from the above results it was obvious that its mode of operation was the reduction of any chlorine gas formed during oxidation. It was decided after this part of the work that the reducing agent with a concentration of 3000mg/L would be used to reduce the chlorine produced in the oxidation chamber back to chloride ions.

3.8.2.1 Effect of 3000mg/L $NH_2OH.HCl$ placed in the acid on chloride interference

The optimized concentration (3000mg/L) of the reducing agent was prepared and placed with the acid used for carbonate and bicarbonate conversion to carbon dioxide (see figure 5). This was undertaken to eliminate any possible counter action between the reducing agent and the oxidizing agent in the UV chamber.

Table 18

The effect of $NH_2OH.HCl$ on carbon signals for both IC and KHP
(Peak area x 10^7)

[C] mg/L	DDW +(IC) (±1 SD) n=4	$35^0/_{00}$ NaCl solution + (IC) (±1 SD) n=4	$35^0/_{00}$ NaCl solution + (IC) $NH_2OH.HCl$ (±1 SD) n=4	$35^0/_{00}$ NaCl solution + (KHP) $NH_2OH.HCl$ (±1 SD n=4)
5	2.4(0.2)	2.9(0.2)	2.8(0.4)	2.9(0.1)
10	5.1 (0.5)	5.6 (0.3)	5.3 (0.1)	5.5 (0.2)
15	6.8 (0.4)	7.0 (0.6)	7.0 (0.3)	6.9 (0.4)
20	8.7(0.4)	8.9(0.4)	8.9 (0.4)	8.8 (0.4)
25	9.7 (0.5)	9.8 (0.1)	9.9 (0.2)	9.9(0.2)

In general, peak areas for the standards under the different conditions specified in table 18 varied from each other, the $\%Cl_{ox}$ are given in table 19. The variation caused by residual chloride interference after the addition of $NH_2OH.HCl$, made the two types of standards (IC & KHP) prepared in $35^0/_{00}$ NaCl solution to be slightly different from the corresponding standards prepared in DDW. The above observation has been substantiated by an ANOVA test (see appendix 6.0), performed on the peak areas for all the conditions specified in table 18. The outcome of the test signified the presence of chloride interference on the standards without $NH_2OH.HCl$.

In table 19, the interference by chloride on the carbon signal decreased as the concentration of IC increased even in the presence of $NH_2OH.HCl$. In other words, the interference by chloride on the standards after the addition of the reducing agent was not significantly different from the interference by chloride in the standards without the reducing agent (see section 3.7). In other words, the

choices to use the reducing agent or not depend on the analyst because the masking effect of IC on chloride interference was equivalent to the reducing capacity of $NH_2OH.HCl$ on chlorine gas. In this project we have decided to adapt the masking effect of IC on chloride interference because of the above reason and the fact that it was simpler than the use of the reducing agent.

Table 19

The effect of $NH_2OH.HCl$ on chloride interference on standards prepared in $35^0/_{00}$ NaCl solution

[C] mg/L	$35^0/_{00}$ NaCl solution + (IC) $\%Cl_{ox}$	$35^0/_{00}$ NaCl solution + (KHP) + $NH_2OH.HCl$ $\%Cl_{ox}$	$35^0/_{00}$ NaCl solution + (IC) + $NH_2OH.HCl$ $\%Cl_{ox}$
5	20	16.6	19.1
10	4.4	3.9	7.6
15	3.2	3.1	2.1
20	2.1	2.9	1.3
25	1.4	2.2	1.7

3.8.3 The effect of the micro-porous tubing (Accurel PP Type S6/2, 0.2μm pore size; Enka) on chloride interference

One of the methods suggested in this project to deal with chloride interference was the use of micro-porous tubing, see figure 5. The 20cm porous tubing was placed after the UV chamber to eliminate gases like chlorine and oxygen that were formed in the UV chamber. The objective here is to demonstrate the

micro-porous tubing's capacity to eliminate chloride interference. The tubing was porous therefore gases like chlorine and oxygen produced in the oxidation chamber (Koshy *et al.*, 1992) should pass through the pores.

When the micro-porous tubing was attached to the line after the UV chamber the carbon standards (5-15mg/L) made in the $35^0/_{00}$ NaCl solution exhibited chloride interference ($\%Cl_{ox}$) less than 10%. The average $\%Cl_{ox}$ was 5% for that range of carbon standards. The trend was that at 5 and 10mg C/L (IC), the $\%Cl_{ox}$ was less than the $\%Cl_{ox}$ at 15mg C/L. When the accurel was removed the $\%Cl_{ox}$ observed was similar to that obtained in section 3.7. That is as the concentration of inorganic carbon (IC) increased the $\%Cl_{ox}$ decreased, see figure 16. The micro-porous tubing had the capacity to eliminate most of the chlorine produced in the oxidation chamber. The results in table 20 showed that when the micro-porous tubing was placed after the UV chamber the $\%Cl_{ox}$ was reduced in all the $35^0/_{00}$ NaCl solution standards (IC).

Table 20

Effect of the micro-porous tubing on chloride interference on carbon standards prepared in DDW and 35$^0/_{00}$ NaCl solution

[C] mg/L	DDW mm (w/o) (±1SD) n=10	35$^0/_{00}$ NaCl solution mm (w/o) (±1SD) n=10	DDW mm (w) (±1SD) n=10	35$^0/_{00}$ NaCl solution mm (w) (±1SD) n=10	%Cl_{ox} (w) (±1SD) n=10	%Cl_{ox} (wo) (±1SD)
5	40.0(0.2)	48.4(0.3)	42.5(0.2)	44.4(0.2)	5(2)	21 (2)
10	73.7(0.1)	87.5(0.1)	71.6(0.1)	73.3(0.2)	2(1)	19(1)
15	126.9(0.1)	140.6(0.1)	118.4(0.2)	128.5(0.1)	9(4)	11(2)

(wo)- without micro-porous tubing, (w)-with micro-porous tubing

Note: Peak heights were measured instead of peak areas because a flat bed chart recorder was used instead of an integrator.

However, the important point to note is that as the level of IC increased to 15mg/L the difference between the %Cl_{ox} obtained with and without the micro-porous tubing dropped dramatically to 2%. This difference of 2% was not significant when compared to the difference in %Cl_{ox} at 5 and 10mg/L (IC) with and without the micro-porous tubing.

The above results implied that when dealing with water samples that have low levels of IC, it would be advisable to use the micro-porous tubing to minimize the chloride interference. At the higher range of IC the choice to utilize, the micro-porous tubing or numerical correction as used in this project depends on the analyst. However, in developing countries as in the case of the South Pacific the numerical correction for chloride interference is appropriate, because the micro-porous tubing is very expensive and is not readily available. However,

when the micro-porous tubing is available it can be used with the numerical method in the following manner. For the range of carbon standards investigated in this project, the mean $\%Cl_{ox}$ was 5%. This could be translated using the equation in figure 14 and it would be equivalent to 11mg/L of inorganic carbon (IC). The IC (11mg/L) value could be added to the experimentally determined IC_m of any particular saline water sample and the final IC_m value could be used to determine the experimental $\%Cl_{ox}$. If the combination is taken, chloride interference would be small, since an increase in IC would result in a decrease in chloride interference as explained in section 3.7.

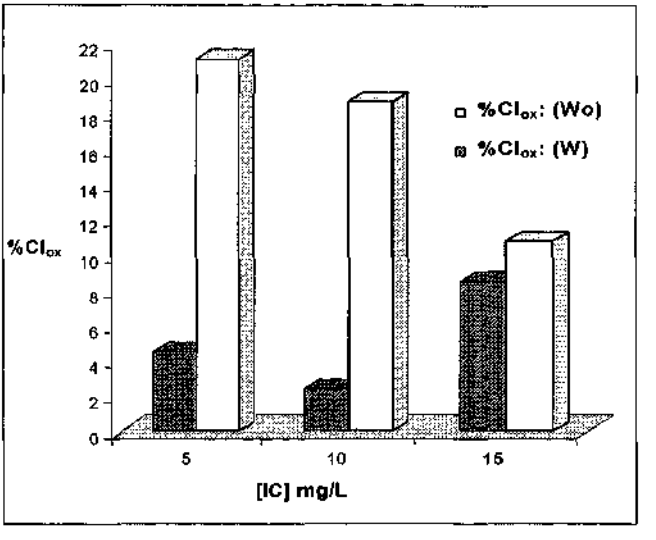


Figure 16 Plot of $\%Cl_{ox}$ versus carbon concentration with (w) and without (wo) the micro-porous tubing

3.9 Gas diffusion and Conductivity detection

A gas diffusion membrane was used to separate the donor and acceptor streams (see figure 5). A number of different methods of separation were used in other applications (Ruzicka and Hansen, 1981). Gas diffusion was considered to be highly selective because few species could be generated as gases at room temperature (Motomizu *et al.*, 1987). Various types of membranes had been used. These included silicon, rubber and micro porous tetrafluoroethylene (PTFE) which was the most versatile of them all and was used in this project.

The carbon dioxide diffused across the membrane to the acceptor stream (DDW) and changed its conductivity. The acceptor stream was directed to a custom-built conductivity cell, that detected the change in conductivity. The change in conductivity was proportional to the quantity of analyte present in the sample or standard. The use of DDW as the receptor for CO_2 resulted in a negligible background conductance but baseline fluctuations were still observed because of ions adsorbed on to the surface of the electrodes and minute impurities in the DDW. Unlike a similar method by (Kuban & Dasgupta, 1993), where DDW was used as the receptor in the acceptor stream the FIA method used in this project did not have any serious problem with its baseline. Factors like the type of membrane, the temperature of the water bath and length of the reaction coil could affect diffusion in general. However, of all the factors mentioned, the temperature of the donor stream (which is dependent on the temperature of the water bath) was the most effective in enhancing diffusion

(see section 3.1). The enhancement of diffusion was due to the acceleration in the production of volatile compounds and increment of the partial pressure of the donor stream and the diffusion coefficient (Cardwell *et al.,* 1994). In a study where volatile acids were separated from wines, the use of a diffusion membrane resulted in the excellent separation of the volatile acids (Barros & Tubino, 1992).

The main disadvantage of a diffusion membrane is that the different species of interest have to be gaseous, consequently, all other gases had to be removed because gases (not necessarily acidic) have been observed to cause positive changes to the conductivity of the acceptor stream in this FIA system. The preceding observation was made possible by deliberately introducing air bubbles into the carrier stream. In a method developed for total carbon dioxide and ammonia, hydrogen sulfide was removed by the addition of zinc ions, since hydrogen sulfide was also capable of diffusing across the membrane (Hall and Alter, 1992). It might not be possible to remove all interfering gases.

In the FIA manifold used in this work, diffusion and conductivity detection occurred at two different places. Diffusion and detection can be combined to enhance signal sensitivity (Johnson *et al.,* 1992). When these processes occur at two different places, there will be a loss of kinetic information and dilution of the sample's analyte signal (Pavon *et al.,* 1992). The dilution process also contributed to moderate detection limit exhibited by this FIA system. The minimization of this dilution process would improve the limit of detection (Johnson *et al.,* 1992). It is not quite clear whether less soluble gases like

carbon dioxide would dissolve in the acceptor stream in time for detection, if the two processes are to be combined.

Conductimetric detection of the carbon signal in this project had some advantages over other forms of detection like spectrophotometry and potentiometry. First, the detector was simple and was constructed of Perspex glass with four platinum electrodes. This conductivity detector was far cheaper than the average detectors for spectrophotometry, coulometry and potentiometry. The above advantages might not be of any significance in well-developed laboratories, but the impact they have on this FIA method's application in a developing laboratory could not be ignored. Perhaps the most important advantage of conductimetric detection was that it had better day to day reproducibility, sensitivity and detection limits than the other forms of detection like spectrometry and potentiometry (Kuban & Dasgupta, 1993). The data in terms of peak area reported in this work were actually conductivity changes in the acceptor stream that were initially detected by the custom built conductivity detector.

3.10 DOC measurement

The prime objective of this part of the project was to do a baseline study of DOC in the Suva lagoon. The period of sampling was not adequate to make future predictions on the DOC levels in the Suva lagoon. In addition, a minor comparison was made between the DOC data obtained from this FIA system and the Shimadzu 2000-UV HTCO unit.

The modified method was used to analyze for DOC levels on selected sites in and around the Suva harbor and Laucala bay that received organic substances from in shore sources. The sampling of the sites was carried out over a period of fourteen weeks (April – August, 1998). In this time frame, sampling was alternated between coastal sites and offshore sites within Laucala bay and Suva harbor (see figure 10). The coastal sites were sampled for eight weeks and the offshore sites were sampled for six weeks.

3.10.1 Comparison of the DOC data obtained from the FIA manifold and the Shimadzu 2000-UV HTCO unit

The discussion in this part of the work on DOC will be based on the average DOC values obtained for each individual method of DOC determination. The above approach was suitable because of the standardizing effect of using averages as opposed to the use of raw data for comparative work (Damond & Harvey, 1987 and Skoog & Leary, 1992). Furthermore, the use of averages for comparative work between WCO and HTCO methods on DOC data were done

by a number of research workers (Gershey *et al.*, 1979, Riley & Skirrow, 1975, Sugimura & Suzuki, 1988, Wangersky, 1993, Tugrul, 1993, Hedges *et al.*, 1993, Chen & Wangersky, 1993, Miller *et al.*, 1993, Sharp *et al.*, 1993b&c and Tupas *et al.*, 1994). The reported averages of the data obtained for the FIA method used in this work were transformed by a statistical procedure (square root transformation, see appendix A 6.0).

Table 21

The average DOC values for the Sites using the FIA manifold used in this project and the average DOC values obtained from a Shimadzu 2000-UV HTCO unit

Sites	FIA Method Raw data [DOC] mg/L (±1SD) n=32	FIA Method Transformed data [DOC] mg/L (±1SD) n=32	Shimadzu 2000-UV HTCO unit data [DOC] mg/L (±1SD) n=20	[FIA – HTCO]x100 / HTCO (±1SD) n=10
Kinoya outfall	15(11)	13(4)	12(1)	8(4)
200m Kinoya outfall	18(14)	16(4)	11(1)	31(8)
Nukulau passage	10(11)	9(3)	9(1)	0
Centra hotel	0.8(0.2)	0.8(0.1)	0.8(0.1)	0
200m Nabukalou creek	19(10)	18(3)	1.0(0.4)	1700(6)
Mosquito island	19(13)	18(3)		
Tradewinds	9(11)	8(2)	3(1)	167(4)
Vugalei bridge	6(6)	5(1)	3(1)	67(2)
Tamavua river	8(5)	8(1)	2(1)	300(2)
Nabukalou creek	7(7)	7(1)	11(2)	-36(4)
Nasese	5(6)	4(1)		
Suva point	8(9)	7(2)	1.0(0.1)	600(5)

Note: With the Shimadzu 2000-UV HTCO unit DOC data reported were averages of two sets by 5 replicate analyses.
The Shimadzu 2000-UV HTCO unit belonged to a Japanese Aid programme based at Monfort boys Town.

The raw average DOC data obtained from the FIA system was transformed so that the large variations in terms of the standard deviations quoted for the raw averages could be reduced, consequently making the data statistically acceptable for comparison (Damond & Harvey, 1987). The large variations in the raw averages indicated the large influence of land based sources of DOC

on the DOC present in the Suva lagoon (this would be discussed in the next section). The transformed DOC data was essentially the same as the raw average data according to an F-test performed on the two sets of data (see appendix 6). The only marked difference in the raw and transformed data was the generally low standard deviations quoted for the transformed data. The similarity between the above sets of data was also evident from the similar correlation coefficients (R^2=0.7) calculated for the individual plots of raw and transformed averages against their standard deviations (figures 17 & 18). Because of the demonstrable similarity between the raw and the transformed data, it was acceptable to compare the two sets of data (FIA system & Shimadzu 2000-UV) using the FIA transformed averages and the average DOC data from the Shimadzu 2000-UV HTCO unit.

The variation of the DOC data with respect to the individual methods of (FIA & Shimadzu 2000-UV) of DOC determination used in this work was statistically insignificant (ANOVA, see appendix 6). However, there were some disparities between the data from the FIA system and the Shimadzu 2000-UV HTCO unit mainly with the coastal sites (Suva point [4], 200m Nabukalou [7], Nabukalou creek [8], Tamavua river [9] and Tradewinds [11]). The coastal sites are essentially estuaries and the above sites reflected their estuarine nature by registering generally low salinity in the range of 23 to 34psu. Estuaries generally have higher concentrations of colloidal DOC than pure marine waters and colloidal DOC have sparing susceptibility to all forms of oxidation (Miller *et al.*, 1993 and Lee & Henrichs, 1993). Apart from the negative difference registered

by the HTCO unit for site 11(see table 21) all the other sites with positive differences indicated that for those sites the FIA system was

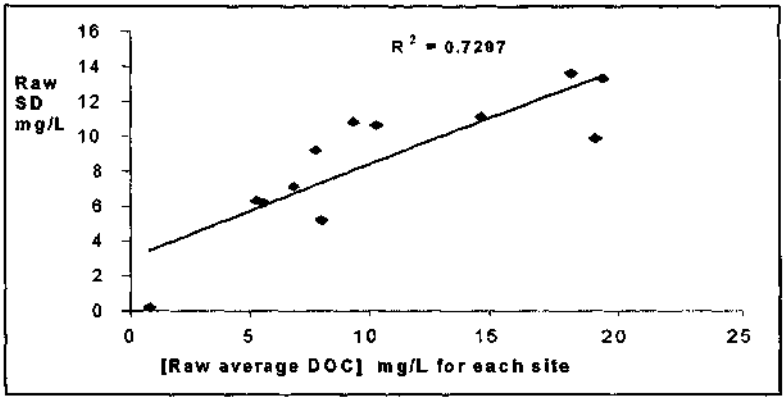


Figure 17 Standard deviations versus DOC concentration for the DOC raw data

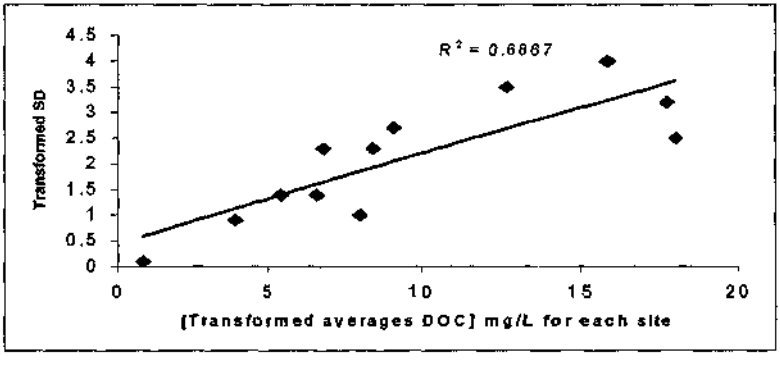


Figure 18 Standard deviations versus DOC concentration for the DOC transformed data

measuring more DOC than the HTCO unit. The coastal sites were expected to have high levels of DOC (Stumm & Morgan, 1981 and Libes, 1992) and the DOC measurement by the FIA system was supporting the preceding assertion. The above results indicated that colloidal DOC might have been oxidized by the FIA system. On the other hand, the Shimadzu 2000-UV HTCO unit might have been partially oxidizing the DOC in the seawater and estuarine water samples because of the frequent instrument "breakdowns" when the seawater and estuarine samples were analyzed. Furthermore, there was a weak but positive correlation between the average DOC data obtained through the FIA system and the Shimadzu 2000-UV HTCO unit (see figure 19).

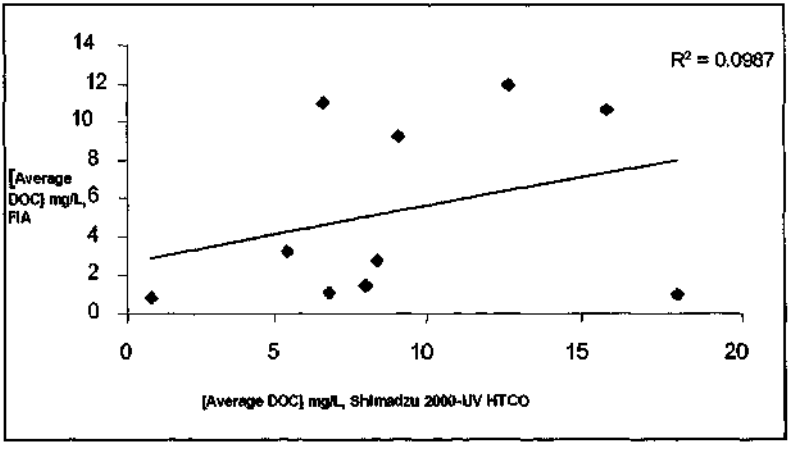


Figure 19 Average FIA DOC data versus Average Shimadzu 2000-UV DOC data

The oxidation efficiency of the Shimadzu 2000-UV HTCO unit was comparable to that of the FIA system when the samples from offshore sites were analyzed. Two sites (Nukulau passage & Centra hotel) registered similar DOC values

irrespective of the method. The oxidation efficiency of the HTCO unit was observed to be negatively affected when the estuarine and coastal waters were injected as samples. It was later found that the platinum catalyst used in the Shimadzu 2000-UV HTCO unit was usually clogged with salt residues and this caused the incomplete DOC oxidation and the poor maintenance of the HTCO unit's baseline. The above problem became so frequent that only two sets of random DOC analyses were done. The clogging of the platinum catalyst was persistent albeit the presence of an in-built halogen scrubber. On the other hand, both methods generally showed high DOC values for the sites receiving direct organic discharge (Kinoya outfall, 200m Kinoya outfall and Nabukalou creek) and lower DOC values for those sites perceived to be far from the organic discharge (Centra hotel and Nukulau passage). The preceding observation showed that the FIA system was suitable for the quantitative determination of DOC in coastal and estuarine waters.

The disparity of the DOC values obtained from the HTCO unit and the FIA system described in this work was probably caused by the incomplete oxidation of DOC by HTCO unit. The other reason for incomparable DOC values between HTCO and WCO methods is the effect of unaccounted blanks (Hedges *et al.,* 1993). In this work the effect of blanks was negligible because the differences tabulated in table 20 were not constant as expected of circumstances where the disparities between WCO and HTCO methods were caused by blanks (Miller *et al.,* 1993). Furthermore, the data from both methods (FIA system & Shimadzu 2000-UV HTCO unit) were corrected for the blanks (reagent, water and instrument) in terms of the Y intercepts of the calibration

standard curves used. The Y intercepts of the calibration curves are reliable estimates of the total blank value (Skoog & Leary, 1992).

3.10.2 DOC variation in the sites sampled as determined by the FIA system

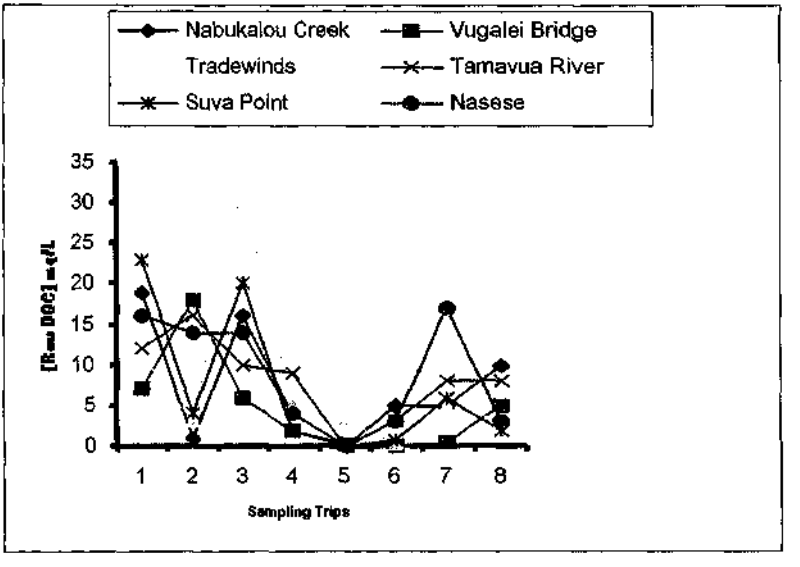
It is essential to note here that this was a baseline DOC study of selected sites in the Suva lagoon and not a comprehensive study of the temporal and spatial variation of DOC in the Suva lagoon. The discussion had been categorized into coastal and offshore sites to ensure clarity. The coastal sites referred to were those sites at the interface of the land and the sea and the offshore sites referred to were those sites further out of the coastal waters. The sites were intentionally sampled on fine days although it did not matter if it rained a few days before sampling. It has been argued that the DOC present in coastal waters originated from terrestrial sources like sewage outfalls, rivers, streams, creeks and industrial effluents (Stumm & Morgan, 1981, Riley & Chester, 1971 and Libes, 1992). On the other hand DOC could also be produced *in situ* by phytoplankton and the degradation of organic matter by microorganisms (Thurman, 1985 and Libes, 1992).

The results of this work in figures 19 and 20 demonstrated a wide variation of DOC on each site at each time of sampling. The large variation of DOC indicated that the input from land based sources like creeks, rivers and storm waters run off significantly influenced the DOC levels present at each site. The

above observation was expected because the sites were at the interface of the Suva landmass and the coastal waters.

3.10.2.1 Coastal sites

The DOC with respect to each site sampled varied considerably on each day of analyses (see figure 19). The DOC in each site ranged from levels less than the detection limit of the FIA system to a maximum of 35mg/L. There wasn't any fixed pattern of DOC apart from the wide variation in DOC levels caused by the input from the landmass of Suva.



Note: The rainfall data is given in the appendix with DOC data on each sampling trip

Figure 20 DOC data for the coastal sites

The sites were in fact point sources of organic matter. The sites were in or at river mouths (Tamavua and Vugalei Bridge), in a creek or at its opening (Nabukalou creek and Tradewinds) and near storm water outlets (Nasese and Suva point). There were direct organic discharges into the sites, consequently it was not seen necessary to actually take samples from the land-based sources. The greatest DOC variations were observed in all the sites at sampling trips 1, 3 and 7(see figure 20). In all the above trips the Suva area experienced rainy weather on a range of 1-5mm three days prior to the sampling day (Fiji Meteorological Service, 1998). Consequently, the rain accelerated the input of DOC in to the sites (Clair & Erhman, 1996). The sampling trips 1, 3 and 7 showed on average DOC levels greater than 10mg/L. The preceding DOC level (10mg/L) was usually associated with estuarine water without any obvious pollution (Head, 1976). By taking 10mg/L as the normal DOC level for the sites sampled in this work, it would be appropriate to label all the sites on sampling trips 1,3 and 7 as being polluted from the DOC input from the landmass of Suva. Tamavua river exhibited a nearly consistent DOC level around 10mg/L through out the sampling period apart from the huge drop exhibited by all sites during sampling trip 5. The preceding observation for the Tamavua river was consistent with the assertion by Libes (1992) that DOC levels in rivers tend to show minor changes in DOC levels when there is rain. No specific reasons were given for the consistent levels of DOC in rivers although factors like the rapid movement and coagulation of terrestrial DOC upon mixing with cations like Ca^{2+} and Mg^{2+} associated with rainy weather and saline waters respectively might have diluted the DOC present at the site (Libes, 1992). The Tamavua

river site was within a part of the river that has a constant interchange with the sea (high levels of cations).

During sampling trip 5, all the sites registered very low levels of DOC that were not detected by the FIA system except for the Tradewinds site which had 3mg/L of DOC. In the three days prior to this sampling trip, the Suva area experienced an average of 0.3mm of rain. Consequently, the Suva lagoon received less surface runoff and this factor contributed to the low DOC values registered by the sites. Apart from the rain and the subsequent increase in organic input to the sites, the sites that are near productive sources of DOC (*e.g.* creeks) seemed to maintain DOC levels greater than the method detection limit of the FIA system. The site near Tradewinds showed a higher DOC level than the other sites probably because of the fact that it was an opening of a brackish creek to the sea, therefore it maintained a reasonable level of DOC in the absence of surface run off. Salt marshes including mangrove swamps are productive sites of DOC (Lal, 1990). Furthermore, the Tradewinds site was close to a hotel, a fishing company wharf and a number of yachts were moored in the vicinity of the site from which organic discharge to the site were very likely. Furthermore, the site had limited interaction with the open sea, consequently the discharge from the creek remained fairly longer at the site, albeit tidal movements.

During sampling trip 2, the Nasese, Tamavua river and Vugalei bridge registered DOC levels around 15mg/L whilst the rest of the sites had DOC levels in the range of 3 to 4mg/L. There wasn't any significant rain (average of

0.1mm) three days prior the day of sampling and it was expected that all sites would register DOC levels less than 10mg/L. On the contrary, Nasese, Tamavua and Vugalei bridge register DOC levels greater than 10mg/L because they have freshwater input from the storm water outlet, a river and a mangrove swamp. These freshwater sources did not necessarily stop discharging into the sites in the absence of any significant form of rain apart from some light showers prior to the time of sampling.

Generally, during the sampling trips 4, 6 and 8 there were no significant rain (0.2mm - 0.4mm) in the last seventy two hours prior the sampling of the sites. Consequently, all sites registered DOC levels less than 10mg/L. Even with these sampling trips, those sites that continually have fresh water discharge like Nabukalou creek, Tamavua river, Vugalei bridge and Tradewinds registered DOC levels greater than the DOC levels for sites like Suva point and Nasese which strongly depend on DOC input from the storm waters apart from the natural background DOC. The freshwater discharges in these sites were generally high in organic matter (Naidu *et al.*, 1989) therefore, higher DOC levels were expected.

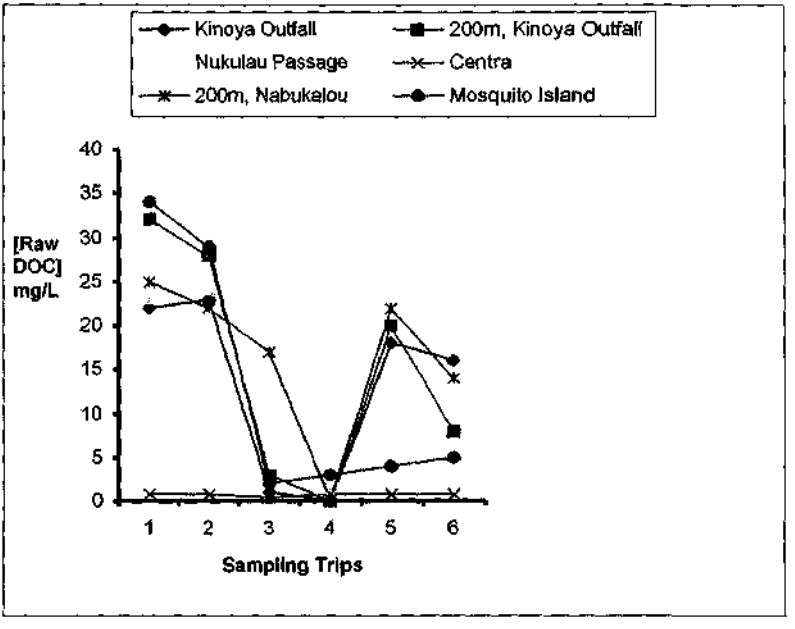
The general trend was that fine weather was usually associated with DOC levels less than 10mg/L and wet weather that results in significant surface run off could double or even triple the DOC levels in the sites. It would be incorrect to ascribe the background DOC in the sites to be around 10mg/L because in the absence of significant surface runoff, there were still slight discharges from the storm water outlets and furthermore sites in the creeks and river continually

have freshwater input. Random dissolved oxygen (DO) measurements of the sites registered DO levels in the range of 5-8mg/L. Independent DO measurements around the Laucala bay by the staff of Kinoya sewage treatment plant registered a similar range of DO (Australia, Department of Transport and Construction, 1982). The above range of DO was close to the expected DO level of seawater at 25^{0}C (Manahan, 1994) which is 8mg/L. The sites could not be described as being oxygen deficient because the samples were collected as surface samples, which generally have good aeration due to wave action. The direct dissolution of oxygen in the sites was possible because the sites were shallow, usually less than one meter in depth. However, the registration of DO levels around 5mg/L indicated that DOC oxidation by microorganisms could have utilized some oxygen, although the use of oxygen for animal respiration and poor aeration could also cause reductions in the DO levels in the sites. Furthermore, the slightly warm waters observed at the sites (26^{0}C) might have halted the dissolution of oxygen (Manahan, 1994).

3.10.2.2 Offshore sites

These offshore sites were situated in the Suva lagoon in the range of 0.1km to 5km from the shoreline. The sites sampled with the exception of the site near Centra hotel registered varied levels of DOC on each sampling trip. The large variations shown by these sites indicated the significance of the terrestrial organic input on the levels of DOC present in each site (see figure 21). The above observation was also seen with the coastal sites discussed in the previous section. The input of organic matter into the Suva lagoon was

predominantly through the discharge from the Rewa river, Vunivadra tributary, Kinoya outfall, Tamavua river, Nabukalou creek and the storm water runoff from the greater Suva area (Australia, Department of Transport and Construction, 1982 and Naidu *et al.*, 1989).



Note: The rainfall data is given in the appendix with DOC data on each sampling trip

Figure 21 DOC data for the offshore sites

The site near Centra hotel maintained a DOC level near 0.8mg/L throughout the period of study. The above site was about 300m from the shoreline therefore it was expected to have high levels of DOC on each time of sampling. There are a number of possible explanations for the registration of such low DOC levels by the site near Centra hotel. The fact that the site was situated in one of the

passages where there is constant water movement towards the inner Suva harbor at high tide and outwards to the barrier reefs at low tide could have left this site with consistent low DOC level (Kumar, 1999). In other words, the water movements initiated by high and low tides as well as wind action could have driven the top layer of the seawater (which usually has the terrestrial water input) outwards from the site (Australia, Department of Transport and Construction, 1982). On the other hand, the continual interchange of seawater (more cations like Mg^{2+} and Ca^{2+}) and the freshwater from the storm water outlet near the hotel could have coagulated the DOC input from the outlet upon receipt at the site (Libes, 1992). Consequently, lesser DOC was present in the water column of the site near Centra hotel.

During sampling trips 1 and 2, all the sites apart from the site near Centra hotel registered DOC levels greater than 20mg/L. On both trips, the Suva area experienced rain (4mm – 5mm) in the last seventy two hours before sampling resulting in increased surface runoff from the rivers, storm water outlets and creeks in to the Suva lagoon. Therefore most of the sites registered high DOC levels. During the above trips (1 & 2) the site near Mosquito Island and the site 200m from the Nabukalou creek registered the highest levels of DOC than the other sites. The site at Kinoya outfall was expected to have higher DOC levels on the above trips because of the continuous discharge from the outfall (Per comm., Shaihnaz) and the added DOC from the surface runoff originating from the surrounding coastline and the Vunivadra tributary. There is a possibility that the discharge from the outfall dispersed to the surrounding areas giving rise to the high levels of DOC registered at the site 200m from the outfall. Likewise, the

site 200m from the Nabukalou creek registered high levels of DOC during the sampling trips 1 and 2 because of the dispersion of the organic discharge out to the sea caused by wave action and receding tides. Furthermore, with increased surface runoff it was possible that the site 200m from the sewage outfall had in its vicinity higher levels of organic matter originating from the discharge from the Vunivadra tributary given its proximity to the observed path of riverine discharge.

The site at Nukulau passage unexpectedly registered high DOC levels in sampling trips 1 and 2 although it was the furthest site from the landmass of Suva. The high DOC levels registered by the site at Nukulau passage probably arose from discharge from the Rewa river that was usually driven by the southeast trade winds which predominantly blow toward the Laucala bay (Australia, Department of Transport and Construction, 1982 and Kumar, 1999). Consequently, the Nukulau site becomes an entry point for the Rewa river discharge into the Laucala bay. The backward movement of surface water into the bay through the Nukulau passage become more pronounced when the tide comes into the bay (Kumar, 1999). On the other hand, at low tide Nukulau passage and Nukubuco passage become the major exit points of the water from Laucala bay to the open sea. As a result it would be possible to have high levels of DOC on any particular day. Furthermore, surface runoff from Nukulau island increased by rain prior the sampling trips 1and 2 could also increase the levels of DOC in the Nukulau passage. During the above trips the site near Mosquito island also registered high DOC levels because the site was in a channel that connects the bay of island to the open sea and it is highly probable that the

surface run off from the surrounding coastline pass through this site. On the other hand, the site 200m from the Nabukalou creek also registered high levels of DOC because of the increased discharge from the Nabukalou creek, Suva fish market and the possible re-suspension of organic matter in the water column caused by the movements of ships and motorized boats. The above site was close to the Suva main wharf.

During sampling trip 3, the sites at Nukulau passage and 200m from the Nabukalou creek registered DOC levels between 10mg/L and 20mg/L. The rest of the sites registered DOC levels less than 5mg/L. The effect of surface run off was minimal here, although light showers (average, 0.8mm) occurred within the seventy two hours before sampling. However, the sampling trip coincided with receding tide. Consequently, the sites at Nukulau passage and 200m from the Nabukalou creek experienced high levels of DOC because of the dispersion of organic matter from the continuous discharge from sources like the Kinoya sewage outfall, Vunivadra tributary and the Nabukalou creek. In other words, the outward movement of the surface water caused by the receding tide dispersed the organic discharges from in shore sources to the sites further out in the lagoon. On the other hand, the sites at Kinoya outfall, near Mosquito island, 200m from Kinoya and the site near Centra hotel experienced DOC deficiency.

During sampling trip 4, the sites generally registered one of the lowest DOC range in all the sampling trips in the study. The low DOC levels were probably due to the insufficient surface run off prevalent because of the generally fine

weather that prevailed seventy two hours before sampling although brief showers (0.4mm) occurred. On the contrary, the site at Kinoya outfall was expected to maintain a reasonable level of DOC around 10mg/L, because of the continuous discharge from the sewage outfall.

The sampling trips 5 and 6 took place after a couple of rainy days (0.2mm – 1.0mm) and the rain increased the surface runoff to the Suva lagoon. As a result, most sites generally registered high DOC levels than on sampling trip 4. The above observation is consistent with the work by Clair & Erhman which stated that surface runoff could increase DOC levels in coastal waters (Clair & Erhman, 1996). Furthermore, these two sampling trips were taken at high tide, consequently sites (see figure 10) close to the Suva landmass apart from the site near Centra hotel registered higher levels of DOC than those sites further out into the Suva lagoon. The preceding result was a consequence of the concentration of the surface run off near the Suva landmass caused by the high tide.

Generally, the offshore sites exhibited DOC levels that were influenced by the surface runoff from the Suva landmass. Furthermore, the movements of seawater in the Suva lagoon caused by tides and wind action also influenced the amount of DOC present in a site. In contrast to the coastal sites, tides were equally important as the effect of rain on the level of DOC in any coastal water. More accurate estimates of the DOC levels in the Suva lagoon could be made with a longer DOC monitoring study, which was outside the scope of this project.

3.10.3 Average hydrographic parameters

Table 22

Hydrographic parameters of the sites monitored

Sites	Temperature/^{0}C (±1SD)	pH (±1SD)	Conductivity/mS/cm (±1SD)	Salinity/psu (±1SD)	Average % freshwater dilution
1	27 (1)	7.0(0.9)	50(3)	32(1)	9
2	27 (1)	7.8(0.6)	50(4)	32(3)	9
3	25(1)	7.9(0.6)	49(6)	32(2)	9
4	27(2)	8.0(0.2)	45(11)	29(6)	17
5	28(2)	8.2 (0.2)	45(10)	28(6)	20
6	26(1)	7.9(0.5)	53(2)	33(2)	6
7	27(1)	7.9(0.5)	53(2)	33(2)	6
8	26(2)	7.9(0.2)	39(13)	24(9)	31
9	26(2)	7.8(0.2)	49(8)	32(4)	9
10	26(2)	8.0(0.2)	49(8)	32(4)	9
11	27(2)	8.1(0.1)	53(2)	34(1)	3
12	26(1)	7.9(0.4)	58(3)	34(1)	3

Note: The % freshwater dilution was calculated based on the seawater without dilution having a salinity of 35 practical salinity units (psu), see appendix 6 for a sample calculation

All the sites registered salinity values less than the salinity (35psu) of pure marine seawater (Campbell & Meadows, 1988). The above observation indicated that the sites received sigficant levels of freshwater from the landmass of Suva. Those sites that have continuous freshwater discharge from creeks and rivers (Centra hotel, Tamavua river and Nabukalou creek) registered the largest percentages of freshwater dilution (see table 22). The range of pH exhibited by the sites was from pH 7.0 to pH 8.2, the preceding range was close

to the pH of oceanic waters (pH 7.5- pH 8.2) (Campbell & Meadows, 1988 and Fergusson, 1990). However, some of the sites exhibited pH levels as low as pH 7 because of the freshwater input from the landmass of Suva. The offshore sites generally have higher salinity and conductivity than the coastal sites because of the high levels of ionic species such as HCO_3^-, Na^+ and Cl^- present in predominantly marine waters. The temperature remained fairly constant at about 26°C.

3.10.4 General discussion on the Samples analyzed

DOC monitoring of the study area (Laucala bay and Suva harbor) had not been done conclusively in the past except for a preliminary study by (Hansen & Lausten 1995). The accuracy of the data cannot be assured to any extent, however, the above study was the only one in which DOC measurements were carried out. The method they utilized was the one developed by (Koshy *et al.*, 1992). The DOC values for some of the sites monitored in this project were three to five times greater than values obtained by (Hansen & Lausten 1995) for the same sites. The differences could also be a result of the preliminary nature of the previous work and possibly due to the increase in DOC as a consequence of the increase in waste discharged into Laucala bay and Suva harbor usually associated with the increase in population near coastal areas (Stumm & Morgan, 1981).

The lack of established DOC data of the Suva lagoon impaired comparative studies to verify the data obtained in this project. To put some reliability on the

data obtained through this FIA system the samples were also analyzed twice with a Shimadzu 2000-UV HTCO analyzer. Some of the sites like Kinoya outfall (1), Centra (6) and Nukulau passage (3) showed similar DOC values from both methods. On the other hand, the HTCO unit developed many problems like the clogging of the catalyst and the poor maintenance of the baseline after several marine samples were analyzed. The above problems warranted the continuous availability of qualified technicians to attend to such problems. On the other hand, the modified FIA method used in this project did not have the above problems. However, the important aspect of the HTCO results with respect to the results obtained from this FIA method, was that they both showed high DOC levels for polluted sites and low DOC levels for the less polluted sites. The above observation indicated the suitability of the FIA system described in this work for the quantitative determination of DOC in estuarine and coastal waters.

Table 23

DOC data obtained for estuarine and marine water samples

Type of sample	Type of instrument/method	[DOC] mg/L	Reference	year
Nearshore Oceanic water	Ampoulated persulfate oxidation(WCO)	1.59	Sharp *et al.*	1993
"	Shimadzu TOC 500(HTCO)	1.992	"	"
"	Japanese HTCO unit	3.672	"	"
Riverwater	Japanese HTCO unit	2.136	"	"
"	Shimadzu TOC 500(HTCO)	1.320	"	"
Estuarine water	Suzuki HTC unit(HTCO)	4.320	Miller *et al.*	1993
"	Shimadzu TOC 500(HTCO)	1.920	"	"
"	UV-Persulfate(WCO)	1.80	"	"
"	**FIA* (This project)**	**6.5**		**1998**
Oceanic water	Shimadzu TOC 5000(HTCO)	0.876	Sharp *et al.*	1993b
"	Dohrman DC-190(HTCO)	0.744	"	"
"	Persulfate oxidation(WCO)	1.008	"	"
"	Ionics TC-TOC 555 (HTCO)	0.936	"	"
"	**FIA* (This project)**	**12.5**		**1998**

Note FIA: DOC value obtained from the work done in this project: Estuarine (mean, coastal sites), oceanic water (mean, Offshore sites)

In table 23, the average DOC values obtained from the work done in this project were generally higher than those reported in the literature for similar water samples. The high DOC values reported in this project could be a result of the fact that the other DOC data were collected from estuarine and oceanic waters of metropolitan countries that have comprehensive sewage treatment plants. Consequently, most effluents from the land were low in terms of their DOC

levels. On the other hand, most of the organic effluents from the landmass of Suva to the Suva harbor and Laucala bay were not treated.

All the sites studied in this project were close to the land thus, input from it significantly influenced the DOC determined for the sites. The focus of the discussions on the site's DOC levels was based on the input sources from the land than on natural sources of DOC in them. The premise for that approach in the discussions was the fact that this DOC data was reflective of substantial land input (Riley & Chester, 1971 and Stumm & Morgan, 1981) given the large variations on each day of sampling. However, there is little information about the separate contribution from the natural and anthropogenic sources found in the total DOC we have been able to measure in the Suva lagoon.

CHAPTER 4

CONCLUSIONS

The modified FIA method used in this work had a method detection limit (MDL) of 0.8mg C/L, a carbon recovery of 98±9% and a sample throughput of 60 samples per hour. The sample throughput and carbon recovery of this modified FIA method were comparable to the sample throughput and carbon recovery of the FIA manifold described by (Koshy *et al.,* 1992) which were 98% and 45 samples per hour respectively. On the other hand, the modified FIA method had higher MDL than the FIA method described by (Koshy *et al.,* 1992) implying that this modified FIA method was slightly lower in sensitivity than its predecessor.

The modified FIA method also suffered from chloride interference, but the interference by chloride ($\%Cl_{ox}$) was masked to levels as low as 1% with inorganic carbon (IC) levels greater than 8mg/L. The interference by chloride is related to the level of IC in an estuarine or coastal water sample by the following equation ($Y = 166x^{-1.5}$, $Y = \%Cl_{ox}$ and $x = [IC]$). Because of the high levels of IC in most coastal and marine waters (Manahan, 1994), the modified FIA method could be used for the determination of DOC in these type of water samples because chloride interference could be reduced significantly.

The combination of the TiO_2 catalyst with the reduced oxidant solution (50% oxidant strength solution) increased both the carbon recovery and chloride

interference. The level of chloride interference was increased by a factor of 12%-51% from the levels of chloride interference observed with the 100% oxidant strength solution alone on different levels of organic carbon. In other words the above combination did not alleviate the interference by chloride but rather it enhanced it.

$NH_2OH.HCl$ could reduce the chloride signal by 81±11%. In the presence of varying amounts of carbon the reducing agent ($NH_2OH.HCl$) reduced chloride interference in the range of 80% to 98%. In other words, the carbon present in the standards also assisted the reducing agent in dealing with chloride interference. However, the combined capacity of the reducing agent and the level of carbon in the standards to minimize chloride interference was similar to the masking effect of IC on chloride interference alone.

The insertion of the micro-porous tubing immediately after the UV chamber reduced chloride interference to an average level of 5%. This indicated that, the interference by chloride was minimized by an average of 95%. The major drawback of this micro-porous tubing in its application was the fact that any slight irregular flow (increase in the internal pressure of the lines initiated by minor blockage) can result in the permeation of both chlorine gas and the solution passing through it. This had resulted in the reduction of the carbon signal detected by the conductivity detector.

The reducing agent and the micro-porous tubing were adequate to minimize chloride interference, however the above approaches of dealing with chloride

interference were not incorporated into the modified method. Instead of the two options investigated specifically for their reduction capability of chloride interference, the masking effect of IC on chloride interference was incorporated into the modified FIA method. The masking effect of IC on chloride interference was incorporated because of its simplicity in application, superior capacity in reducing chloride interference than the other two approaches and its (IC) generally high concentration in most estuarine and coastal waters.

The baseline DOC study in this work indicated that the Suva lagoon received a significant amount of DOC from the landmass of Suva. Factors like rain, tide and current movements in the lagoon significantly influenced the concentration of DOC present in the water columns of the sites monitored. The sites monitored registered DOC levels in the range of 0.8mg/L to 35mg/L. An average rainfall as low as 0.1mm in the three days prior to the sampling day could double or triple the levels of DOC determined at these sites. Furthermore, the sites near or in the rivers, creeks and storm water outlets which continuously discharge to the Suva lagoon maintained DOC levels greater than 0.8mg/L in the absence of any significant rain.

The modified FIA method measured DOC levels that were comparable to the DOC levels obtained from an established Shimadzu 2000-UV HTCO unit. Although the correlation between the average data from the two different methods was weak, it was still a positive correlation and for some of the sites, both methods showed very similar DOC values on each day of sampling.

Recommendations

Future investigation into the involvement of chloride in the measurement of DOC using the FIA system described in this work should focus on the following areas.

- A second diffusion manifold could be placed after the UV chamber instead of the micro-porous tubing. This manifold should eliminate the gases (including chlorine) formed as a result of the persulfate photooxidation of the DOC present in estuarine and coastal water samples.

- The modified FIA method should be used for the long term monitoring of DOC in the Suva lagoon, so that predictions could be made about the DOC budget of the lagoon and the adverse and positive effects of the DOC like oxygen depletion and the complexation capacity of the lagoon for heavy metals and organic pollutants like pesticides (Stumm & Morgan, 1981).

- The Ghost peaks should also be investigated, to ascertain their origin.

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APPENDIX

A 1.0

Typical plots for 1, 2, 16, 24 mg C/L standards prepared in DDW and 35$^{0}/_{00}$ NaCl solution

Note:

- The standards were injected (analyzed) at least 4 times, the peak areas of each run was printed immediately after each peak.
- The peaks that were labeled as SSW refer to the standards prepared in the 35$^{0}/_{00}$ NaCl solution and the peaks labeled as DDW or D.D.H_2O referred to the standards prepared in distilled deionised water. The peaks were of the corresponding standards prepared in the two different solvents (DDW and SSW) were placed immediately after one another for easy comparison
- The operating parameters of the integrator were as follows:

Attenuation 2^= 10
Chart speed CHT SP= 0.3
Area reject AR REJ= 35000
Threshold THRSH= 0
Peak width PK WD= 0.50

.625	4037053	PU	.419	88.42845
1.061	528181	I UH	.138	11.57158

TOTAL AREA=4565534
MUL FACTOR=1.0000E+00

* RUN # 170 AUG 8, 1997 10:16:18
START
~~0.643~~ ~~0.730~~ 1ppm c d.o w RT 0.533 keyet!
STOP 0.730

RUN# 170 AUG 8, 1997 10:16:18

AREA%

RT	AREA	TYPE	WIDTH	AREA%
.533	1398878	PU	.181	30.40608
.730	3201774	I UP	.293	69.59392

TOTAL AREA=4600653
MUL FACTOR=1.0000E+00

* RUN # 171 AUG 8, 1997 10:21:35
START
~~0.736~~ 0.695 1ppm c d.o w
STOP

RUN# 171 AUG 8, 1997 10:21:35

AREA%

```
* RUN # 185        AUG  8, 1997  11:06:26
START
STOP                0.695 (PPM C S S W)
```

```
RUN#   185          AUG  8, 1997  11:06:26

AREA%
      RT       AREA TYPE  WIDTH       AREA%
    .695   10107640   BV   .418    93.08384
   1.105     756946 I VH   .116     6.91616

TOTAL AREA=1.0945E+07
MUL FACTOR=1.0000E+00
```

```
* RUN # 186        AUG  8, 1997  11:10:03
START
STOP                0.685 (PPM C S S W)
```

```
RUN#   186          AUG  8, 1997  11:10:03

AREA%
      RT       AREA TYPE  WIDTH       AREA%
    .242    450978   BP   .144     4.54643
    .685   9468416 I PH   .403    95.45357

TOTAL AREA=9.9194E+06
MUL FACTOR=1.0000E+00
```

```
* TIME 9  INTG # 9  0
* RUN # 187        AUG  8, 1997  11:13:48
START
STOP                0.698 (PPM C S S W)
```

```
RUN#   187          AUG  8, 1997  11:13:48

AREA%
      RT       AREA TYPE  WIDTH       AREA%
    .698   11031308 I VH   .452   100.00000

TOTAL AREA=1.1031E+07
MUL FACTOR=1.0000E+00
```

```
* RUN # 182        AUG  8,
START
STOP                0.700
```

```
RUN#   182          AUG

AREA%
      RT       AREA TYPE
    .700   10210304 I PH

TOTAL AREA=1.0210E+07
MUL FACTOR=1.0000E+00
```

```
* TIME 3  INTG # 9  0
* RUN # 183        AUG  8,
START
STOP                0.711 (
```

```
RUN#   183          AUG  (

AREA%
      RT       AREA TYPE  L
    .711   9456026 I PH

TOTAL AREA=9.4560E+06
MUL FACTOR=1.0000E+00
```

```
* TIME 4  INTG # 9  0
* RUN # 184        AUG  8,
START
STOP                0.698 (P
```

```
RUN#   184          AUG  0

AREA%
      RT       AREA TYPE  W
    .699   10381448 I VH

TOTAL AREA=1.0381E+07
MUL FACTOR=1.0000E+00
```

```
* TIME 5  INTG # 9  0
```

.730 9113331 I VH .440 100.00000

TOTAL AREA=9.1133E+06
MUL FACTOR=1.0000E+00

* RUN # 195 AUG 8, 1997 11:48:35
START
0.695 2ppmc D.D.W
STOP

RUN# 195 AUG 8, 1997 11:48:35

AREA%

RT	AREA	TYPE	WIDTH	AREA%
.685	9082746	I VH	.440	100.00000

TOTAL AREA=9.0827E+06
MUL FACTOR=1.0000E+00

* RUN # 196 AUG 8, 1997 11:51:09
START
0.709 2ppmc D.D.W
STOP

RUN# 196 AUG 8, 1997 11:51:09

AREA%

RT	AREA	TYPE	WIDTH	AREA%
.709	9594672	I PH	.477	100.00000

TOTAL AREA=9.5847E+06
MUL FACTOR=1.0000E+00

* RUN # 197 AUG 8, 1997 11:54:23
START
0.683 2ppmc D.D.W
STOP

RUN# 197 AUG 8, 1997 11:54:23

AREA%

RT	AREA	TYPE	WIDTH	AREA%
.683	9039494	I VH	.437	100.00000

TOTAL AREA=9.0395E+06

* RUN # 201 AUG 8, 199
START
0.705 ugmw
STOP

RUN# 201 AUG 8, 1

AREA%

RT	AREA	TYPE	WIDT
.735	8511394	I VH	.44

TOTAL AREA=8.5114E+06
MUL FACTOR=1.0000E+00

* RUN # 202 AUG 8, 199
START
0.695 2ppm
STOP

RUN# 202 AUG 8, 1

AREA%

RT	AREA	TYPE	WIDT
.685	9621504	I BH	.43

TOTAL AREA=9.6215E+06
MUL FACTOR=1.0000E+00

* RUN # 203 AUG 8, 199
START
0.725 2ppm
STOP

RUN# 203 AUG 8, 1

AREA%

RT	AREA	TYPE	WIDT
.725	9635462	I VH	.44

TOTAL AREA=9.6355E+06
MUL FACTOR=1.0000E+00

START

RUN# 210 AUG 8, 1997 12:39:19

AREAX

RT	AREA	TYPE	WIDTH	AREAX
.709	12587564	I UH	.485	100.00000

TOTAL AREA=1.2588E+07
MUL FACTOR=1.0000E+00

* RUN # 211 AUG 8, 1997 12:41:39
START
0.718 3ppmc O.O.W
STOP

RUN# 211 AUG 8, 1997 12:41:39

AREAX

RT	AREA	TYPE	WIDTH	AREAX
.718	13077160	I UH	.461	100.00000

TOTAL AREA=1.3077E+07
MUL FACTOR=1.0000E+00

* RUN # 212 AUG 8, 1997 12:47:16
START
0.751 2ppmc S.S.W
STOP

RUN# 212 AUG 8, 1997 12:47:16

AREAX

RT	AREA	TYPE	WIDTH	AREAX
.751	13190464	I PH	.417	100.00000

TOTAL AREA=1.3190E+07
MUL FACTOR=1.0000E+00

* RUN # 213 AUG 8, 1997 12:49:49
START
0.700 2ppm S.S.W
STOP

RUN# 216 AUG 8, 1

AREAX

RT	AREA	TYPE	WIDT
.715	14876160	I UH	.48

TOTAL AREA=1.4876E+07
MUL FACTOR=1.0000E+00

* PH. WO 0.2 @
* RUN # 217 AUG 8, 1997
START
0.720
STOP

RUN# 217 AUG 8, 19

AREAX

RT	AREA	TYPE	WIDTH
.720	13230148	I BH	.419

TOTAL AREA=1.3230E+07
MUL FACTOR=1.0000E+00

* RUN # 218 AUG 8, 1997
START
0.724 2pl
STOP

RUN# 218 AUG 8, 1997

AREAX

RT	AREA	TYPE	WIDTH
.724	13454880	I UH	.440

TOTAL AREA=1.3455E+07
MUL FACTOR=1.0000E+00

* RUN # 219 AUG 8, 1997 1.
START
0.719 2ppmc
STOP

RUN# 219 AUG 8, 1997

AREA%

RT	AREA	TYPE	WIDTH	AREA%
.176	134967	BP	.117	.51291
.417	88964	PV	.112	.33809
1.009	25635664	VV	.504	97.42246
2.060	454323	I VP	.223	1.72655

TOTAL AREA=2.6314E+07
MUL FACTOR=1.0000E+00

* RUN # 13 JUN 19, 1997 13:10:18
START
~~0.415~~ 0.920 16ftMC D.D.H2O
~~STOP~~

RUN# 13 JUN 19, 1997 13:10:18

AREA%

RT	AREA	TYPE	WIDTH	AREA%
.415	134698	BV	.088	.26281
.920	48876736	VV	.525	95.07411
1.804	1235571	VV	.180	2.40341
2.006	1162103	I VH	.212	2.26050

TOTAL AREA=5.1409E+07
MUL FACTOR=1.0000E+00

* RUN # 14 JUN 19, 1997 13:13:04
START
0.943 16ftMC D.D.H2O
STOP

RUN# 14 JUN 19, 1997 13:13:04

AREA%

RT	AREA	TYPE	WIDTH	AREA%
.943	42967488	I BB	.470	100.00000

TOTAL AREA=4.2967E+07
MUL FACTOR=1.0000E+00

* RUN # 15 JUN 19, 1997 13:17:46
START

~~STOP~~

RUN# 15 JUN 19, 1997 13:

AREA%

RT	AREA	TYPE	WIDTH	A
1.116	64409184	SBH	.530	96.3
1.989	1510197	SHH	.103	2.2
2.170	895535	ISHH	.130	1.3

TOTAL AREA=6.6815E+07
MUL FACTOR=1.0000E+00

* RUN # 16 JUN 19, 1997 13:20:
START
~~0.306~~ 1
STOP

RUN# 16 JUN 19, 1997 13:2

AREA%

RT	AREA	TYPE	WIDTH	ARE
.306	87782	BP	.097	.147
.560	336111	PP	.281	.564
1.360	59073664	ISPB	.506	99.287

TOTAL AREA=5.9498E+07
MUL FACTOR=1.0000E+00

* RUN # 17 JUN 19, 1997 13:24:31
START
~~0.075~~ 1.1.
STOP

RUN# 17 JUN 19, 1997 13:24:

AREA%

RT	AREA	TYPE	WIDTH	AREA%
.075	58995	BB	.137	.09025
.614	52352	PH	.072	.08009
1.112	65258208	ISHH	.546	99.82970

TOTAL AREA=6.5370E+07
MUL FACTOR=1.0000E+00

* RUN # 34 JUN 19, 1997 14:28:29
START
0.222 1.028 16PPMC S-S H_2O
STOP

RUN# 34 JUN 19, 1997 14:28:29

AREA%

RT	AREA	TYPE	WIDTH	AREA%
.222	4870896	BP	.639	4.85024
1.028	95555008	ISPH	.617	95.14976

TOTAL AREA=1.0043E+08
MUL FACTOR=1.0000E+00

* RUN # 35 JUN 19, 1997 14:31:29
START
0.141 1.015 16PPMC S-S H_2O
STOP

RUN# 35 JUN 19, 1997 14:31:29

AREA%

RT	AREA	TYPE	WIDTH	AREA%
.141	181350	BP	.173	.26322
.528	47197	PP	.094	.06850
1.015	68668672	ISPH	.508	99.66829

TOTAL AREA=6.8897E+07
MUL FACTOR=1.0000E+00

* RUN # 36 JUN 19, 1997 14:34:06
START
0.215 0.990 16PPMC S-S H_2O
STOP

RUN# 36 JUN 19, 1997 14:34:06

AREA%

RT	AREA	TYPE	WIDTH	AREA%
.215	66918	BP	.082	.10742
.538	73275	PP	.074	.11762
.990	62158016	ISPH	.511	99.77498

TOTAL AREA=6.2298E+07
MUL FACTOR=1.0000E+00

1.801	1900697	SHH	.302	2.12737
2.295	410965	ISHH	.146	.45998

TOTAL AREA=8.934SE-07
MUL FACTOR=1.0000E+00

* RUN # 42 AUG 5, 1997 12:14:51
START
0.890 24 ppm C D·D·W
STOP

RUN# 42 AUG 5, 1997 12:14:51

AREAX

RT	AREA	TYPE	WIDTH	AREAX
.274	211507	PH	.111	.23924
.890	88:95456	ISHH	.725	99.76077

TOTAL AREA=8.8407E+07
MUL FACTOR=1.0000E+00

* RUN # 43 AUG 5, 1997 12:17:53
START
0.878 24 ppm C D·D·W
STOP

RUN# 43 AUG 5, 1997 12:17:53

AREAX

RT	AREA	TYPE	WIDTH	AREAX
.087	5150	BB	.037	.00573
.878	89799936	SPH	.762	99.67222
2.442	290180	ISHH	.108	.32209

TOTAL AREA=9.009SE+07
MUL FACTOR=1.0000E+00

* RUN # 44 AUG 5, 1997 12:20:58
START
0.932 24 ppm C D·D·W

RUN# 44 AUG 5, 1997 12:20:58

AREAX

* RUN # 39 AUG 5, 1997 12:03:05
START
0.926 16 ppm D·
STOP

RUN# 39 AUG 5, 1997 12:03:05

AREAX

RT	AREA	TYPE	WIDTH	AREAX
.160	185873	BV	.100	.15997
.926	64754080	VV	.723	97.84326
2.161	1321489	I VH	.327	1.99677

TOTAL AREA=6.6181E+07
MUL FACTOR=1.0000E+00

* RUN # 40 AUG 5, 1997 12:08:52
START
0.950
STOP

RUN# 40 AUG 5, 1997 12:08:52

AREAX

RT	AREA	TYPE	WIDTH	AREAX
.095	28211	BH	.050	.02877
.950	95729600	SHH	.780	97.64029
2.298	2285312	ISHH	.388	2.33092

TOTAL AREA=9.8043E+07
MUL FACTOR=1.0000E+00

* RUN # 41 AUG 5, 1997 12:11:54
START
0.870 24
STOP

RUN# 41 AUG 5, 1997 12:11:54

AREAX

RT	AREA	TYPE	WIDTH	AREAX
.086	45444	BB	.070	.05086
.250	24601	BP	.061	.02753
.870	86963200	SPH	.733	97.35430

STOP

RUN# 156 AUG 6, 1997 17:17:11

AREAX

RT	AREA	TYPE	WIDTH	AREAX
.140	214811	BV	.119	.35726
1.057	87559114	VV	.557	99.64219

TOTAL AREA=9.7974E+07
MUL FACTOR=1.0000E+00

---

* RUN # 157 AUG 6, 1997 17:20:50
START
1.031 24 ppm CS SW
STOP

RUN# 157 AUG 6, 1997 17:20:50

AREAX

RT	AREA	TYPE	WIDTH	AREAX
.198	2276177	BP	.195	2.47576
1.052	86956768	PV	.352	94.52051
2.348	1338531	VV	.344	1.45573
2.671	1425664	I VH	.219	1.55003

TOTAL AREA=9.1977E+07
MUL FACTOR=1.0000E+00

---

* RUN # 158 AUG 6, 1997 17:23:48
START
1.058 24 ppm
RT 1.0
STOP

RUN# 158 AUG 6, 1997 17:23:48

AREAX

RT	AREA	TYPE	WIDTH	AREAX
.159	9446	PB	.049	.00911
.358	60940	BV	.063	.05877
1.056	46851368	VV	.459	45.18156
1.158	53179712	VH	.463	51.30038
2.431	3516290	I VH	.301	3.38997

TOTAL AREA=1.0370E+08
MUL FACTOR=1.0000E+00

---

* RUN # 159 AUG 6, 1997 17:24:28
START
1.133 24 ppm CS SW
STOP
RT 0.992
1.133

RUN# 159 AUG 6, 1997 17:24:28

AREAX

RT	AREA	TYPE	WIDTH	AREAX
.343	466503	BV	.106	.45553
.362	299395	VH	.095	.38495
.992	38296214	BMH	.352	42.03824
1.133	49986911	IBMF	.459	54.10850

TOTAL AREA=8.9040E+07
MUL FACTOR=1.0000E+00

---

* RUN # 160 AUG 6, 1997 17:27:33
START
1.055 24 ppm CS
STOP

RUN# 160 AUG 6, 1997 17:27:33

AREAX

RT	AREA	TYPE	WIDTH	AREAX
.250	55451	BP	.073	.05873
1.055	91526992	PV	.904	97.71141
2.307	2097714	I VH	.381	2.22801

TOTAL AREA=9.3269E+07
MUL FACTOR=1.0000E+00

A 1.0

Typical plots for 1, 2, 16, 24 mg C/L standards prepared in DDW and 35‰ NaCl solution

Note:

- The standards were injected (analyzed) at least 4 times, the peak areas of each run was printed immediately after each peak.
- The peaks that were labeled as SSW refer to the standards prepared in the 35‰ NaCl solution and the peaks labeled as DDW or D.D.H_2O referred to the standards prepared in distilled deionised water. The peaks were of the corresponding standards prepared in the two different solvents (DDW and SSW) were placed Immediately after one another for easy comparison
- The operating parameters of the integrator were as follows:

Attenuation 2^= 10
Chart speed CHT SP= 0.3
Area reject AR REJ= 35000
Threshold THRSH= 0
Peak width PK WD= 0.50

Sample Analysis / Standards for Calibration (DDW)
30/4/98

Power Failed
MAY 9, 1998 11:18:11

WORK

* [illegible]
PEAK DETECTIVITY: 1244

ZERO = 0, -11.179
HIT ZP = 10
CHT SP = 0.5
RP RCT = 450000
TRPCH = 0
FE.QU = 0.50

* PLOT
STOP

* RUN # 105 MAY 9, 1998 11:53:56
START

0.7001 Zppmc DDW
STOP

RUN# 105 MAY 9, 1998 11:53:56

HKPHZ
RT HKPH TYPE WIDTH HKPHZ
7001 1165434 T 88 BIX 100 100000

TOTAL HKPH=1 1665407+07
MID THICTOR=1 000007+00

* RUN # 106 MAY 9, 1998 11:55:41

RUN# 106 MAY 9, 1998 11:55:41

RECHX

FT	RECH TYPE	WRITTEN	RECHX
875	11692648 I 8H	675	100 00000

TOTAL RECH= 1 1692F+07
MAX FRE TOP= 1 00000F+00

* RUN # 107 MAY 9, 1998 11:58:06
START

STOP K 875 2ppm CDW

RUN# 107 MAY 9, 1998 11:58:06

RECHX

FT	RECH TYPE	WRITTEN	RECHX
875	9742U35 I 8P	487	100 00000

TOTAL RECH= 9 742U+06
MAX FRE TOP= 1 00000+00

* RUN # 108 MAY 9, 1998 11:59:59
START

STOP K 875 2ppm CDW

RUN# 108 MAY 9, 1998 11:59:59

RECHX

FT	RECH TYPE	WRITTEN	RECHX
875	11602368 I 8H	554	100 00000

TOTAL RECH= 1 U602+07
MAX FRE TOP= 1 00000+00

* RUN # 109 MAY 9, 1998 12:04:09
START

STOP K 900 5ppm CDW

RUN# 109 MAY 9, 1998 12:04:09

RECHX

[illegible]

[illegible]

* RUN # 110 MAY 9, 1998 12:10:49
START

STOP и 894 Sppmc DDW

RUN# 110 MAY 9, 1998 12:10:49

RESULTS

P1	RESULT	TYPE	UNITS	RESULTS
894	2.94405.03	L PR	SYN	[illegible]

TOTAL RESULT=2.19410E+07
MUL FACTOR=1.00000E+00

[illegible]

* RUN # 111 MAY 9, 1998 12:10:17
START

STOP и 410 Sppmc DDW

RUN# 111 MAY 9, 1998 12:10:17

RESULTS

P1	RESULT	TYPE	UNITS	RESULTS
295	1.18755E	PR	.127	9.63850
483	2.27710E-02	L BP	.526	95.56173

TOTAL RESULT=2.38795E+07
MUL FACTOR=1.00000E+00

* RUN # 112 MAY 9, 1998 12:11:36
START

STOP и .880 Sppmc DDW

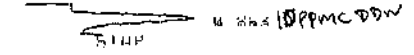
RUN# 112 MAY 9, 1998 12:11:36

RESULTS

P1	RESULT	TYPE	UNITS	RESULTS
.880	2.18280E-03	L BR	.582	100.00000

TOTAL RESULT=2.18280E+07
MUL FACTOR=1.00000E+00

```
*  RUN #  113      MAY  9, 1998  12:16:08
START
```

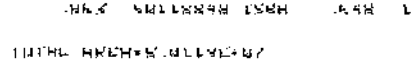



```
RUN#    113            MAY  9, 1998  12:16:08

AREA=
      PT        AREA TYPE   WIDTH        AMOUNT
    .0613   5811.5848 ESPH    .438   100.00000

TOTAL AREA=5.0115E+07
MUL FACTOR=1.00000E+00
```

```
*  RUN #  114      MAY  9, 1998  12:18:54
START
```

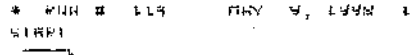



```
RUN#    114            MAY  9, 1998  12:18:54

AREA=
      PT        AREA TYPE   WIDTH        AREA%
    .0598   5128.7520 ESPH    .414   100.00000

TOTAL AREA=5.1288E+07
MUL FACTOR=1.00000E+00
```

```
*  RUN #  115      MAY  9, 1998  12:21:55
START
```




```
RUN#    115            MAY  9, 1998  12:21:55

AREA=
      PT        AREA TYPE   WIDTH        AREA%
    .0588   4982.1712 ESPH    .386   100.00000

TOTAL AREA=4.9821E+07
MUL FACTOR=1.00000E+00
```

```
*  RUN #  116      MAY  9, 1998  12:24:22
START
```

STOP

RUN# 116 MAY 9, 1998 12:24:22

AREA%

P7	AREA	TYPE	WIDTH	AREA%
.992	60945926	ISBR	.812	100.00000

TOTAL AREA=6.0494E+07
MUL FACTOR=1.0000E+00

* RUN # 117 MAY 9, 1998 12:28:11
START

0.998 10ppmC DDW

STOP

RUN# 117 MAY 9, 1998 12:28:11

AREA%

P1	AREA	TYPE	WIDTH	AREA%
.990	49287520	ISBR	.605	100.00000

TOTAL AREA=4.9288E+07
MUL FACTOR=1.0000E+00

* RUN # 118 MAY 9, 1998 12:33:58
START

0.871 15ppmC DDW

STOP

RUN# 118 MAY 9, 1998 12:33:58

AREA%

P1	AREA	TYPE	WIDTH	AREA%
.871	55483520	ISBP	.669	100.00000

TOTAL AREA=5.5484E+07
MUL FACTOR=1.0000E+00

* RUN # 119 MAY 9, 1998 12:36:57
START

0.888 15ppmC DDW

STOP

AREA%

RT	AREA	TYPE	WIDTH	AREA%
.[illegible]	[illegible]	[illegible]	.764	100.000000

TOTAL AREA=[illegible]E+07
MUL FACTOR=1.00000E+00

* RUN # 120 MAY 9, 1998 12:59:51
START

0.[illegible] 15ppmc DDW

STOP

RUN# 120 MAY 9, 1998 12:59:51

AREA%

RT	AREA	TYPE	WIDTH	AREA%
.[illegible]	[illegible]	[illegible]	.626	100.000000

TOTAL AREA=[illegible]E+07
MUL FACTOR=1.00000E+00

* RUN # 121 MAY 9, 1998 12:42:59
START

0.781 15ppmc DDW

STOP

RUN# 121 MAY 9, 1998 12:42:59

AREA%

RT	AREA	TYPE	WIDTH	AREA%
.781	[illegible]	[illegible]	.617	100.000000

TOTAL AREA=6.[illegible]E+07
MUL FACTOR=1.00000E+00

* RUN # 122 MAY 9, 1998 12:47:19
START

0.869 20ppmc DDW

STOP

RUN# 122 MAY 9, 1998 12:47:19

AREA%

RT	AREA	TYPE	WIDTH	AREA%
.869	[illegible]	[illegible]	.598	100.000000

TOTAL AREA=[illegible]E+07

* RUN # 124 MAY 9, 1998 12:49:36
START

0.695 20ppmcDDW

STOP

RUN# 124 MAY 9, 1998 12:49:36

AREAS

RT	AREA	TYPE	WIDTH	AREA%
.695	9849792	BBA	.617	100.00000

TOTAL AREA=9.84979E+07
MUL FACTOR=1.00000E+00

* RUN # 124 MAY 9, 1998 12:52:10
START

0.914 20ppmcDDW

STOP

RUN# 124 MAY 9, 1998 12:52:10

AREAS

RT	AREA	TYPE	WIDTH	AREA%
.914	8917291 6	BBA	.633	100.00000

TOTAL AREA=8.91729E+07
MUL FACTOR=1.00000E+00

* RUN # 125 MAY 9, 1998 12:55:36
START

0.879 20ppmcDDW

STOP

RUN# 125 MAY 9, 1998 12:55:36

AREAS

RT	AREA	TYPE	WIDTH	AREA%
.879	7489 9294	BBA	.622	100.00000

TOTAL AREA=7.48992E+07
MUL FACTOR=1.00000E+00

0.999 65ppm c DDW

STOP

RUN# 126 MAY 9, 1998 14:00:50

AREAS

PT	AREA	TYPE	WIDTH	AREA%
.999	1121998760	VBR	.854	100.00000

TOTAL AREA=1.12199E+09

MUL FACTOR=1.00000E+00

* RUN # 127 MAY 9, 1998 14:02:59

START

0.999 25ppm c DDW

STOP

RUN# 127 MAY 9, 1998 14:03:59

AREAS

PT	AREA	TYPE	WIDTH	AREA%
.999	1096659000	VBR	.846	100.00000

TOTAL AREA=1.09667E+09

MUL FACTOR=1.00000E+00

* RUN # 128 MAY 9, 1998 14:06:52

START

0.992 ~~[illegible]~~ 2.5ppm c DDW

STOP

RUN# 128 MAY 9, 1998 14:06:52

AREAS

PT	AREA	TYPE	WIDTH	AREA%
.992	1264842000	VBR	.820	100.00000

TOTAL AREA=1.26484E+09

MUL FACTOR=1.00000E+00

* RUN # 129 MAY 9, 1998 14:09:22

START

0.999 2.5ppm c DDW

STOP

A 3.0

A Typical set of data for DOC analysis on a set of samples

Note:

- The seawater samples were injected (analyzed) four times, the peak area of each run was printed immediately after each peak.
- The peaks that were labeled as "No oxidant" referred to the runs that involved the acidification of the samples to quantify the measure inorganic carbon (IC_m).
- The peaks that were labeled as " Full FIA system referred to those runs (peaks) where the total carbon measured (TC_m) were quantified (both the acid and the oxidant were used).
- The difference between TC_m and IC_m gave the peak area (carbon signal) equivalent to the DOC present in the seawater sample prior to correction for chloride interference.

The operating parameters of the integrator were as follows:

Attenuation 2^= 10
Chart speed CHT SP= 0.3
Area reject AR REJ= 35000
Threshold THRSH= 0
Peak width PK WD= 0.50

Sample Analysis

```
HREHX
      RT        HREH TYPE  WIDTH       HREHX
    .000   92419912 1SPH    .000   100.00000

TOTAL HREH=9.24195E+07
MUL FACTOR=1.00000E+00


*


POWER FAILED
MAY  9, 1998  13:12:29


KPCHK

*  RUN #   120      MAY  9, 1998  15:15:42
START
```

0 071 — STOP — 0 071 Light House No overlap

```
RUN#   120            MAY  9, 1998  15:15:47

HREHX
      RT        HREH TYPE  WIDTH       HREHX
    071   45710412 1SPH    .001   100.00000

TOTAL HREH=4.57104E+07
MUL FACTOR=1.00000E+00


*  RUN #   121      MAY  9, 1998  15:18:00
START
```

0 0400 — STOP — 0 0400 Light house @ 130

```
RUN#   121            MAY  9, 1998  15:18:00

HREHX
      RT        HREH TYPE  WIDTH       HREHX
    040   45704294 1SPH    .002   100.00000

TOTAL HREH=4.57042E+07
MUL FACTOR=1.00000E+00


*  RUN #   122      MAY  9, 1998  15:20:48
START
```

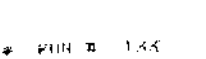
0 044 — Light house @ 150

RUN# 1.42 MAY 9, 1998 15:20:44

RECORD
FT RECN TYPE WIDTH RECORD
RSV 44445426 USER 596 1UN 000000

TOTAL RECORD= 4 44465,+00
MIN FRC TOP=1 00000+00

* RUN # 1.43 MAY 9, 1998 15:25:28
START



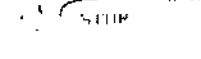
and 2nd Light house at 130

RUN# 1.43 MAY 9, 1998 15:25:28

RECORD
FT RECN TYPE WIDTH RECORD
RSV 45791,44 USER 617 1UN 000000

TOTAL RECORD= 5 5791,0+00
MIN FRC TOP=1 00000+00

* RUN # 1.44 MAY 9, 1998 15:29:41
START



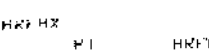
and 4th Nabulesi opp/fm at 130

RUN# 1.44 MAY 9, 1998 15:29:41

RECORD
FT RECN TYPE WIDTH RECORD
4TH 55796432 USER 635 1UN 000000

TOTAL RECORD= 5 5796,0+00
MIN FRC TOP=1 00000+00

* RUN # 1.45 MAY 9, 1998 15:42:25
START



and 4th Nabulesi opp/fm at 130

RUN# 1.45 MAY 9, 1998 15:42:25

RECORD
FT RECN TYPE WIDTH RECORD
4TH [illegible] USER 638 1UN 000000

[illegible]

[illegible]

* [illegible] # 136 MAY 9, 1998 13:35:19

START

[illegible] Nabukelow opp/fm as 130

STOP

[illegible] 136 MAY 9, 1998 13:35:19

[illegible]

RT	[illegible]	TYPE	[illegible]	[illegible]
995	5455/457	[illegible]	621	[illegible]

[illegible]

[illegible]

* [illegible] # 137 MAY 9, 1998 13:58:13

START

[illegible] Nabukelow opp/fm as 130

STOP

[illegible] 137 MAY 9, 1998 13:58:13

[illegible]

RT	[illegible]	TYPE	[illegible]	[illegible]
995	[illegible]	[illegible]	618	[illegible]

[illegible]

[illegible]

* [illegible] # 138 MAY 9, 1998 14:41:04

START

[illegible] Nabukelow opp/fm as 130

STOP

[illegible] 138 MAY 9, 1998 14:41:04

[illegible]

RT	[illegible]	TYPE	[illegible]	[illegible]
995	4[illegible]/36	[illegible]	587	[illegible]

[illegible]

[illegible]

* RUN # 139 MAY 9, 1998 13:58:04
START

STOP

885 TRAVEL LODGE

RUN# 139 MAY 9, 1998 13:58:04

RRFR%

P1	RRFR	TYPE	STATE	RRFR%
885	55029496	TSRP	885	100 00000

TOTAL RRFR=5 5029E+07
MIN FRACTOR=1 00000E+00

* RUN # 140 MAY 9, 1998 14:00:49
START

STOP

885 TRAVEL LODGE 6 130

RUN# 140 MAY 9, 1998 14:00:49

RRFR%

P1	RRFR	TYPE	STATE	RRFR%
885	51926496	TSRP	885	100 00000

TOTAL RRFR=5 1926E+07
MIN FRACTOR=1 00000E+00

* RUN # 141 MAY 9, 1998 14:03:56
START

STOP

885 TRAVEL LODGE 6 130

RUN# 141 MAY 9, 1998 14:03:56

RRFR%

P1	RRFR	TYPE	STATE	RRFR%
885	51589016	TSRP	885	100 00000

TOTAL RRFR=5 1589E+07
MIN FRACTOR=1 00000E+00

* RUN # 142 MAY 9, 1998 14:06:22
START

885 TRAVELLODGE 6 130

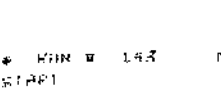
RUN# 142 MAY 9, 1998 14:06:24

AREAS

RT	AREA	TYPE	WIDTH	AREAX
885	66548816	CSPA	698	100 00000

TOTAL AREA=5.65296E+07
MUL FACTOR=1.00000E+00

* RUN # 143 MAY 9, 1998 14:12:52
START



N 481 swa point on 130

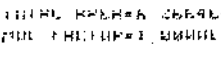
RUN# 143 MAY 9, 1998 14:12:52

AREAS

RT	AREA	TYPE	WIDTH	AREAX
981	62668872	CSPA	662	100 00000

TOTAL AREA=6.26688E+07
MUL FACTOR=1.00000E+00

* RUN # 144 MAY 9, 1998 14:16:09
START



N 997 swa point on 130

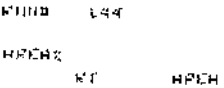
RUN# 144 MAY 9, 1998 14:16:09

AREAS

RT	AREA	TYPE	WIDTH	AREAX
997	99110816	CSPA	699	100 00000

TOTAL AREA=9.91108E+07
MUL FACTOR=1.00000E+00

* RUN # 145 MAY 9, 1998 14:19:19
START



N 878

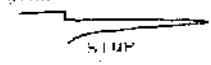
RUN# 145 MAY 9, 1998 14:19:19

AREAS

RT	AREA	TYPE	WIDTH	AREAX
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TOTAL APEA=5.9210E+07
MUL FACTOR=1.0000E+00

* RUN # 146 MAY 9, 1998 14:21:48
START



0.900 Save point

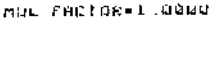
RUN# 146 MAY 9, 1998 14:21:48

APEAS

PT	APEA	TYPE	WIDTH	APEAX
.900	5933613.0	1SBH	.624	100.00000

TOTAL APEA=5.9336E+07
MUL FACTOR=1.0000E+00

* RUN # 147 MAY 9, 1998 14:26:25
START



0.900 Nukulan Passage in 130

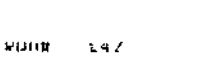
RUN# 147 MAY 9, 1998 14:26:25

APEAS

PT	APEA	TYPE	WIDTH	APEAX
.900	6775802.2	1SBH	.623	100.00000

TOTAL APEA=6.7758E+07
MUL FACTOR=1.0000E+00

* RUN # 148 MAY 9, 1998 14:29:19
START



0.900 Nukulan Passage

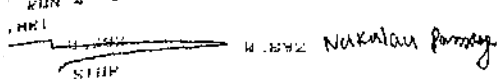
RUN# 148 MAY 9, 1998 14:29:19

APEAS

PT	APEA	TYPE	WIDTH	APEAX
.900	7753763.6	1SBH	.726	100.00000

TOTAL APEA=7.7538E+07
MUL FACTOR=1.0000E+00

RUN # 149 MAY 9, 1998 14:22:08
START

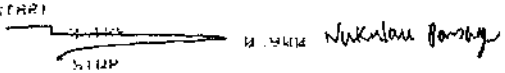


RUN# 149 MAY 9, 1998 14:22:08

AREA%				
MT	AREA	TYPE	WIDTH	AREA%
.892	24999544	DSPH	.638	100.00000

TOTAL AREA=2.4999E+07
AUC FACTOR=1.0000E+00

* RUN # 150 MAY 9, 1998 14:25:18
START



RUN# 150 MAY 9, 1998 14:25:18

AREA%				
MT	AREA	TYPE	WIDTH	AREA%
.900	25602698	DSPH	.652	100.00000

TOTAL AREA=2.5602E+07
AUC FACTOR=1.0000E+00

* RUN # 151 MAY 9, 1998 14:41:29
START

RUN# 151 MAY 9, 1998 14:41:29

AREA%				
MT	AREA	TYPE	WIDTH	AREA%
.907	30194682	DSPH	.638	100.00000

TOTAL AREA=3.0195E+07
AUC FACTOR=1.0000E+00

* RUN # 152 MAY 9, 1998 14:44:24
START

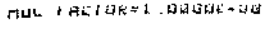
RUN# 152 MAY 9, 1998 14:44:24

AREAX

RT	AREA	TYPE	WIDTH	AREAX
.906	82654400	DSBB	.652	100.00000

TOTAL AREA=8.2654E+07
MUL FACTOR=1.00000E+00

* RUN # 153 MAY 9, 1998 14:49:25
START



0.905 Varesi River

STOP

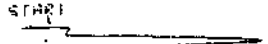
RUN# 153 MAY 9, 1998 14:49:25

AREAX

RT	AREA	TYPE	WIDTH	AREAX
.905	87421552	DSBB	.681	100.00000

TOTAL AREA=8.7432E+07
MUL FACTOR=1.00000E+00

* RUN # 154 MAY 9, 1998 14:52:17
START



0.990 Varesi River

STOP

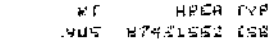
RUN# 154 MAY 9, 1998 14:52:17

AREAX

RT	AREA	TYPE	WIDTH	AREAX
.990	66268928	DSBP	.526	100.00000

TOTAL AREA=6.6269E+07
MUL FACTOR=1.00000E+00

* RUN # 155 MAY 9, 1998 14:57:08
START



0.997 ~~Varesi Rio~~ Tributaria 2 T30

STOP

RUN# 155 MAY 9, 1998 14:57:08,

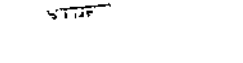
AREAX

RF	HPER	TYPE	WIDTH	HPER%
.997	89158848	DSPH	.745	100.00000

TOTAL HPER=8.9159E+07
MUL FACTOR=1.0000E+00

* POST
STOP

* RUN # 156 MAY 9, 1998 15:01:01
START



Trade winds Mixo

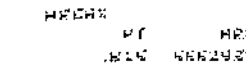
RUN# 156 MAY 9, 1998 15:01:01

HPER%

RF	HPER	TYPE	WIDTH	HPER%
.816	66629376	DSPH	.632	100.00000

TOTAL HPER=6.6629E+07
MUL FACTOR=1.0000E+00

* RUN # 157 MAY 9, 1998 15:04:18
START



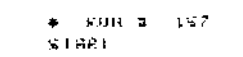
RUN# 157 MAY 9, 1998 15:04:18

HPER%

RF	HPER	TYPE	WIDTH	HPER%
.988	66657888	DSPH	.632	100.00000

TOTAL HPER=6.6658E+07
MUL FACTOR=1.0000E+00

* RUN # 158 MAY 9, 1998 15:07:18
START



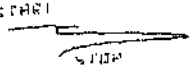
Trade winds

RUN# 158 MAY 9, 1998 15:07:18

HPER%

RF	HPER	TYPE	WIDTH	HPER%
[illegible]	[illegible]	DSPH	.632	100.00000

* RUN # 159 MAY 9, 1998 15:10:14
START

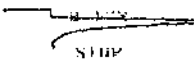


RUN# 159 MAY 9, 1998 15:10:14

RPCH#				
NT	RPCH TYPE	DIOTA	RPCH#	
.997	STRUJNNN DEPH	.1003	100.00000	

INTCHL RPCH=5.17052E+07
MUL FACTOR=1.00000E+00

* RUN # 160 MAY 9, 1998 15:10:44
START

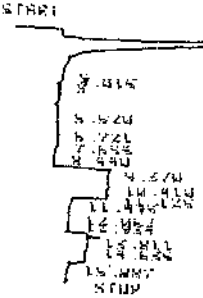


RUN# 160 MAY 9, 1998 15:10:44

RPCH#				
NT	RPCH TYPE	DIOTA	RPCH#	
.996	SNNNNJSN DEPH	.1004	100.00000	

INTCHL RPCH=5.95982E+07
MUL FACTOR=1.00000E+00

* RUN # 161 MAY 9, 1998 15:21:58
START



RUN# 161 MAY 9, 1998 15:21:58

RT	APER	TYPE	WIDTH	APERX
.825	6756400	SBR	.550	55.72367
5.815	714929	SPR	.660	.58944
9.570	1740254	BP	1.556	1.92478
10.410	879802	DP	.598	7.25265
11.125	1088568	UP	.481	8.97319
11.495	400947	PD	.316	.25057
12.067	718711	DP	.792	.59255
12.924	527888	UP	.414	.44290
13.811	2661928	SPR	.584	11.22718
14.625	1514509	SBR	1.855	12.48694
15.887	1149440	TSBP	.812	.94767

TOTAL APER=1.21296E+08
MUL FACTOR=1.00000E+00

* RUN # 162 MAY 9, 1998 15:40:21
START

0.898 Tradewinds @ 160, Full FIA system

RUN# 162 MAY 9, 1998 15:40:21

APERX

RT	APER	TYPE	WIDTH	APERX
.828	7299649	DSBR	.581	100.00000

TOTAL APER=7.29964E+07
MUL FACTOR=1.00000E+00

* RUN # 163 MAY 9, 1998 15:43:07
START

0.835 Tradewinds @ 160 Full FIA System

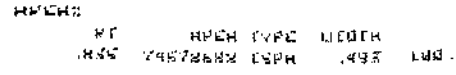
RUN# 163 MAY 9, 1998 15:43:07

APERX

RT	APER	TYPE	WIDTH	APERX
.835	7457682	DSPR	.493	100.00000

TOTAL APER=7.45768E+07
MUL FACTOR=1.00000E+00

* RUN # 164 MAY 9, 1998 15:45:46
START



0.825 Full FIA system

TOTAL
MUL FACTOR=1.0000E+00

* RUN # 168 MAY 9, 1998 15:57:08
START

STOP 0.271 Nawasi River Full PIA system

RUN# 168 MAY 9, 1998 15:57:08

AWCR%

PT	APCR	TYPE	WIDTH	APCR%
.271	1.2091E+09	DSPR	.472	100.0000

TOTAL APCR=1.2091E+09
MUL FACTOR=1.0000E+00

* RUN # 169 MAY 9, 1998 15:59:59
START

STOP 0.271 Nawasi River Full PIA system

RUN# 169 MAY 9, 1998 15:59:59

AWCR%

PT	APCR	TYPE	WIDTH	APCR%
.271	1.5598E+09	DSPR	.419	100.0000

TOTAL APCR=1.5598E+09
MUL FACTOR=1.0000E+00

* RUN # 170 MAY 9, 1998 16:04:59
START

STOP 0.558 Nukulau Passage Full PIA

RUN# 170 MAY 9, 1998 16:04:59

AWCR%

PT	APCR	TYPE	WIDTH	APCR%
.558	1.2782E+09	DSPR	.481	100.0000

TOTAL APCR=1.2782E+09
MUL FACTOR=1.0000E+00

* RUN # 171 MAY 9, 1998 16:07:51
START

0.896 Nukulau Passage
Full FIA System

STOP

RUN# 171 MAY 9, 1998 16:07:51

AREAS

RT	AREA	TYPE	WIDTH	AREAS
.996	12684966	ISBN	.451	100.00000

TOTAL AREA=1.2684E+08
MUL FACTOR=1.0000E+00

Actually
Tamavua R

* RUN # 172 MAY 9, 1998 16:10:55
START

0.808 Nukulau Passage
Full FIA System

STOP

RUN# 172 MAY 9, 1998 16:10:55

AREAS

RT	AREA	TYPE	WIDTH	AREAS
.808	12721648	ISBN	.456	100.00000

TOTAL AREA=1.2722E+08
MUL FACTOR=1.0000E+00

* RUN # 173 MAY 9, 1998 16:12:29
START

0.848 Nukulau Passage
Full FIA System

STOP

RUN# 173 MAY 9, 1998 16:12:29

AREAS

RT	AREA	TYPE	WIDTH	AREAS
.848	11995428	ISBN	.446	100.00000

TOTAL AREA=1.1995E+08
MUL FACTOR=1.0000E+00

* RUN # 174 MAY 9, 1998 16:17:27
START

0.859 Suva point Full FIA System

STOP

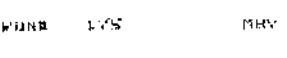
RUN# 174 MAY 9, 1998 16:17:27

AREA%

RT	AREA TYPE	DEPTH	AREA%
.859	72259988 ISBH	.552	100.00000

TOTAL AREA=7.2259E+07
MUL FACTOR=1.00000E+00

* RUN # 175 MAY 9, 1998 16:20:12
START



0.862 Suvapent Full FIA system

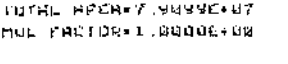
RUN# 175 MAY 9, 1998 16:20:12

AREA%

RT	AREA TYPE	DEPTH	AREA%
.859	79099264 ISBH	.548	100.00000

TOTAL AREA=7.9099E+07
MUL FACTOR=1.00000E+00

* RUN # 176 MAY 9, 1998 16:22:54
START



0.861 Suvapent Full FIA system

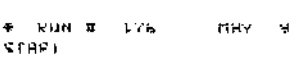
RUN# 176 MAY 9, 1998 16:22:54

AREA%

RT	AREA TYPE	DEPTH	AREA%
.861	76202112 ISBH	.559	100.00000

TOTAL AREA=7.6202E+07
MUL FACTOR=1.00000E+00

* RUN # 177 MAY 9, 1998 16:27:03
START



0.864 Nabukalon opp/Sm Full FIA systems

RUN# 177 MAY 9, 1998 16:27:03

AREA%

RT	AREA TYPE	DEPTH	AREA%

TOTAL AREA=6.1453E+07
MUL FACTOR=1.0000E+00

* RUN # 178 MAY 9, 1998 16:29:53
START
STOP 0.876 Nabukelan opp/for full FIA system

RUN# 178 MAY 9, 1998 16:29:53

RPLHZ

PT	AREA	TYPE	WIDTH	RPLHZ
1.876	5750828	USER	.546	100.00000

TOTAL AREA=5.7508E+07
MUL FACTOR=1.0000E+00

* RUN # 179 MAY 9, 1998 16:32:22
START
STOP 0.855 Nabukelan opp/for full FIA system

RUN# 179 MAY 9, 1998 16:32:22

RPLHZ

PT	AREA	TYPE	WIDTH	RPLHZ
.855	7116562	USER	.555	100.00000

TOTAL AREA=7.1165E+07
MUL FACTOR=1.0000E+00

* RUN # 180 MAY 9, 1998 16:35:01
START
STOP 0.879 Nabukelan opp/for full FIA system

RUN# 180 MAY 9, 1998 16:35:01

RPLHZ

PT	AREA	TYPE	WIDTH	RPLHZ
.879	5833520	USER	.571	100.00000

TOTAL AREA=5.8335E+07
MUL FACTOR=1.0000E+00

* RUN # 181 MAY 9, 1998 16:59:15
START
STOP 0.874 Light House full FIA system.

RUN# 181 MAY 9, 1998 16:59:15

APERX

RY	APER	TYPE	WIDTH	APERX
.874	5551987E	1SPH	.887	100.00000

TOTAL APER=5.55198E+07
MUL FACTOR=1.00000E+00

* RUN # 182 MAY 9, 1998 16:91:41
START
STOP 0.858 Lighthouse full FIA system

RUN# 182 MAY 9, 1998 16:91:41

APERX

RY	APER	TYPE	WIDTH	APERX
.858	5512614E	1SPH	.896	100.00000

TOTAL APER=5.51261E+07
MUL FACTOR=1.00000E+00

* RUN # 183 MAY 9, 1998 16:99:14
START
STOP 0.885 Lighthouse full FIA system

RUN# 183 MAY 9, 1998 16:99:14

APERX

RY	APER	TYPE	WIDTH	APERX
.885	5212613E	1SPH	.871	100.00000

TOTAL APER=5.21261E+07
MUL FACTOR=1.00000E+00

* RUN # 184 MAY 9, 1998 16:97:15
START
STOP 0.875 Lighthouse full FIA system

TOTAL HPCR=4.7879E+07
MUL FACTOR=1.0000E+00

* RUN # 188 MAY 9, 1998 16:58:24

START

0.867 Naverse Full FVM System

STOP

RUN # 188 MAY 9, 1998 16:58:24

HPCRX

VC	HPCR	TYPE	WIDTH	HPCRX
0.867	47879.04	DSBH	.561	100.00000

TOTAL HPCR=4.7879E+07
MUL FACTOR=1.0000E+00

*

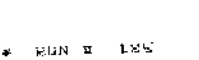
RUN# 184

APCHX

PC	APCH	TYPE	WIDTH	APCHX
.875	41287264	ESPH	.551	100.00000

TOTAL APCH=4.12872E+07
MUL FACTOR=1.00000E+00

* RUN # 185 MAY 9, 1998 16:51:04
START



0.876 Noscope Full FIA System

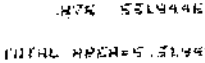
RUN# 185 MAY 9, 1998 16:51:04

APCHX

PC	APCH	TYPE	WIDTH	APCHX
.876	55194469	ESPH	.592	100.00000

TOTAL APCH=5.51946E+07
MUL FACTOR=1.00000E+00

* RUN # 186 MAY 9, 1998 16:52:50
START



0.855 Noscope Full FIA system

RUN# 186 MAY 9, 1998 16:52:50

APCHX

PC	APCH	TYPE	WIDTH	APCHX
.855	47760128	ESPH	.555	100.00000

TOTAL APCH=4.77601E+07
MUL FACTOR=1.00000E+00

* RUN # 187 MAY 9, 1998 16:55:58
START

0.881 Noscope Full FIA System

RUN# 187 MAY 9, 1998 16:55:58

APCHX

PC	APCH	TYPE	WIDTH	APCHX
.881	48698272	ESPH	.559	100.00000

A 4.0

Typical "Ghost Peak" plots for selected sites

Note:

- The seawater samples were injected (analyzed) four times, the peak area of each run was printed immediately after each peak.
- The seawater samples were neither acidified (measure IC_m) nor analyzed using the "Full FIA" system (measure TC_m).
- The seawater samples were analyzed under certain conditions specified on the peaks "untreated" (injected directly after filteration), "bubbled with nitrogen gas for 15 minutes" (degassed) and "bubbled with nitrogen gas for 15 minutes + moderately heated" (degassed and heated). The UV source was also switched on and off.
- The operating parameters of the integrator were as follows:

Attenuation 2^= 10
Chart speed CHT SP= 0.3
Area reject AR REJ= 35000
Threshold THRSH= 0
Peak width PK WD= 0.50

START

STOP Light House No oxidant & acid UV off

[illegible] APR 10, 1998 04:57:[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

START

STOP Light House conditions as in 601
No oxidant & acid UV off
(untreated)

[illegible] APR 10, 1998 04:53:46

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

START

STOP Light House as 601
No oxidant & acid, UV off
(untreated)

[illegible] APR 10, 1998 05:07:[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

START

STOP Light House as 601
No oxidant & acid, UV off (untreated)

PLOT 204 APR 10, 1995 08:00:52

APFA

01	APFA T PF	WIDTH	APFA	
[illegible]	[illegible]	50	00.00000	

TOTAL APFA=[illegible]
DIV FACTOR= 0.00000E+00

* PLOT 5 ABF APR 10, 1995 08:07:04
START
0.000 Light House as 601
STOP
NO oxidant & acid, UV off (untreated)

PLOT ABF APR 10, 1995 08:07:04

APFA

01	APFA T PF	WIDTH	APFA	
[illegible]	[illegible]	25	100	00.000

TOTAL APFA=[illegible]
DIV FACTOR= 0.00000E+00

* PLOT 5 ABA APR 10, 1995 08:10:11
START
0.000 Light House as No oxidant & acid, UV on, w/Bath 56°C
STOP
(untreated)

PLOT ABA APR 10, 1995 08:10:11

APFA

01	APFA T PF	WIDTH	APFA	
[illegible]	[illegible]	25	100	00.000

TOTAL APFA=[illegible]
DIV FACTOR= 0.00000E+00

* PLOT 5 ABC APR 10, 1995 08:13:58
START
0.000 Light house as 606
STOP
NO oxidant & acid, UV on
- untreated)

PLOT ABC APR 10, 1995 08:13:58

APFA

PT	AREA	TYPE	WIDTH	AREA
216	[illegible]	I BR	387	100 [illegible]

TOTAL AREA=[illegible]
100 FACTOR= 0.0000E+00

* RUN # 608 APR 10, 1998 05:14:47
START

START # Light House on 606
No oxidant & acid, UV on
(Unwected)

RUN # 608 APR 10, 1998 05:14:47

AREA:

PT	AREA	TYPE	WIDTH	AREA
445	[illegible]	I BR	387	100 [illegible]

TOTAL AREA=[illegible]
100 FACTOR= 0.0000E+00

* RUN # 609 APR 10, 1998 05:16:37
START

START # 445 Light house on 606, No oxidant & Acid, UV on
(Unwected)

RUN # 609 APR 10, 1998 05:16:37

AREA:

PT	AREA	TYPE	WIDTH	AREA
445	[illegible]	I BR	387	100 [illegible]

TOTAL AREA=[illegible]
100 FACTOR= 0.0000E+00

* RUN # 610 APR 10, 1998 05:21:10
START

START # 445 Lami (Tumaruna bridge) condition as in 606, No oxidant &
(River) UV on, (Unwected)

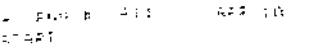
RUN # 610 APR 10, 1998 05:21:10

AREA:

PT	AREA	TYPE	WIDTH	AREA
445	[illegible]	I BR	387	100 [illegible]

TOTAL AREA=[illegible]
100 FACTOR= 0.0000E+00

* RUN # A12 APR 10, 1998 05:24:13
START



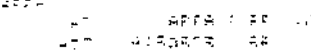
RUN A12 APR 10, 1998 05:24:13

AREA

RT	AREA	* RF	WIDTH	AREA
606	4150875	RP	512	100.00000

TOTAL AREA=4150875
DIL FACTOR= 00000.00

* RUN # A13 APR 10, 1998 05:26:18
START



RUN A13 APR 10, 1998 05:26:18

AREA

RT	AREA	* RF	WIDTH	AREA
606	5454088	RP	583	100.00000

TOTAL AREA=5454088
DIL FACTOR= 00000.00

* RUN # A14 APR 10, 1998 05:27:45
START

RUN A14 APR 10, 1998 05:27:45

AREA

RT	AREA	* RF	WIDTH	AREA
606	5307728	RP	565	100.00000

TOTAL AREA=5307728
DIL FACTOR= 00000.00

APR 10, 1998 05:57:15

AREA

	AREA	TYPE	WIDTH	AREA%
[illegible]	[illegible]	BP	[illegible]	100.00000

TOTAL AREA=[illegible]
[illegible] [illegible]E+00

APR 10, 1998 05:33:43

Tamavua Bridge 614 (river) No oxidant, acid, UV off

APR 10, 1998 05:33:43

AREA

	AREA	TYPE	WIDTH	AREA%
442	3457298	I BP	304	100.00000

TOTAL AREA=3457298
[illegible] [illegible]E+00

APR 10 1998 05:47:00

Tamavua Bridge 614 (River) No oxidant acid, UV off

APR 10, 1998 05:47:00

AREA

	AREA	TYPE	WIDTH	AREA%
555	5714786	I BP	[illegible]	100.00000

TOTAL AREA=5714786
[illegible] [illegible]E+00

APR 10 1998 05:45:17

Naboukadou MH No oxidant & acid 36°C UV off (untreated)

APR 10 1998 05:45:17

AREA

	AREA	TYPE	WIDTH	AREA%
541	5861069	I BP	444	100.00000

TOTAL AREA=5261069
MUL FACTOR= 0000E-00

* RUN # [illegible] APR 10 1998 [illegible]
START
[illegible] 0.[illegible] Nabonkalou MH as 620
No incident & acid, nv off
(Unknotted)

RUN# [illegible] APR 10, 1998 05:47:[illegible]

AREA:

AT	AREA TYPE	WIDTH	AREA:
[illegible]	[illegible]4717 I BP	[illegible]	100.00000

TOTAL AREA=[illegible]4717
MUL FACTOR= 0000E-00

* RUN # [illegible] APR 10, 1998 05:49:41
START
[illegible] 0.49[illegible] Nabonkalou MH as 620
No incident & acid, nv off
(Unknotted)

RUN# [illegible] APR 10, 1998 05:49:41

AREA:

AT	AREA TYPE	WIDTH	AREA:
49[illegible]	[illegible]7115[illegible] I BP	[illegible]	100.00000

TOTAL AREA=[illegible]7115[illegible]
MUL FACTOR= 0000E+00

* RUN # [illegible] APR 10, 1998 05:52:51
START
[illegible] 0.49[illegible] Nabonkalou MH as 620
No incident & acid, nv off
(Unknotted)

RUN# [illegible] APR 10, 1998 05:52:51

AREA:

AT	AREA TYPE	WIDTH	AREA:
49[illegible]	[illegible]0[illegible]994 I BP	[illegible]	100.00000

TOTAL AREA=[illegible]0[illegible]994
MUL FACTOR= 0000E-00

* RUN # 614 APR 10, 1998 05:53:43
START

STOP 0.505 Naboukalou mH @ 620
No oxidant & acid, uv off
(Unheated)

RUN# 614 APR 10, 1998 05:55:43

AREA

RT	AREA	TYPE	WIDTH	AREA%
.505	7009875	I BP	.400	100.00000

TOTAL AREA=7009875
NUL FACTOR=1.00000E+00

* RUN # 615 APR 10, 1998 05:56:47
START

STOP 0.537 Naboukalou mH UV on No acid & oxidant 50°c
(Unheated)

RUN# 615 APR 10, 1998 05:56:47

AREA

RT	AREA	TYPE	WIDTH	AREA%
.537	5112355	BV	.240	100.00000

TOTAL AREA=5112355
NUL FACTOR=1.00000E+00

* RUN # 616 APR 10, 1998 05:58:55
START

STOP 0.555 Naboukalou mH @ 625
No oxidant & acid, uv on
(Unheated)

RUN# 616 APR 10, 1998 05:58:55

AREA

RT	AREA	TYPE	WIDTH	AREA%
.555	3441134	I BV	.375	100.00000

TOTAL AREA=3441134
NUL FACTOR=1.00000E+00

* RUN # 617 APR 10, 1998 06:01:00
START

[illegible] (Unheated)

No oxidant & acid, UV on

RUN [illegible] APR 10, 1998 06:01:00

AREA

	AREA	TYPE	WIDTH	AREA%
[illegible]	1017998	BP	[illegible]	100.0000

TOTAL AREA=1017998
TOTAL FACTOR=1.0000E-03

RUN [illegible] APR 10, 1998 06:02:01

Nabankalam MH 0.625
No oxidant & acid, UV on
(Untreated)

RUN [illegible] APR 10, 1998 06:02:01

AREA

	AREA	TYPE	WIDTH	AREA%
[illegible]	4457648	BPB	.193	67.8143
[illegible]	2121962	TBPH	.146	32.5787

TOTAL AREA=6579610
TOTAL FACTOR=1.0000E+00

RUN [illegible] APR 10, 1998 06:06:10

Nabankalam MH, No oxidant & acid, UV on
(Untreated)

RUN [illegible] APR 10, 1998 06:06:10

AREA

	AREA	TYPE	WIDTH	AREA%
[illegible]	484797	BP	.198	100.0000

TOTAL AREA=484797
TOTAL FACTOR=1.0000E+00

RUN [illegible] APR 10, 1998 06:10:11

Nabankalam MH No oxidant and acid UV on 50°C
Not filled

RUN [illegible] APR 10, 1998 06:10:11

AREA

	AREA	TYPE	WIDTH	AREA%
.618	4004378	T BP	.384	100.00000

TOTAL AREA=4004378
NOL FACTOR=1.0000E+00

Run # 631 APR 10, 1998 06:11:53
START
STOP 0.611 Nabankalou mH a 630, NO oxidant & acid
N_2-bubbled, UV on

Run # 631 APR 10, 1998 06:11:59

AREA

	AREA	TYPE	WIDTH	AREA%
.611	5973802	T PB	.567	100.00000

TOTAL AREA=5973802
NOL FACTOR=1.0000E+00

Run # 632 APR 10, 1998 06:13:51
START
STOP 0.618 Nabankalou a 630, NO oxidant & acid
N_2-bubbled UV on

Run # 632 APR 10, 1998 06:13:51

AREA

	AREA	TYPE	WIDTH	AREA%
.618	4077534	T BP	.387	100.00000

TOTAL AREA=4077534
NOL FACTOR=1.0000E+00

Run # 633 APR 10, 1998 06:13:51
START
STOP 0.614 Nabankalou mH a 630, NO oxidant & acid
N_2-bubbled, UV on.

Run # 633 APR 10, 1998 06:13:51

AREA

	AREA	TYPE	WIDTH	AREA%
.614	4086133	T BP	.365	100.00000

TOTAL AREA=4086133

* RUN # 644 APR 10, 1998 07:03:22
START
STOP 0.530 lighthouse @ 643, N2-bubbled, No oxidant added
UV-off

RUN# 644 APR 10, 1998 07:03:22

AREA
PT AREA TYPE WIDTH AREA%
.530 3770045 I BP .347 100.00000

TOTAL AREA=3770045
VOL FACTOR=1.0000E+00

* RUN # 645 APR 10, 1998 07:05:02
START
STOP 0.534 lighthouse @ 643 N2-bubbled, No oxidant added
UV-off

RUN# 645 APR 10, 1998 07:05:02

AREA
PT AREA TYPE WIDTH AREA%
.534 4930960 I BP .345 100.00000

TOTAL AREA=4930960
VOL FACTOR=1.0000E+00

* RUN # 646 APR 10, 1998 07:06:50
START
STOP 0.545 lighthouse @ 643 N2-bubbled, No oxidant added
UV-off.

RUN# 646 APR 10, 1998 07:06:50

AREA
PT AREA TYPE WIDTH AREA%
.545 4370701 I BP .436 100.00000

TOTAL AREA=4370701
VOL FACTOR=1.0000E+00

* RUN # 647 APR 10, 1998 07:10:37
START

		AREA TYPE	WIDTH	AREA
316	3787210	I BP	145	100.00000

TOTAL AREA=3787210
MUL FACTOR=1.00000E+00

RUN # 651 APR 10, 1998 07:17:16
START
0 473 Nebulization MH No oxidant & Acid N2 bubbled + boiled

RUN # 651 APR 10, 1998 07:17:16

AREA:

		AREA TYPE	WIDTH	AREA
492	3507385	I BP	260	100.00000

TOTAL AREA=3503385
MUL FACTOR=1.00000E+00

RUN # 651 APR 10, 1998 07:18:11
0 479 Nebulization MH @ 651, NO oxidant + acid, N2 bubbled + boiled

RUN # 651 APR 10, 1998 07:18:11

AREA:

		AREA TYPE	WIDTH	AREA
478	3078641	I BP	230	100.00000

TOTAL AREA=3078641
MUL FACTOR=1.00000E+00

RUN # 651 APR 10, 1998 07:19:39
START
0 42 Nebulization MH @ 651, NO oxidant & Acid, UV on N2 - bubbled + boiled.

RUN # 651 APR 10, 1998 07:19:39

AREA:

		AREA TYPE	WIDTH	AREA
447	3171321	I BP	241	100.00000

TOTAL AREA=3171321
MUL FACTOR=1.00000E+00

A 5.0

Raw DOC data for the sites on each day of sample analysis

Note:

- The DOC values tabulated were the actual DOC levels measured in each site on each sampling trip
- The rainfall data given were the actual data for the 3 days before the sampling trip. The sampling trips were intentionally made on fine days.

A 6.0

Statistical analysis + sample calculation of the average freshwater dilution of the seawater samples collected

- **Square root transformation**
- **F- Test**
- **ANOVA (Analysis of variance)**
- **Average freshwater dilution**

Square root transformation

The raw DOC data had to be transformed statistically because the raw means and their errors in terms of their standard deviations (SD) were dependent on each other. For example, a large mean will have a large standard deviation whilst a small mean will have a small standard deviation. Furthermore, the errors were in some cases equivalent to the raw means. Because of the above factors, the data was transformed through square root transformation to stablish the errors (SD) and to ensure that their values are smaller than the transformed means.

Sample calculation

Raw datum : a.....0.778

Transformation: $\sqrt{a + 1}$.....$\sqrt{0.778 + 1} = 1.333$

All the individual datum for DOC at sites monitored were transformed in the above manner. From the transformed data, the square roots means (SRM) and square root standard deviations (SSD) were calculated.

To revert to the original form of the data, the SRM and SSD were squared.

$(SRM)^2$..... Transformed mean

$(SSD)^2$.....Transformed standard deviation

F - Test

The test was to determine any differences in the variances $(SD)^2$ of sample populations, (e.g. variances in the carbon recoveries of the FIA method used in the project and the FIA method used by (Koshy *et al.*, 1992).

FIA method used in this project :

Variance: 82.81

FIA method (Koshy *et al.*,1992)

Variance: 24.01

F_{test}=82.81/24.01 = 3.44, $F_{critical}$ 6,6 =4.2

Ho = The variances of the two sets of recoveries are equal, at 95% confidence interval. Since F_{test} is less than $F_{critical}$, we accept Ho.

Raw DOC data:

Variance: 36.60

Transformed DOC data:

Variance: 30.25

F_{test}=36.60/30.25=1.21, $F_{critical}$=2.82 (95% confidence interval)

$F_{test} < F_{critical}$, Therefore, there is no significant difference between the two sets of data

Raw DOC for each day of four replicate analysis for the sites monitored in the project

Note: <MDL, the DOC present was below the method detection limit of the FIA system.

The rainfall data was the average for the 3 days before sampling, the sampling of the sites was intentionally done on fine days. A period of 3 days was chosen because there was no information available on the flushing rate of the Suva lagoon. The rainfall data was obtained from the (Fiji Meteorological Department, 1996) in Nadi.

Sites	**DOC levels (mg C/L) on each sampling trip**							
Date and sampling trip #	12/4 **1**	30/4 **2**	9/5 **3**	28/5 **4**	11/6 **5**	28/7 **6**		
Rainfall/mm	**5.1**	**4.0**	**0.8**	**0.4**	**1.1**	**0.2**		
Kinoya outfall	22.22	23.22	0.89	<MDL	18.36	16.24		
200 m Kinoya	32.02	28.31	2.81	<MDL	20.43	8.46		
Nukulau passage	22.80	23.63	10.80	1.13	10.24	2.40		
Centra	0.88	0.78	0.48	0.84	0.82	0.76		
200 m Nabukalou	25.37	21.57	16.96	0.18	22.23	14.27		
Mosquito island	33.59	29.17	2.10	3.43	4.28	5.42		
Date and sampling trip #	5/4 **1**	20/4 **2**	5/5 **3**	19/5 **4**	20/6 **5**	27/6 **6**	5/8 **7**	29/8 **8**
Rainfall/mm	**5.1**	**0.1**	**1.3**	**0.4**	**0.3**	**0.4**	**1.8**	**0.2**
Nabukalou creek	19.30	0.97	16.35	3.92	<MDL	4.71	5.20	10.40
Vugalei bridge	6.88	18.07	5.90	2.39	0.19	0.05	0.40	4.89
Tradewinds	10.62	2.92	32.49	4.85	3.41	0.25	5.21	3.42
Tamavua river	12.06	15.98	10.15	9.05	<MDL	3.08	8.23	7.82
Suva point	22.6	4.20	20.49	2.09	<MDL	0.70	6.19	2.16
Nasese	16.31	14.23	13.91	3.71	<MDL	3.14	17.21	2.89

Analysis of Variance (ANOVA)

DATA FOR THE EFFECT OF HYDROXYLAMINEHYDROCHLORIDE ON CHLORIDE SIGNAL

A	B	C	D
2.398	2.88	2.795	2.856
5.139	5.635	5.338	5.528
6.802	7.023	7.01	6.942
8.668	8.874	8.939	8.801
9.714	9.849	9.926	9.881

A= DDW standards
B= SSW standards
C=SSW (IC) standards + Hydroxylaminehydrochloride
D=SSW (KHP) standards + Hydroxylaminehydrochloride

Anova: Two-Factor
Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Row 1	4	10.929	2.73225	0.0509349
Row 2	4	21.64	5.41	0.0477247
Row 3	4	27.777	6.94425	0.0102549
Row 4	4	35.302	8.8255	0.0115803
Row 5	4	39.37	9.8425	0.0083363
Column 1	5	32.741	6.5482	8.4688632
Column 2	5	34.261	6.8522	7.5894017
Column 3	5	34.008	6.8016	8.1421883
Column 4	5	34.008	6.8016	7.6724583

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	127.387602	4	31.8469	3673.099	2.06632E-18	3.25916005
Columns	0.2824498	3	0.09415	10.858891	0.000978664	3.4902996
Error	0.1040437	12	0.00867			
Total	127.774098	19				

CARBON RECOVERIES OF MODEL ORGANIC COMPOUNDS VIA THREE METHODS

Compound	FIA (Project)	KOSHY	BECKMAN
Citric acid	102.8	106	108
Thiourea	101.9	101	100
Sodium acetate	94.9	102	106
KHP	105	103	0
Urea	105.9	104	102
D-Glucose	93.4	96	102
Nicotinic acid	80.3	92	100

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Row 1	3	316.8	105.6	6.88
Row 2	3	302.9	100.9667	0.903333333
Row 3	3	302.9	100.9667	31.60333333
Row 4	3	208	69.33333	3606.333333
Row 5	3	311.9	103.9667	3.803333333
Row 6	3	291.4	97.13333	19.45333333
Row 7	3	272.3	90.76667	98.16333333
Column 1	7	684.2	97.74286	82.20952381
Column 2	7	704	100.5714	23.95238095
Column 3	7	618	88.28571	1524.571429

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	2829.666667	6	471.6111	0.813738365	0.57926739	2.99611713
Columns	579.5466667	2	289.7733	0.499987538	0.618631967	3.88529031
Error	6954.733333	12	579.5611			
Total	10363.94667	20				

MEASUREMENT OF CHLORIDE INTERFERENCE ON CARBON SIGNAL

DDW	SSW
0.384	1.023
0.595	1.209
0.951	1.655
0.964	1.363
1.268	1.692
1.778	2.378
3.479	3.686
6.319	6.597
8.843	8.943

Anova: Two factor without replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Row 1	2	1.407	0.7035	0.2041605
Row 2	2	1.804	0.902	0.188498
Row 3	2	2.606	1.303	0.247808
Row 4	2	2.327	1.1635	0.0796005
Row 5	2	2.96	1.48	0.089888
Row 6	2	4.156	2.078	0.18
Row 7	2	7.165	3.5825	0.0214245
Row 8	2	12.916	6.458	0.038642
Row 9	2	17.786	8.893	0.005
Column 1	9	24.581	2.731222	8.774995444
Column 2	9	28.546	3.171778	7.770679694

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	132.183781	8	16.52297	727.8036567	1.2365E-10	3.43810314
Columns	0.873401389	1	0.873401	38.47157161	0.00025871	5.31764499
Error	0.181620111	8	0.022703			
Total	133.2388025	17				

FIA SYSTEM (TRANSFORMED DOC AVERAGES) AND AVERAGE DOC DATA FROM
SHIMADZU 2000-UV HTCO UNIT

Site	FIA method DOC mg/L	Shimadzu 2000-UV HTCO unit DOC mg/L
Kinoya outfall	13	12
200m Kinoya outfall	16	11
Nukulau passage	9	9
Centra hotel	0.8	0.8
200m Nabukalou creek	18	1
Mosquito island	18	0
Tradewinds	8	3
Vugalei bridge	5	3
Tamavua river	8	2
Nabukalou creek	7	11
Nasese	4	0
Suva point	7	1

Anova: Two-Factor With Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Row 1	2	25	12.5	0.5
Row 2	2	27	13.5	12.5
Row 3	2	18	9	0
Row 4	2	1.6	0.8	0
Row 5	2	19	9.5	144.5
Row 6	2	18	9	162
Row 7	2	11	5.5	12.5
Row 8	2	8	4	2
Row 9	2	10	5	18
Row 10	2	18	9	8
Row 11	2	4	2	8
Row 12	2	8	4	18
Column 1	12	113.8	9.48333	31.13061
Column 2	12	53.8	4.48333	22.76697

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*
Rows	356.8733333	11	32.443	1.512175	0.252037
Columns	150	1	150	6.991525	0.022824
Error	236	11	21.4545		
Total	742.8733333	23			