UNIVERSITY OF SOUTHAMPTON

Occurrence and behaviour of trace metals in coastal waters of Bermuda, and chromium in the Sargasso Sea

by

Douglas Patrick Connelly

A thesis submitted to the University of Southampton for the degree of Doctor of Philosophy.

Department of Oceanography

July 1997

UNIVERSITY OF SOUTHAMPTON

ABSTRACT

FACULTY OF SCIENCE

OCEANOGRAPHY

Doctor of Philosophy

OCCURRENCE AND BEHAVIOUR OF TRACE METALS IN COASTAL WATERS OF BERMUDA, AND CHROMIUM IN THE SARGASSO SEA

by Douglas Patrick Connelly

The distribution of the dissolved and particulate forms of the trace metals, cadmium, copper, lead, manganese and nickel were investigated in the coastal waters of Bermuda over a 3-4 year period; together with salinity, temperature and the nutrients nitrate, nitrite and phosphorus. Trace metal concentrations were determined in the predominantly calcareous sediments of the inshore areas of Bermuda. A selective extraction technique was used to assess the environmental mobility of the metals in the sediments.

Concentration of trace metals in the waters and sediments are generally elevated in the enclosed harbour areas which have high human populations. The concentrations of metals are elevated with respect to the offshore Sargasso Sea water that exchanges with the coastal waters, concentrations of cadmium range from 0.1-2.4 nmol l^{-1}, copper 0.42-60 nmol l^{-1}, lead 0.03-3.5 nmol l^{-1}, manganese 0.3-40 nmol l^{-1} and nickel 0.45-14 nmol l^{-1}.

Most of the metals in the sediments were associated with the non-labile, presumably organic fraction of the sediments. However lead and manganese were associated with the labile fraction of the sediments. An in-depth study of Devil's Hole; a 24m deep basin in Harrington Sound which has a seasonal thermocline, and subsequent anoxia, was undertaken. Results from this study indicated that there was release of dissolved manganese across the anoxic/oxic interface. Reduced manganese was rapidly oxidised to the particulate material in the oxic water column. Data indicated that the sediments can readily release cadmium under both oxic and anoxic conditions. The concentrations of cadmium in St. George's Harbour are found to be elevated with respect to other stations and previous work in the same area.

Inputs of cadmium into the Bermuda coastal zone were found to be from diffuse sources; copper from anti-fouling compound on boats; lead, manganese and nickel showed a strong association with run-off during rain events.

A study of the seasonal trends in the distributions of the metals was performed. Some evidence for seasonal factors was cadmium and manganese, the other metals exhibited no evidence of seasonal trends.

A study of the oceanic distribution of chromium (III) and (VI) was performed at the Hydrostation 'S' site in the Sargasso Sea. Detectable concentrations (>0.03 nmol l^{-1}) of both species were measured at all depths to 2400m. Determination of chromium over an annual period indicates the existence of a seasonal cycle of this element related to a biological component. The concentrations of the reduced chromium (III) in the upper water column were higher during bloom events (upto 2.8 nmol l^{-1} compared to 0.6 nmol l^{-1} under normal conditions). Determination of the concentration of total chromium in deep sediment trap material indicated linkage between upper ocean biological processes and the removal of chromium to the deep ocean. Aeolian sources appear to be the dominant input for chromium, lateral advection is also thought to be important.

Contents

Chapter 1. TRACE METALS IN MARINE ENVIRONMENTS

Chapter 2. THE BERMUDA INSHORE ENVIRONMENT

Chapter 3. EXPERIMENTAL PROCEDURES

Chapter 4. TRACE METALS IN THE BERMUDA COASTAL ZONE

Chapter 5. CHROMIUM IN THE SARGASSO SEA

5.5 Discussion

Chapter 6. CONCLUSIONS

APPENDICES

LIST OF TABLES

Chapter 3

Chapter 4

Chapter 5

CHAPTER 6

LIST OF FIGURES

CHAPTER 2

CHAPTER 3

CHAPTER 4

CHAPTER 5

CHAPTER 6

ACKNOWLEDGMENTS

I am indebted to my supervisor for his support, friendship, guidance and endless patience throughout every stage of this work. Peter's wife Liz and their family deserve a special mention for their generosity in always providing me with a place to stay when in Southampton. I would like to thank Dennis Burton for his advice and comments regarding this work. All of the practical work for this thesis was done at the Biological Station and for that I thank Tony Knap who has been supportive throughout this work and provided encouragement, time, and kept me gainfully employed throughout the process, I owe him a great debt.

There are many people who have helped during various parts of this work, providing support, advice and sample data. I would particularly like to thank all of the members of the BATS group especially Peter Countway and Marta Sanderson for analysing most of the nutrient samples, Fred Bahr and Rod Johnson for providing the CTD data and, Kjell Gunderson and Karen Orcutt for the biological data from the BATS station. I have to thank Nick Bates and Craig Carlson for sitting down on numerous occasions over coffee and discussing the interactions between DOC and bacterial degradation and the possible redox effects. Rod Johnson deserves an extra mention amongst the BATS group for his open door policy, especially with regard to questions of the physical processes in the Sargasso Sea.

Throughout this study I have relied on the help of many of the staff at the Biological Station. Some of this work was performed on the R/V Stommel and I have to thank Bomber Smith and Nancy Stevens for their help in the driving and diving aspects of those trips. There were many people who helped me in the actual collection of the samples and particularly the divers that were needed, most of them were members of the Biological Station's work study programme.

I have to thank my friend Richard Parkes for always supporting me in this endeavor, and Annie Glasspool who always said that it could be done. I have to thank Tim Jickells and his wife Sue for getting me to Bermuda in the first place, and for their encouragement since then. My family have been supportive through the whole of this process and have my love and gratitude

Chapter 1.

Trace metals in marine environments

1.1 Introduction

The ocean can be viewed as a large reaction vessel for trace metals and other compounds (Chester, 1990). There are inputs of components into the reservoir via the atmosphere (Duce *et al.*, 1991), rivers and hydrothermal activity. These compounds may undergo modification in the oceanic environment but ultimately collect in the deep ocean sediments (Davis, 1973). This study is concerned with the geochemistry of metals in the marine environment, this introductory chapter will focus on the sources of trace metals to the ocean and the subsequent changes within the environment.

Trace metals are generally defined as those metals found in the oceanic environment at concentrations less than 1 μmol l^{-1}. Some trace metals, such as iron and zinc, are known to be micro-nutrients for the growth of phytoplankton (Martin *et al.*, 1993). Other elements are bio-limiting at low concentrations and toxic at high concentrations in oceanic environments; copper is a good example of this type (Bruland *et al.*, 1991; Morel *et al.*, 1991). Some metals have so far demonstrated only toxic effects; mercury is one such metal (Bryan, 1976). Some metals exist in natural environments in variable speciation states, and the geochemistry and toxicity of these metals is often dependent on the form that is present in the environment (Cross and Sunda, 1985). Certain trace metals that were previously thought to be toxic to phytoplankton have since been found to be used as substitute metals for elements more commonly viewed as micro-nutrients; cadmium is known to substitute for zinc in certain marine diatom species (Price and Morel, 1990; Morel *et al.*, 1991). It is uncommon to find concentrations of dissolved trace metals in open ocean areas that are at levels known to be toxic (Jickells, 1986). However trace metals in coastal areas can be found at concentrations that are known to be toxic to marine organisms.

1.2 Sources and relative strengths of trace metal inputs to marine environments

There are essentially three major pathways by which trace metals enter the ocean: rivers; atmospheric transport and; vent fluids associated with hydrothermal activity. Riverine input and hydrothermal inputs are generally viewed as point sources: their impact can be very localised. Atmospheric inputs, however can be responsible for the transport of trace metals far from their source, for example, the predominant source of lead to offshore marine locations is via atmospheric transport (Bruegmann *et al.*, 1985). A review of the relative importance of these sources of trace metals is presented below.

Goldberg (1975) estimated that $219*10^{14}$ g of suspended and dissolved river solids potentially enriched with anthropogenic compounds enter the oceans every year. This estimate has recently been recalculated and revised down slightly to $15*10^{15}$ g (Milliman, 1991). However, the input of trace metals and other trace compounds is moderated by interactions that occur at the salt water/fresh water interface. It has been estimated (Balls, 1988) that up to 90% of the trace metals associated with river water are trapped in estuaries. Martin and Thomas (1994) calculate that 75-95% of trace metals are deposited with riverine particulate material on the margins of the world's oceans. The removal of metals from the dissolved phase in estuarine environments is primarily due to adsorption of those metals onto suspended particulate material (SPM) (Balls, 1988): the adsorbed metals are then subject to sedimentation. Since not all trace metals have the same affinity for SPM, this will not be a universal effect. Balls (1988) reported that of the metals studied (cadmium, copper, nickel, zinc, mercury and lead) the most particle reactive metal was lead, while cadmium was the least particle reactive. Patterson *et al.* (1976) observed that for lead 39-56% (in the contaminated coastal waters off California) was associated with particles. In the same study they also demonstrated that the great majority of the lead entering the area was particle associated, with only 11% becoming dissolved in clean seawater.

This view of the estuarine systems of the world acting as filters of anthropogenic trace elements may, however be over-simplistic. Particles and associated metals can be carried across estuaries into open ocean environments. Balls and Topping (1987) found that some metals that were trapped in the Firth of Forth estuary were, over time, flushed out with particles to the North Sea. Once metals have entered the open ocean environment, oceanic circulation and mixing will transport and redistribute metals throughout the water column. The question of particle/water interaction will be discussed in more detail later (section 1.3.2).

Atmospheric transport is the primary dispersive route by which trace metals can enter the marine system away from point sources. It has been proposed that for lead, atmospheric inputs represent the major source to the marine environment (Schaule and Patterson, 1981; Breugmann *et al.*, 1985; Lambert *et al.*, 1991). In a recent paper, Duce *et al.* (1991) synthesized all historical data concerned with atmospheric transport and distribution of trace elements. For the trace metals lead, zinc, and cadmium the concensus was that their transport to the ocean was dominated by atmospheric inputs rather than riverine inputs. In contrast the atmospheric and riverine inputs for copper, nickel, arsenic and iron are in roughly equal proportions. Chester *et al.* (1991) identified different regional and seasonal differences in atmospheric inputs of trace metals to the marine system, and suggested that the source region of aerosol material was an important control of inputs to the ocean. In certain remote areas, such as central ocean gyre systems, atmospheric input may be an important source of trace micronutrients and metals that are limiting to primary production, and may be an important stimulant to production in those areas (Cornell *et al.*, 1995).

The determination of the total concentrations of trace metals associated with aerosol material does not give any indication of what fraction will dissolve in seawater. In this respect it is the solubility of the element once it is in the ocean that determines its fate. It is known that aerosol particles undergo changes during transport through the atmosphere. These changes can affect the subsequent solubility of trace metals from the particles when they enter the ocean. Crecelius (1980), with modification later by Chester and Murphy (1988), divided the elements that enter the oceans from the atmosphere into three groups depending on their solubility in seawater: (i) highly soluble elements which include sodium and bromine (greater than 90% is soluble), (ii) relatively soluble (20-90%), including cadmium, zinc, copper and lead, (iii) slightly soluble and insoluble (<10%), including aluminium, iron, lanthanum and hafnium. Statham and Chester (1988) studied the solubility of manganese associated with aerosol particles in both rainwater and seawater and concluded that the pH of the environment was the determining factor for the solubility of the manganese. Low pH environments would increase the solubility of the manganese (and potentially other elements) in the aerosol.

Hydrothermal vents were first discovered in the late 1970s and are thought to be common at spreading centres on seafloor ridges (Corliss *et al.*, 1979; Edmond *et al.*, 1982). The majority of the vents studied have been located around the North and South American continents and along the mid-Atlantic ridge (Libes, 1992). Trace element distributions in the vent area and from the vents themselves have been the subject of some scrutiny (Humphris, 1978; Malahoff, 1982) and there are now some generally accepted theories regarding the trace metal chemistries around the vents. For example It is known that hydrothermal vents are a source for manganese; indeed one of the methods used to locate hydrothermal activity is the detection of high concentrations of manganese in the lower water column (Klinkhammer, 1980; Hydes *et al.*, 1986). Vent fluids have also been found to be enriched with iron, lithium, barium, nickel and cobalt, although these metals are thought to be rapidly precipitated in the area around the vent or to be taken up by other minerals (Humphris, 1978).

Hekinian *et al.* (1983) analysed vent fluids and made estimates of the concentration of metallic elements entering the ocean around the vents. The estimates were very crude but they calculated that in the region of 100 kg day^{-1} of these metals was coming from the vents to the world's oceans. It is thought that the majority of the trace metals released from the vents is deposited in the area close to the vents (German *et al.*, 1995) and as such may not represent a strong source of dissolved trace metals to the marine environment. The question of the importance of vents on a global scale for trace elements is still unresolved.

1.3 Behaviour and distribution of trace metals in oceanic environments

1.3.1 Trace metal classification

In the open ocean trace metals behave in ways that can be characterised as belonging to one of three groups: (i) conservative metals; (ii) metals that have a nutrient like distribution and; (iii) metals that are rapidly removed from the water column by scavenging processes (Bruland, 1983; Burton and Statham, 1986).

The first group are essentially unreactive metals and their concentration in marine systems is constant relative to salinity: elements such as rubidium and cesium are in this group. These elements have long residence times in the ocean, generally greater than 10^5 years.

The second group of metals are those that show a nutrient type distribution. This group was sub-divided by Bruland (1983) into labile nutrient types, refractory nutrient types and those that show a combination of both types of behaviour. The labile nutrient types have a distribution in the water column like nitrate and phosphate; a surface depletion followed by rapid recycling in the upper waters, below the mixed layer, with a mid-depth concentration maximum. This type of behaviour is reported for cadmium (Boyle *et al.*, 1976; Bruland, 1980; Boyle and Huested, 1983; Kremling and Pohl, 1989), however this association varies from ocean to ocean (De Baar *et al.*, 1994), differences are thought to be due to the mixing of different water masses in the water column and biological cycling effects (Kudo *et al.*, 1996). Metals having a refractory nutrient type behaviour have water column distributions similar to silicate; an example is zinc (Bruland and Franks, 1983). Zinc appears to be associated with the skeletal parts of siliceous organisms and typically shows depletion in the surface layer and regeneration to dissolved forms at depth. Nickel demonstrates a combination of both types of behaviour with both a shallow and deep water regeneration cycle, Boyle and Huested (1983) reported that nickel is correlated with both phosphate and silicate. These nutrient type elements have oceanic residence times that are of the order of 10^3-10^5 years.

Scavenged metals are those that are rapidly removed from waters in association with particulate material in the water column; aluminium is a good example of this type of metal (Measures *et al.*, 1986). Lead has been found to also be readily scavenged in the water column (Lambert *et al.*, 1991; Flegal *et al.*, 1993) and is used in this study as a representative of this type of metal. Due to this scavenging the elements in this group have relatively short oceanic residence times, generally $<10^3$ years.

1.3.2 Metal association with particles and colloids: solid/dissolved phase interactions

From the discussion at the beginning of this chapter, it is evident that there is removal of most of the trace metals from riverine sources flowing into the ocean occurs in the estuarine environment (Balls, 1988). In the open ocean there are processes that occur to prevent the concentrations of trace metals increasing to levels approximating calculated solubility equilibrium conditions. This process was termed the "great particle conspiracy" by Turekian (1977). There are two main sources of particle in the open ocean environment (cosmic dust is a third, but is thought to be a minor component); those produced from biological activity and those derived from crustal sources by direct-fall out from aeolian dust sources (Jickells *et al.*, 1990) or by advective transport from shelf areas.

It appears that those metals exhibiting a nutrient type distribution are probably associated with biologically produced material. Martin (1970) proposed that copepod skeletons falling through the water column removed trace metals by direct adsorption onto the surface of the skeletal material, this direct adsorption was later calculated, by use of models, to be unimportant in the removal of metals from the dissolved phase to the particulate (Balistrieri *et al.*, 1981). This particle adsorption is now thought to occur mainly by uptake onto organic films that coat particles (Balistrieri *et al.*, 1981; Goldberg *et al.*, 1988). Removal of trace metals from the dissolved phase during phytoplankton bloom events is well reported (Noriki *et al.*, 1985; Wangersky *et al.*, 1989), for example Noriki *et al.* (1985) report rapid removal of dissolved cadmium into the particulate phase during a bloom event and that the rate of that removal is dependent on the strength of the biological affinity of the trace metals. Price and Morel (1990) have also reported that cadmium is actively taken up by diatom species and can be used as an analogue for the micro-nutrient zinc. Gonzalez-Davila (1995) discussed the role that phytoplankton have in the control of heavy metals in seawater, the conclusion was that the phytoplankton are able to passively adsorb and actively assimilate trace metals as well as release compounds capable of binding trace metals into the seawater.

Zooplankton can act to remove trace metals from the water column by repackaging the phytoplankton and their associated trace metals into faecal pellets which are capable of sinking through the water column (Cherry *et al.*, 1978; Lambert *et al.*, 1991). Recycling of the metals from these pellets can occur throughout the water column. For example Fisher *et al.* (1991) determined that cadmium and zinc were readily remobilised but other elements such as cobalt and silver had the potential to be carried for thousands of meters to the sediments. The lighter particles as they fall through the water column in the open ocean environment undergo dramatic changes in composition. Up to 95% of the organic matter is degraded in the surface water of the oceans and the result is that material associated with this material is released back to the dissolved phase (Chester, 1990).

Our understanding of the transfer of metals from the dissolved phase to particulate material in the water column has benefited greatly from the investigation of radionuclides in the water column (Broecker and Peng, 1982; Bacon and Anderson, 1982). The original concept was that trace elements were adsorbed onto the surface of particles by a passive processes such as the adsorption by and with hydrous iron oxides on particle surfaces (Hem, 1977). More recently it has been determined that particles in surface waters become covered in an organic coating and these coatings are responsible for the sorption of metals on particle surfaces (Goldberg *et al.*, 1988). Honeyman *et al.* (1988) proposed that the determining factor for the removal of particle reactive trace elements from the water column in open ocean environments was the concentration of particles; and that this was controlled by surface coordination and colloidal reaction chemistries.

The use of the thorium series of nuclides for modeling the removal of trace metals from seawater probably represents an upper limit for the rate of removal; these nuclides are highly particle reactive and other trace elements will not be as rapidly removed from the water column to the particulate phase. Most of the earlier work was concerned only with the adsorption (and subsequent removal of the particles and trace metals associated with those particles) of trace metals from the water column. More recent investigations have been concerned with the reverse of this process, ie. the recycling of the metals from the particles into the dissolved phase, and this has been examined by scavenging models (Clegg and Whitfield, 1990, 1991).

The use of sediment traps has increased our understanding of the interactions between dissolved trace metals and particles, and provided data for models involving the estimation of fluxes of trace metals and other elements from surface waters. Deuser and Ross (1980) first proposed that there was a linkage in the concentrations of falling material caught in sediment traps and the biological processes in the upper water column. By combining these flux rates to the concentration of trace elements in the material it has been possible to estimate the residence times of particulate bound metals in the upper ocean environments (Jickells *et al.*, 1984). There is much debate concerning the accuracy and validity of applying data from sediment traps to any of these scavenging processes and even to the idea that sediment traps represent an accurate determination of upper ocean processes (Gust *et al.*, 1994; Siegel and Deuser, In press).

The definition of dissolved and particulate is purely operational. Commonly the dissolved phase is determined as those metals that are in solution after the sample has passed through a 0.4-0.5 µm filter. There is growing evidence that there are particles and associated trace metals in the water column which pass through these filters and will be defined as dissolved. These particles are colloidal in nature and have size range of 1 nm-1 µm (Muller, 1996), although there are various different size classifications reported in the literature. Often the size class used is dependent on the method used for the collection of the particles, for example Moran *et al.* (1996) use a size grouping of 10000 nominal molecular weight-0.2 µm because they used cross flow filtration to concentrate and collect the particles. These colloidal particles have been found in large numbers (10^6-10^9 l^{-1}) in both Atlantic and Pacific Oceans (Wells and Goldberg, 1991, 1992). They have a very large surface area and so may be important in the removal of trace metals from seawater.

Recent data (Martin *et al.*, 1995) indicates that for some metals, such as iron, lead and manganese, in one inshore basin (the Venice lagoon) greater than 50% of the trace metals formerly designated as dissolved are actually present in association with colloidal material. Similar patterns have been found for estuarine environments (Benoit *et al.*, 1994; Wen *et al.*, 1996). The importance of colloids in the ocean cycling of trace metals is not yet well understood and more studies are necessary to determine how important colloidal material is in open ocean environments.

1.3.3 Redox and photochemical changes in the water column

Changes in the redox conditions in the water column can bring about changes in the solubility of certain "redox sensitive" trace metals. There are areas in the world's oceans where there are anoxic conditions that can result in reducing conditions in the water column, while there are also micro zones around and inside particles undergoing strong organic matter breakdown that are reducing (Libes, 1992).

Manganese and chromium are two metals that are present in oxic and anoxic ocean environments in two stable species; manganese (II) and chromium (III) in anoxic conditions and, manganese (IV) (manganese III is an intermediate but unstable species) and chromium (VI) in oxic environments. The reduced manganese is soluble in seawater whereas the reduced chromium is particulate, oxidised manganese is adsorbed onto particulate material whereas chromium (IV) is soluble in seawater. The behaviour of manganese in the water column and the controlling factors for the distribution of the two species (II and IV) are reasonably well understood. It is thought that there is a photoreduction of the manganese (IV) during daylight periods, possibly mediated by the presence of organic acids or photochemically produced hydrogen peroxide (Spokes and Liss, 1995), followed by the bacterial oxidation back to manganese (IV) during night hours (Sunda and Huntsman, 1990). The control of chromium in the water column and distributions between the two most common redox species (III and VI) are less well understood and will be explored in this study.

The role of photochemistry in trace metal geochemistry in the open ocean is topical and the mechanisms for such reactions are under investigation. As well as the proposed role of photochemistry in the control of dissolved manganese in the upper ocean (Sunda and Huntsman, 1990; Spokes and Liss, 1994) there is discussion concerning the role such reactions have in the control of iron in oceanic environments (Johnson *et al.*, 1994). The importance of photochemistry is only now becoming understood. In this study the potential role that this type of reaction could have in the open ocean distribution of chromium will be discussed in more detail (chapter 6).

1.4 Trace metal behaviour in near-shore environments

1.4.1 Sediment/water column interactions

In coastal areas the interactions between the sediments and the overlying water column are of paramount importance. From the discussion of open ocean environments presented earlier, the binding of metals to particles by whatever method (passive uptake, biological incorporation, etc.) removes the metals from the water column and the ultimate sink for metals in marine environments is the sediment. In coastal areas there is more of a dynamic interplay between the sediment and the water column above that sediment, and the sediments can be both a sink and a source for trace metals. The coastal environment differs from the oceanic environment in that it is usually more biologically productive than the adjoining open ocean environments due to the inputs of nutrients from land run-off and sedimentary inputs during the degradation of organic matter at the sediment/water interface (Gerringa and Cambon, 1991).

The reactions that occur at the sediment/water interface are complex and varied: Santschi *et al.* (1990) present an excellent summary of the multifarious reactions and processes that drive the changes and exchanges that occur at the sediment/water interface. Elements that arrive at the surface of the sediments in association with particles are either held in the sediments or released as the particles are diagenetically altered (Santschi *et al.*, 1990). Metals that are known to have an organic or direct biological relationship in the upper water column are processed along with the organic matter; for example, copper is released from sediments with the degradation of organic matter (Gerringa and Cambon, 1991). For metals to accumulate and be buried in the sediments, they have to be associated with a refractory component and/or be in an area where the inputs of sedimentary material are greater then the rate of diagenetic release of the metals.

Work has been performed to distinguish what phase metals are associated with in sediments. Generally this involves the use of selective extraction procedures. Some of these are simple one stage extraction procedures (Chester and Hughes, 1967) while others are more complex and attempt to determine the phase associations in more detail (Tessier *et al.*, 1979). These leaching methods for the interpretations of geochemical processes in sediment material have come under some criticism (Martin *et al.*, 1987; Nirel and Morel, 1990); the benefits and drawbacks of these methods are discussed in greater detail in chapter 3. This is not to infer that the release of trace metals to the dissolved phase is the only way that metals can be distributed through the environment; direct transport of sediment material in the form of resuspended particulate matter is also thought to be important (Balls and Topping, 1987).

Certain metals such as manganese and chromium are directly controlled by the redox conditions in both sediments and the water column. In sediments that become anoxic, for example, due to the depletion of oxygen by aerobic bacteria in the breakdown of organic carbon, manganese and iron are released into the dissolved phase from sediment particles (Gerringa, 1991). This can also lead to the release of other metals associated with iron and manganese; such as copper and nickel (Sawlan and Murray, 1983). In most sediments that lie below oxygenated waters manganese and iron are released in the lower anoxic sediment and then precipitated at the oxic sediment/water interface, effectively removing other trace metals due to adsorption onto the oxy-hydroxide surfaces of iron and manganese. The differing oxidation rates of iron and manganese {iron being oxidised at a rate greater (Salomons and Förstner, 1984) than manganese (Emerson *et al.* 1979)} can result in a release of reduced manganese into overlying oxygenated waters without an associated release of iron (Dehairs *et al.* 1989).

Changes in distribution of trace metals across oxic/anoxic interfaces can produce useful data for trace metal geochemists. There have been numerous studies performed in anoxic basins aimed at interpreting the geochemical nature of trace metals therein (Lewis and Landing, 1982; Boulegue, 1983; Kremling, 1983b; Dyrssen and Kremling, 1990). There are competing factors at play in the behaviour of trace metals in such environments: the concentration of hydrogen sulphide controls whether the metals are bound as insoluble sulphides (generally lower hydrogen sulphide concentration) or as soluble bi- and poly-sulphides (greater concentrations of hydrogen sulphide) (Kremling, 1983b).

1.4.2 Carbonate sediment systems

The majority of studies concerned with the behaviour of trace metals in marine systems have been performed in those areas that are predominantly siliclastic in nature. Carbonate dominated systems in coastal regions, while uncommon, are not rare yet there are few studies of the distribution of trace metals in such environments. The main source of carbonate material in the environment is the biota. The predominant species in the open ocean are the coccolithophores (Chester, 1990), while in coastal regions such as those found in Bermuda, there are a multitude of carbonate producing organisms, from the free living and attached *Foraminifera* to benthic calcareous algae such as some members of the *Chlorophyta*. The majority of the inshore sediments in Bermuda are dominated by carbonate grains produced by these two families (Pestana, 1993). The carbonates are produced either by directly removing calcium carbonate from the seawater and precipitating it as skeletal material or these primary produced grains are bioeroded to produce secondary grains (Pestana, 1993). The grains once formed are altered in their make-up by the actions of wind and tide and are broken into smaller and smaller pieces, until silt and mud size particles are produced.

There is evidence that in anoxic waters and sediments a shift in the partial pressure of carbon dioxide can result in the dissolution of calcium carbonate (Balzer and Wefer, 1981), with the subsequent release of trace metals associated with them. This process of dissolution of calcium carbonates in sediments is questionable, and there are conflicting views. Sulphate reduction in sediments should lead to an increase in alkalinity and a lower pH according to equation 1.1

$$\begin{aligned} &{}^{1}\!/_{53}(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + SO_4^{2-} \rightarrow \\ &2HCO_3 + HS^- + {}^{16}\!/_{53}NH_3 + {}^{1}\!/_{53}H_3PO_4 + H^+ \qquad 1.1 \end{aligned}$$

This should result in an increase in carbonate precipitation due to the increase in alkalinity (Berner, 1971), but may also produce a dissolution of carbonates in the early stages of the reduction (Morse and Mackenzie, 1990). Although it is thought that the predominant control of many trace metals in the marine environment is by the uptake of metals by organic compounds as coatings on particles or hydrous iron/manganese oxide precipitates (James *et al.*, 1993; Martin *et al.*, 1995), there is some evidence for the direct adsorption of metals onto carbonate grains (Martin and Knauer, 1983; Van Der Wiejden, 1994). Carbonates themselves may therefore play an important role in the geochemistry of certain trace metals, particularly in nearshore or coastal carbonate dominated environments (Wartel *et al.*, 1990).

1.5 Overview of previous trace metal investigations in the Bermuda coastal environment

The largest study of the Bermuda coastal environment was initiated in 1975 by the Bermuda Biological Station. This study was titled the Bermuda Inshore Waters Investigation (BIWI) and continues, albeit in a changed form, today. The BIWI study was a multi-disciplinary attempt to assess the environmental quality of the Bermuda coastal environment (Morris *et al.*, 1977). The study covered a large number of parameters both physical (temperature, salinity currents) and chemical (nutrients, dissolved organic matter), as well as an analysis of the morphology and morphometry of the inshore waters. Barnes and Bodungen (1978) and Bodungen *et al.* (1982) explored the continuation of a reduced BIWI monitoring programme and in-depth studies of certain pollution related topics. Although there was a minor investigation of trace metals as part of this study there was no detailed study of trace metals in the coastal area until Lyons *et al.* (1980) and Lyons *et al.* (1983). These studies were concerned with trace metal fluxes and distributions in the coastal sediments of Bermuda.

Jickells and Knap published two papers that were predominantly concerned with trace metal distribution and control; Jickells and Knap (1984) and Jickells *et al.* (1986). These studies were concerned with trace metal distributions in the water column and underlying sediments. There was no investigation of the interactions between particulate material in the water column and the dissolved trace metals, which would clearly help resolve the role of particles in the cycling of metals between the water column and the sediments.

1.6 Overview of past trace metal investigations in the Sargasso Sea

The largest data set for trace metals in the Sargasso Sea is from the thesis work of Jickells (1986) concerned with the distribution of trace elements at the Hydrostation 'S' site in this area. There have been many other published works concerned with trace metals in the Sargasso Sea (Boyle *et al.*, 1981; Sherrell and Boyle, 1992; Moran and Buesseler, 1992). None of these have considered the distribution of redox sensitive chromium. The only references to the oceanic concentrations of this element in this area are one surface measurement by Sherrell and Boyle (1988), and reference to surface concentrations in a paper by Jeandel and Minster (1987). The study of redox sensitive species in an oligotrophic oceanic environment, such as the Sargasso Sea, should allow a distinction to be made between direct oxygen concentration mediated redox effects and those redox changes brought about by biological mechanisms and/or photochemistry.

1.7 Research objectives

The first research objective was to determine the geochemical behaviour of the trace metals, cadmium, copper, lead, manganese and nickel in coastal waters and carbonate sediments around Bermuda. These metals are important in that they are considered potential pollutants and metals such as cadmium are coming under increasing environmental legislation in other areas of the world (Environment Department, 1987). Bermuda presently has no water quality criteria for the marine environment, although there is pressure to institute a "clean water act". Recent concern over lead and other air pollutants have led to the introduction of a clean air act (Bermuda Government, 1994) with strict standards for the emission of potential pollutants to the local environment.

A sub-objective was to do a detailed study in one of the inshore basins (Harrington Sound) that occasionally undergoes stratification, and becomes anoxic in the lower water column. Concentrations of trace metals in the water column, both dissolved and particulate, were determined. This will allow the investigation of the impact of changing redox conditions on metal behaviour. A laboratory based study of the changes in the geochemical nature of trace metals under periods of anoxia was also performed.

The second main research objective was a study of the oceanic distribution and changing redox state of chromium at an oligotrophic open ocean site in the Sargasso Sea. The control of distribution of chromium between the two main occurring species, chromium (III) and chromium (VI), is not understood. The data produced in this study will be used to determine what the relative concentrations of these species are and what factors control that speciation.

The thesis structure is as follows:

In Chapter 2 a general overview of the sampling locations of the inshore waters are presented.

Chapter 3 reviews the commonly used methods for the analysis of trace metals in seawater and sediments. The methods used in this study are described together with a laboratory based experimental study focused on the uptake and release of trace metals from sedimentary material from two stations on the Bermuda platform.

Chapter 4 discusses the results of the geographic, seasonal and inter-annual distribution of trace metals, nutrients, salinity and pigments around the Bermuda inshore platform. Also presented are the results of the laboratory experiments studying the release and uptake of trace metals by the sediments. Included in this Chapter is a study of the Harrington Sound system, with a seasonal thermocline and periodic anoxia in the lower water column. Data is presented for the mixed conditions in the Sound, when the environment is stratified, and from studies performed using sediment traps.

Chapter 5 describes and discusses an offshore investigation in the Sargasso Sea of the distribution of chromium. Data is presented for an annual study of the distribution of the two commonly occurring species of chromium (III and VI), as well as the distribution of the chromium under spring bloom conditions. Interpretation and discussion of the data is presented and an hypothesis is presented concerning the biological control of chromium speciation in seawater.

Chapter 6 provides conclusions on the work done, and suggests future directions for research.

Chapter 2.

The Bermuda Inshore Environment

2.1 Introduction to Bermuda

The Bermuda islands are formed from an extinct volcano that is thought to be the result of a "hot spot" that moved below the plate approximately 52 million years ago. Bermuda is a chain of between 130 and 150 islands (Morris *et al.*, 1977, Hayward *et al.*, 1991), with a total area of approximately 50km^2. The volcanic mount is now topped by a layer of calcium carbonate (mainly limestone), with a maximum depth of less than 100m. The islands are thought to be the southern ridge of the volcano: this would make the mouth of the volcano where the northern platform area is today.

The submarine platform on which the islands sit, is ringed by a coral reef. The total area of this platform is 720km^2. (See Figure 2.1) The population of Bermuda is estimated to be 60,000 (BDA Govt. 1994), this means that Bermuda, with over 1100 people per km^2, is one of the most densely populated places on earth. In addition there are approximately 600,000 tourists who visit the island each year.

The economy of Bermuda is based upon tourism and international business registration. With the exception of the diesel powered electricity generating plant, and a new (1994) mass burn municipal waste incinerator there are no major industries on the island. Bermuda has no rivers and only very small amounts of standing freshwater, the majority of drinking water is obtained by collecting rainwater from the house roofs and subsequent storage under the homes. Sewage systems in Bermuda are somewhat rudimentary. In general householders have a septic tank underneath the house into which the sewage goes, from where it seeps through the porous rock into the groundwater or the seawater. A good review of this operation and the subsequent potential for groundwater contamination can be found in Simmons (1987). The corporations of St. George's and Hamilton have a rudimentary sewerage system, the sewage is collected, macerated, chlorinated then pumped offshore with no further treatment. The total sewage entering the Bermuda marine zone is around 5.5 million gallons per day during the peak tourist season, this drops to around 3.5 million gallons per day outside of the tourist season.

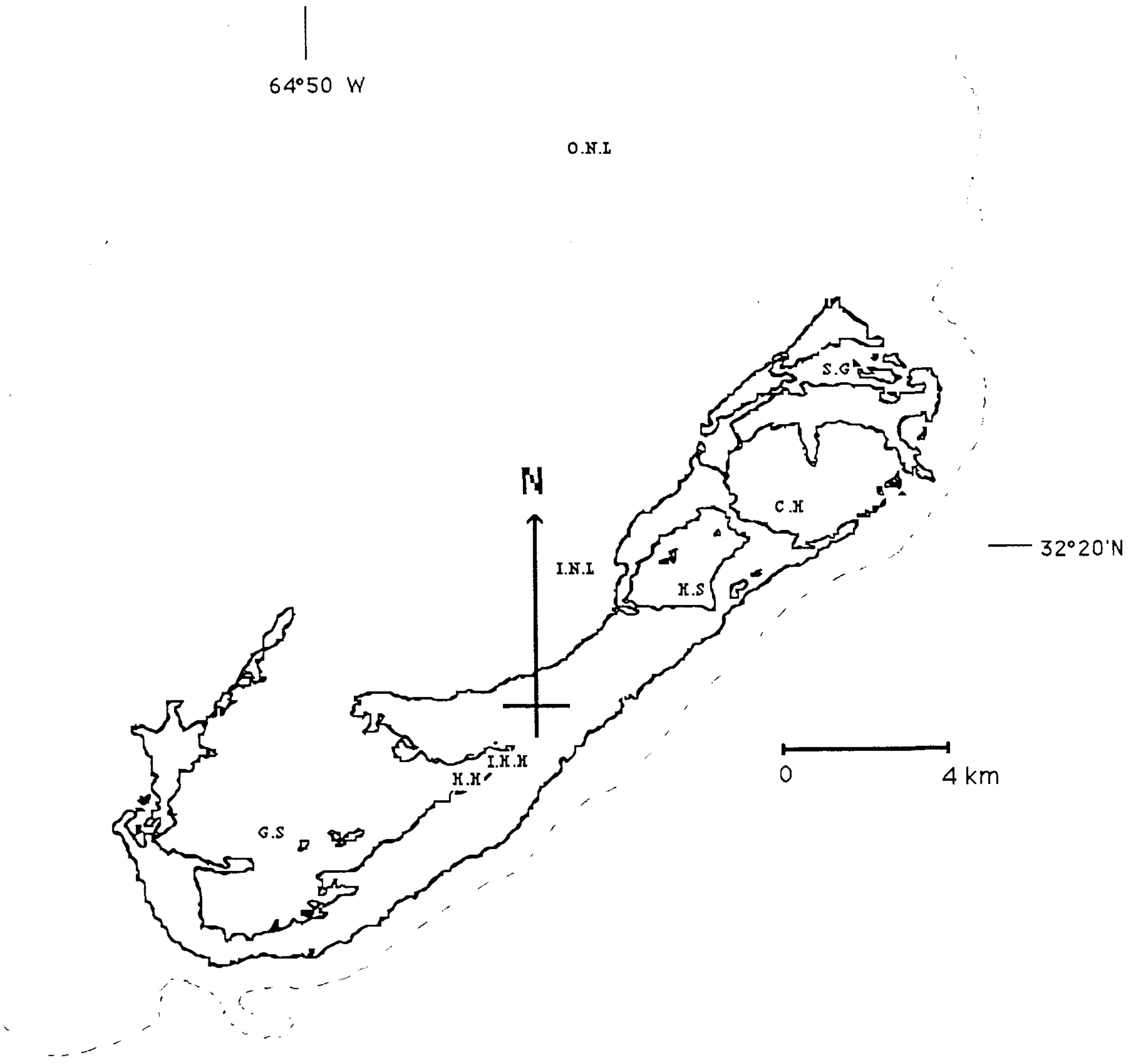

Figure 2.1. Map of Bermuda showing study sites

S.G.- St. George's

C.H.- Castle Harbour

H.S.- Harrington Sound

G.S.- Great Sound

H.H.- Hamilton Harbour

I.H.H.- Inner Hamilton Harbour

I.N.L.- Inner North Lagoon

O.N.L.- Outer North Lagoon

2.2 General hydrological and geological properties of the Bermuda inshore waters and surrounding areas

Bermuda is on an area of weak convergence, between the northwestward flowing equatorial current in the summer months and eddies that arise from the Gulf stream and approach the area from the east in the winter months. Bermuda is in the sub tropical frontal zone (25°N and 33°N) (Bates, 1995), an area of transition between the relatively productive northern waters and the oligotrophic waters to the south of this area. The Sargasso Sea area is one of the most studied areas of ocean in the world, and there are presently two long term projects occurring there, the Bermuda Atlantic Time Series (BATS) and the Hydrostation S programme. These programmes and the results from them are discussed in more detail in the section concerning the offshore distribution and redox mediated speciation changes of chromium.

As one would expect the inshore waters of Bermuda show distinct seasonal patterns in temperature. During the winter months the temperatures can fall as low as 16°C and in the summer can exceed 30°C. Salinity in the inshore areas is dependent on freshwater inputs from rainfall and groundwater inputs.

As previously discussed, the sediments in Bermuda are dominated by biogenically produced carbonates. Bigelow (1905) recognised three sediment types in the Bermuda inshore area:

1. Blue Muds - found in the enclosed inshore areas of Bermuda, these sediments typically have a sparse fauna.

2. White Marls - Found in the deeper areas of the inshore waters, composed of fine sands, very little associated fauna.

3. Shell sands - Found in the shallower areas in the inshore waters, typically very coarse with high numbers of faunal species.

The stations used for this study are those that were used in an earlier study, and form part of the Bermuda Inshore Waters Investigation (BIWI). They were chosen to represent the different inshore marine environments that are found in Bermuda. The sites will now be discussed in more detail on an individual basis.

2.3 Study sites

2.3.1 St. George's Harbour

St. George's harbour was formed as a topographic low between the island dune ridges. The area of the harbour is approximately 2.7 km^2 with a mean depth of 5.9 m and a maximum depth of 16.8 m. The depth at the sampling site is 14 m. Flushing time for the harbour is estimated to be 20 days with a direct exchange with the open ocean through a channel that is dredged for boat traffic, this channel has been widened by 8 m in the summer of 1995.

The sediments are typified by coarse shell sands in the channel entrance, with areas of fine sediments (both blue muds and white marls) in the deeper areas and more enclosed back areas of the harbour.

There is an active boatyard on the North side of the harbour that could offer a direct source of metals into the harbour. The commercial wharf area in St. George (Penno's Wharf), is the main point of discharge for gravel and aggregate that arrives in Bermuda for the building industry. This aggregate can often be bottom ash from incinerators and this, depending on source, could provide metals to the harbour due to runoff from the wharf. The sediments are 2-3 m thick and are composed of fine dark silts with a large proportion of fine white marl (Von Bodungen *et al.*, 1982). The sediments are well mixed due to the large amount of shipping activity that takes place in the harbour. In 1994 there were 131 ships that entered St. George's harbour and 997 visiting yachts.

2.3.2 Castle Harbour

Castle Harbour is a flat bottomed area that is thought to have arisen from reef formation and sedimentation. The area of Castle Harbour is 11.6 km^2 with a mean depth of 7.8 m and a maximum depth of 15.5 m, the study site has a depth of 12.5m. This Harbour is well flushed by waters from both the North lagoon and the open ocean to the south, with an estimated residence time of 23 days. The sediments are dominated by calcareous deposits, mainly shells and coral fragments, with finer silt and clay sized sediments in the deeper areas and directly off the dump site.

There is very little development around the harbour, although there is an airport and a metals dump to the east of the site. The metals dump is a major source of metals to the harbour and there are several studies that have looked at the dispersion of metals from this source. (Barnes and Bodungen, 1982; Jickells and Knap, 1984; Knap *et al.*, 1991). From the summer of 1995 this site is being used as a depository for the concreted ash from the mass burn incinerator.

2.3.3 Harrington Sound

Harrington Sound is one of the most enclosed coastal areas of the island with an area of 4.8 km^2, a mean depth of 20m and a maximum depth of 25m. Due to the enclosed nature of the site the flushing time of the water is 140 days or more (Barnes and Von Bodungen, 1978). The sampling site is situated at the southern end of the sound at Devil's Hole. This is the deepest part of the sound, with a depth of 25m. Devil's Hole is unique to Bermuda in that it has a seasonal thermocline. The water below the thermocline has been known to become anoxic. There are three sedimentary zones recognised in Harrington Sound (Neuman, 1965), dependent on depth.

(i) A shallow sandy zone in waters less than 10m in depth.
(ii) In waters greater than 10m the amount of sand is reduced and fine material increases, this area is sub-divided into an *Oculina* (*Oculina* is a small, generally less than 30cm, branched coral of the order Faviidae) zone in the 10-17m depths, typified by large amounts of *Oculina* debris and mussel shells.
(iii) In waters greater than 17m there is a sub-thermocline zone, where the clay and silt size fractions dominate, the only coarse fractions present are derived from mollusc shell debris.

Harrington Sound will be discussed in more detail in the section regarding the study on Devil's Hole.

2.3.4 Great Sound

The site in the Great Sound is situated to the eastern edge of the channel that continues into Hamilton Harbour. The area of the Great Sound is 24.6 km^2, with a mean depth of 5.7m and a maximum depth of 23.5m, the study site is 15 m deep, The sediments are coarse shell sands although there are areas in the channels and back waters where more fine grained sediments dominate. The flushing time of the Great Sound is estimated to be 22 days with direct exchange to the waters of the North lagoon. The passing ship activity causes the sediments to become well mixed.

2.3.5 Hamilton Harbour

Hamilton Harbour is potentially the area of Bermuda most affected by anthropogenic activities. The area of Hamilton Harbour is 2.7 km^2, and the mean depth in the harbour is 7.3 m, with a maximum depth of 17.1 m. There are two sites of study in the harbour (see Fig 1) which are designated Hamilton Harbour and Inner Hamilton Harbour. Both of these sites have been shown to have elevated metal levels (compared to the North Lagoon area) in previous studies (Jickells and Knap, 1982; Burns *et al.*, 1990). The sediments in the harbour are of a fine particulate nature. As is the case with the St. George site, the shipping activity in the harbour results in the sediments being well mixed.

2.3.6 North Platform

The north platform or lagoon area has an area of 665.4 km^2 with a mean depth of 8.5m and a maximum depth of 22m. The platform is not thought to be subject to any upwelling process, and new computer models of the area support this assumption (Johnson. per. comm.). The currents across the area are predominantly controlled by winds and in the absence of any wind it is a relatively static system.

The platform is dominated by sediments that are coarse shell sand. There are two stations on this platform area chosen for this study. The Inner North Lagoon station is outside the entrance to the inlet that feeds water into the Harrington Sound area. The Outer North Lagoon station is 6 miles offshore almost at the edge of the reef platform, this is thought to be representative of an offshore environment in terms of water borne contaminants.

Chapter 3.

Experimental Procedures

3.1 Aspects of contamination control

Data reported for trace metals in the environment since the 1970s show a decrease in reported concentrations (Topping, 1986). This is due in part to improvements in analytical capability, mostly as a result of advances in "clean" sampling and analytical protocols. This "clean" sampling and analysis is performed with minimum exposure to potential contamination sources.

The two most common forms of contamination that can occur during the collection and analysis of environmental samples are termed adventitious and systematic. Adventitious contamination is caused by such things as: boats used in the collection of samples, the collection vessel itself, and the improper handling of the sample in the laboratory. Adventitious contamination is often indicated by data that has random errors. Systematic contamination is often caused by the use of impure reagents in the analysis of the samples. Systematic errors are commonly those that are non-random in nature. An excellent review of contamination and methods of reducing such contamination can be found in Howard and Statham (1993).

In this study all equipment that was to come into contact with the media to be analysed was thoroughly cleaned using the following protocol.

(i) A wash or soak in Aquet (a non-ionic metal free detergent).
(ii) A Q-Water rinse followed by a soak for a week in 50% HCl.
(iii) A Q-Water rinse and a week soaking in 10% HCl.
(iv) A further Q-Water rinse and a week soaking in 1% Ultrex HNO_3.
(v) A rinse in sub-boiling distilled water (SBDW), and then air dried under a laminar flow hood in the clean room.

Some sample equipment such as pipette tips and collection vials for the back extraction of seawater samples (see section 3.3.2) were stored in 1%(v/v) Ultrex HNO_3 and rinsed in SBDW just prior to use. Nuclepore filters, used for the filtration of the collected seawater, were soaked for 1 week in 2N HCl then stored in a 1% Ultrex HNO_3 solution. Before use they were rinsed in SBDW, dried in a laminar flow hood and weighed in sealed filter boxes. Where possible all procedures were performed in a clean room, and usually under a laminar flow hood within that clean room.

3.2 Sampling methodology

3.2.1 Collection and storage of seawater samples

To reduce the chance of adventitious contamination a pole sampler was used in this study to collect the samples of seawater from the front of the boat. In the laboratory, equipment was used that was composed of Teflon or polyethylene, as these are materials that can be easily cleaned of metals. Recently it has been reported that some of those materials that were previously thought of as having a low contamination potential may be important sources of contamination for certain elements; high density polyethylene (HDPE) has been reported to be a potentially significant source of zinc contamination, as well as chromium and aluminium (Howard and Statham, 1994).

The sampling bottle was placed into the water upside down and inverted to fill at a depth of at least 10cm: this was to avoid collection of the surface microlayer that is known to have higher concentrations of trace elements than the water column below it (GESAMP, 1995). The samples collected were filtered in the clean room through a 0.4 µm Nuclepore filter to remove any particulate matter from the sample, 100ml of SBDW was then passed through the filter to remove any salt residues. The vacuum system used for the filtration of the seawater was that described by Jickells (1986). The samples were acidified with 1ml of Ultrex HNO_3, this serves to maintain the trace metals in solution by mass action. After acidification the samples were stored until they were extracted. This method of storage has been shown to be effective for at least 2 years and does not alter the recovery of metals present (Kremling 1983a). The acidification can lead to the leaching of metals that are in the walls of the HDPE bottles; as a result of this some of the samples were contaminated with zinc, from this and possibly other sources, and this analyte was not determined in this study.

3.2.2 Collection and storage of sediment samples

Collection of the sediment samples was performed by divers: this was better than using a grab sampler as the chances of contamination can be reduced. The samples were collected into clean glass bottles and capped while at the bottom. The sediment was collected from the top 1cm to 3cm by scraping the bottle along the surface of the sediment. Care was taken to ensure that there was minimal contact with dive equipment especially lead weight belts; where possible such weights were plastic coated. This collection could result in the collection of anoxic sediments from lower down in the sediments, this is probably not a problem in the oxic Bermuda sediments, with the exception of Harrington Sound samples.

Samples were chilled when received on deck and then taken to the laboratory, where samples were freeze dried and then ground with a clean agate pestle and mortar to produce a homogeneous sample. Large pieces of debris, such as broken coral branches, were removed before grinding. Samples were stored in pre-cleaned resealable polyethylene bags until analysis.

3.2.3 Collection of ancillary data

3.2.3.1 Physical parameters

Temperature was analysed at each site using an electronic thermometer (± 0.1°C) and recorded along with the weather conditions. Boating activity in the area was recorded as was any recent ship passage. This may be important as it resuspends the bottom sediments. Secchi depth samples were recorded with a 0.5m secchi disc.

3.2.3.2 Salinity samples

Samples for salinity analysis were collected into 250ml borosilicate glass bottles. The screw thread was wiped with a low lint tissue after sampling to reduce the chance of salt crystal formation around the cap which could result in evaporation of the sample due to an improper seal. The bottles were then tightly capped. The caps for the bottles have a plastic insert to improve the sealing process. The samples were kept at room temperature until analysis, generally within 2 weeks. Determination of salinity is discussed later in this chapter.

3.2.3.3 Nutrient samples

Samples for nutrient analysis were collected in 60ml amber bottles. The samples were chilled on deck and frozen immediately on return to the laboratory. The analysis of these samples was performed within 1 month. The determination of nutrients is discussed later in this section.

3.2.3.4 Chlorophyll samples

Sample collection for analysis of chlorophyll involved the collection of 2 litres of seawater. The samples were filtered on deck through 45mm Whatman GF/F filters. The filters were folded, placed into foil envelopes and chilled on the boat then stored in liquid nitrogen in the laboratory until analysis. Chlorophyll analysis is presented later in this chapter.

3.3 Analysis of seawater for dissolved trace metals

3.3.1 Introduction

The presence of large amounts of interfering elements in seawater coupled with extremely low concentrations of the analytes of interest presents the analyst doing trace metal determinations in the water column with a difficult and complex problem. Advances in analytical instrumentation have resulted in a variety of methods that can be used to determine the concentrations and phase associations (i.e. solid/dissolved, complexed/non-complexed) of trace metals. Some of the more commonly used methods of analysis are graphite furnace atomic absorption spectroscopy (GFAAS) after preconcentration and separation of the metals from the seawater (Jickells and Knap, 1984; Statham, 1985; Backstrom and Danielsson, 1990), flame atomic absorption spectroscopy (Sturgeon, 1989), electrochemical techniques such as anodic stripping voltammetry (ASV) and cathodic stripping voltammetry (CSV) (e.g. Riso *et al.*, 1990; Skwarzec *et al.*, 1988; Van Den Berg, 1986; Muller and Kester, 1990), inductively coupled plasma-mass spectroscopy (ICP-MS), X-ray fluorescence (XRF), instrumental neutron activation analysis (INAA) and stable isotope dilution spark source mass spectrometry (SIDMS) (Mykytiuk *et al.* 1980.).

The most widely utilised technique is atomic absorption spectroscopy (AAS); both flame and graphite furnace modes. Although direct analysis using GFAAS and flame AAS has been reported for the analysis of contaminated seawater in the past (Sturgeon, 1989; Hoenig *et al.*, 1991), the low levels of the elements of interest combined with the high levels of interfering ions often do not permit a direct determination of metals in seawater from relatively uncontaminated environments.

To overcome these problems, methods must be developed that allow the concentration of the analytes of interest and remove the interfering matrix. Commonly used methods are: (1) ion exchange resins, both in column methods and batch extractions (Fang *et al.*, 1987,1988, 1990; Pai, 1988; Pai *et al.*, 1988; Vermieren *et al.*, 1990; Kantipuly *et al.*, 1990; Blain *et al.* 1991: Baffi *et al.* 1992); (2) coprecipitation methods such as cobalt/ammonium pyrrolidine dithiocarbamate (APDC) (Boyle and Edmond, 1977; Boyle *et al.*, 1986); (3) complexation followed by collection on resins (King and Fritz, 1985; Van Geen and Boyle, 1990; Lui and Huang, 1992); and (4) a variety of chelation-solvent combinations, such as APDC/Methyl IsoButyl Ketone (MIBK - new nomenclature 4-methyl-2-pentanone) (Sturgeon *et al.*, 1980) and APDC-diethylammonium diethyldithiocarbamate (DDDC)/Freon (Tappin, 1988). A review of these methods can be found in Hall (1991). Dithiocarbamate derivatives, such as APDC/DDDC, are the most widely used complexing agents, although the solvent used to separate the complexed metals varies.

Since the initial use of 4-methyl-2-pentanone by Kinrade and Van Loon (1974), there has been some discussion pertaining to the accuracy of using MIBK as a solvent (for trace metal determination) since seawater is somewhat soluble in MIBK, and there is a risk of matrix transfer to the final extract (Magnusson and Westerlund, 1981). Freon TF (1,1,2 trichloro-1,2,2, trifluoroethane) has been used as the solvent phase since it is inert, has a low solubility in water and is non-toxic (Tappin, 1988; Hall 1991). Chloroform has been used successfully as a solvent for metal/complex extraction in Bermuda (Jickells and Knap, 1984; Jickells, 1986) and elsewhere (Bruland *et al.*, 1979). Magnusson and Westerlund (1981) showed that when using chloroform it was important to increase the time taken during the back-extraction step, this was because the dithiocarbamates are more stable in chloroform than in other used solvents.

Within the Montreal Protocol, signatory countries are expected to phase out the use of chlorofluorocarbon compounds and other radiatively important trace species (RITS) (Ozone Secretariat, 1993). Bermuda is one of the signatories of the protocol and as such it was decided that the APDC/DDDC-freon system should not be used. Instead an APDC/DDDC-chloroform technique, with back extraction into nitric acid, was used in this study. This has been proven to be successful in the past (Jickells and Knap, 1984). Care was taken with chloroform due to its suspected carcinogenic effects; with such consideration in mind chloroform proves to be an acceptable solvent.

3.3.2 Analytical procedures

3.3.2.1 Preparation of chemicals

Sub-boiling distilled water (SBDW)

Sub-Boiling Distilled Water was produced in the laboratory using a Quartz system similar to that described by Tappin (1988). Milli-Q water is poured into a quartz flask where it is heated by the action of two infra-red lamps. The water evaporates, condenses on a quartz cold finger and then drips through a collection tube and into a bagged clean Teflon bottle. This system was set up in a clean room environment to reduce possible contamination problems. Since fresh water is in short supply in Bermuda, a recirculating system using ice cooled fresh water was established rather than using a mains supply water system.

Isothermally Distilled Ammonia solution (ID-NH_4OH)

The ammonia solution used for the neutralisation of an acidified seawater sample was prepared from analytical grade ammonia solution. A FEP beaker containing SBDW was placed in an airtight container with a beaker of analytical grade ammonia, and left for approximately two days, after which replacement fresh ammonia solution was put in place. During this time the ammonia partitions between the SBDW and the ammonia solution and forms ID-NH_4OH. This was then decanted into a FEP bottle, capped and stored until use.

Chloroform

HPLC grade chloroform was cleaned by adding 20 ml l^{-1} of 50% HCl; this mixture was shaken and the acid discarded. This process was repeated twice. The chloroform was then washed with 20-30 ml of SBDW three times to remove any remaining acid. The clean chloroform thus produced was stored in a glass (amber coloured) and Teflon dispenser, a pump mechanism is used to dispense the chloroform, all parts of the pump are glass or Teflon.

Mixed Complexant

The mixed complexant used in the extraction of metals from seawater samples was prepared using a solution of 2% (w/v) analytical grade APDC and 2% (w/v) DDDC, in 3.5% (w/v) NaCl. The complexant is made up into a NaCl solution because this has been shown to convert any cadmium in the solution into a colloidal form which is then removed in the next stage (Tappin, 1988). The solution was filtered through a Whatman #1 filter paper, the filtrate was collected and poured into a teflon separatory funnel. 5ml of the purified chloroform was added and the funnel shaken for 6 minutes, the chloroform was then discarded. This process was repeated three times to ensure complete removal of metals. The complexant was stored in a teflon bottle, refrigerated, and used within 24-36 hours.

3.3.2.2 Preconcentration and removal of trace metals from seawater

Using a plastic frame it was possible to manually shake 10 samples simultaneously, this usually meant that 8 samples and 2 blanks could be extracted for each process run. All of the FEP separatory funnels (and other equipment used for this method) were cleaned by the procedure outlined in section 3.1. As an additional contamination control measure the funnels were also taken through an extraction run. This involved adding 4ml of the mixed complexant and 7ml of the chloroform to the empty funnels. The funnels were shaken for 6 minutes and then the contents discarded. This process was performed after each set of 10 samples had been run.

A sample of 70ml of seawater was placed into each funnel; 2 were left empty at this stage, these were the blanks for each run. Since the samples of seawater were acidified it was necessary to bring the pH to the optimum range for the trace metal complexation (8-8.5). Sub-samples of the seawater were removed, generally 20ml, and taken for pH analysis. The amount of ID-NH_4OH necessary for the required pH change was measured and the amount needed for the 70ml samples was calculated. This amount was then added to the seawater samples: the operational blanks did not receive this ammonia. The funnels were shaken thoroughly to ensure total pH equilibration. Mixed complexant (4 ml) was added and the samples were shaken. Chloroform was then added (7ml), and the funnels were closed and shaken for 6 minutes. Shaking was interrupted once to open the funnels to allow the release of pressure that had built up. The funnels were then left for 5 minutes for the aqueous layers to separate. The chloroform layer was poured into screw-topped plastic vials and care was taken not to allow any transfer of the seawater into the vials at this time. A further 4ml of chloroform was added to the funnels, they were then closed and the shaking process was repeated. The second chloroform aliquot was combined with the first and the vial closed. The seawater in the funnels was then discarded and the funnels cleaned as outlined above.

Due to the unstable nature of the chloroform (evaporative loss being the major problem) the extracts were subjected to a back extraction process. This removes the metal ions from the solvent and leaves them in an acidic solution which is more stable than the original solvent. There are basically two methods for doing this: the solvent can be evaporated and then the residue taken up into a small amount of acid; or more commonly, acid is added to the solvent and the metals are removed from the solvent and carbamate complex. The evaporation method can result in the loss of volatile metal ions such as lead and potentially cadmium.

The back extraction was investigated to determine the optimum efficiency. There was discussion by Magnusson and Westerlund (1981) concerning the optimal time necessary to remove the metals from the solvent/complexant mix when using chloroform as the solvent. To determine the efficiency of the back extraction triplicate samples of NASS 2 certified reference material (National Research Council, Canada) were analysed in the usual way as outlined above, the samples were back extracted into a nitric acid solution. The back extraction was performed three times and the aliquots of nitric acid were analysed separately, the data for the analysis is shown in Figure 3.1 for the trace metals copper, nickel and lead, recovery is on a cumulative percentage basis.

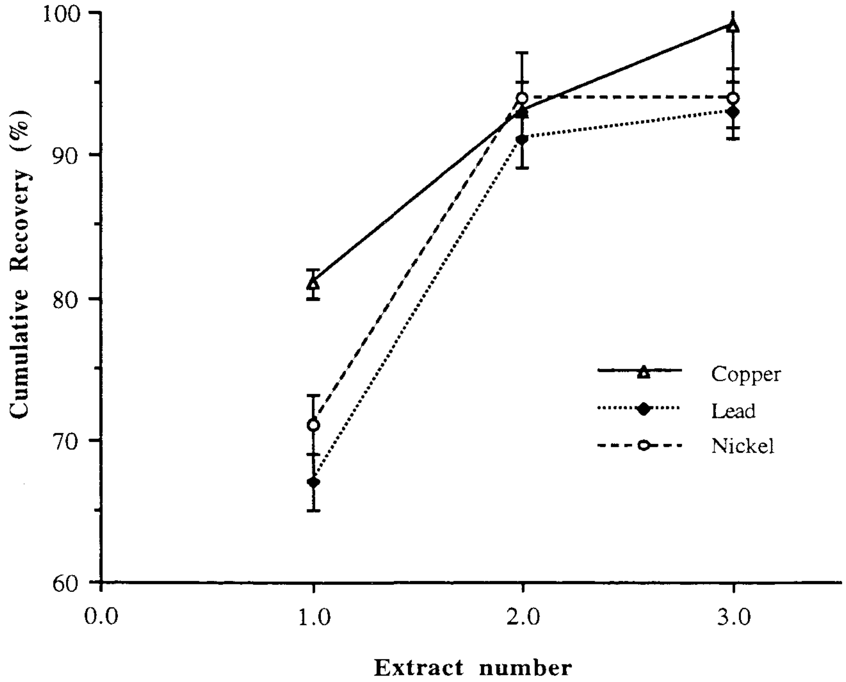

Figure 3.1. Cumulative recovery for copper, lead and nickel using sequential back extractions (error bars are ± 1 s. dev.).

From this Figure it can be seen that the back extraction has to be a two stage process to enable full recovery of the analyte of interest. A three stage process is not thought to be necessary as generally less than 5% of the analyte remains in solution, and each extraction step increases the potential for contamination.

The optimised back extraction was performed by adding 20µl of concentrated nitric acid to the vials containing the solvent phase. The vials were shaken for 6 minutes and then

180µl of SBDW was added to the vials and they were subjected to a further 6 minutes shaking. The vials were then allowed to stand for 5 minutes after which time the acidic aliquot on the surface of the solvent was removed by pipette to a clean polyethylene vial. The process of acidification and shaking was repeated and the two aliquots of the acidic metal containing solution were combined. 1 ml of SBDW was then added to the vials to bring the final concentration to 1.4ml, producing a concentration factor of 50. The vials were labeled and closed, placed in tray, bagged and stored in a refrigerator to reduce the potential for evaporative loss and contamination.

3.3.2.3 Determination of trace metals in seawater by Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)

All of the seawater extracts were analysed for trace metals using GFAAS. A Perkin-Elmer 1100B AAS equipped with an HGA-700 graphite furnace and an AS-70 autosampler was used. All analyses were performed using pyrolytically coated L'Vov platforms and tubes. The programmes used in the determination of trace metals are shown in Table 3.1.

Element	Cadmium	Copper	Lead	Manganese	Nickel
Wavelength	228.8	324.8	283.3	279.5	232.0
Lamp energy	4	15	10	20	25
Drying °C	140	140	140	140	140
Ramp (sec)	15	15	15	15	15
Hold (sec)	15	15	15	15	15
Ashing °C	850	1000	700	1400	1400
Ramp (sec)	20	20	20	20	20
Hold (sec)	10	10	20	15	10
Standing °C	20	20	20	20	20
Ramp (sec)	5	5	5	5	5
Hold (sec)	4	4	4	4	4
Atomisation°C	1650	2300	1800	2200	2500
Ramp (sec)	0	0	0	0	0
Hold (sec)	3	4	3	3	3
Clean °C	1800	2500	2000	2400	1650
Ramp (sec)	2	2	2	2	2
Hold (sec)	3	3	3	3	3

Table 3.1. Programmes used for GFAAS analysis.

A mixed stock standard was prepared from commercially purchased atomic absorption standards. This was 100 $\mu g\ l^{-1}$ of each metal and was referred to as the stock standard. On a daily basis, working stock standards were prepared to a concentration of 10 $\mu g\ l^{-1}$. This was used for calibration of the instrument. The working stock was used for the primary standard on the GFAAS. The auto sampler was programmed to produce serial dilutions of this working stock. Matrix modification was utilised where the recommended by the manufacturer. All analyses were performed with deuterium arc lamp background correction. All data was produced in hard copy and then converted to nmol l^{-1} using a computer spreadsheet programme. Each concentrate was analysed in triplicate on the AAS; any sample that had a relative standard deviation (r.s.d) greater than 10% within the triplet was re-analysed.

3.3.3 Quality control procedures for the analysis of trace metals in seawater

For every set of analyses performed, an analysis of the certified reference material NASS 2 was performed (National Research Council, Canada). This was analysed as if it were a sample and all procedures were the same as for a sample. This material was also preserved with nitric acid in the same way as were the samples in this study. Blanks were determined in the way outlined in the extraction procedure by running an extraction process with just chloroform and the mixed complexant. The limit of detection for the procedure is calculated as three times the value of the standard deviation value for the blank. The quality of the standards prepared in this laboratory were checked using commercially purchased detection limit control samples from Perkin Elmer Corporation. This laboratory is also part of a United States Environmental Protection Agency intercomparison study for the analysis of trace metals in freshwater. Although this is a non-marine water study it serves as a good check of the efficiency of the GFAAS analysis and standard preparation. A summary of data for the quality control programme for this study can be found in Table 3.2.

Element	Blank result (Between batch)	Recovery of metals from NASS 2	Precision data (Between batch)	Detection limit (Between batch)
Cadmium	0.04±0.03	92.50%	0.75±0.08	0.09
Copper	0.16±0.14	102.70%	10.34±1.35	0.42
Lead	0.07±0.01	92.30%	0.15±0.01	0.03
Manganese	0.10±0.10	90.90%	3.57±0.42	0.3
Nickel	0.43±0.15	95.70%	1.72±0.44	0.45

Table 3.2. Blanks, Recovery, Precision and detection limit for seawater analysis (nM, ± values are 1 standard deviation values n=5).

3.4 Analysis of sediments for trace metals

3.4.1 Introduction

Any discussion of the trace metals in seawater in a shallow coastal environment must also consider the distribution and concentrations of trace metals in the sediments below these waters, and in the suspended particles in the water column. Bottom and suspended sediments are considered to be the most important controlling factor for trace metals in such environments, as they can potentially act as both a sink via the interaction of the dissolved trace metals with the particles in the water column, or a source through benthic releases (Santschi *et al.*, 1990). The interactions between dissolved trace metals in the water column and particles within the water column are complex, as they are controlled by factors related to the suspended particulate material such as composition of the particles, and size (Burton *et al.*, 1993). There is also a strong argument that those metals presently described as dissolved, may be partly bound to colloidal sized suspended particulate matter (Benoit *et al.*, 1994a) that passes the presently used 0.45μm filters, but can be important in the subsequent removal of trace metals to the sediments (Martin *et al.*, 1995).

Bermuda sediments are predominantly calcareous in nature. The source of the sediment material is primarily biological, with the most important species producing the sedimentary grains being *Halimeda, Foraminifera* and *Penicillus*. Calcareous remains of these species can represent up to 80% of carbonates in some locations around Bermuda, the remainder being composed of carbonates from other species, organic matter and unidentified sedimentary material (Pestana, 1993).

There have been several different approaches for the determination of trace metals in sediments. Loring and Rantala (1988, 1990) recommend a total digestion using hydrofluoric acid in association with another mineral acid (in a Teflon pressurised digestion vessel, commonly known as a "bomb"). Their reason for a total analysis is the inability of other commonly used acids (nitric, nitric/perchloric, and aqua regia) alone to digest the silicates and other refractory oxides. However other investigators (Jickells and Knap, 1983; Krumgalz and Fainshtein, 1989) have used nitric acid alone and their results show high recoveries and precision for this technique. In particular Krumgalz and Fainshtein (1989) presented a series of experiments that used a certified reference material and showed no significant difference, with the notable exception of iron, between experimental results and reference material concentrations. The iron is most likely incorporated in the silicate lattice, which is not fully decomposed by nitric acid. Since the sediments in Bermuda are dominated by calcareous material and a supply of ultrapure nitric acid was available (Baker Ultrex II), it was decided to use Teflon "bombs" with nitric acid as the digestion agent. A similar approach was taken by Jickells and Knap (1984), and in a later study (Knap *et al*, 1991) in which data was included showing good recovery of trace metals from certified reference material.

Of prime importance to the majority of environmental scientists is not the total metal content in sediments but the environmental availability of those metals. The availability of metals to the environment and the organisms within it is thought to be predominantly determined by the phase association that the metal has within those sediments. The metals can be absorbed directly onto the surface of particles (Calmano *et al.*, 1992) in association with iron/manganese oxy-hydroxides (Hem, 1977) bound to the carbonate fraction in sediments (Morse, 1986), associated with the organic matter in the sediments (Balistrieri *et al.*, 1981), associated with sulphide minerals (Morse, 1994), or lattice bound with the silicates in the sediments. Experimental methods have been sought that enable the differentiation of the phase association of the metals within the sediments (e.g. Chester and Hughes, 1967; Tessier *et al.*, 1979; Rosental *et al.*, 1986). These can be a simple one stage digestion (Loring and Rantala, 1990) or a sequential multiple chemical attack (Tessier *et al.*, 1979; Valin and Morse, 1982; Kumar, 1987; Hirner, 1991; Rule and Alden, 1992).

One of the earliest investigations of this type was the work by Chester and Hughes (1967). They used a mixture of acetic acid and hydroxylamine hydrochloride to distinguish between metals held in various phases in the sediment. Thus they separated those trace metals associated with ferro-manganese compounds, carbonates, and adsorbed onto mineral surfaces, from the more strongly held metals in association with organic matter and those that can be termed "residual" (probably mainly within the alumino-silicate lattices in the sediments). This approach to the selective removal of metals from the sediments was also tried by later investigators (Tessier *et al.*, 1979; Rosental *et al.*, 1986; Rule and Alden, 1992), often with changes and additional leaching agents to identify further the metal/sediment interactions. Tessier *et al.* (1979) in particular pursued a more elaborate path. They attempted to separate the metals from the sediments into five fractions:

(1) Exchangable: the metals were extracted by mixing the sediment with magnesium chloride solution at room temperature for one hour.

(2) Carbonate bound: the metals were extracted by leaching the sediment with 1M sodium acetate (pH 5 adjustment made with acetic acid) at room temperature and with continuous agitation.

(3) Iron/manganese oxide bound: the metals were extracted using either a mixture of 0.3M sodium thiosulphate, 0.175M sodium citrate and 0.025M H-citrate, or a 0.04M hydroxylamine hydrochloride solution in 25% (v/v) acetic acid. This was performed at 96°C, and under constant agitation.

(4) Organically bound: the metals were extracted using a mixture of nitric acid and hydrogen peroxide at 85°C, followed by the addition of 3.2M ammonium acetate in 20% (v/v) nitric acid.

(5) Residual: the remaining metals were extracted using a mixture of hydrofluoric and perchloric acids.

Recently this analytical procedure has been criticized (Rapin *et al.*, 1986; Martin *et al.*, 1987; Kersten and Forstner, 1987; Nirel and Morel, 1990; Hirner, 1992). The main objections arise from the pretreatment and sample collection of the sediments which can result in changes in the partitioning of metals in sediments, as well as the potential for metals to redistribute to different phases during the chemical attack. Kheboian and Bauer (1987) noted that the sequential extraction regimes used may not be totally specific for the phases of interest and there could be possible problems in the interpretation of any data produced from sequential extraction techniques. This is particularly likely when the more selective methods are used, such as the Tessier *et al.* (1979) multi-stage sequential attack.

The commonly employed methods of collection can result in changes in the oxic state of the samples, as can the common preservation techniques (freezing, air drying, oven drying and freeze drying). Rapin *et al.* (1986) investigated the effect of various pretreatment regimes on the recovery of trace metals from the sediments. They recommended that the best method for sample storage (if the sample cannot be analysed immediately after collection) was freezing or short term wet storage at 1-2°C. They determined that the fractions most susceptible to change were fractions 1 and 2 in the sequential extraction suggested by Tessier *et al* (1979).

The present knowledge of trace metal distributions between various phases in carbonate dominated systems is minimal. The only study for which there is any data regarding an investigation of carbonate systems by use of a sequential extraction method is that of Ripley (1992). This study looked at the phase association of the trace metals, lead, cadmium, nickel, copper, zinc and iron, in sediments taken from the Bermuda platform area. The study used the same sequential extraction technique as that employed by Tessier *et al.* (1979).

As pointed out by Martin *et al.* (1987), these methods may not give a realistic view of the bioavailability of metals in sediments; however they can give an operationally defined distribution of the metals. Unfortunately there is little data in the literature that has used certified reference material and presented the results of any of the sequential extraction procedures. Loring and Rantala (1988) report the results of an intercomparison exercise for trace metals. In this paper there was data presented for the extraction of certified reference material in dilute (25%v/v) acetic acid. The conclusion was that the results for the intercomparison were unacceptable for this type of extraction due to the lack of precision in the results. Krumgalz and Fainshtein (1989) also presented the results of the extraction of certified reference materials using the hydroxylamine hydrochloride/acetic acid method. As one would expect, the values were lower than the reported total values. Unfortunately there was no further discussion of this aspect of the data.

The conditions for the experiments must be controlled so that there is no variation in, e.g., the time for the extraction, the temperature for the extraction and the size class of the sediment sample analysed. In most of the reported studies there are similarities in the sample procedure but the differences could be extremely important. One good example of this is a comparison of the sequential extraction methodologies used by Tessier *et al.* (1979) with that used by Rosental *et al.* (1986). Tessier *et al.* (1979) used the sequential technique outlined above, consisting of a 5 stage attack, whilst Rosental *et al.* (1986) used a three stage attack that effectively groups the first three defined fraction of Tessier *et al.* (1979) into one group; the two remaining fractions are the organic (and sulphidic) fraction and the residual. The sediments in these two studies are very different, one is riverine sediment (Tessier *et al.*, 1979) and the later study uses a marine sediment. While it is useful to compare studies it must be remembered that there are different conditions used at all stages of most of the published sequential extraction methods. Discussion and comparison of data obtained from different studies must be interpreted with care, and only in a general sense.

For this present study, an investigation of the partitioning of trace metals in the sediments was undertaken. In light of the arguments listed above (with relation to multi-stage extraction techniques) a simpler sequential technique was investigated, namely the hydroxylamine hydrochloride/acetic acid extraction discussed by Chester and Hughes (1967, see above). The data presented by Rapin *et al.* (1986) indicated, with reference to Tessier *et al.* (1979), that if the samples are freeze dried there should be no change in the recovery of metals in fraction 3. Since this method will leach those metals described as fractions 1 and 2, as well as the metals associated with fraction 3, there should be few problems with freeze drying the sediments.

3.4.2 Analytical procedure for the analysis of total trace metals in sediments

3.4.2.1 Preparation of chemicals

The only chemical used in the determination of total metals in sediments is Ultrex nitric acid. This is commercially produced and has a certified low trace metal content.

3.4.2.2 Digestion procedure for total trace metals

Approximately 0.5g of homogenised sediment is weighed accurately into to a clean teflon digestion bomb. Sufficient Ultrex nitric acid is added to the bomb in a dropwise manner to stop the sedimentary material effervescing; this is performed in the clean room. Due to the calcareous nature of the sediments around Bermuda, this addition of acid causes the samples to effervesce and it is necessary to be careful to prevent the sample from effervescing out of the bomb. On occasions when this happened the sample was discarded, a clean bomb chosen and the process restarted. It generally took around 1 hour to add around 1ml of the acid to the bomb. The actual amount of acid added was not critical as correction for volume is performed after digestion. The bombs were then sealed and heated at 120°C for at least 6 hours. The samples were commonly left overnight in the oven. After this time the bombs were removed from the oven and allowed to cool at room temperature. The bombs were carefully opened and then Q-water added to the acid mixture. The solution was then poured into a polyethylene storage vial and weighed. The final weight of the solution was recorded. The samples were generally clear at this stage: only for the Hamilton Harbour and St. George's Harbour samples was there residual material in the samples. This was a small fraction (<0.1%) of the original sample weight. Blanks were produced by passing acid through the process, in all cases the blank produced undetectable concentrations of the metals studied.

3.4.3 Analysis of sediments for labile trace metals

3.4.3.1 Preparation of chemicals

Acetic acid

Ultrex grade acetic acid was purchased commercially. A 35% (v/v) solution was made using SBDW in the clean room and the solution stored in clean teflon bottles.

Hydroxylamine hydrochloride solution

A 25% (w/v) solution of pure hydroxylamine hydrochloride was prepared using SBDW, into a teflon bottle. The original Sigma chemical was found to be contaminated with zinc and cadmium, various suppliers were tried and the Baker 99.9% grade was found to be the least contaminating.

Mixed reagent

A mixed reagent of 150ml of the hydroxylamine hydrochloride solution and 350ml of the acetic acid solution was prepared and stored in a FEP bottle.

3.4.3.2 Extraction procedure for labile trace metals in sediments

The sediments were freeze dried and ground. Approximately 0.5g of the sediment was accurately weighed into a 50ml conical centrifuge tube and 25ml of the mixed reagent was slowly added to the tubes. The sediment effervesced, as it did with the nitric acid digestion due to the high carbonate content, so the addition of the mixed reagent was performed slowly. The tubes were left open in the clean room until the frothing had ceased (generally 1-1.5 hours). The tubes were capped and shaken on a wrist shaker for 4 hours. The tubes were then centrifuged using a lab top centrifuge (5000 rpm) for 15 minutes and the supernatant poured off into 50ml teflon beakers. 1ml of Ultrex nitric acid was added and the samples were evaporated on a hot plate in the clean room to near dryness. The samples were diluted with 10ml of SBDW. and analysed in the same way as the samples for total metals (see next section). The matrix that remains is acidic (pH approximately 2.5).

3.4.4 Determination of trace metals in leach and total digest samples by Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)

Standards were prepared in the same manner as outlined in Section 3.3.2.3. The analysis of the samples was performed by the method of standard additions. This was thought to be necessary due to the complex nature of the matrix that was produced by the digestion process. The autosampler was programmed to perform this standard addition analysis. This method of analysis produces a 4 point calibration curve for each sample and as such replication of the analysis for the samples is unnecessary.

The GFAAS analysis was performed using the same programmes given in Table 3.1. The solution data was converted to µg/g of sediment using a spreadsheet programme which takes into account the initial sediment weight digested and the final volume of digest.

3.4.5 Quality control procedures

Quality control for the determination of total metals in the sediments was performed in three ways. The first was the use of the certified reference material MESS 1 (National Research Council, Canada). This was analysed in the same way as the samples. There are no reference materials for calcareous sediments. Blank estimates were made using clean Teflon bombs, adding the acid and treating this solution in the same way as samples. Recovery estimates were produced by analysing samples from the certified reference material MESS-1, five times. Precision data was obtained by analysing a sample of Bermuda sediment five times. The data for these procedures are found in Table. 3.3.

Element	MESS-1 Certified values	MESS-1 Measured Conc.	Blank data	Precision data	Detection limit
Cadmium	0.59±0.1	0.53±0.02	0.01±0.02	0.49±0.02	0.06
Copper	25.1±3.8	23.3±0.63	0.01±0.01	7.76±0.21	0.03
Lead	34±6.1	32.3±0.84	0.07±0.01	7.70±0.2	0.03
Manganese	513±25	490±0.4	0.02±0.08	11.2±0.4	0.16
Nickel	29.5±2.7	31.7±1.9	0.02±0.01	1.33±0.08	0.3

Table 3.3. MESS-1 certified values, measured concentrations, blank data, precision data and detection limits (3 times the std. dev. of the blank) for the determination of trace metals in sediments (all data $\mu g\ g^{-1}$, n=5, ± 1 standard deviation).

The generally lower recoveries for the metals (with the exception of nickel) probably reflect incomplete recoveries from silicate lattices not destroyed by the digestion process.

The main problem with any quality control assessment for the labile metal extraction system is that there is no available certified reference material. Blanks are determined by taking the chemicals through the process and then analysing for concentrations of metals. Precision for the method is estimated by analysing subsamples from the same sediment sample a number of times (St. George's Harbour). The data for the precision and blank determination are in Table. 3.4.

Element	Blank data	Precision data	Detection limit
Cadmium	0.06±0.07	0.26±0.06	0.21
Copper	0.05±0.01	1.65±0.03	0.03
Lead	0.03±0.02	7.33±0.09	0.06
Manganese	0.05±0.02	58.1±1.8	0.06
Nickel	0.01±0.03	1.36±0.04	0.09

Table 3.4. Blank determination, precision data and detection limit for the partial extraction method (all data $\mu g\ g^{-1}$, n=5, ±1 standard deviation).

3.5 Collection and analysis of suspended particulate material for trace metals

3.5.1 Introduction

Chapter 1 discussed the potential role that falling particles have in the removal of trace metals from the water column. With this in mind an investigation of the trace metal loading of the particulate material in the Bermuda inshore waters was undertaken.

3.5.2 Collection of samples

The seawater samples collected for dissolved trace metals were filtered through 0.4μm Nuclepore filters. These filters were previously dried in the clean room, weighed on a Cahn microbalance and stored in polycarbonate filter holders. The samples were filtered in the clean room as described in section 3.2.1. The rinsed filters were returned to the filter boxes and dried in the clean room to constant weight. The filters were digested with Ultrex nitric acid in the same Teflon bombs that were described in Section 3.4.2.2. The bombs were sealed and heated to 120°C for at least 6 hours, and as was the case for the sediments they were generally left overnight to ensure full digestion. The bombs were cooled and opened: the solution inside was clear, indicating that the digestion process was complete. The solution was poured into a polyethylene storage bottle and made up to approximately 5ml with SBDW on a balance: the mass of final solution was recorded.

3.5.3 Determination of trace metal concentration

Due to the general lack of an interfering matrix in the analysis of filters, the trace metal concentrations were determined using the direct calibration method, as was used in the analysis of seawater concentrates (Section 3.3.3).

3.5.4 Quality control

There is no commercially produced reference material for suspended particulate material. Blank determination was performed by analysing clean filters in the same way the sample filters were digested.

3.5.5 Calculation of suspended particulate material trace metal loading

A spreadsheet programme (Microsoft Excel) was used to convert the $\mu g\ l^{-1}$ value obtained from the GFAAS into $\mu g\ g^{-1}$ of metal in particulate material.

3.6 Analysis of samples for ancillary data

3.6.1 Salinity determination

A Guildline model 8400 AutoSal salinometer was used for the determination of salinity. The salinity is determined by conductivity using 4 conductivity cells. The analysis is quick, with a throughput of 25-30 samples per hour. Calibration was performed using IAPSO standard seawater. Salinity can be determined with an accuracy of 0.001.

3.6.2 Nutrient determination

Analysis of the nutrients for the inshore waters was performed using a Technicon autoanalyser II. A full description of the methodologies used for this can be found in the JGOFS manual (IOC 1994); they are generally based on methods published by Strickland and Parsons (1972). The methods are colorimetric, and have been shown to be reliable for the concentrations of nutrients encountered in this study. Detection limit for the phosphate determination is 0.03 $\mu mol\ l^{-1}$ and 0.01 $\mu mol\ l^{-1}$ for the nitrate/nitrite and nitrite determinations. Quality control is performed by the analysis of low nutrient surface seawater from the BATS station as a blank and by comparing analyses for deep water samples from the BATS study site, where nutrient concentrations are assumed to be constant. Frequent inter-laboratory comparisons of nutrient samples are performed as part of the BATS study and this reduces the potential for systematic error in the colorimetric analysis.

3.6.3 Pigment analysis

The GF/F filters collected for pigment analysis were placed in centrifuge tubes with 5ml of 100% acetone, sonicated for 5 minutes then sealed with parafilm and left overnight to extract the pigments. The samples were centrifuged to prevent filter particles from interfering with the fluorometric determination. Analysis of the pigments was performed using a Turner fluorometer. The samples were read and then 2 drops of 10%

HCl added and the fluorescence read again. Concentrations of chlorophyll a and phaeopigments were determined using the equation 3.1:

$$Chl(\mu g/l) = \left(\frac{F_m}{F_m - 1}\right) \times (F_o - F_a) \times K_x \times \left(\frac{vol_{ex}}{vol_{filt}}\right)$$

$$Phaeo\ (\text{chl equiv.weights}) = \left(\frac{F_m}{F_m - 1}\right) \times \left[(F_m * F_a) - F_o\right] K_x - vol_{ex}$$

Equation 3.1

where:

F_m = acidification coefficient (F_o/F_a) for pure chlorophyll a (usually 2.2)

F_o = reading before acidification

F_a = reading after acidification

K_x = door factor from calibration calculations

vol_{ex} = extraction volume

vol_{filt} = sample volume

Quality control for this method is performed by analysis by the spectrophotometric technique of Strickland and Parsons (1972), of commercially purchased chlorophyll a standards and intercomparison studies with other laboratories.

3.6.4 Determination of carbonate content of sedimentary material

Sediment was collected as outlined in section 3.2.2. A subsample of each sediment weighing approximately 10mg was taken from the sediment sample. This was weighed and placed on a filter and the filter and sediment was weighed. The sediment was then treated with 10% analytical grade HCL, until all effervescence had stopped. The filter and sediment that remained was washed with Q-Water, dried and re-weighed. The difference between the starting weight of sediment and the final weight is assumed to be the weight of carbonate in the sample. This method can lead to an over estimate of the amount of carbonate material present in a sample due to dissolution of organic material and other non-carbonate components of the sediments. A refinement of this method involved placing the sample in a gas jar with fuming HCl, then weighing the sample after decomposition of the carbonate.

The problem with the fuming method is that the calcium carbonate forms calcium chloride, which was washed away in the previous method, in this method there may be an overestimate of sample weight because of this. Analysis of 10 samples by both of these methods produced a less than 5% difference between them. The loss of soluble material from the samples using the quicker wet method may not be as important for samples analysed here as the carbonates are the predominant (>90%) component of the sediments.

3.6.5 Determination of organic carbon in sedimentary material

Carbon and nitrogen contents of the sediment samples were determined using a Leeman elemental analyser. Two samples of each sediment were taken, one was weighed and analysed directly, the other was weighed and fumed with concentrated HCL to remove the carbonates and then the sediments were analysed using the analyser. This method produces results that can then be used for organic C:N comparisons. Data for this analysis produced less than 15% differences for replicate samples. Full details of the use of the CHN analyser can be found in the JGOFS manual (IOC, 1994).

Chapter 4.

Trace metals in the Bermuda Coastal Zone

4.1 Introduction

The study of the trace metals cadmium, copper, nickel, lead and manganese in the coastal zone is approached from three directions

i) A laboratory study to investigate the factors that lead to the uptake or release of trace metals from natural sediments to seawater.

ii) A study of Devil's Hole; a periodically anoxic basin in Harrington Sound. Differences in metal behaviour between mixed and stratified conditions are investigated, along with a study of sedimenting material.

iii) The analysis of samples (both water and sediment sample) taken from the coastal zone over a period of three and a half years, and the interpretation of this data in terms of cycling sources and sinks.

It is possible, using simulated environments, to study factors influencing trace metal uptake and release by sediments. These experiments can take the form of enclosure experiments such as the use of Lund tubes in freshwater systems (Reynolds *et al.*, 1985), or the manipulation of whole environments such as the lakes experimental area in Canada (Malley and Mills, 1992). For marine studies it is nearly impossible to use enclosure systems such as the Lund tubes because of tidal and other (advection properties, weather etc.) considerations. More commonly tanks or large scale mesocosm experiments (Amdurer *et al.*, 1982) are utilised in marine studies, where sediments are exposed to seawater and the behaviour of the trace metals is studied. This approach is appropriate here as it is easier to control the environmental factors. There will obviously be differences in temperature, light and physical agitation relative to sediments in natural marine environments. The use of benthic chambers can overcome some of these problems (Ciceri *et al.*, 1992), although since they are essentially enclosure experiments there are problems with maintaining conditions within the chambers to be representative of conditions external to the chamber e.g. light, hydrodynamics and oxygen regime. Details of these experiments will be presented in Section 4.2.

Harrington Sound (Fig. 4.1) represents a unique situation within the Bermuda marine environmental system as it is the most enclosed of the four Bermuda basins (St. George's Harbour, Castle Harbour and Great Sound/Hamilton Harbour being the other three). The area of the Sound is approximately 5 km^2 with a mean depth of 20 m and its

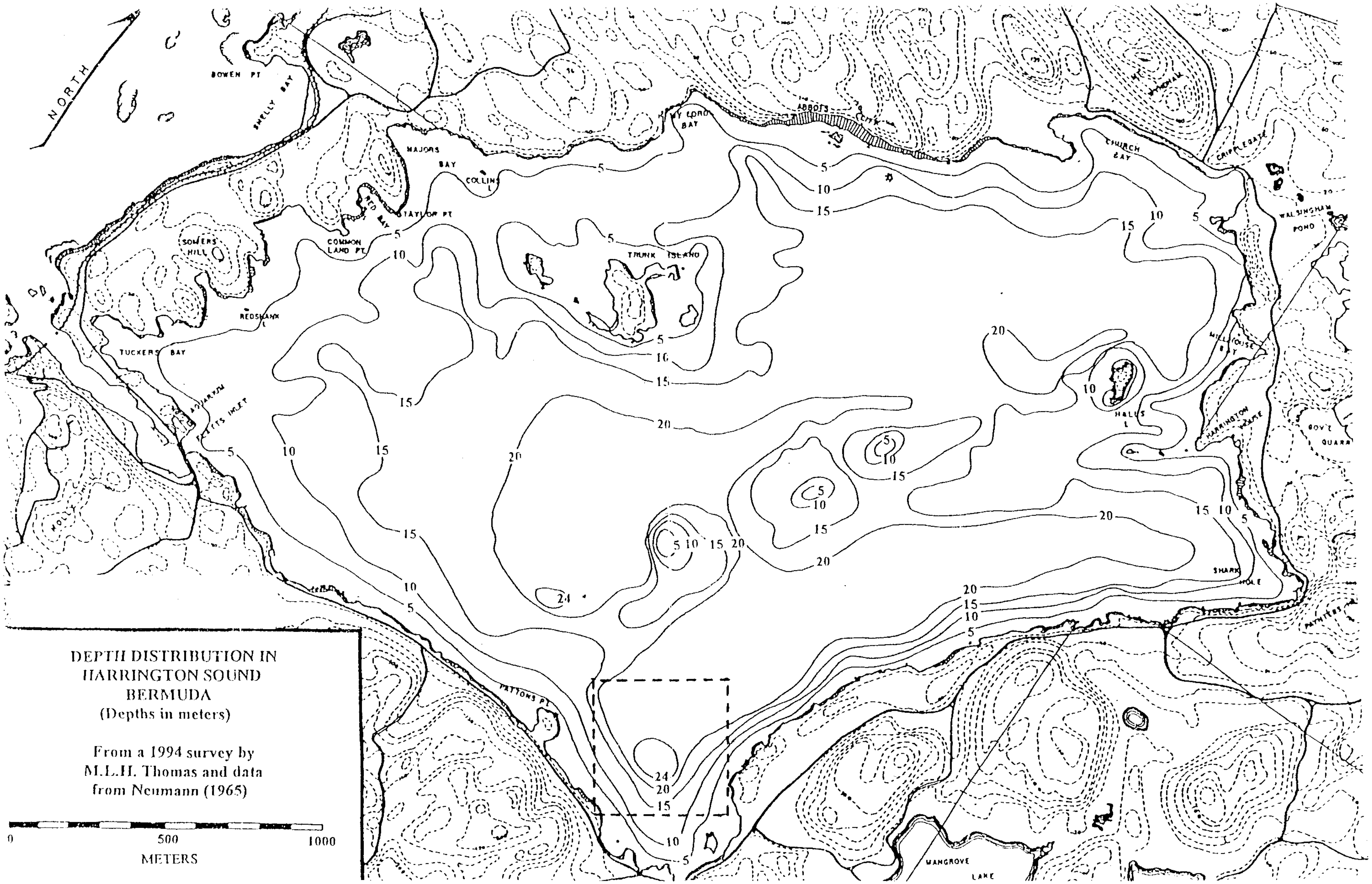

Figure 4.1 Bathymetric map of Harrington Sound (Devils hole marked in hatched box)

volume is estimated to be $70 * 10^6 m^3$. The location within the sound for this study was Devil's Hole, in the south eastern part of the sound; with a maximum depth of 25m.

Up to 50% of the water exchange of Harrington Sound is thought to occur through the Flatts inlet. The remaining exchange is via ground water exchange or with the surrounding ocean water. The residence time of the water in Harrington Sound was estimated by Morris *et al.* (1977) to be 120-140 days, and by Barnes and Bodungen (1978) at greater than 140 days. The tidal range in the Sound is the lowest amongst the inshore basins, with an average of only 20 cm between tides (Morris *et al.*, 1977). The bathymetry of the Sound area results in Devil's Hole being separated, at depth, from the remainder of the Sound by a submarine ridge at a depth of around 15-20m; this reduces the potential for deeper water mixing in the Devil's Hole basin (Figure 4.1). The bathymetry of the site combined with the enclosed nature of the Harrington Sound basin can result in a seasonal thermocline developing in Devil's Hole: this was present in 1993, 1995 and again in 1996 (personal observation). Once the water column has become stratified there is the potential for the waters below the thermocline to become sub-oxic or even anoxic.

Previous studies in the Harrington Sound area have concentrated on the general conditions in the Sound as a whole (Wefer *et al.*, 1981, Thomas, 1991) and the Devil's Hole area in particular (Jickells and Knap, 1984). There have been no detailed studies of the behaviour of trace metals in the Devil's Hole area between mixed water column conditions and stratified conditions. While it is thought that there are limited areas of anoxia in other areas of Bermuda (Jickells and Knap, 1984), Devil's Hole exhibits this regularly. This area provides an opportunity to investigate anoxia in a carbonate dominated system, and the knowledge gained can be used to assess the importance of such processes in other areas of the coastal zone.

Comparing and contrasting behaviour of metals across oxic/anoxic interfaces has been performed in many areas e.g. Saanich Inlet in Canada (Emerson *et al.*, 1979, Jacobs and Emerson, 1982; Francois, 1988), the Baltic Sea (Kremling, 1983b; Dyrssen and Kremling, 1990), the anoxic basins in the Mediterranean (Lange *et al.*, 1990) and the Black Sea (Lewis and Landing, 1992). Some of these environments, such as the basins in the Mediterranean and the Black Sea are permanently anoxic at depth while others, such as the Saanich Inlet have an annual development of an anoxic water mass. The oxic/anoxic interfaces have provided valuable information regarding the distributions of those metals that undergo redox changes (e.g. manganese in the study by Lange *at al.*, 1990), but, as will be shown here, changes to these redox sensitive metals can affect the distributions of other associated metals.

The study outlined in Section 4.3 investigates the geochemistry of the Devil's Hole area in more detail. Emphasis is placed on the distribution of trace metals between the dissolved and the particulate phases, as well as the composition of the sinking particulate material that forms the sediments.

The only previous work that investigated, in detail, the distribution of trace metals in the Bermuda coastal zone is that of Jickells and Knap (1984). This earlier study looked at the concentrations of dissolved metals as well as the total metals in the sediments. The present study additionally considers the role that particulate material has in the distribution of trace metals in the coastal zone of Bermuda. The numbers and frequency of collection of samples in this present study should allow an investigation of any seasonal patterns in trace metals that may be present in the coastal zone. The laboratory experiment along with the investigation of the situation in Devil's Hole should enable a more detailed and descriptive insight into the geochemistry of trace metals in the Bermuda coastal zone, and thus explain the observed metal distributions found in the study area, and so all three topics have been combined in this chapter.

4.2 Experimental investigations of water column/sediment interactions in the Bermuda system

4.2.1 Experimental design and procedure

Samples of sediment were collected using a Van Veen grab sampler from St. George's Harbour, to represent a contaminated sediment, and the outer North Lagoon area, to represent a relatively uncontaminated sediment. Clean HDPE buckets (15 liters in volume), similar to those used by Church *et al.* (1986) for the study of trace metal distribution in rain, were cleaned and separated into two groups of four buckets. All of the buckets were filled with 15 litres of seawater collected from the outer north lagoon area, from the front of the boat to reduce contamination from the boat itself. The buckets were covered to prevent particles dropping in them, aerated and left for one week to allow equilibration of the seawater. 250ml samples of water were removed from all buckets, filtered and analysed, according to Section 3.3 for dissolved trace metals to determine the initial metal concentrations. Following this two separate experiments were performed designated A and B below.

A Three buckets were spiked with metals according to the concentrations shown in Table 4.1 and then 1kg of North Lagoon clean wet sediment was added. The metal concentrations were chosen to reflect field stations typified by moderate contamination. The buckets were gently (resuspension of sediments was minimal) aerated for two weeks and samples of seawater collected, filtered (0.4µm Nuclepore filters), acidified and stored. After the 2 weeks the aeration process was stopped and the air above the seawater was replaced with nitrogen and the buckets sealed for 2 weeks to allow anoxic conditions to develop. A positive pressure of nitrogen was maintained on top of the water column to prevent the diffusion of oxygen into the buckets.

Element	Concentration
Cadmium	0.38±0.04
Copper	13.89±1.19
Lead	3.33±0.2
Manganese	7.47±0.95
Nickel	3.50±0.51

Table 4.1. Initial measured concentrations of metals in tank experiment A (nmol l^{-1}, n=4).

B Three buckets of seawater had 1kg of the St. George's sediment added. These buckets were treated in exactly the same way as in experiment A, they were first subjected to oxic conditions then forced anoxia. The initial concentrations of metals in the water was as shown at time 0 in Table 4.3.

In each of the experiments there was a fourth bucket that was treated in the same way as the other buckets but contained no sediment; this therefore acted as an experimental control and was used to account for metals that may leach from the buckets or conversely be absorbed by the walls of the buckets. Both sets of buckets were stored in a laboratory area and thus subjected to regular diel variations in light, although the temperature was maintained at 21°C ± 2°C.

Samples were taken for nutrient analysis as well as for determination of pH; salinity measurements were used to check that there were no significant losses of water due to evaporation over the experimental period. The sediments in both experiments were analysed for total metal loading as well as organic carbon content and carbonate content.

4.2.2 Results of the laboratory study

The initial analysis of the sediments used in the laboratory study (total values) shown in Table 4.2

Element	Test A	Test B
Cadmium	< d.l	0.22±0.08
Copper	0.25±0.09	12.0±0.15
Lead	0.8±0.34	41.9±0.87
Manganese	1.22±0.05	29.9±7.60
Nickel	0.17±0.06	1.74±0.17
Org. Carbon (%)	1.2±.2	3.8±0.4

Table 4.2.Initial concentrations of trace metals and percentage organic matter in sediments used in the laboratory experiments (all metal data μg g^{-1} sediment ± 1 std. dev.; n=5).

The changes in dissolved metal concentrations during the experiments are shown in Table 4.3. Time 0 is the starting parameters, Time 1 is after 2 weeks and Time 3 is under anoxic conditions (oxygen concentrations <0.5 μmol kg^{-1}).

	Time 0	Time 1	Time 2
Experiment A			
Cadmium	0.38 ± 0.2	1.01 ± 0.2	< d.l
Copper	13.9 ± 1.19	32.8 ± 7.8	31.0 ±6.49
Lead	3.33±0.2	1.01 ± 0.2	0.51±0.01
Manganese	7.47 ± 0.95	2.12 ± 0.1	13.49±0.7
Nickel	3.5 ± 0.51	23.3 ± 2.58	6.35±0.41
Experiment B			
Cadmium	0.32 ± 0.1	0.67 ± 0.1	1.66 ± 0.35
Copper	7.85 ± 2.64	37.2 ± 2.85	108.7 ± 21.24
Lead	0.70 ± 0.34	2.34 ± 0.34	3.57 ± 1.06
Manganese	5.10 ± 0.4	1.89 ± 0.16	3.88 ± 0.73
Nickel	6.51 ± 0.68	21.0 ± 7.55	6.13 ± 0.68

Table 4.3. Results of the dissolved trace metal analysis for the laboratory experiments. (All data nmol l^{-1}± 1 std. dev.; n=3.)

This data is also shown in Figure 4.2 for experiment A and Figure 4.3 for experiment B.

Data on nitrate, nitrite and phosphate was also obtained for the tank experiments (Table 4.4)

	Time 0	Time 1	Time 2
Experiment A			
Nitrate	0.04±0.02	0.02±0.02	0.02±0.02
Nitrite	<d.l	0.01±001	0.03±0.02
Phosphate	<d.l	<d.l	<d.l
Experiment B			
Nitrate	0.03	0.08±0.02	0.06±0.02
Nitrite	<d.l	0.03±0.01	0.08±0.02
phosphate	<d.l	<d.l	<d.l

Table 4.4. Results of the nutrient analysis for the laboratory experiments (all data expressed in µmol l^{-1}, n=4).

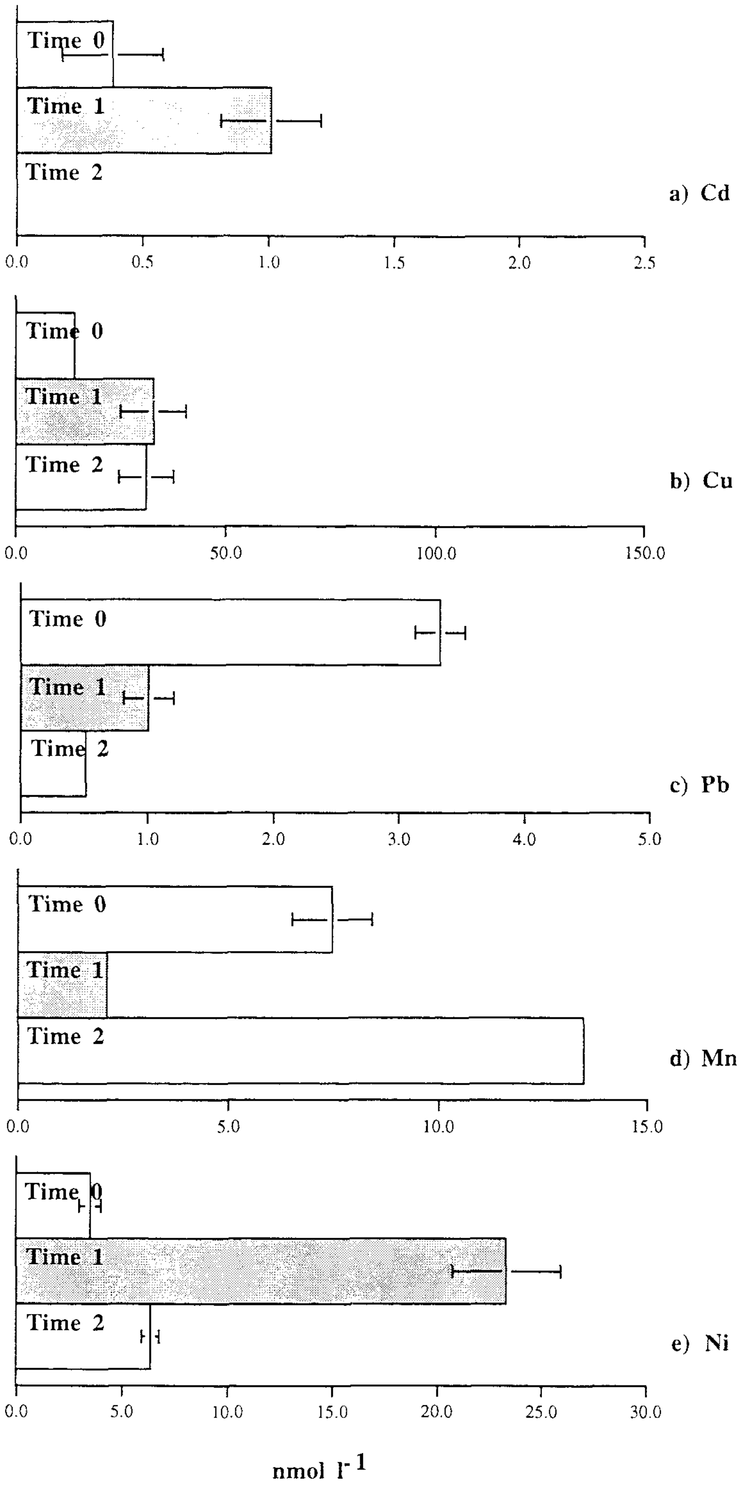

Figure 4.2 Results for tank experiment A (all data nmol l^{-1}, Time 0=start of experiment. Time 1= two weeks and Time 2 is after anoxia)

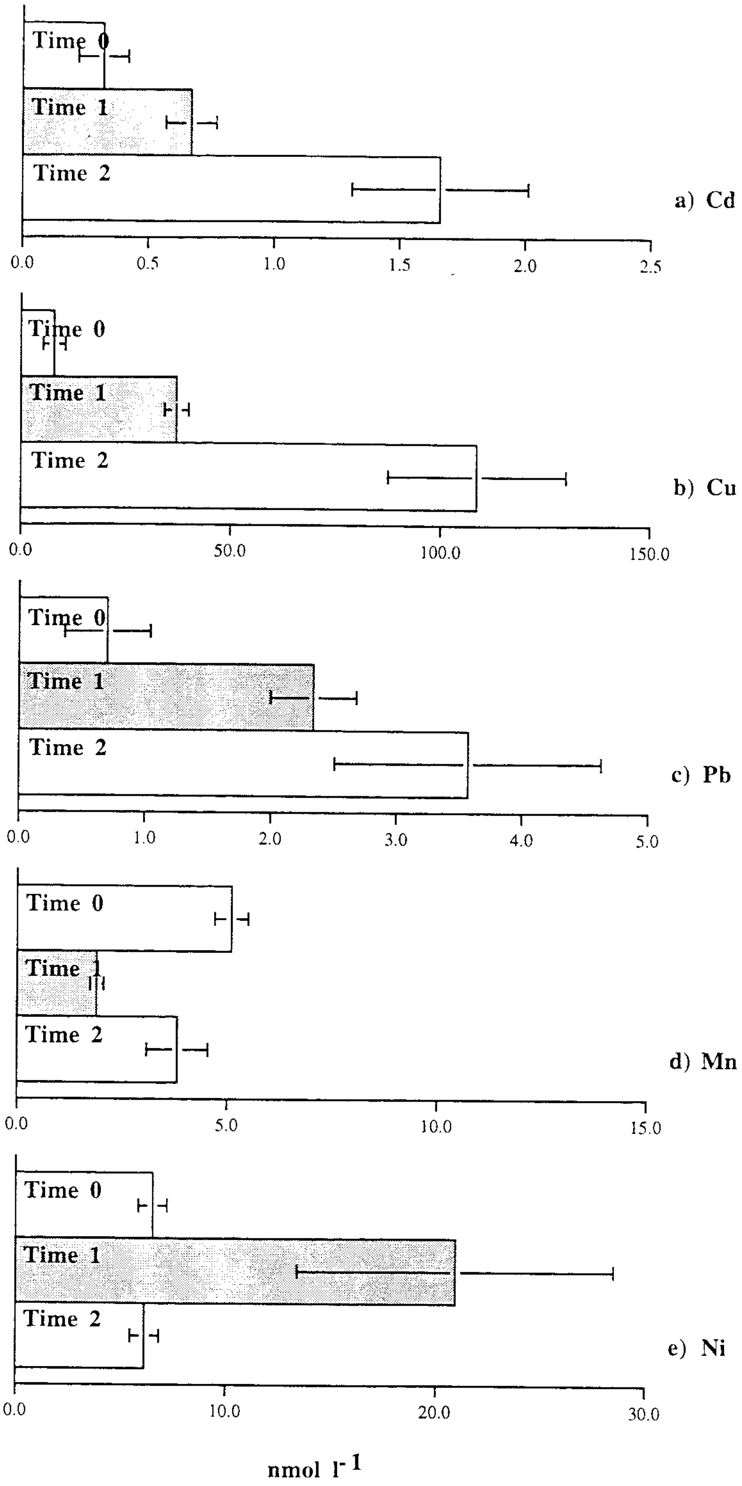

Figure 4.3 Results for tank experiment B (all data nmol l^{-1} ± 1sd, Time 0=start of experiment. Time 1=after two weeks and Time 2 is after anoxia)

For experiment A there is an initial increase in the concentrations of dissolved cadmium, copper and nickel after addition of the sediment, and both lead and manganese underwent significant decreases ($p<0.05$). After the system had undergone a period of anoxia the cadmium concentration fell below the detection limit. Dissolved copper is not significantly changed ($p<0.05$) compared to before the anoxic period but is still higher than in the initial spiked seawater. The dissolved lead concentration is significantly lower ($p<0.05$) than it was before the period of anoxia and lower than the initial spike of lead in the water. Dissolved manganese increased significantly ($p<0.05$) when the sample became anoxic. Dissolved nickel decreased under the anoxic conditions, but was still significantly higher ($p<0.05$) than the initial concentration of nickel added.

For experiment B, dissolved cadmium increased significantly during the two stages of the experiment. Dissolved copper demonstrated similar behaviour to the cadmium with significant increases ($p<0.05$) over all the experimental conditions. Dissolved lead initially increased in the first part of the experiment, there was a further increase during the second stage but this change was not significant ($p<0.05$). Dissolved manganese initially decreased during the first stage of experiment B but increased significantly ($p<0.05$) during the anoxic period. Dissolved nickel behaved as it did in experiment A with an initial large increase in dissolved concentrations, followed by a decrease during the period of anoxia.

The nutrient concentrations in experiment A remained low or below the level of detection ($0.01\mu mol\ l^{-1}$) over the whole period of the experiment. For experiment B there was a decrease in the concentration of the nitrate and an increase in the concentration of the nitrite, particularly during the anoxic period of the experiment. The phosphate remained below the levels of detection throughout this experiment.

4.2.3 Discussion

The results from the tank experiments can be used to give an insight into the geochemical processes at work in the control of trace metals in the Bermuda inshore water area. It is probably incorrect to assume that the tank experiments reflect any natural conditions that may exist in the Bermuda inshore environment, however they can provide a useful insight into shorter term processes.

Cadmium

For experiment A, with uncontaminated sediment and seawater that was artificially spiked with trace metals, there was an increase in the concentration of dissolved cadmium in the overlying water over the first stage of the experiment under oxic conditions. The concentrations of dissolved cadmium dropped below detection limits when the experiment was subjected to anoxic conditions, possibly suggesting that the cadmium is forming insoluble sulphide compounds that are then being deposited to the sediments (Borg and Jonsson, 1996).

For experiment B, with St. George's sediment, which has elevated concentrations of trace metals and uncontaminated seawater, there was a release of cadmium from the sediment under both oxic and anoxic conditions. Although both experiments were determined to be anoxic, there may have been differences in the degree of evolution of sulphide.

In contrast to the first experiment presented here, Boulegue (1983) described the behaviour of cadmium under anoxic conditions and found that the release and uptake of cadmium from and by sediments was not affected by anoxia. He deduced that the cadmium in anoxic environments was complexed by thiosulphate and the solubility of the cadmium was not altered as a result of this complexation. There is an increase in the concentration of dissolved cadmium under both experimental conditions for experiment B: this could be due to the breakdown of POC complexed cadmium in the relatively organic rich St. George's sediments combined with the formation of thiosulphate complexes.

This is in contrast to work by Elderfield *et al.* (1981) and later work by Pederson et al. (1989), who described the distribution of cadmium, in coastal waters under anoxic conditions, in terms of a process of insoluble sulphide formation and subsequent removal to the sediments. Westerlund *et al.* (1986) described a series of flux experiments and reported that under anoxic conditions the concentration of dissolved cadmium in the water column decreased; they proposed that this was due to the formation of insoluble cadmium sulphides, experiments by Borg and Jonsson (1996) support this insoluble cadmium sulphide formation theory. Experiment B in this study appears to indicate that the formation of insoluble sulphides is not the controlling factor for the cadmium here, as there is continued release of cadmium during the anoxic period. This could be explained if the sediments were not anoxic enough for the production of sulphide that would then remove the cadmium, that the release of cadmium by the breakdown of organically bound cadmium is greater than the formation of the cadmium sulphide, or there is formation of soluble thiosulphate complexes of cadmium. These laboratory experiments indicate that the sediments are a potential source of dissolved cadmium to the overlying water column. For experiment B there was release of cadmium under all conditions.

Copper

Studies of the behaviour of copper across anoxic interfaces have produced a confused pattern of possible controlling reactions. Gaillard *et al.* (1989) determined that the main factor preventing the release of copper from sediments was the binding with insoluble iron sulphide complexes under anoxic conditions. The formation of these complexes prevented the release of dissolved copper from sediments. Kremling (1983b) proposed that the control of copper in anoxic waters was dependent on the concentration of hydrogen sulphide present. At high concentrations of sulphide the copper forms bisulphide and chloride complexes that are insoluble and at lower concentrations close to the oxic/anoxic interface the copper forms soluble poly-sulphide complexes. Oezteurk *et al.* (1995) investigated the distribution of metals between the dissolved and particulate phase in a water profile through an anoxic brine, and they found that the dissolved copper was high in the oxic waters but lower in the anoxic waters. They accredited this to the formation of insoluble copper sulphides, however there was little change in the particulate bound copper in their study to lend support to this theory.

In contrast to this data Lyons *et al.* (1980) found that the anoxic sediments of Devil's Hole, Bermuda were a source of copper to the anoxic waters above the sediments. They suggested that this was due to polysulphide complex formation and the subsequent release of these complexes.

The results for copper in the tank experiments show a release of copper from the sediments in both experiments under oxic conditions. In the first experiment when the tanks became anoxic there was no further increase or decrease of dissolved copper in the overlying water. This may be due to one of two processes: the copper may have reached a pseudo-equilibrium between the sediment and the dissolved phase, or there may be further release due to organic degradation with the released copper forming, or becoming bound to, insoluble sulphides. The second experiment revealed that the concentration of copper continued to increase even under the anoxic conditions. The mobilisation of copper from sediments has been previously reported (Westerlund *et al.*, 1986; Zwolsman *et al.*, 1996), via the degradation of organic matter. There is the possibility that even though there is some evidence that the tank experiments in this study were anoxic (see section on manganese), they may not have been sufficiently anoxic to allow for the production of insoluble metal sulphides.

Nickel

The rapid release of nickel from the sediments during the oxic stage of both experiments supports work performed by Gerringa (1990), who found release of nickel from sediment slurries to the dissolved phase due to the aerobic degradation of organic matter in the sediments. Huynh-Ngoc *et al.* (1989) investigated the sediments off the coast of Monaco, and found that under oxic conditions the dissolved nickel concentrations in the pore waters were elevated 30 times over the concentrations in the water column; hence they deduced that the sediments would be a source of nickel to the overlying seawater.

There was a decrease in the concentration of dissolved nickel in the water of the tanks during the anoxic phase of the experiment. This may reflect sulphide complex formation and removal from the water, although this is not certain because there was no associated decrease of copper. One reason for the difference in behaviour may be that copper is being released by the aerobic and anaerobic degradation of the organic material in the sediments, but is then forming complexes with dissolved organic material in preference to sulphides. Copper has been found associated with strong organic carbon complexes in both surface water particulates and deep sea sediments (Chester *et al.*, 1988). Nickel, however, could be forming sulphide complexes preferentially to other complexes. This hypothesis is in contrast to observations by Dyrssen and Kremling (1990) who found that for the anoxic waters in the deeper waters of the Baltic Sea, copper forms insoluble sulphides at a greater rate than nickel.

Lead

The results from the first tank experiment show there is a decrease of dissolved lead during the oxic stage. The dissolved lead decreases further after the tank becomes anoxic. For experiment B there is an increase in the concentration of dissolved lead during oxic conditions. When the tank goes anoxic there appears to be a continued increase in the dissolved concentration, although this is not statistically significant ($p < 0.05$).

This data would seem to support the work performed by Ciceri *et al.* (1992), who in experiments using benthic chambers determined that there was a mobilisation of lead from sediments as the organic matter in the sediments was degraded. They suggested that soluble ligands were formed during this degradation process and further noted that the lead associated with the suspended matter in the water column also increased over the time frame of the experiment. Gaillard *et al.* (1986) found a similar trend but determined that there would be a decrease of dissolved lead when the water column became anoxic, due to the formation of insoluble sulphide complexes. These findings are contrary to that made by Gerringa (1990), who determined that the concentrations of dissolved lead above a sediment remained constant even when the organic matter within that sediment was degraded. His explanation for this was that the newly liberated lead (formerly associated with the organic matter) immediately formed insoluble salts or oxides within the sediments.

Manganese

The tank experiments lend support to the idea that the distribution of manganese in the coastal waters of Bermuda is primarily controlled by redox changes. For both experiments there is a decrease in the dissolved phase manganese during the initial aerobic stage of the experiment. That this occurred in the second experiment indicates that the sediments are not saturated with respect to manganese, even though the sediment used in this experiment represents the highest loading of manganese among the study stations. This implies that the sediments have a high carrying capacity for manganese. The anaerobic phase of the experiment saw an increase in the dissolved phase manganese in both of the experiments, presumably due to the reduction of manganese (IV) to the soluble manganese (II).

4.3 Trace metal geochemistry in Devil's Hole, Harrington Sound.

The sampling programme that was used for the other stations in this study also included Harrington Sound (Chapter 3). Since the Sound is not visited by any large vessels (entrance to the Sound is blocked by a bridge at Flatts Inlet, maximum height approximately 3 m), sediment resuspension due to shipping activity is not important. Therefore it was possible to carry out an investigation of rate of sedimentation and the geochemical nature of that sedimenting material.

Sediment traps have come under increasing criticism in recent years: problems include whether the traps are efficient collectors of falling material in the water column (Buessler *et al.*, 1994); whether the collected material undergoes changes once it is in the traps, from the feeding and excretion processes of zooplankton (Hansell and Newton, 1994) and whether the traps are a true reflection of upper water column processes (Siegel *et al.,* 1990). One of the problems is that it is basically impossible to compare different trap designs and therefore there is no method of quality control for such trap data (Gust *et al.*, 1994). However, with all these caveats it is still possible to use the data obtained from deployed traps in a relative way (Jickells *et al.*, 1996). Since the role of this particular study is to look at gross changes in fluxes of particles over short depth and time scales, and the geochemistry of that particulate material, there is the potential for some useful data to be collected.

4.3.1 Collection and analysis of settling particles.

Moored sediment traps were utilised which were made from cleaned PVC pipes (cleaned by soaking in 10% HCl for 24 hours before use then washed with Q-water) suspended at a known depth by a surface float and held in place, with the wire taut, by a weight. The traps used are the same as those used by Knauer and Martin (1983).

The trap is a very simple design, and where possible any metallic components of the trap were covered in plastic tape. The weight used was plastic coated and the rope used was Kevlar. These precautions were taken to reduce the potential for contamination. The trap depth was 18m to avoid being too close to the sediment with the consequent potential for resuspended sediment material to be collected, whilst being just below the depth of any seasonal thermocline that may form (generally the thermocline forms between 15 and 17m). This depth was chosen to be within the anoxic zone when such conditions arise. The traps were not treated with any poison as this would be one extra source of contamination and experimental artifact for the trace metals. A test was performed where the traps were left in the field for periods of time ranging from 1 day to 3 days to determine if any material was lost over time, and there were no significant losses over the three day time period relative to a single day's flux; it is assumed that the rain rate remained constant over the collection period.

The main problem with the sediment traps deployed at this location was the loss of three trap systems; this led to fragmentation of the sampling programme. The reasons for the losses were storms (2 sets of traps) and removal by fishermen (1 set). Unavailability of the materials used for the construction of the traps led to delays in deployment of new traps and so the samples were taken at irregular periods through the year. In total 13 samples were collected from the traps; the dates are shown in Table 4.5. The times of sampling are representative of mixed and summer water column conditions.

Date	Period	Days deployed
30/11/94	Winter	3
3/12/94	Winter	3
10/12/94	Winter	4
14/12/94	Winter	4
9/1/95	Spring	3
13/1/95	Spring	4
19/1/95	Spring	2
30/1/95	Spring	3
29/8/95	Summer	3
6/9/95	Summer	3
3/10/95	Summer	3
6/10/95	Summer	3
9/10/95	Summer	3

Table 4.5. Sediment trap sampling dates with deployment time

The sedimentary material was analysed for total concentrations of metals (section 3.4.2.2) and partially bound metals (section 3.4.3.2). In addition, total organic carbon was determined using the method outlined in section 3.6.5. The sediment collected was dried at room temperature in the clean room and weighed; from this the rate of sedimentation expressed as g $m^{-2}d^{-1}$ was determined.

During the summer of 1996 a thermocline formed. To study the distribution of trace metals and nutrients through the water column vertical samples were taken using a clean

Teflon lined Niskin bottle, on a Kevlar hydrowire. The bottle was lowered by hand from the boat and then tripped with an all brass messenger. The weight on the end of the line was covered in plastic to reduce the potential for contamination from that source. Surface samples were taken immediately on arrival at the station to prevent any contamination that may leach from the boat when it is sitting on the station. Samples were taken approximately every 5 m down the water column (at the approximate depth of the thermocline the sampling depth intervals were decreased to allow fine scale depth changes to be determined).

Aliquots were taken at each of the depths for oxygen analysis (first water from the Niskin bottles, duplicate samples) and fixed on deck using the Winkler method (Strickland and Parsons, 1972). The Niskin was moved away from the oxygen sampling area to avoid contamination by the manganese in the Winkler reagent and one litre of water was taken for trace metals and treated as outlined in section 3.2.1; 60ml samples were collected for nutrient analysis, and salinity samples were also collected from each depth. The temperature was measured within each oxygen sample bottle at the time of collection to allow for the determination of the oxygen anomaly. A portable CTD (conductivity, temperature and depth instrument package) was also utilised at this site to gain a profile of salinity and temperature as well as density (derived later) for the water column. Mixed samples were taken in winter of 1995.

4.3.2. Results for background data for Devil's Hole study.

The organic carbon content and the sedimentation rate for the samples collected for Devil's Hole are shown in Table 4.6.

Date	% Organic C	Sedimentation rate
30/11/94	27.1	1.43
3/12/94	39.6	2.52
10/12/94	29.3	1.85
14/12/94	30.1	3.19
9/1/95	40.3	2.32
13/1/95	29.3	2.16
19/1/95	29.6	2.17
30/1/95	28.2	1.55
29/8/95	29	1.22
6/9/95	28.9	0.99
3/10/95	27.3	1.10
6/10/95	26	0.43
9/10/95	27.4	0.34

Table 4.6 Organic carbon and sedimentation rate for Devil's Hole samples (sedimentation rate in g m^{-2} d^{-1})

The background data from the study of Devil's Hole can be seen in Figure 4.4. This is a summary of the temperature, salinity, oxygen, and the nutrient data. The metal data is discussed later in this chapter for each metal. It can be seen from Figure 4.4. that when the basin is stratified the thermocline occurs at a depth of 18-20m, with the oxygen concentration dropping to zero between that point and 24m. The concentration of phosphate is little changed by the onset of anoxic conditions. Nitrate concentrations are generally higher during mixed conditions. Nitrite concentrations are higher in the lower water column (below 15m) during stratified conditions, although there is a drop in nitrite concentration at 24m.

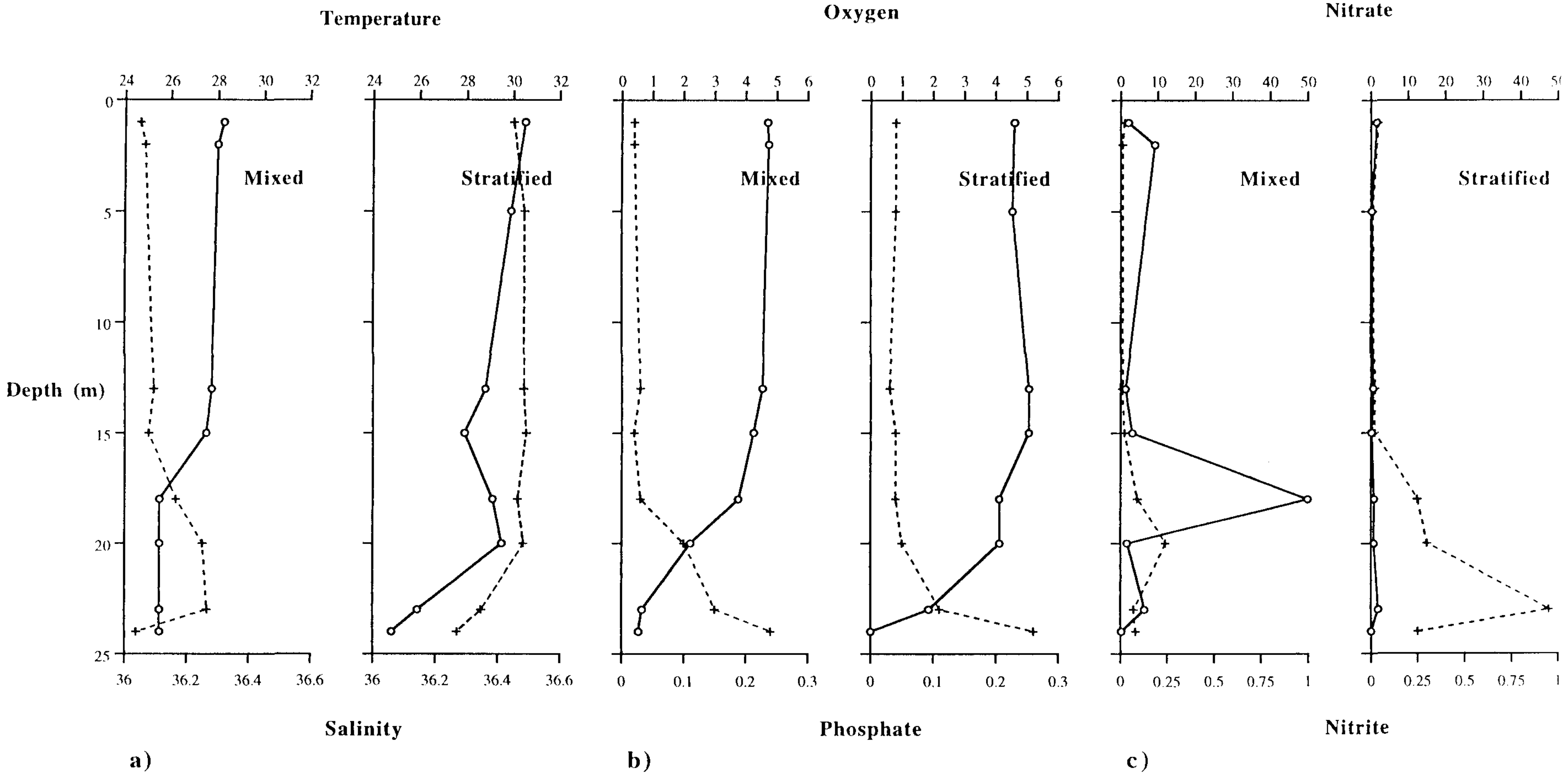

Figure 4.4. Accessory data for the Devils Hole study- **a)** temp °C (solid) salinity (dashed), **b)** oxygen ml l^{-1} (solid) phosphate µmol l^{-1}(dashed), **c)** nitrate (solid) and nitrite (dashed) µmol l^{-1}.

4.4.3 Results for trace metal study in Devil's Hole

Cadmium

The data for the Harrington Sound study into the cadmium associated with sediment trap material is presented in Figure 4.5.

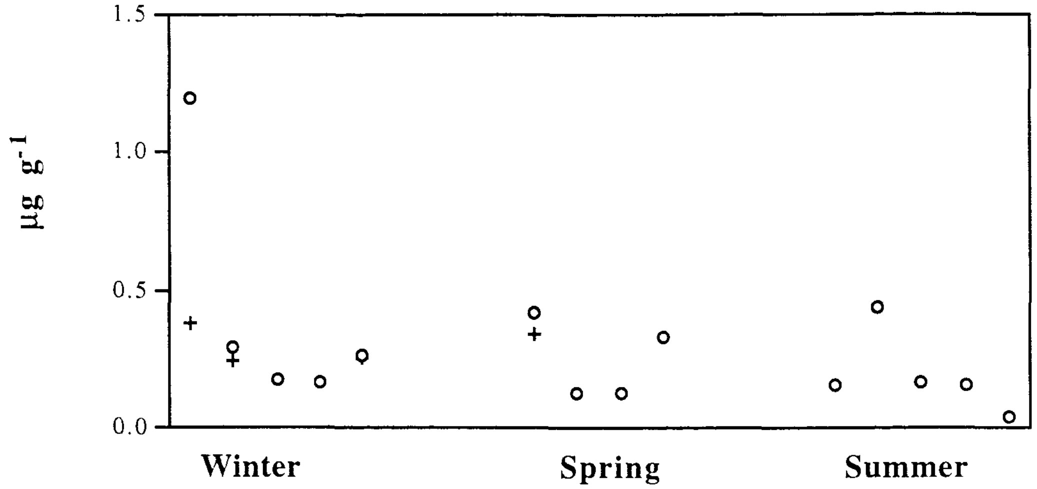

Figure 4.5. Total (o) and labile (+) cadmium concentrations in trap material from Harrington Sound (all data expressed in units of µg g^{-1} of dry material)

There is one immediate relationship in this data that is evident in Figure 4.5. For the majority of the samples there was no detectable cadmium released by the partial extraction method. This is probably a reflection of the high detection limit of 0.21 µg g^{-1} for cadmium using the selective extraction technique. There is detectable cadmium measured by the partial extraction process in two of the four winter samples and also the first Spring sample. The possible reasons for this are discussed in detail later.

The data obtained for the water column distributions of dissolved and particulate cadmium under mixed and summer conditions is presented in Figure 4.6a and b. Dissolved cadmium is above the limits of detection during mixed conditions, and the particulate bound cadmium is found at detectable concentrations at all depths except 15 and 23m.

During summer anoxic conditions the dissolved cadmium is below the limits of detection (0.09 nmol l^{-1}) between 15 and 23 m, after which the concentrations increase. Above 15 m the concentrations of dissolved cadmium are similar in both mixed and stratified conditions. The particulate bound cadmium is present in detectable concentrations throughout the water column with the exceptions of 5m and 23 m. There is a large peak in particulate cadmium at a depth of 15m.

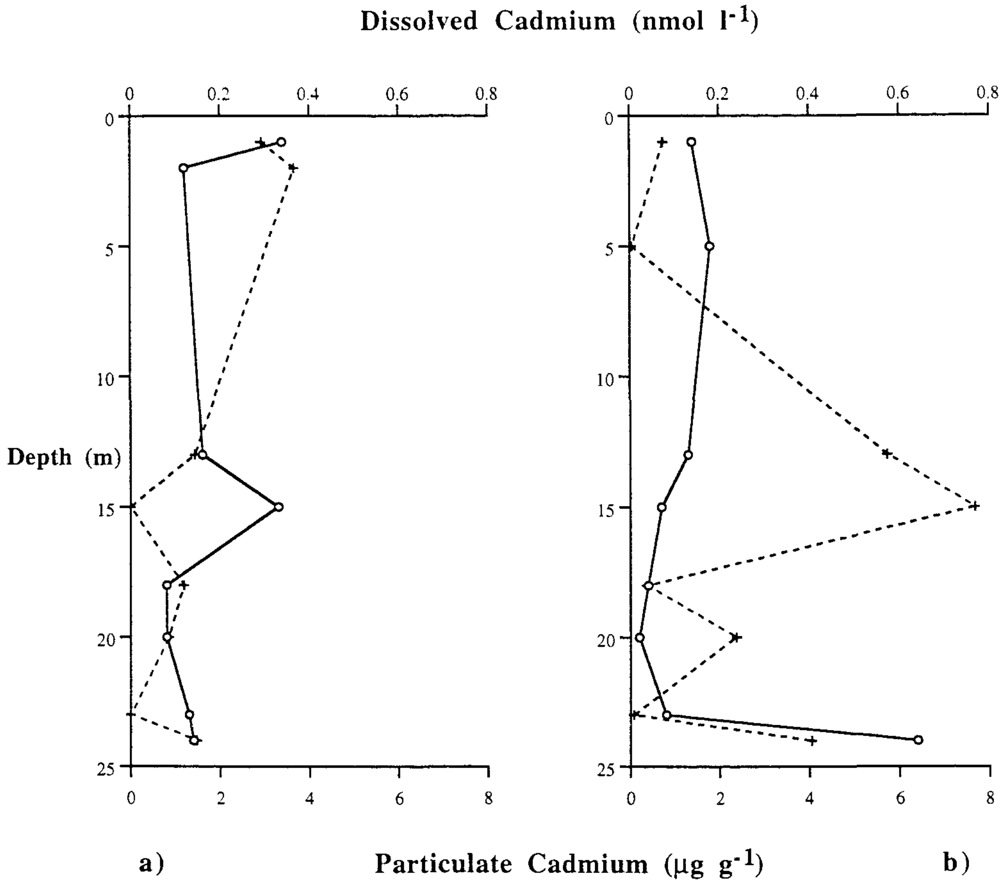

Figure 4.6 Dissolved (solid-nmol l^{-1}) and particulate (dashed-μg g^{-1}) cadmium in Harrington Sound. **a**) mixed and **b**) stratified conditions.

Copper

The data for the copper associated with sediment trap material is presented in Figure 4.7.

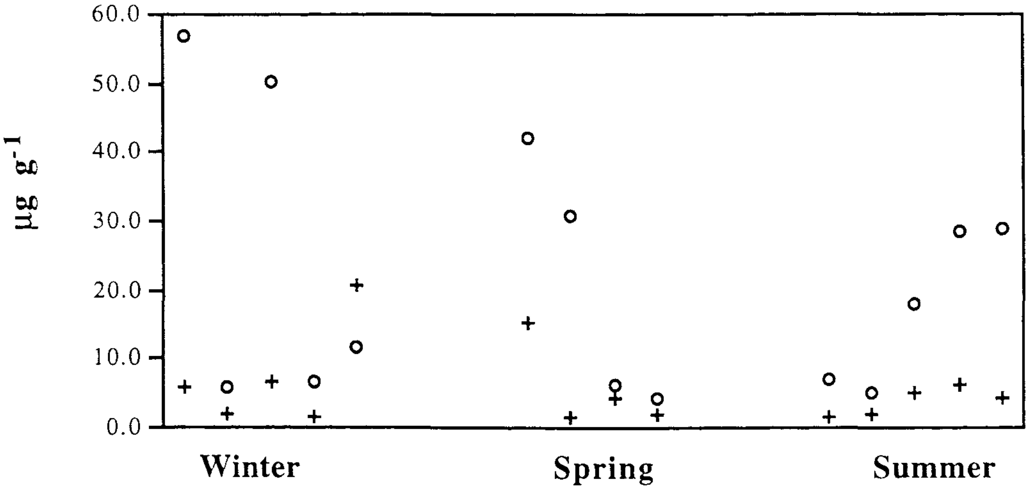

Figure 4.7. Total (o) and labile (+) copper concentrations in trap material from Harrington Sound (all data expressed in units of μg g^{-1} of dry material)

Total copper is variable between samples. The last winter samples have less total copper than labile copper, this is due to either an incomplete digestion for the total copper or contamination by copper during the partial extraction technique. Overall there is no obvious relationship between the total and labile copper.

The results for the distribution of dissolved and particulate copper during mixed and summer conditions can be seen in Figure 4.8. Dissolved copper does not vary dramatically between mixed and summer conditions (with the exception of high dissolved copper in the surface waters during stratified conditions, probably the result of contamination from the boat anti-fouling paint). There are higher concentrations of particulate associated copper present throughout the water column during the mixed conditions.

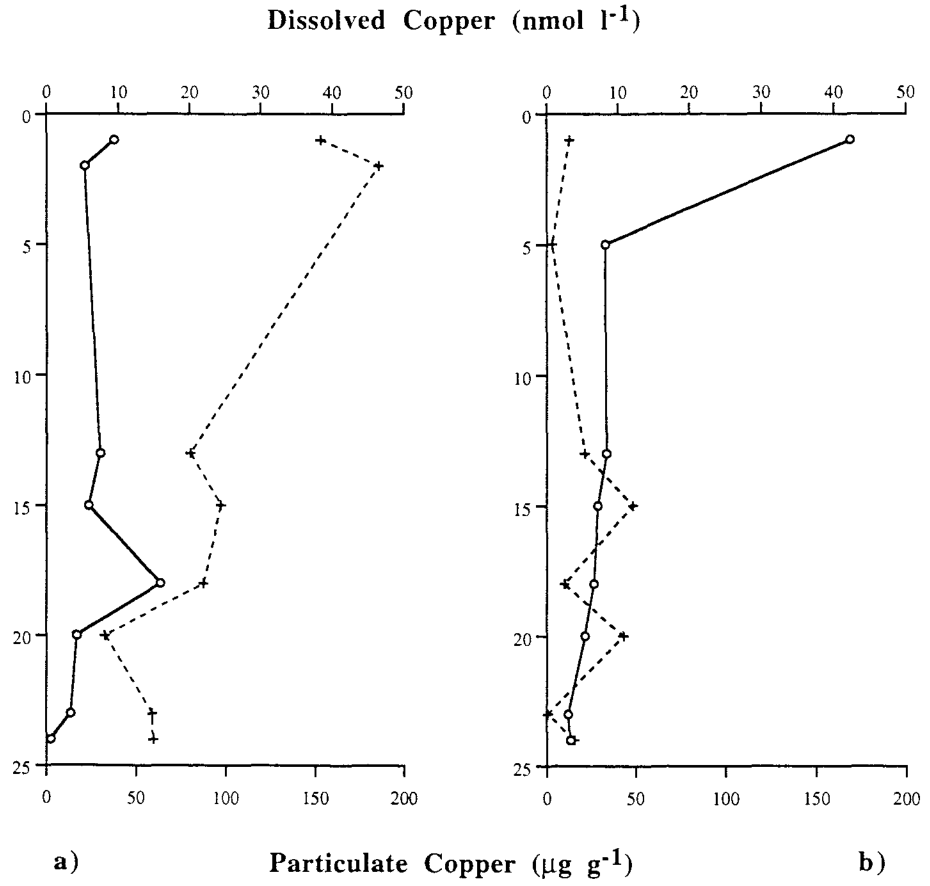

Figure 4.8 Dissolved (solid-nmol l^{-1}) and particulate (dashed-$\mu g\ g^{-1}$) copper in Harrington Sound. **a**) mixed and **b**) stratified conditions.

Nickel

The data for the nickel in the sediment trap material can be seen in Figure 4.9.

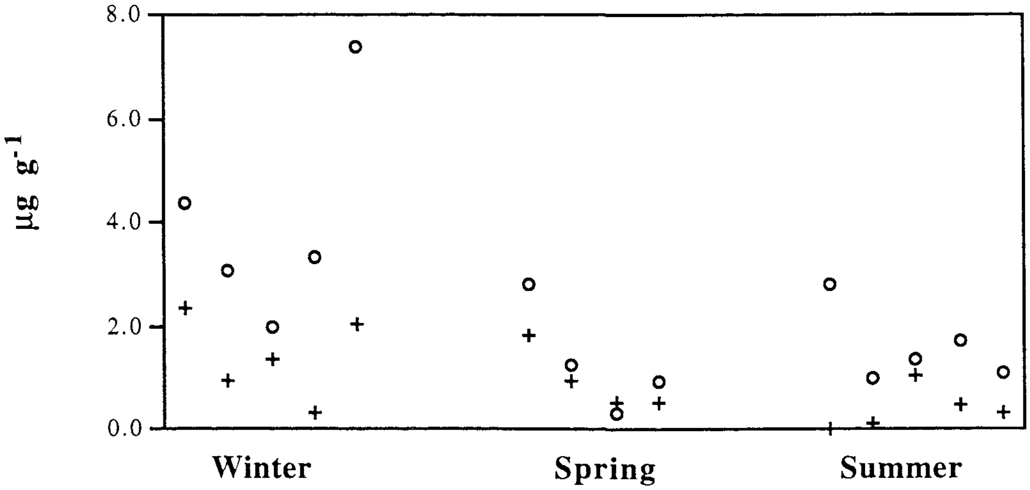

Figure 4.9. Total (o) and labile (+) nickel concentrations in trap material from Harrington Sound (all data expressed in units of μg g^{-1} of dry material)

From Figure 4.9 it can be seen that there is a high degree of variability in the data. As was the case for copper, there is one sample (in this case the third during the Spring period) that has a higher labile nickel than total nickel, this could be due to the reasons discussed above for a similar problem with the copper data.

The results for the distribution of dissolved and particulate nickel during mixed and summer conditions can be seen in Figure 4.10. There is a large peak in dissolved nickel during mixed conditions at a depth of 3m, this is most likely due to contamination. The concentrations of particulate nickel are below detection (0.30 μg g^{-1}) in the upper water column during mixed conditions, with the exception of a peak at 18 m at this time. There is very little variability in the water column distribution of dissolved and particulate nickel during stratified conditions.

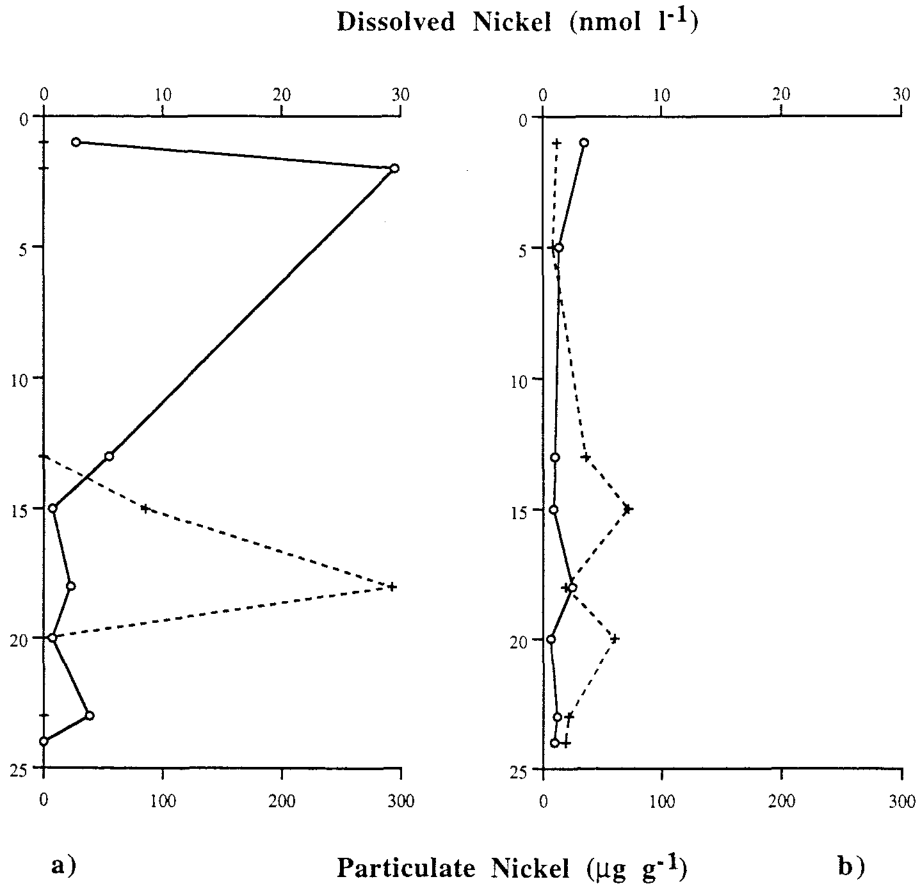

Figure 4.10 Dissolved (solid-nmol l^{-1}) and particulate (dashed-µg g^{-1}) nickel in Harrington Sound. **a**) mixed and **b**) stratified conditions.

Lead

The data for lead associated with the sediment trap material from Harrington Sound is given in Figure 4.11.

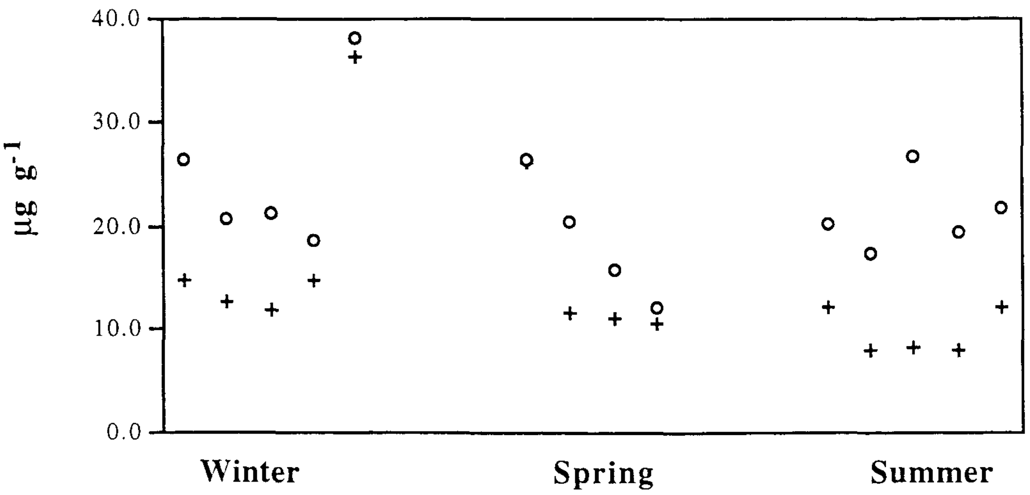

Figure 4.11. Total (o) and labile (+) lead concentrations in trap material from Harrington Sound (all data expressed in units of μg g^{-1} of dry material)

The total lead concentrations compared to the labile lead concentrations are similar over the whole study period. There is an indication that there is less lead associated with the labile phase relative to that associated with the residual material during the summer period, although this difference is not significant at the $P<0.05$ level.

Dissolved lead concentrations in mixed and summer conditions are similar (Figure 4.12.), with the exception of a large surface water concentration during stratified conditions. Particulate lead is high in the surface waters during mixed conditions, but below 5m the data is similar during mixed and summer conditions.

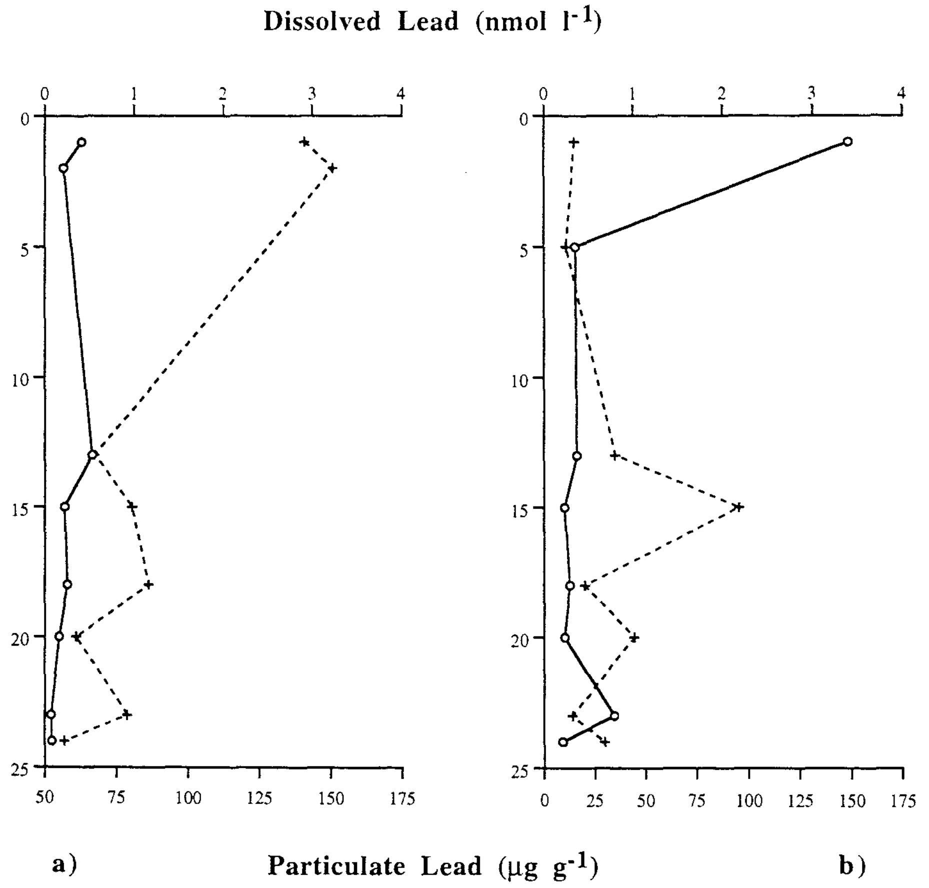

Figure 4.12 Dissolved (solid-nmol l^{-1}) and particulate (dashed-µg g^{-1}) lead in Harrington Sound. **a**) mixed and **b**) stratified conditions.

Manganese

Data on manganese in particulate material collected in the sediment traps from Devil's Hole, Harrington Sound is shown in Figure 4.13.

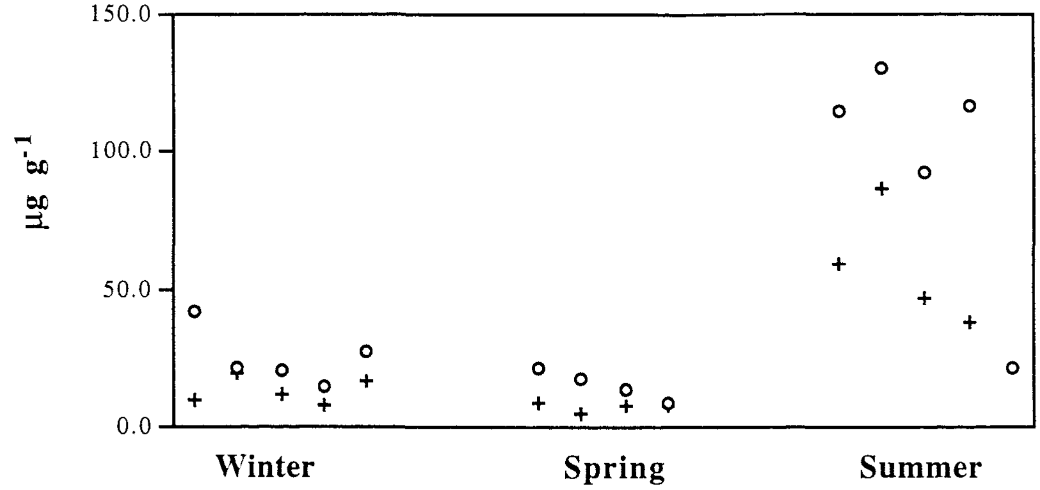

Figure 4.13. Total (o) and labile (+) manganese concentrations in trap material from Harrington Sound (all data expressed in units of $\mu g\ g^{-1}$ of dry material)

From this data it is evident that there is a distinct difference between the samples taken in summer compared to the other two periods of the year. During the summer there a smaller fraction of manganese released using the partial extraction technique (ie. that termed labile).

Data for dissolved and particulate manganese during mixed and summer conditions in Devil's Hole can be seen in Figure 4.14, and it is evident that their distributions are mirror images. During summer conditions the most obvious feature is the large increase in the concentration of dissolved manganese in the bottom waters. The distribution of particulate manganese during this time is not as variable through the water column as it was under a mixed regime, but there is a marked peak in concentration at 15m .

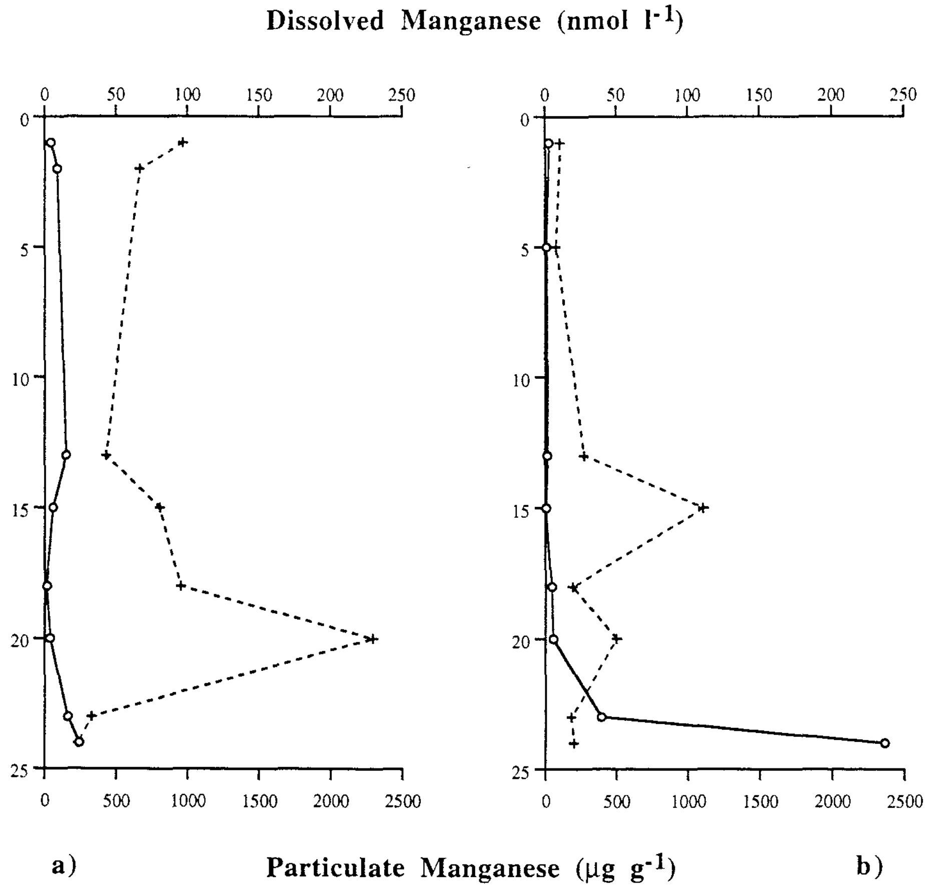

Figure 4.14 Dissolved (solid-nmol l^{-1}) and particulate (dashed-$\mu g\ g^{-1}$) manganese in Harrington Sound. **a**) mixed and **b**) stratified conditions.

4.3.4 Discussion

Cadmium in the sediment trap material shows no overall correlation with the other metals in the study, the sedimentation rate or concentration of organic carbon. There is a peak in the concentration of cadmium in the trap material collected on 30/11/94 that corresponds to both a period of high sedimentation rate and to a high concentration of organic carbon in the trap material. This may indicate an association of cadmium with phytoplankton since this trap material may be the result of a bloom in the upper water column. Evidence for this is also found in the high concentrations of chlorophyll reported for this station during January 1995. This is by no means certain as there are other times during the study when there are high organic carbon concentrations and high sedimentation rates but no elevated cadmium concentrations.

The cadmium data from the sediment traps indicate that during the time of maximum sedimentation rate there is a decrease in the ratio of labile to total cadmium, this is reversed during the summer/early period. This could be due to the presence of a halocline in the Sound. This halocline would reduce the sedimentation rate, and some of the loosely bound cadmium would be released by diagenetic processes at work in this part of the water column (from Table 4.6 it is seen that the sedimentation rate is lower during the period the thermocline is in place). Added to this is evidence that particles do not drop immediately through the water column but can be maintained in the surface waters by turbulent mixing processes (Alldredge *et al.*, 1987) and hence stay above the thermocline where processes leading to the removal of cadmium could occur. The sedimentation rate (Table 4.6) is lower during the period designated as summer samples, indicating that this retardation in falling rate at the thermocline may be occurring

Cadmium removal from particulate matter at the halocline is not supported by the data for the dissolved cadmium profile under stratified conditions. Particulate cadmium decreases below 15m but increases at 20m, there is however no associated increase or decrease in dissolved cadmium, with the exception of a large increase at 24m. One explanation for this lack of agreement between less cadmium in particulate matter and a decrease in dissolved cadmium, could be that the dissolved cadmium is rapidly removed from the water column by the phytoplankton. Phytoplankton are still present in the water column in sufficiently high enough numbers to produce saturated oxygen concentrations (oxygen anomaly = 126.2% at 13m depth). Phytoplankton are known to concentrate cadmium, blooms have been studied and reveal that they are responsible for the removal of dissolved cadmium from the water column (Noriki *et al.*, 1985), added to this is evidence that cadmium is readily scavenged from surface waters in association with fecal pellets (Fisher *et al.*, 1991). One further factor that could have a role in the distribution of cadmium and other metals is the potential for advective transport of the metals to and from the study area. The role of advective transport has been found to be important in other areas (Hall, 1993).

There is an increase in dissolved cadmium concentrations at the very bottom of the water column during summer conditions. This indicates a release of cadmium from the sediments, either through degradation of organic matter and/or release from the more mobile phases in the sediments. The latter process would help explain the lack of partially extracted cadmium found in this sediment material. The release of cadmium from sediments has been reported in other marine and estuarine environments (Emerson *et al.*, 1984; Zwolsman *et al.*, 1996) and was explained by the release of cadmium by the degradation of organic material in the sediments, and the oxidation of sulphides. This field data is supported by the tank data for experiment B that showed a release of cadmium from contaminated sediments during anoxic conditions, or as discussed below a release from the sinking biogenic debris reaching the sediments.

The decrease in the particulate bound cadmium at 24m lends further evidence to the idea that the cadmium in association with sedimenting material is mobilised as dissolved cadmium. Organic carbon content of the sedimenting material is generally in the 20-40% range, whilst the organic carbon in the surface sediments in Devil's Hole is around 2-3%, which indicates that the degradation of organic matter and release of any associated metals is a rapid process, and there is no long term accumulation of organic matter in the sediments.

The concentration of total copper in the sediment trap material is variable throughout the study. Unlike the cadmium there is always a fraction of the copper that is defined as labile. This fraction does not change in as periodically a distinct way as was the case with the cadmium. The concentration of labile copper in the sedimenting material is fairly constant this probably reflects the association of copper with organic matter in this material; the organic content of the sedimenting material is higher than the receiving sediments and the copper is assumed to be associated with organic matter.

During summer conditions there is no significant difference in dissolved copper concentration throughout the water column, with the exception of the high concentration in the surface waters. These data are in contrast to earlier results (Dyrssen and Kremling, 1990), who found that there was a large decrease in the concentration of dissolved copper in anoxic waters which they ascribed to the removal of copper onto freshly formed iron sulphide particles. That study was performed in the strongly sulphidic waters of the Baltic; differences in observations may be due to the concentration of sulphide not being as high in Harrington Sound.

Particulate copper is higher during the mixed conditions. The lower salinity in the surface waters at this time indicate that there may have been an input of freshwater due to a rain event, this could have increased the concentration of particulate bound copper due to run-off from the surrounding catchment. The data from the field experiments indicate that the release of copper from sediments in Harrington Sound is unaffected by changes from oxic to anoxic conditions.

The ratio of total to partially bound nickel is variable under conditions of high and low sedimentation rates. Generally though there is a larger fraction of nickel associated with the labile phase during the Spring period. The highest total nickel concentrations in the sediment trap material were found in samples collected on 14/12/94; at this time the sedimentation rate was high and the organic carbon in the trap material was low. This indicates that nickel during this time is probably not related to the biological processes in the upper water column. This date corresponds to a time when there was high rainfall associated with a storm (2.7cm on 13/12/94 the last winter sample; unpublished personal data). This is the only period of the study where there was such high rainfall and as such it is likely that runoff or rainfall or a combination of both is responsible for the high nickel concentration in the sedimenting material. However, since rainfall contains low concentrations of particulate material the source of the nickel is particles that have entered Harrington Sound in runoff from the surrounding area.

This similarity of concentrations of nickel between oxic and anoxic environments has been reported by both Dyrssen and Kremling (1990) and Oezteurk (1995) who found that dissolved nickel concentrations changed very little between an oxic anoxic water masses in the systems studied. There is no evidence in the current study to support the idea that the sediments are a source of dissolved nickel to the overlying water column. This is in contrast to the results for the tank experiment data and that of Lapp and Balzer (1993) who reported that under oxic conditions pore water fluxes from sediment could be high. However, their sediments were not dominated by calcareous material.

Lead concentrations in the sediment trap material from Harrington have variable proportions of labile and total phases. The highest concentration of lead in the trap material is coincident with the highest concentration of nickel, and probably also indicates runoff into the Sound following rainfall events. The majority of lead during this period is in the labile phase. This is not unexpected since the main source of lead in

Bermuda appears to be from vehicular emissions and the lead in those emissions is associated with lead bromide/ chloride complexes (Finlayson-Pitts and Pitts, 1986) that readily form carbonate complexes (Rosental *et al.*, 1986), which would then fall to the sediments in the inshore area of Bermuda.

During periods of high sedimentation rate (Table 4.6) there is a greater proportion of lead in the labile fraction, and when the sediment rate decreases, the amount of labile lead, as a percentage of total lead, decreases. Early work (Martin, 1970) indicates that there is passive adsorption of lead onto falling particles in the water column. It is possible that these falling particles are consumed by zooplankton and then the lead will be associated with the organic component and as such would be classed as total by the digestion technique used here. This consumption could occur at the top of the thermocline where the particles slow down. Repackaging of the smaller particles into fecal pellets would increase the weight of the particles so that when there is a thermocline present the majority of the particles passing though the thermocline are the heavier fecal pellets, within which the lead is organically associated. This is most likely due to a shielding effect rather than lead/organic complexes. Lee and Fisher (1996) determined that metals associated with the structural components of phytoplankton cells were not released by microbial digestion, and were consumed by zooplankton and converted to rapidly falling fecal pellets.

There is little data reported in the literature regarding the behaviour of lead across oxic/anoxic interfaces. Oezteurk (1995) reported that dissolved lead in anoxic water forms insoluble sulphides, thus reducing the concentration of dissolved lead in those environments. In this present study dissolved lead concentrations do not appear to be strongly influenced by the onset of anoxia during stratification. However, the decrease in dissolved lead and increase of particulate lead at the 24m depth could indicate formation of insoluble sulphides as reported by Oezteurk (1995). Westerlund *et al.* (1986) report that there is little release of lead from coastal sediments using benthic chambers, and from laboratory experiments it was suggested that any lead released would form salts or oxides (Gerringa, 1990) which would be held in the sediments. The high surface particulate lead concentrations during mixed conditions could be due to run-off as was reported for the sediment trap material, although there is no corresponding increase in particulate nickel concentrations.

The association of high manganese concentration in the trap material with periods of low sedimentation rate could be indicative of repackaging of material above the thermocline. As was discussed in the paragraph concerning nickel, the presence of the thermocline reduces the sinking rate of small particles due to the density gradient. It could be proposed that there is a release of reduced and hence soluble manganese (II) below the interface that crosses to the oxic water mass where it is rapidly bound to the high concentrations of calcite or is oxidized to particulate manganese (IV). The higher residence time of the smaller particles in the water column allows for a longer time for manganese scavenging before the particles pass through the thermocline.

During mixed conditions in Harrington Sound the relatively high concentration of manganese at a depth of 13m in Devil's Hole may be due to lateral advection of manganese (dissolved) rich water from the surrounding areas, where manganese was released from reducing sediments. During anoxic conditions the massive increase in dissolved manganese is due to reduction of particulate manganese (IV). Whilst there is a slight decrease in the particulate manganese in this zone, solid phase manganese is still present. This indicates that the majority of this manganese is released from the reducing sediments and not from the particles in the water column.

4.3.5 Summary

From the work presented here cadmium in Harrington Sound is associated with the organic component of the particulate material. The release of the cadmium into the dissolved phase occurs via the breakdown of the organic matter, either in the water column during down-column degradation, or at the sediment water interface. In the Bermuda coastal zone this degradation of organic material is rapid. The distribution of copper between dissolved and particulate phases is related to the organic content of the sediments. The distribution of copper and nickel between the dissolved and particulate phase is unaffected by a change from oxic to anoxic conditions. There is evidence that the main source of nickel to the Harrington Sound basin is in run-off during rain events. Like nickel the concentrations of lead are associated with run-off events in the basin. Lead appears to be unaffected by changes from oxic to anoxic conditions. The distribution of manganese between the dissolved and particulate phase is dependent on the redox state of the water column and the sediments; under reducing conditions the manganese is predominantly in the reduced (Mn II) form, under oxic conditions the manganese is associated with the carbonate material in the water column. The main problem with the work from this study is that this is not a totally stratified system; although the oxygen concentrations in the lower water column are low, at 23m there is still detectable oxygen. This work needs to be repeated comparing a more obviously stratified water column.

4.4 Inshore waters study-data base for metals

Data for the concentrations of dissolved trace metals and trace metals associated with suspended particulate matter can be found in Appendix 1. All of the data is presented in graphical format later in this chapter.

The whole data set for dissolved and particulate metals was subjected to cross correlation matrix analysis using the statistical package Statview 512. This was to determine if there were any obvious relationships between the components of the data set. The results of this cross correlation analysis can be found in Appendix 2. Only correlation results that were greater than 0.7 were considered significant and will be discussed in the text.

The data for the metals in the sediments, both total and those extracted by the partial extraction technique are in Appendix 3, and this data is presented in graphical format for each metal in this chapter.

There is a large degree of variability in the dissolved metal data. This is due in part to samples being collected at different points of the tidal cycle from month to month. For a station such as St. George's this will be particularly important as samples taken on an incoming tide will contain a higher proportion of 'cleaner' offshore water. Conversely samples taken at the low point in the tidal cycle will be representative of water that has been in that locale for an extended time and could have been impacted by higher metal inputs as runoff from the surrounding land areas, or from the sediments at the station. This will, to a varying degree, be important for all of the stations studied.

To test this idea the concentration of metals against the time of the tidal cycle was plotted (Figure 4.15). The data for St. George's was originally used but due to the complex nature of the water mass flow around St. George's (R. Johnson. pers. comm.) Great Sound was thought to offer a better chance of determining the influence of tidal cycle on the distribution of the metals. The data are presented for all of the metals in Great Sound (Figure 4.15). There is no obvious strong relationship between the tidal state (time 0 hour is high tide, 6 hour is low) and the distribution of dissolved trace metals. This indicates that there are multiple factors involved in the distribution of trace metals in the coastal zone, some of these will be explored in this discussion.

It is common (Balls, 1988, 1990; Tappin *et al.*, 1995) to use the suspended particulate material and the concentration of dissolved trace metals to calculate a distribution

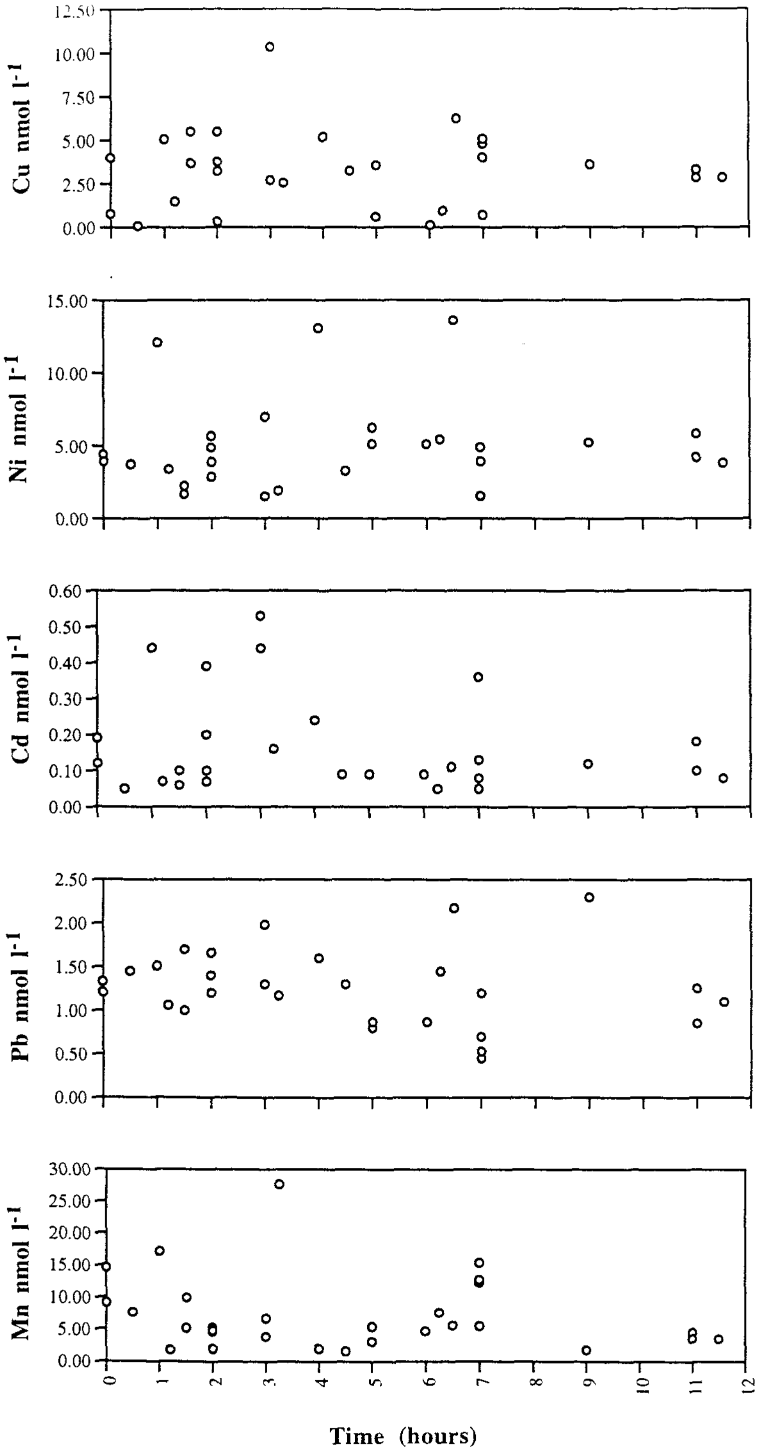

Figure 4.15 Plot of metal concentrations against tidal cycle (0 - high tide, 6 - low tide) for Great Sound.

coefficient (K_d) for the separation of a metal between the dissolved and the particulate phases in seawater. The K_d is calculated according to equation 4.1 (Balls, 1988):

$$K_d=(P*10^6)/C_D \qquad 4.1$$

where

P = concentration of trace metals in particulate material ($\mu g\ g^{-1}$)
C_D = dissolved metal concentration ($ng\ kg^{-1}$)

The K_d is based on the assumption that there is instantaneous and reversible equilibrium between the dissolved and particulate phases, all particle surfaces are alike and complex speciation of the dissolved element is not present (Millward, 1995; Williams, 1995). The seasonal variability of the data for dissolved and particulate material may be more readily interpreted by use of K_d values (Tappin *et al.*, 1995), and this will be discussed in more detail later.

Table 4.7 gives a summary of LogK_d values for the data set in this study.

	log K_d Cd	log K_d Cu	log K_d Ni	log K_d Pb	log K_d Mn
Mean	4.51	5.97	5.35	5.44	5.30
±1 s.d.	0.68	0.83	0.67	0.62	1.73

Table 4.7. Summary data for log K_d values from the inshore waters.

4.4.1 Cadmium

4.4.1.1 Results

The data for dissolved and particulate cadmium in the water column are shown in Figure 4.16 a-h. Dissolved cadmium concentrations while variable, are higher in the St. George's station than the other 7 stations (up to 2.4 nmol l^{-1}). The cadmium associated with the suspended particulate matter (spm) exhibits large degrees of variability at all stations.

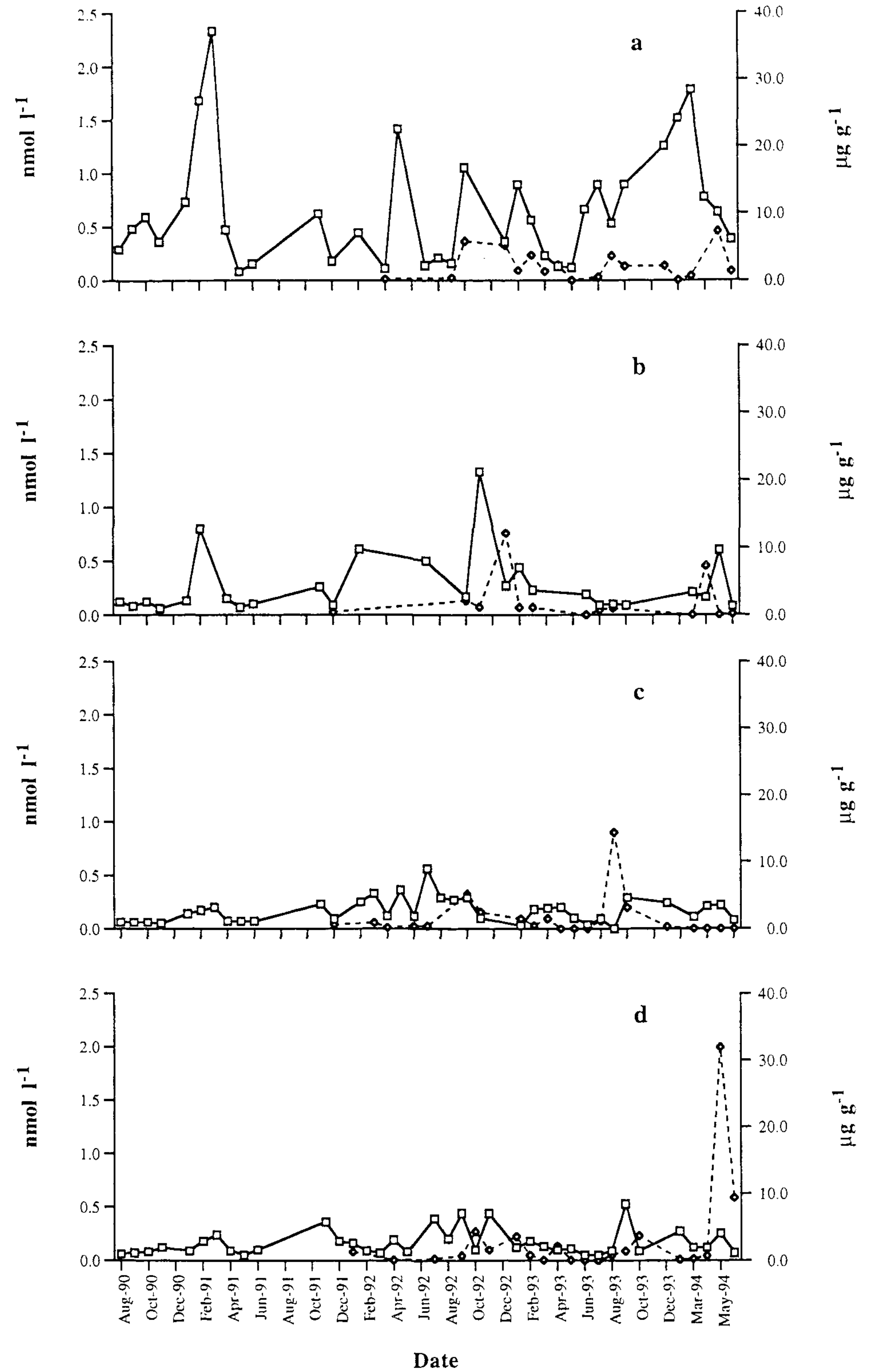

Figure 4.16.
Monthly distribution of dissolved cadmium (solid line) and cadmium associated with suspended particulate material (dashed line) in a) St. George's Harbour; b) Castle Harbour; c) Harrington Sound and d) Great Sound.

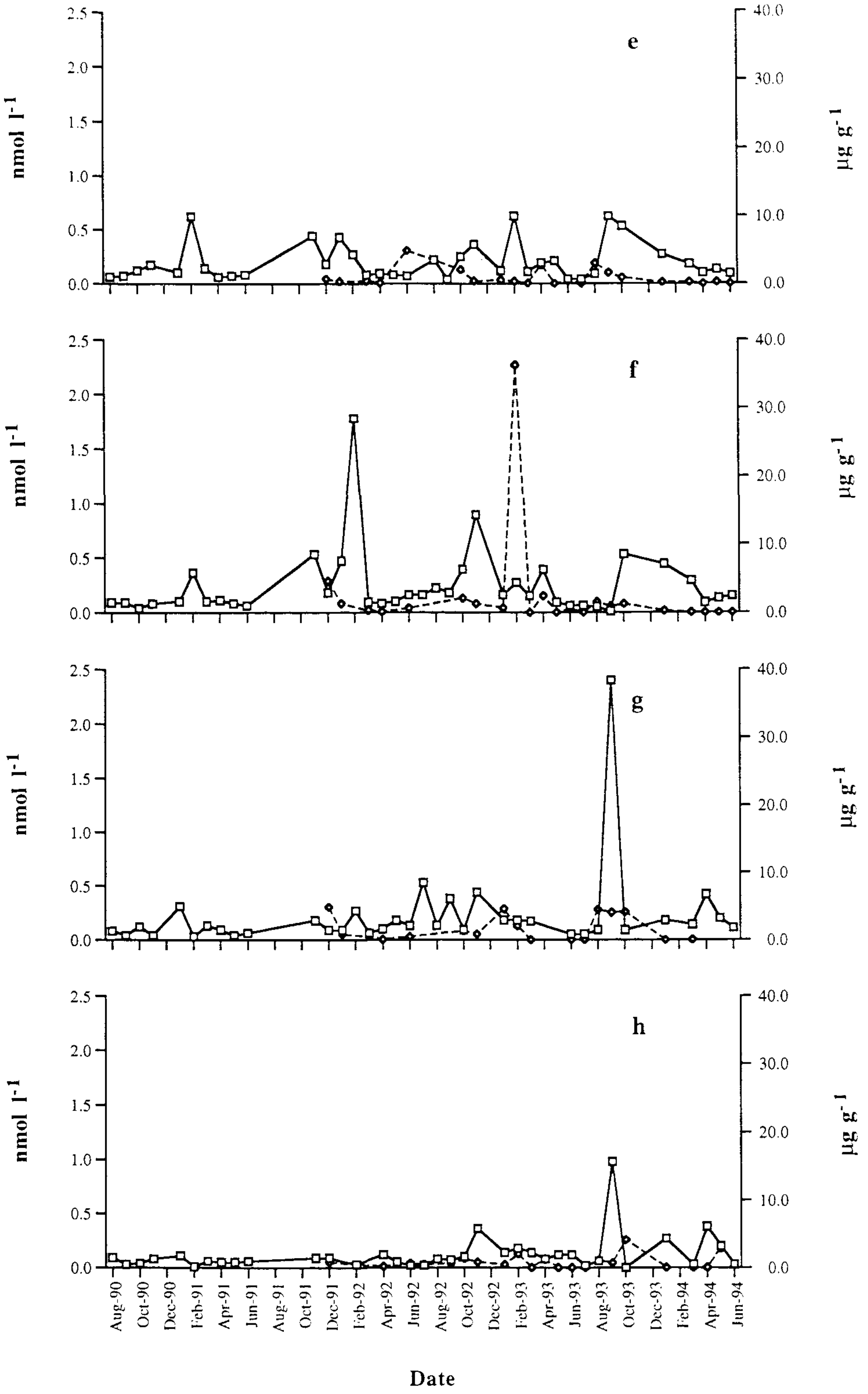

Figure 4.16 cont'd.
Monthly distribution of dissolved cadmium (solid line) and cadmium associated with suspended particulate material (dashed line) in e) Hamilton Harbour; f) Inner Hamilton Harbour; g) North Lagoon and h) Outer North Lagoon.

The data obtained for the study of the cadmium associated with sediment material in the Bermuda coastal zone is presented in Figure 4.17. For all of the stations the concentration of cadmium extracted from sediments using the partial extraction process was below the limits of detection (0.21µg g^{-1}), so the discussion is concerned with only total cadmium. The highest concentrations of cadmium in sediments were found in the St. George's Harbour station. Both of the Hamilton Harbour stations (e and f) are similar. Concentrations in the North Lagoon stations (g and h) are below the limits of detection for this total digestion method (0.06 µg g^{-1}).

4.4.1.2 Discussion

Dissolved cadmium concentrations show distinct spatial distributions. St. George's Harbour has the highest concentrations of cadmium of all the sites studied, 0.7±0.6 nmol l^{-1}. Concentrations at the stations in this study do not differ greatly from each other or from the data collected by Jickells and Knap (1984), with the exception of St. George's where the concentration reported here is 0.7 nmol l^{-1} compared to an earlier value of 0.09 nmol l^{-1}. The data for the current study is comparable to other reported concentrations in nearshore waters: Sanudo-Wilhelmy and Flegal (1991, 1996) report concentrations of dissolved cadmium of 0.034-0.26 nmol l^{-1} for Pacific coastal waters, while Tappin *et al.* (1995) reported concentrations of dissolved cadmium up to 0.7 nmol l^{-1} for the North Sea. These areas are closer to potentially large inputs of cadmium, namely North America and Europe respectively. As was discussed in Chapter 2, there is no major industrial activity on the island of Bermuda.

Because of the isolation of Bermuda, its lack of industry and the proximity of the Sargasso Sea, it is perhaps of more relevance to compare the concentrations obtained in this study with the open ocean concentrations found in other studies: Hydes *et al.* (1986) report open ocean surface values of 0.03 nmol l^{-1} cadmium for the mid-Atlantic ridge area of the north Atlantic; Kremling and Pohl (1989) report dissolved concentrations of up to 0.08 nmol l^{-1} for the continental shelf of Europe, and 0.02 nmol l^{-1} for the open ocean waters. Bruland and Franks (1983) report concentrations of 0.002 nmol kg^{-1} for the Sargasso Sea. These concentrations are similar to those obtained for the stations in the North Lagoon area which has a major water exchange with the open Sargasso Sea.

There are only two significant (r=0.70) correlations for cadmium with all of the studied variables over all of the stations in this study. There is a correlation with dissolved copper (r=0.81) in Castle Harbour and a correlation with suspended particulate material (r=0.8) at the Inner Hamilton Harbour station. There is no correlation with phosphate

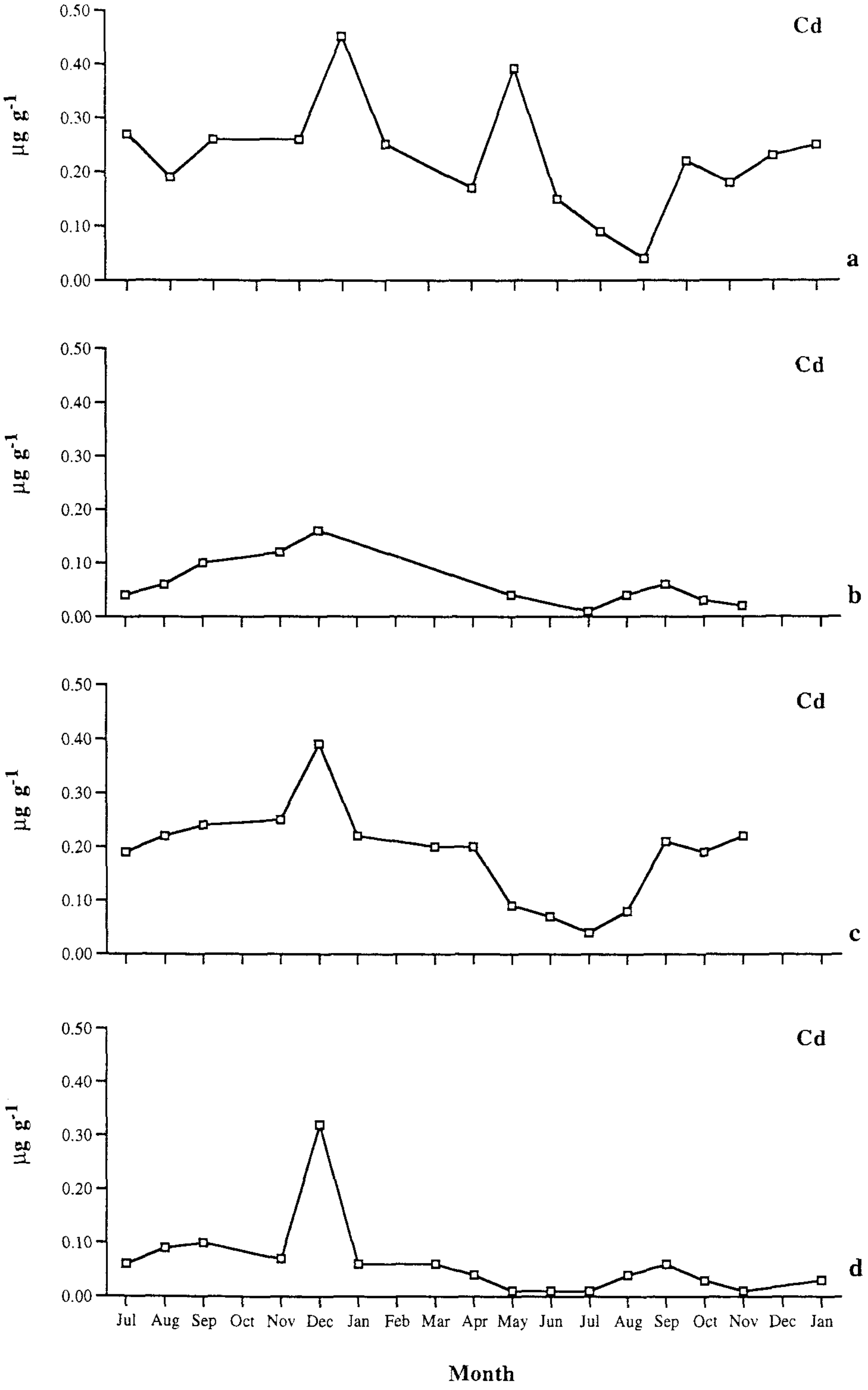

Figure 4.17.
Monthly distribution of total cadmium in sediment material in a) St. George's Harbour; b) Castle Harbour; c) Harrington Sound and d) Great Sound.

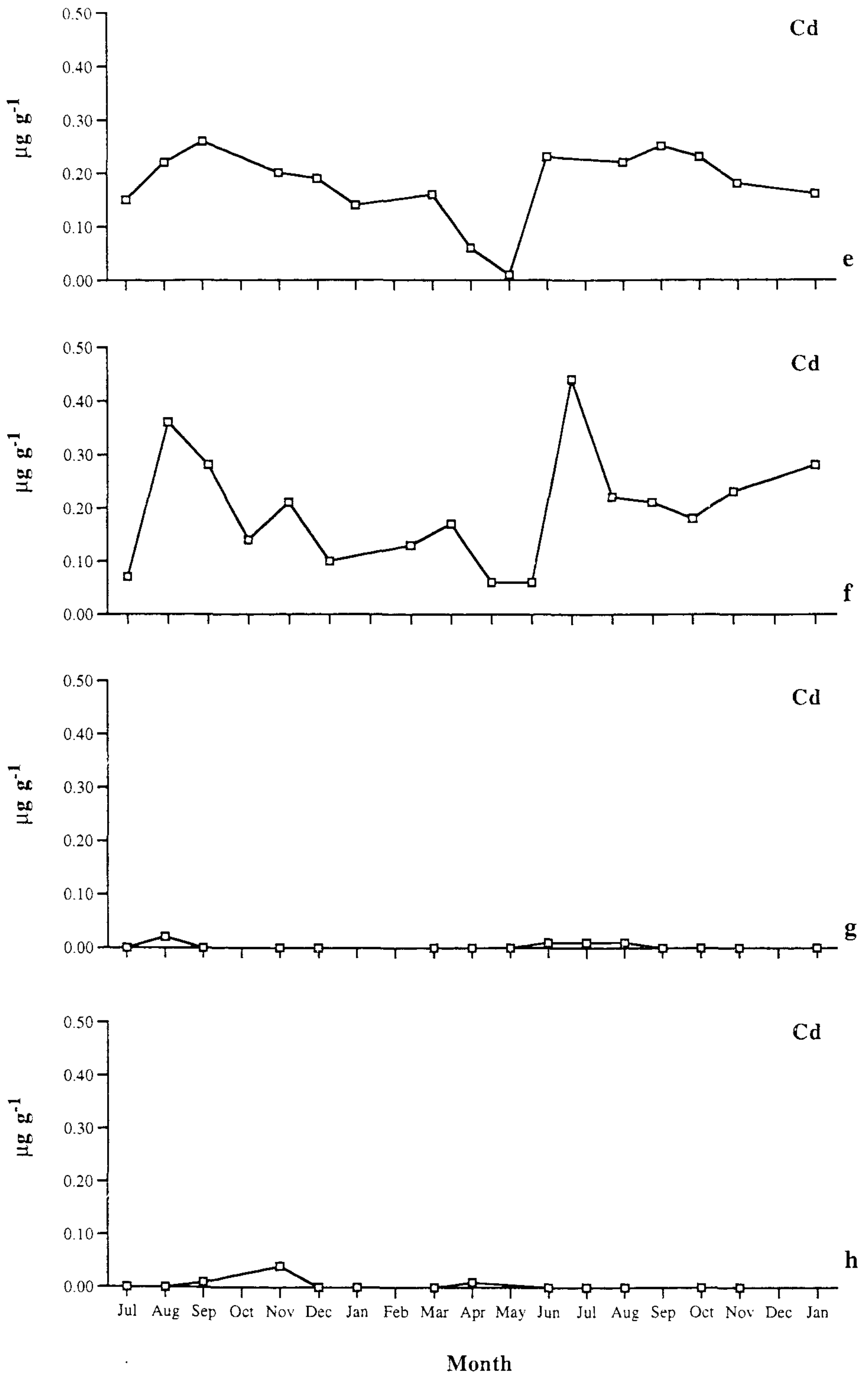

Figure 4.17 cont'd.
Monthly distribution of total cadmium in sediment material in e) Hamilton Harbour; f) Inner Hamilton Harbour; g) North Lagoon and h) Outer North Lagoon.

for any of the stations studied: this is not entirely unexpected as it has been found that the relationship between phosphate and cadmium changes in coastal areas (Jones and Murray, 1984), this is often explained by the fact that in coastal environments there are other factors that affect this relationship, such as inputs of cadmium and vertical mixing of the water column (Ruiz Pino *et al.*, 1990). The correlation of cadmium with suspended particulate matter may simply reflect resuspension of sedimentary material (due to the action of ship passage) which has elevated concentrations of dissolved cadmium (the distribution of cadmium within the sediments is discussed later). Correlation data cannot be assumed to explain in a causal sense what is happening in a system, they can only infer a relationship between the variables.

From the data in Table 4.6 it can be seen that cadmium has the lowest distribution coefficient (K_d) of all the studied metals (log K_d 4.51± 0.68). This implies that the cadmium is less associated with the particulate phase than the dissolved phase, relative to the other metals in this study. This behaviour is commonly reported for cadmium (Balls, 1987, 1988; Hall, 1993; Tappin *et al.*, 1995), as the majority of cadmium is in the form of cadmium-chloro complexes. However, there is evidence that the particulate bound fraction of cadmium can vary from season to season due to the uptake by the biological component in the system, and the concentration of cadmium is elevated in the suspended matter with respect to the sediments. This implies that the suspended matter that is being collected is not just resuspended sedimentary material, although an important caveat to this explanation is that the suspended matter from sediment resuspension is probably the finer fraction of the sediments and this contains more metals relative to the other size fractions (Ripley, 1992), Everaarts and Fisher (1992) reported that there were high concentrations of cadmium (>5μg g^{-1}) in the <63μm fraction of sediments from the Dogger Bank area of the North Sea.

There is evidence that particulate cadmium is associated with the biogenic component of suspended particulate material (Windom *et al.*, 1989). Recently evidence has been presented that cadmium can be used instead of zinc as a micronutrient by certain diatoms (Price and Morel, 1990; Lee *et al.*, 1995). The subsequent removal to the sediments could be in the dead phytoplankton cells. It is also known that cadmium can be scavenged by falling fecal pellets but is rapidly processed by biological breakdown and the cadmium released back to the dissolved phase (Fisher *et al.*, 1991). This probably explains the strong association of the cadmium with the non-labile (as defined by the extraction processes used in this study) fraction of the sediment and reflects this organic association of cadmium. The problem of the high detection limit for the labile cadmium negates an ability to be more positive in this conclusion. MacDonald *et al.* (1991) investigated the distribution of cadmium in the Straits of Georgia, Canada, and found that even though there were recent discharges of cadmium into the water column there was no evidence for a concomitant build up in the sediments. They explained this by the fact that cadmium had a long residence time in the water column, was subject to rapid recycling and as such did not accumulate in the sediments.

Cadmium concentrations in the sediments are higher in Harrington Sound and the Hamilton Harbour stations, compared to the other stations. The data from the partial extraction method indicate that there was no detectable labile cadmium. Since the partial extraction method used dissolved all of the carbonates and probably resulted in the release of metals bound to the surfaces of the sediment particles, it appears that the cadmium is not bound in either of these components of the sediments. It is known from previous work that cadmium can be associated with organic material in sediments: Gerringa (1990) determined that cadmium release from sediments was related in part to the degradation of particulate organic carbon (POC). Results presented here are more in agreement with work from Rule and Alden (1992) who found that the cadmium in sediments was associated with the organic or sulphide component of the sediment.

Rosental *et al.* (1986) and Rifaat *et al.*, (1992) determined that the majority of the cadmium in the sediments was associated with the carbonate phase or the readily released phase of the sediments. Rodger and Davies (1992) found that in sediments collected at a historical sewage dumping site, the majority of cadmium was associated with carbonates. In that study the sediments were predominantly clay and silt with 2-3% organic material. Cadmium has been demonstrated to show an affinity for suspended calcite particles, although it is only loosely held and can be displaced by competition from calcium and magnesium ions in seawater (Kozar *et al.*, 1992a, 1992b). The affinity of cadmium for the hydrolysable sites on particle surfaces under natural environmental conditions was shown to be low in work by Fu and Allen (1992), however these conditions were most likely to be found in freshwater environments and experiments in seawater environments were not performed.

It must be noted that none of these studies were performed in environments that were predominantly calcareous in nature and as such, care must be taken in comparing the results presented here to these other studies. There is reported data for only one study that was undertaken in a mainly carbonate environment: L.A. Hall (1991) examined metal associations in sediments from the Gulf of Paria in Trinidad. For these sediments it was reported that cadmium was associated with the loosely bound fraction of the sediments, such as the carbonates and surface adsorbed species.

There is some evidence that over time metals can change association within the phases of the sediments, through diagenetic changes. Boothman (1988) reported that for sediments collected during the summer months the cadmium was associated predominantly with the organic/sulphide phase, whereas the sediments collected in winter showed an association of cadmium with the more labile phases. This was explained by the oxidation of the organic matter leading to a liberation of the bound cadmium which then re-associates within the sediments but with the more labile phases.

The data for the partial extraction method presented in this work does appear to support the idea that the cadmium is bound to the organic or residual phase of the sediment. When this evidence is combined with that from the Devil's Hole study it is unlikely that carbonates are important sites for cadmium adsorption in sediments and suspended particulate matter in Bermuda.

Whilst the highest concentrations of dissolved cadmium in this present study are found in St. George's Harbour, and these are higher than an earlier study that included this area (Jickells and Knap, 1984), any differences in sediment data are unclear as the earlier study had a high limit of detection (1.2μg g^{-1}) relative to this study.

A study undertaken to determine the source of the cadmium in St. George's Harbour (Connelly, 1993 unpublished Bermuda Government report) determined that there were high concentrations of cadmium in the sediments (generally >1.5μg g^{-1}) in the northeast part of the harbour, in the vicinity of a new boatyard facility. It is assumed that in the construction of this facility, waste that was high in cadmium (probably old Ni/Cd batteries) was used as landfill, this investigation is being continued to include soil samples from this area. Other sources of cadmium around Bermuda are probably from diffuse general anthropogenic activities (incineration and landfill seepage) and runoff.

The sediments have been shown to be a potential source of cadmium, through the tank experiments. The release from the sediments is expected to be through the breakdown of organic bound cadmium (Foerstner *et al.*, 1989). The fact that the highest concentration of dissolved cadmium was found in the area with the highest concentration of sedimentary cadmium may indicate that the sediments are a source of dissolved cadmium. The principal removal route will presumably be via exchange with offshore water that contains less cadmium.

The lack of an inverse correlation of cadmium with salinity would imply that atmospheric wet deposition is not a major source of cadmium in Bermuda. Jickells *et al.* (1984) report that cadmium in rainfall may be significant compared to the open ocean concentrations of this metal. Accordingly rainfall input may be important at the outer North Lagoon station, although it is more likely that the low concentrations of cadmium found at this station are due to the tidal transfer of cadmium from the more polluted inshore stations and mixing with low cadmium offshore waters.

4.4.1.3 Summary

The sources of cadmium in Bermuda appear generally diffuse, with the exception of the input in St. George's Harbour. The low K_d of cadmium indicates that cadmium is predominantly present in the dissolved form in Bermuda waters. The sediments have been shown to be a potential source of cadmium, presumably through the breakdown of organic matter. The principal route for removal of cadmium will be via flushing of the dissolved cadmium out of the area during the tidal cycle. The lack of correlation with salinity implies that atmospheric wet deposition is not a major source of cadmium to the coastal area.

4.4.2 Copper and nickel

Copper and nickel appear to be somewhat conservative in nature in coastal systems (Tappin *et al.*, 1995), although in open ocean environments they show some degree of nutrient type behaviour (Boyle *et al.*, 1981; Bruland, 1980; Morley *et al.*, 1993; Nolting, 1994). As they show similar biogeochemical behaviour the results from these two elements are considered together.

4.4.2.1 Results

The data for dissolved and particulate copper and nickel in the water column are shown respectively in Figure 4.18 (a-h), and Figure 4.19 (a-h).

Dissolved copper concentrations are markedly high in the Hamilton Harbour stations (Fig. 4.18 e, f) relative to the other locations. Concentrations of dissolved copper in St. George's Harbour are lower than the Hamilton Harbour station but higher than the other stations. Concentrations in Great Sound and Harrington Sound (Figures 4.18 c and d respectively) are similar, and higher than copper found at the two North Lagoon stations (g and h) which are comparable to each other except for some lower concentrations found at the Outer North Lagoon station at times. Concentrations of copper associated with suspended particulate matter in the water column are highly variable at all stations. There is no obvious positive correlation between suspended material and dissolved copper, as a result of this large degree of variability in the data..

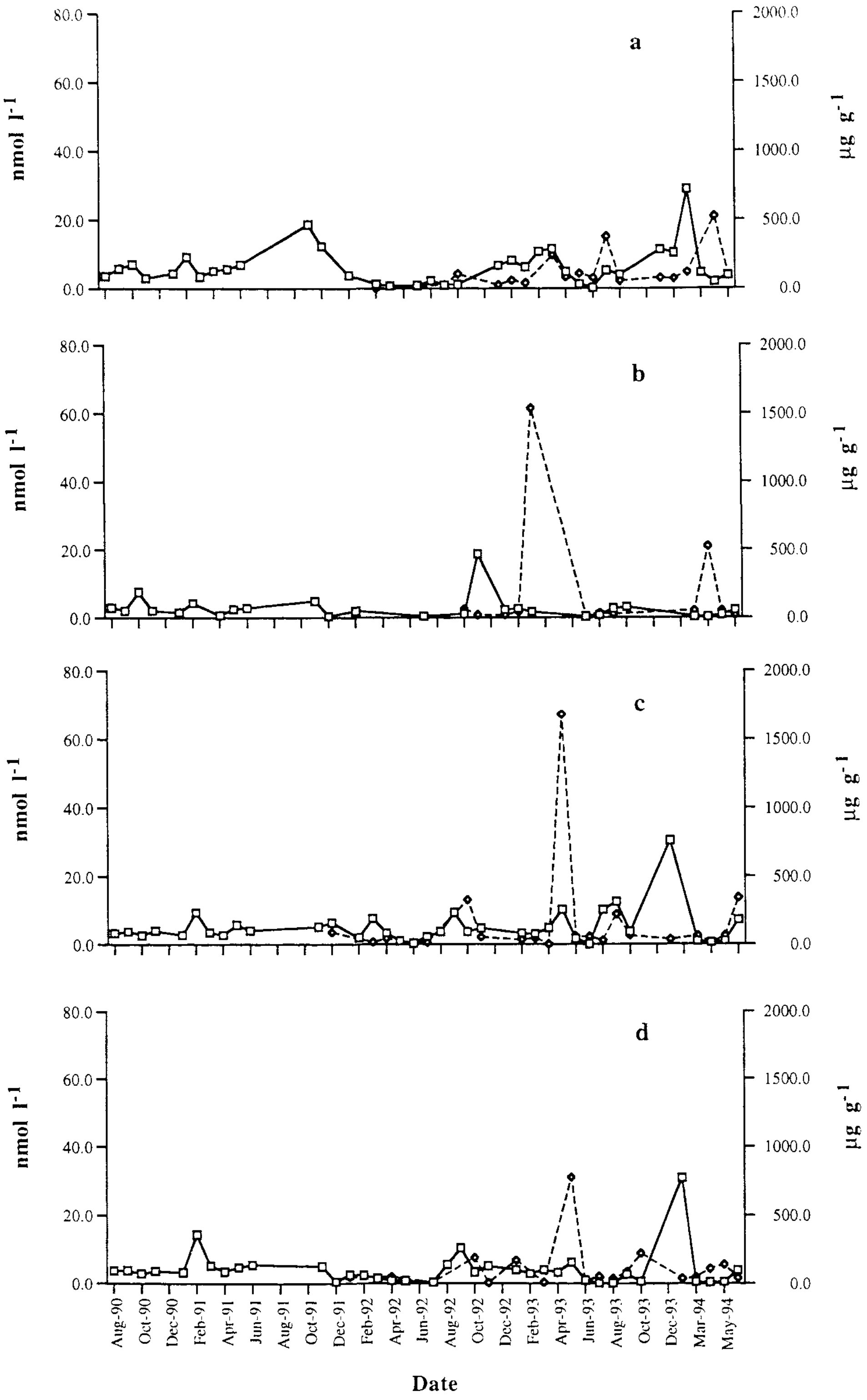

Figure 4.18.
Monthly distribution of dissolved copper (solid line) and copper associated with suspended particulate material (dashed line) in a) St. George's Harbour; b) Castle Harbour; c) Harrington Sound and d) Great Sound.

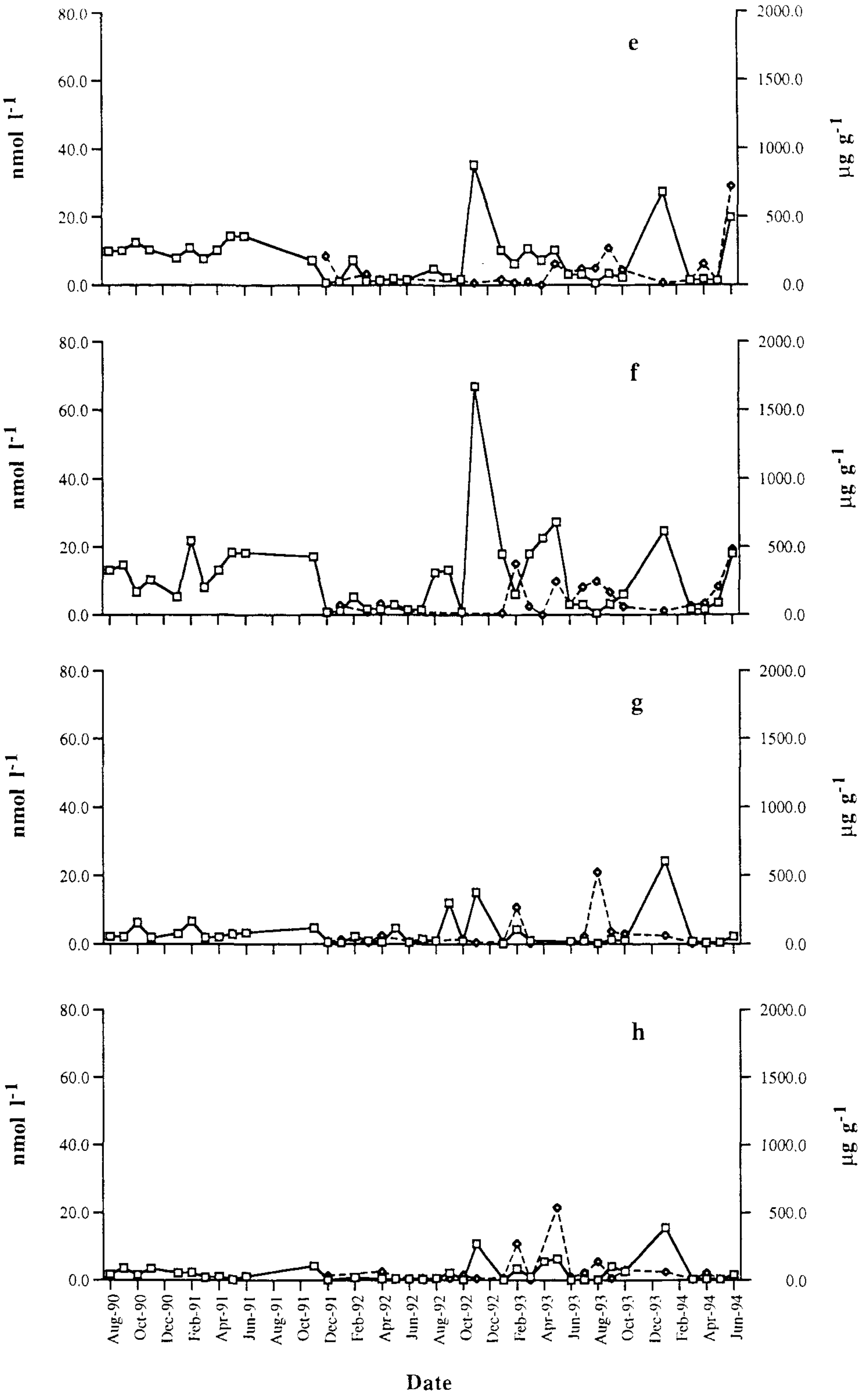

Figure 4.18 cont'd.
Monthly distribution of dissolved copper (solid line) and copper associated with suspended particulate material (dashed line) in e) Hamilton Harbour; f) Inner Hamilton Harbour; g) North Lagoon and h) Outer North Lagoon.

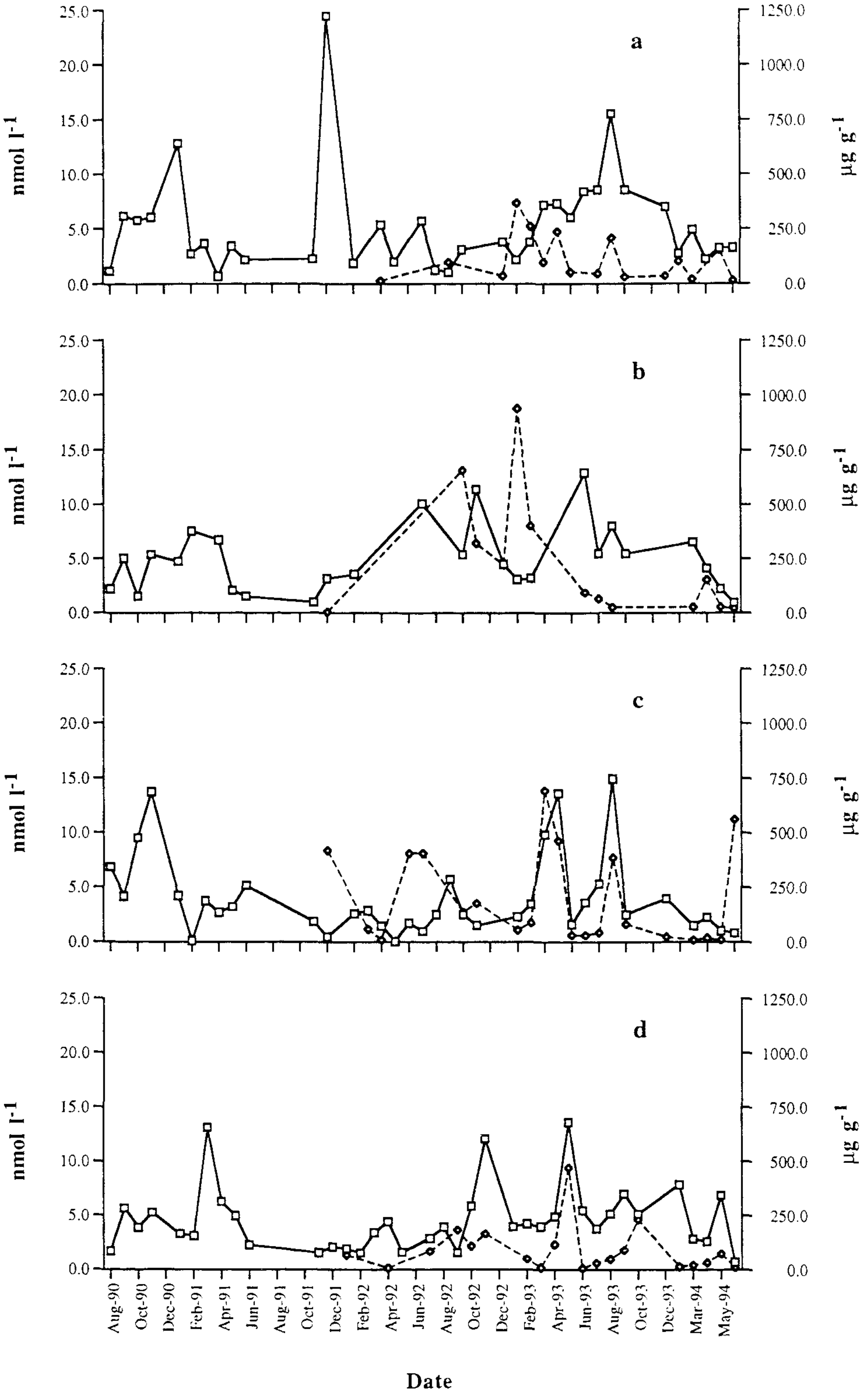

Figure 4.19.
Monthly distribution of dissolved nickel (solid line) and nickel associated with suspended particulate material (dashed line) in a) St. George's Harbour; b) Castle Harbour; c) Harrington Sound and d) Great Sound.

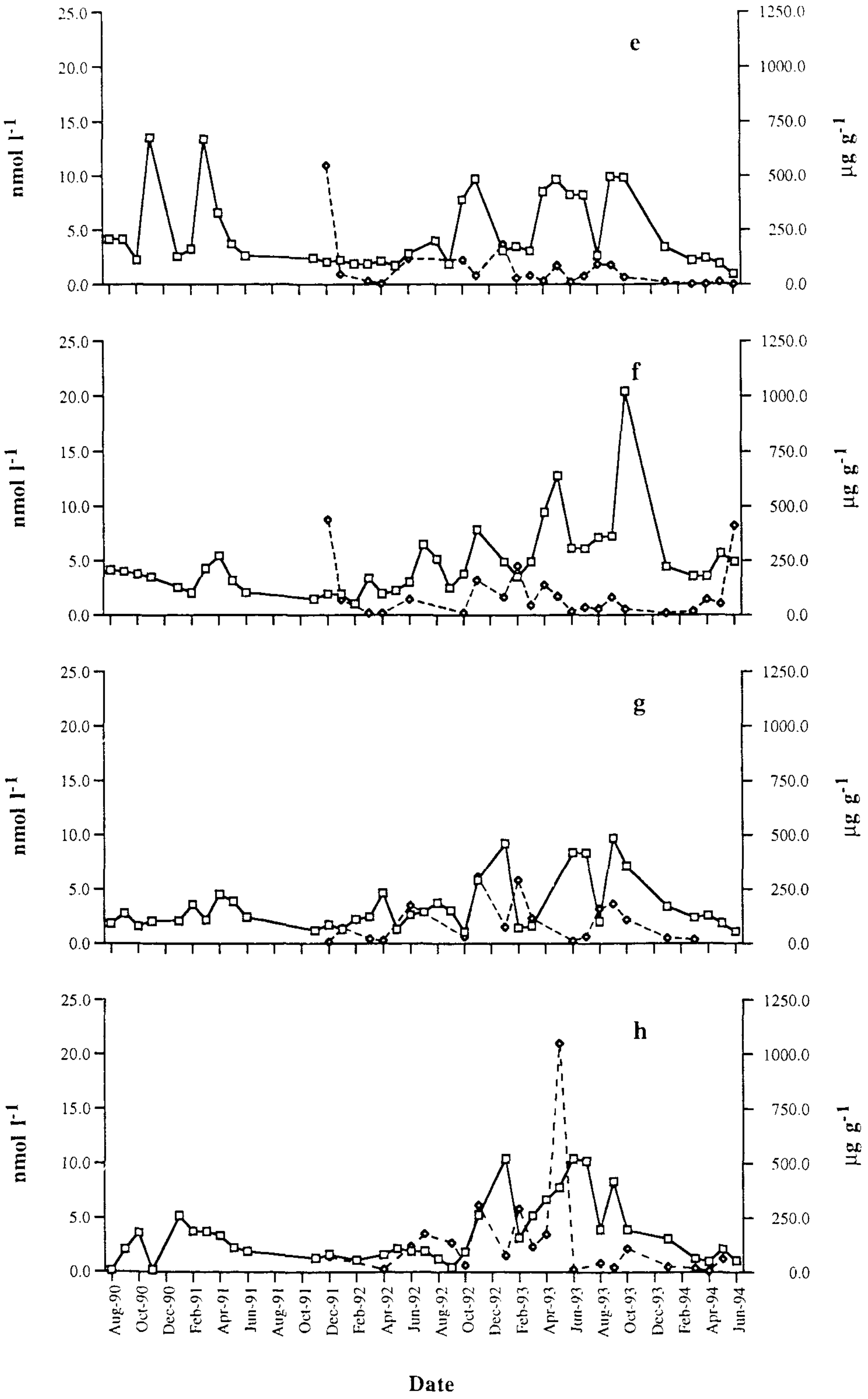

Figure 4.19 cont'd.
Monthly distribution of dissolved nickel (solid line) and nickel associated with suspended particulate material (dashed line) in e) Hamilton Harbour; f) Inner Hamilton Harbour; g) North Lagoon and h) Outer North Lagoon.

The distribution of dissolved nickel between the stations is similar to that of copper. Highest concentrations are found in the Inner Hamilton Harbour station, and the lowest in the North Lagoon stations. As with copper there is no positive correlation between the suspended material in the water column and the concentration of dissolved nickel.

Data for copper in sediments using the labile and total extraction is shown in Figure 4.20 (a-e). Comparing the labile and total extraction processes for copper it is found that for most of the stations for the bulk of the time copper is released using the total extraction method. The highest concentration of copper in sediments is found at the Hamilton Harbour stations, and the lowest in the Outer North Lagoon.

Data for nickel released from sediments using the total and partial extraction is shown in Figure 4.21 (a-e). Total nickel concentrations are similar at all three Harbour stations (a, e and f) and in Harrington Sound (c). As with copper most of the nickel is released using the total extraction technique.

4.4.2.2 Discussion

Average concentrations of dissolved copper are generally lower than those reported by Jickells and Knap (1984) for the stations studied, i.e. 5.1 nmol l^{-1} for St. George's Harbour compared to 10.2 nmol l^{-1} for the earlier study. The stations in this present study that represent less contaminated environments are the North Lagoon stations, where the concentrations of dissolved copper are comparable to the values reported for earlier studies of the Sargasso Sea area, Jickells (1986) reported surface concentrations of copper in the range 1-1.7 nmol l^{-1}.

Dissolved nickel concentrations reported for the present study are consistent between this study and that of Jickells and Knap (1984) for all the stations with the exception of the North Lagoon areas, where the present concentrations, like the copper data, are comparable to those nickel concentrations reported for Sargasso Sea surface waters by Jickells (1986). There are no reported data for dissolved nickel in the earlier inshore waters study (Jickells and Knap, 1984).

There is much debate in the literature as to the possible controlling influence of organic matter on the speciation of copper and nickel (Nimmo *et al.,* 1989; Midorikawa *et al.*, 1992; Hirata, 1992). The stability of the organic complexes of copper and nickel are thought to be different. Nimmo *et al.* (1989) found that for samples from Liverpool Bay 31-41% of the nickel was complexed with stable organic compound while 98-99% of the copper was complexed with organic material as a labile organic species.

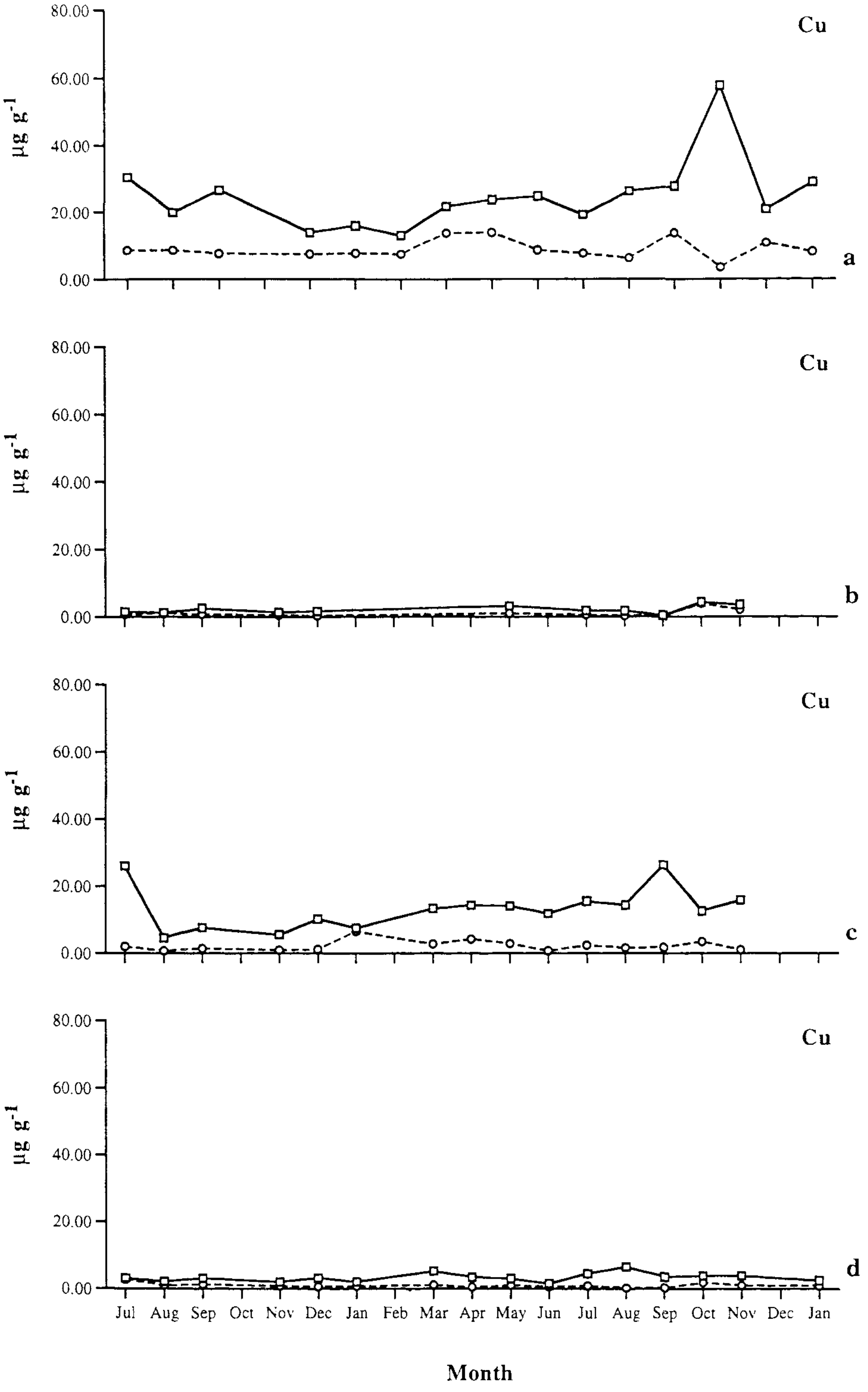

Figure 4.20.
Monthly distribution of total copper (solid line) and partially bound copper (dashed line) in sediment material from a) St. George's Harbour; b) Castle Harbour; c) Harrington Sound and d) Great Sound.

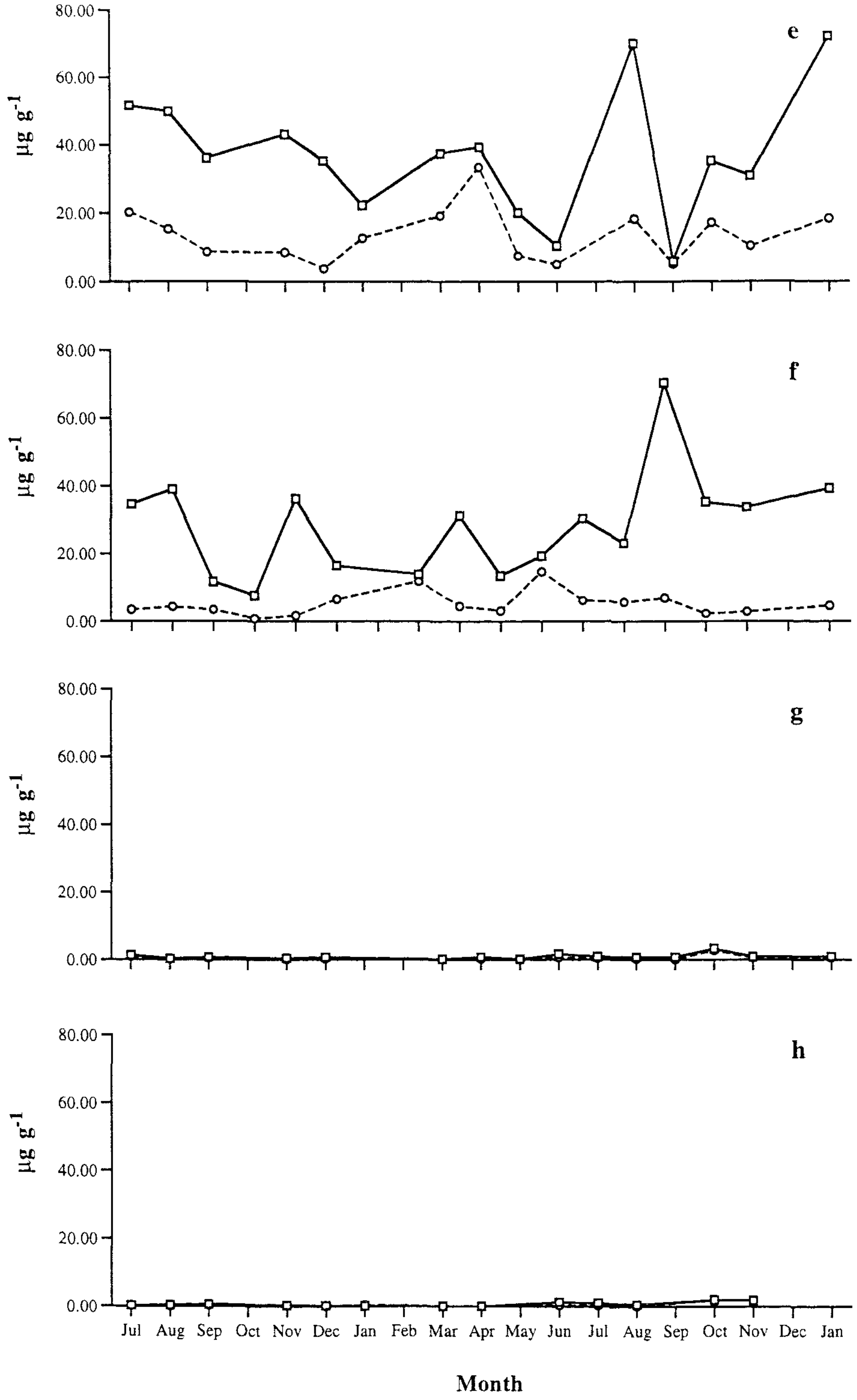

Figure 4.20 cont'd.
Monthly distribution of total copper (solid line) and partially bound copper (dashed line) in sediment material from e) Hamilton Harbour; f) Inner Hamilton Harbour; g) North Lagoon and h) Outer North Lagoon.

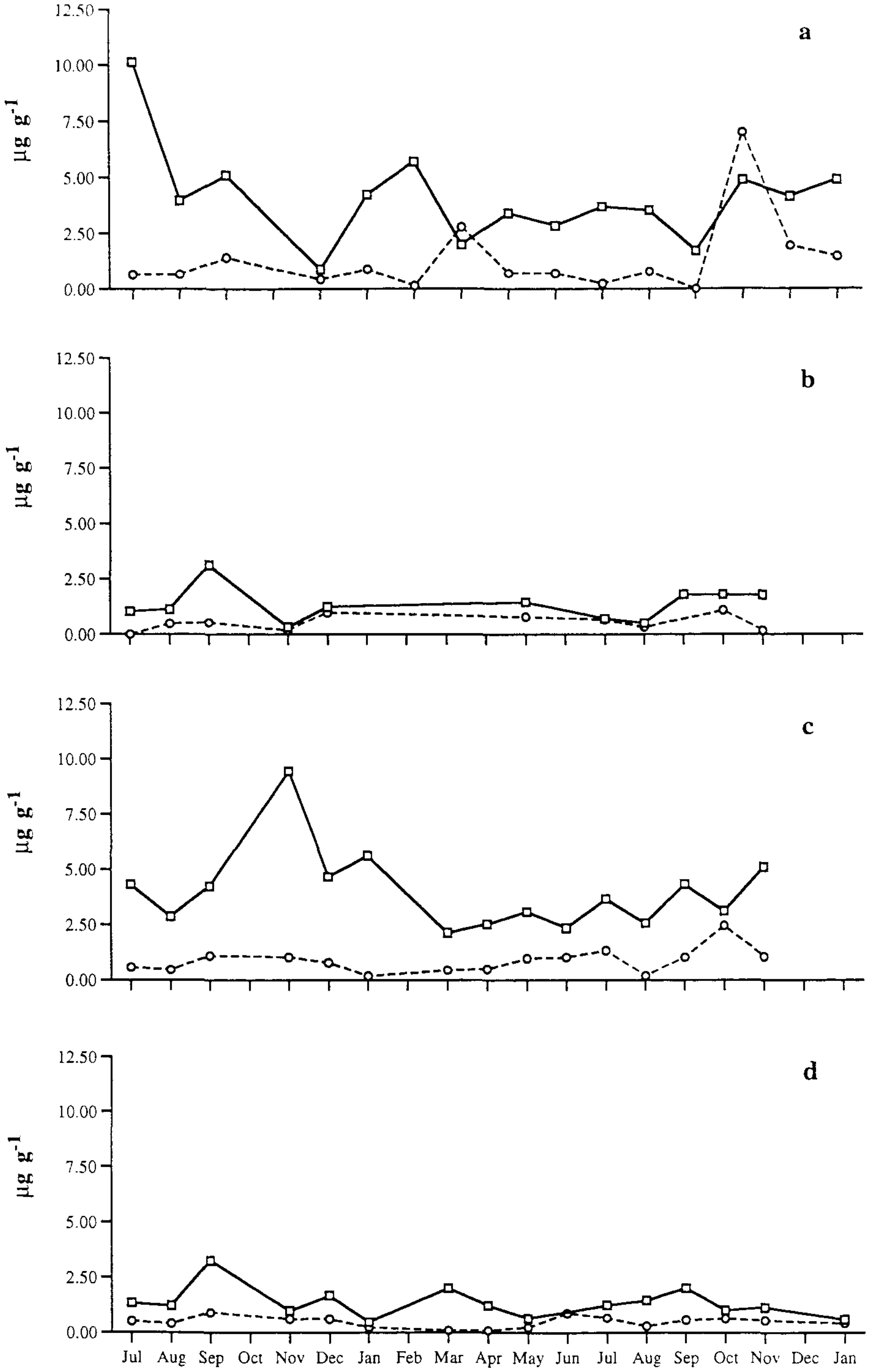

Figure 4.21.
Monthly distribution of total nickel (solid line) and partially bound nickel (dashed line) in sediment material from a) St. George's Harbour; b) Castle Harbour; c) Harrington Sound and d) Great Sound.

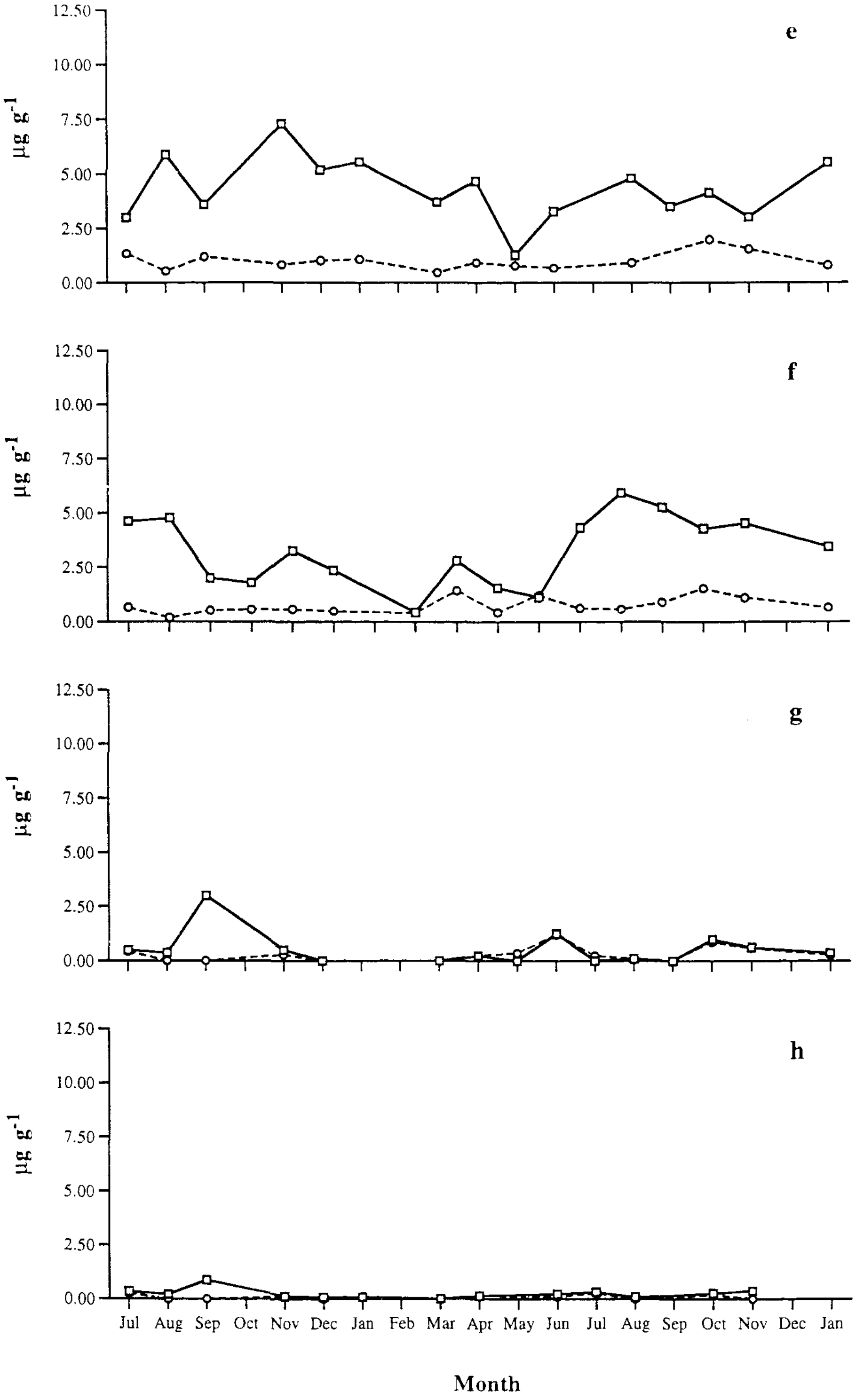

Figure 4.21 cont'd.
Monthly distribution of total nickel (solid line) and partially bound nickel (dashed line) in sediment material from e) Hamilton Harbour; f) Inner Hamilton Harbour; g) North Lagoon and h) Outer North Lagoon.

The nature of these organic compounds is not fully established, and the differences in stability may infer that there is not just one group of organic compounds involved. Midorikawa *et al.* (1992) identified three complexing organic species in seawater that were capable of binding trace metals, and one of these had a high affinity for copper. Hirata (1992) investigated the complexation of metals by one group of organic compounds found in marine systems, the humic acids, in the sea off Japan. He reported that naturally occurring humic acids were enriched with nickel, copper, aluminium, manganese and zinc relative to the sediments in the same area. Sunda and Hanson (1987) and Paulson *et al.* (1994) reported that most of the copper in seawater was bound in organic complexes. The source of this organic material is debatable. It is known that algae are responsible for some of the dissolved organic matter in the ocean. Sunda and Gessner (1989) isolated dissolved organic material from marine fungi that was capable of complexing ionic copper. The nature of the remaining copper that is not complexed with organic material is thought to be predominantly in the form of carbonato (Symes and Kester, 1985) or chloro compounds (Millero and Hawke, 1992).

The behaviour of nickel in the water column is not as well investigated as that of copper. Oh (1991) reported that 21-68% of the nickel in seawater was associated with organic material. Barbeau and Wollast (1994) reported that the abiotic sorption of nickel onto particles was slow in the natural seawater environment. This implies that most of the nickel in the water column is in the dissolved form in the absence of biologically mediated reactions. The concentration of spm is known to have a large effect on the distribution coefficients of metals.

The distribution coefficient for copper (using total leaching) is on average higher than that of nickel (5.97±0.83 c.f. 5.35±0.67). The coefficients reported here are higher than those reported by Balls (1989) and Statham *et al.* (1991), who report 4 - 5 for copper and 4 - 4.5 for nickel. Copper is therefore predominantly associated with the particulate phase in the Bermuda system, with only a narrow range of log K_d values. The K_d value gives no information as to which phase of the particles the copper is bound, there is evidence that there is an association with the organic film on the particles (Goldberg *et al.*, 1988). There is evidence for the rapid uptake of copper by calcite in marine systems (Franklin and Morse, 1982) and whereas this could be an important process in the carbonate dominated system in Bermuda, there is no supporting evidence from the partial extraction data from the sediments. However, Monteny *et al.* (1993) report that the complexation of copper with organic compounds maintains copper in the dissolved phase and is responsible for the conservative nature of copper through estuarine systems.

Both the copper and nickel are more concentrated in the suspended particulate material relative to the sediment material; this is particularly marked in the case of nickel. The degree of enrichment between suspended particulate material and sediment is different for each station, with the suspended particulate material in the less contaminated North Lagoon areas having a greater enrichment compared to the sediments. This may indicate a preferential binding of copper and nickel with the biological component in the suspended particulate material; in the harbour stations it is thought that some of the suspended particulate material is by shipping activity. The relative importance of the biological component would be greater, as observed, at the offshore stations where there would be no "dilution" with resuspended sediment material.

The present study indicates that there is a positive correlation for dissolved copper with dissolved cadmium in Castle Harbour (r=0.84), and a correlation between nickel and copper (r=0.80) at the Outer North Lagoon station. Nickel shows correlations with lead in Harrington Sound (r=0.84) and a multi-correlation with copper, manganese, chlorophyll and salinity (r=0.80, r=0.77, r=0.85 and r=0.71 respectively) for the Outer North Lagoon station. The multi-correlation at the Outer North Lagoon station is interesting- at this station there is less likely to be the large and regular physical disturbance from ship activity that is present at the other stations (with the exception of Harrington Sound and Castle Harbour stations). Overall there is no clear correlation in the data or obvious single process at work for nickel and copper in the Bermuda coastal waters.

Concentrations of copper and nickel in the sediments are elevated in the harbour stations and Harrington Sound. The concentrations of copper are comparable to those obtained by Jickells and Knap (1984), but the range is lower than that reported by Lyons *et al.* (1983) with total concentrations of copper ranging from 21-129 $\mu g\ g^{-1}$ sediment in Hamilton Harbour. The most obvious source in the Harbour areas is the large number of boats on moorings that use copper and tin based anti-fouling paints (Connelly *et al.,* 1997). There are few data with which to compare the current nickel data; Jickells *et al.*, (1986) reported nickel concentrations $< 12.5\ \mu g\ g^{-1}$ in Hamilton Harbour and $< 5\ \mu g\ g^{-1}$ for North Lagoon.

A comparison of data for the partial and total extraction methods indicates that for most stations the ratio of total to labile copper and nickel is high. This implies, as was discussed for the spm above, that copper and nickel are associated with the organic material in the sediments or are associated with the refractory mineral phase (see Chapter 3). Since the sediments in Bermuda are predominantly calcareous in nature, with the remainder being organic matter, this refractory material is insignificant in this study. The lack of refractory material in the sediments therefore supports the idea that the copper and nickel are associated with organic material.

In sequential extraction experiments on other sediment systems this association of nickel and copper with organic material is identified, although Tessier *et al.* (1979) found that only 25% of the copper was associated with the organic material and up to 50% of the nickel was in the residual phase. In contrast Rosental *et al.* (1986) found that 80% of the copper and 60% of the nickel was associated with the organic fraction; the remainder of the copper was associated with the carbonates and the nickel with the refractory material, whilst Gerringa (1990) determined that copper and nickel were strongly associated with organic material in sediments, and suggested that the release of copper was brought about by the degradation of those organic components in the sediments. Kerner and Geisler (1995) suggest that the copper is released as the organic material degrades but that it binds to newly arriving organic material and is not released to the water column until all organic material is degraded. This would occur if the productivity in the water column above the sediments decreased and the supply of organic matter was reduced or stopped (i.e. at the end of a bloom event, or the onset of stratification in the water column above the sediments). The nickel is not so readily released as copper and Gerringa (1990) argued that this was due to differences in the nature of the organic complexes with the metals. In contrast to the findings here and other cited work L.A. Hall (1991) found (using the method of Tessier *et al.* 1979) that in carbonate sediments the copper was associated with the loosely bound phase, and nickel with the organic material.

4.4.2.3 Summary

Copper concentrations, are higher than those of a background concentration (Sargasso Sea water), in the coastal waters of Bermuda and appear to come primarily from the use of copper based anti-fouling paints. The highest concentrations of copper are found in areas that have a high degree of boating activity. There is evidence that the sediments in the inshore areas can act as both a sink and source for dissolved copper. Removal of dissolved copper from the coastal zone will be via flushing during the tidal cycle, and particle deposition of copper to the sediments.

Nickel is thought to come from a variety of diffuse anthropogenic sources. Organic matter appears to play a role in the behaviour of nickel in the Bermuda Coastal Zone and rain events and associated run-off appear to have a strong influence on the distribution of particulate nickel in the inshore waters. Nickel appears to be relatively unaffected by the onset of anoxia in field, although the results from laboratory simulations are contrary to these observations.

4.4.3 Lead

4.4.3.1 Results

Lead concentrations in the water column, both dissolved and associated with spm, can be seen in Figure 4.22. a-h. Dissolved lead concentrations are highest in the Hamilton Harbour/Great Sound basin, and lowest in the North Lagoon. Lead associated with the spm is highest in St. George's Harbour and the Inner Hamilton Harbour, although as with all metals there is a great degree of variability within the data set.

Total lead and labile lead for all stations are shown in Figure 4.23. a-h. Concentrations of total lead are highest at the St. George's and at Hamilton Harbour Stations. There is detectable total lead (>0.03μg g^{-1}) for at least some parts of the year at all Stations, and for all Stations the labile lead represents the majority of the total lead present (>75%).

4.4.3.2 Discussion

Lead is known to be readily bound to particles in the marine environment (Turekian, 1977; Whitfield and Turner, 1987; Lambert *et al.*, 1991). There is detectable (>0.03 nmol l^{-1}) dissolved lead at all stations in this study, with the harbour stations tending to have the highest concentrations. The dissolved lead concentrations reported here are significantly lower than those reported by Jickells and Knap (1984), where concentrations varied between 0.7-5.8 nmol l^{-1}, although it must be pointed out that this was only one sample taken for each of the stations in this earlier study. The concentrations of dissolved lead at the Outer North Lagoon station are comparable with data obtained for the North Atlantic and Sargasso Sea (Boyle and Huested, 1983; Schaule and Patterson, 1983) and indicate that for the purposes of this study this station is representative of an uncontaminated site, and provides oceanic concentrations of lead.

It is interesting to note that the concentrations of dissolved lead are higher in this study than those reported for the North Sea, (0.2 nmol l^{-1}; Tappin *et al.*, 1995), an area that presumably has higher anthropogenic inputs of lead. This may be due to the high concentration of particulate material in the North Sea reported in that study, and the efficient adsorption of the dissolved lead by this particulate material.

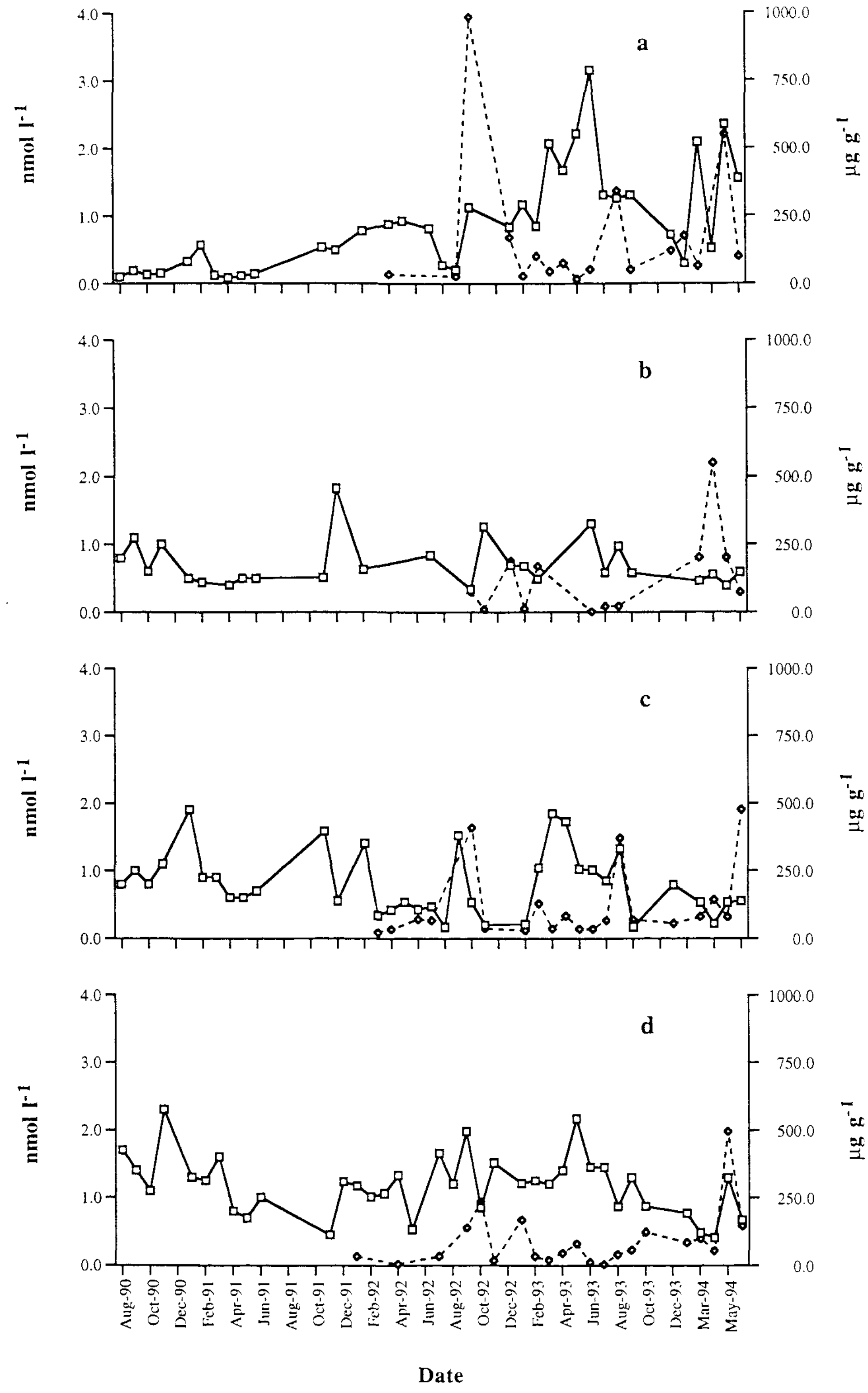

Figure 4.22.
Monthly distribution of dissolved lead (solid line) and lead associated with suspended particulate material (dashed line) in a) St. George's Harbour; b) Castle Harbour; c) Harrington Sound and d) Great Sound.

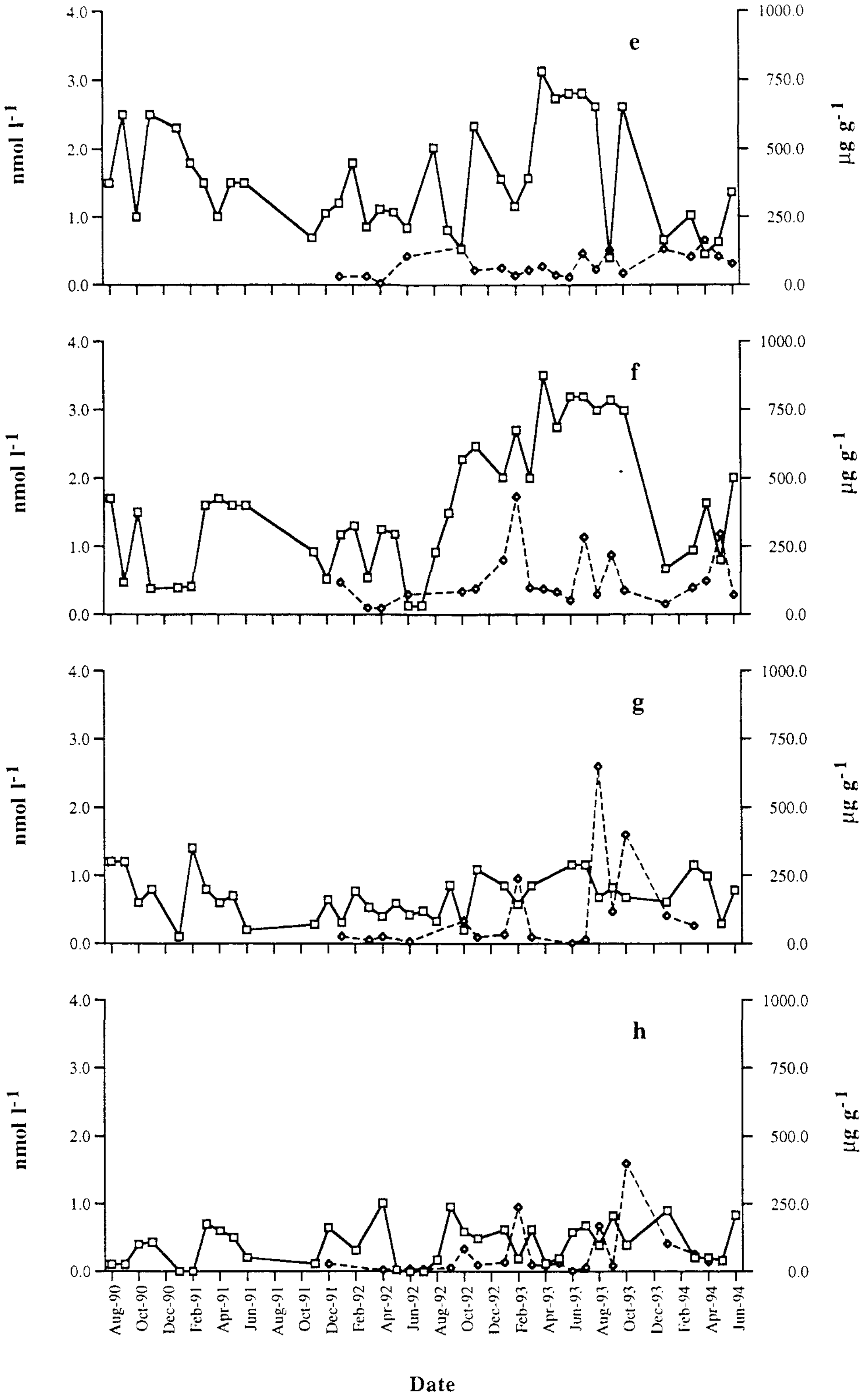

Figure 4.22 cont'd.
Monthly distribution of dissolved lead (solid line) and lead associated with suspended particulate material (dashed line) in e) Hamilton Harbour; f) Inner Hamilton Harbour; g) North Lagoon and h) Outer North Lagoon.

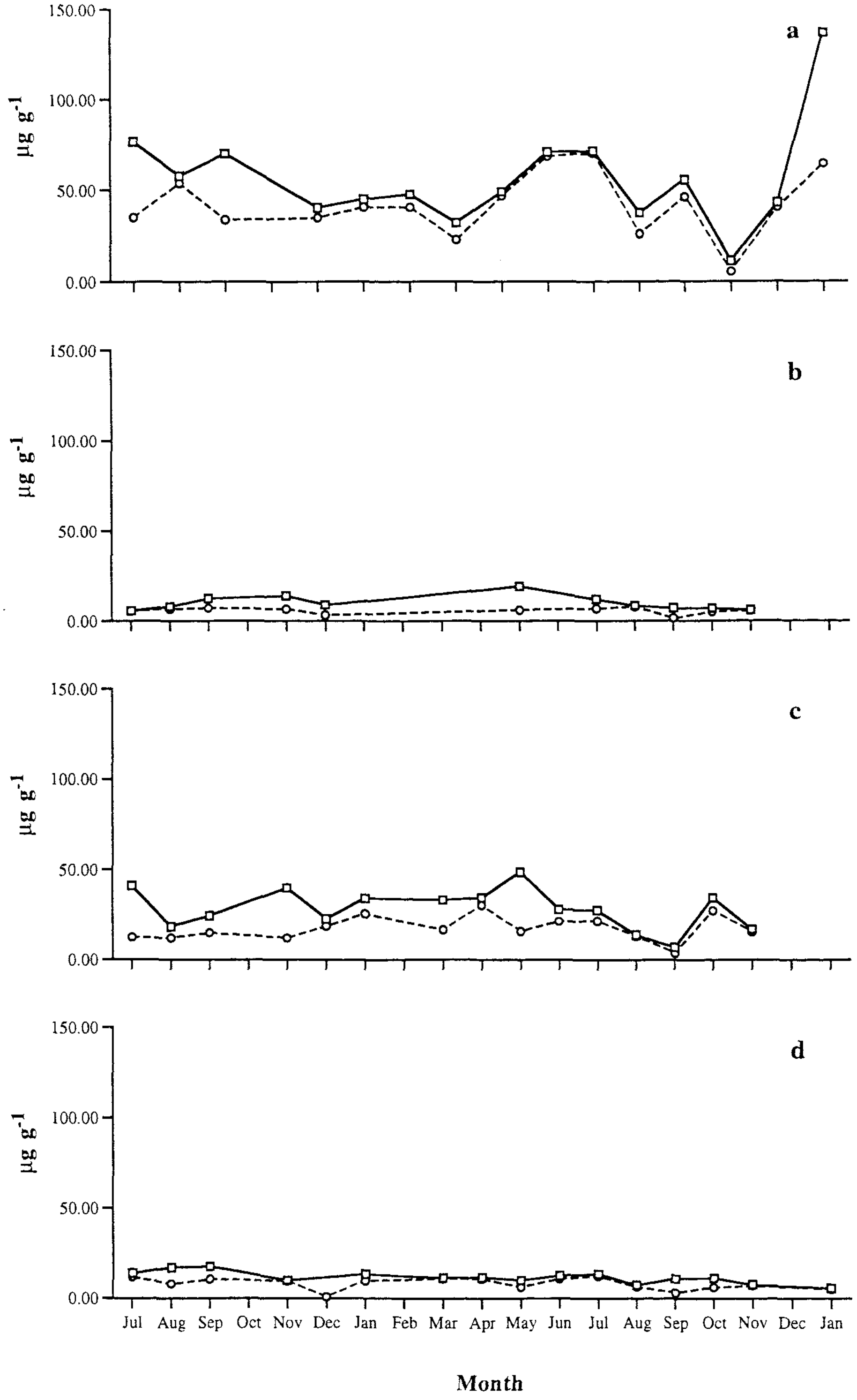

Figure 4.23.
Monthly distribution of total lead (solid line) and partially bound lead (dashed line) in sediment material from a) St. George's Harbour; b) Castle Harbour; c) Harrington Sound and d) Great Sound.

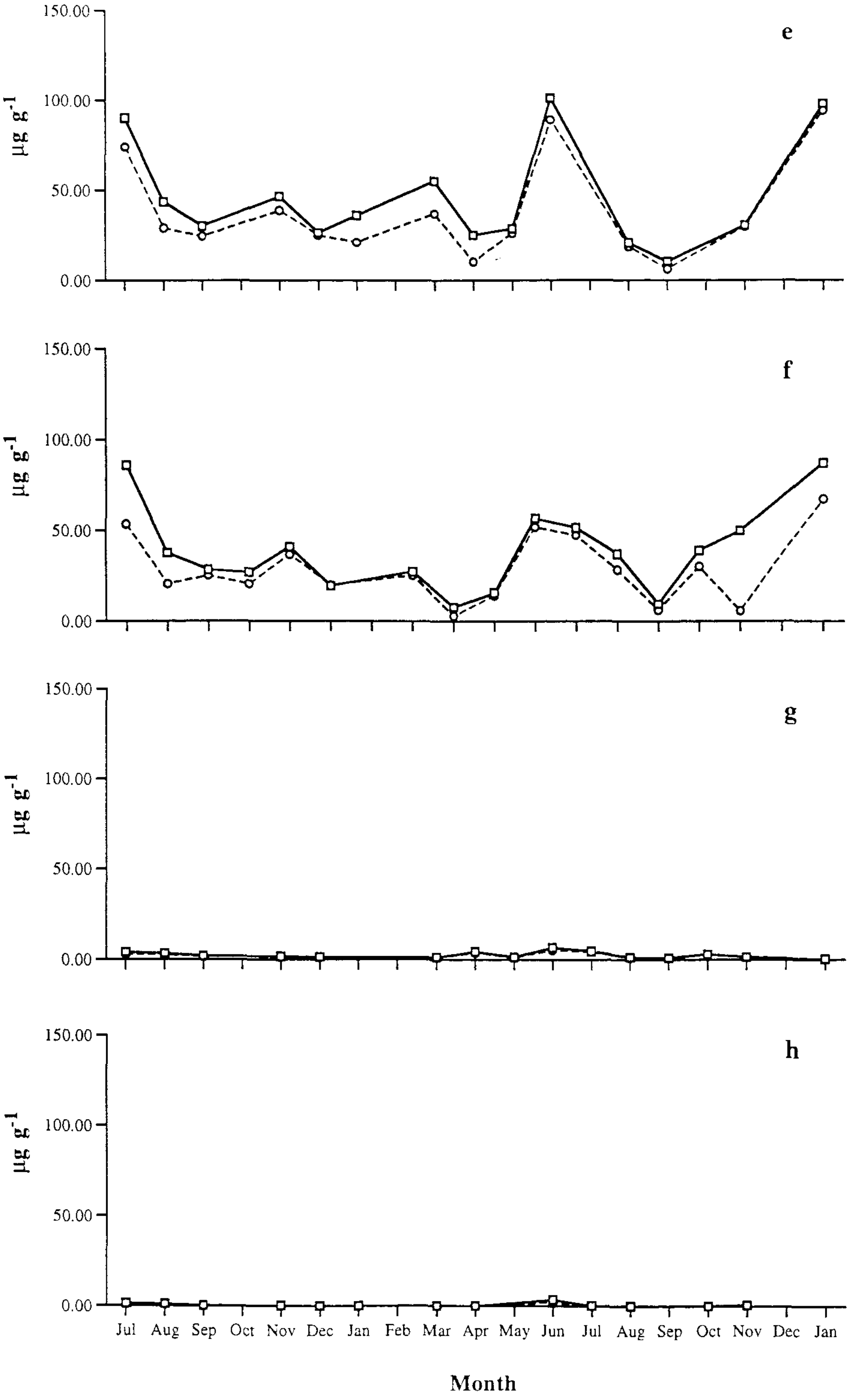

Figure 4.23 cont'd.
Monthly distribution of total lead (solid line) and partially bound lead (dashed line) in sediment material from e) Hamilton Harbour; f) Inner Hamilton Harbour; g) North Lagoon and h) Outer North Lagoon.

The range of K_d values for lead in this study (log K_d approximately 5.4 - 5.7), is narrower than that found for other studies, and is at the lower end of the reported ranges: Balls (1989) reported that the log K_d for lead in a range of different inshore environments around the UK was between 5 and 7, whilst Tappin *et al.* (1995) report log K_d values for the North Sea in the range 5-7.5, with a seasonal difference for the log K_d distribution.

The concentrations of lead in the sediments around Bermuda follow the same trend as the dissolved metal. There are higher concentrations of lead at the St. George's Harbour, Hamilton Harbour and Harrington Sound stations. This is probably a result of two factors. Firstly, the harbours and Harrington Sound have a longer residence time of water than the other stations, and, hence lead introduced to these areas is likely to be incorporated into the sediments before removal by physical flushing processes. Secondly the St. George's Harbour and the two Hamilton Harbour stations are located at the centres of the highest human population density on Bermuda and are also areas with the highest automobile traffic. Harrington Sound, with the longest residence time of all the inshore basins, represents a natural sediment trap; the high concentrations of trace metals here are presumably a reflection of long term accumulation. The depth of water at this station combined with the lack of heavy shipping to disturb the sediments also adds to the potential for long term accumulation of lead and other metals.

The lead concentrations in the sediments for this study are comparable to those obtained by Jickells and Knap (1984), with the exception of the Hamilton Harbour stations which were lower (Jickells and Knap (1984) report a range of concentrations of lead 46-101 $\mu g\ g^{-1}$ sediment). Lyons *et al.* (1983) report concentrations of lead in the sediments of Hamilton Harbour between 105 and 229 $\mu g\ g^{-1}$, significantly higher than this present study and that conducted by Jickells and Knap (1984), although this study used a nitric acid/hydrofluoric acid total digest. This may result in a higher recovery of lead compared to this report and that of Jickells and Knap (1984), both of which used nitric acid only. It is more likely that the samples were taken in a different place within the Harbour.

Tessier *et al.* (1979), Boothman (1988) and Hall (1991) all report that the majority of lead in their study sediments was associated with the residual phase of the sediments. Rosental *et al.* (1986) found that 30% of the lead was associated with the carbonates, 45% with the residual phase and up to 20% was associated with the organic/sulphide phase. Scoullos (1986), using sediments from the coastal zone of Greece, found that 40% of lead was associated with the organic/sulphide phase and 30% was associated with the iron/manganese coatings and the carbonates. Giani *et al.* (1994) report that lead in sediments from the Northern Adriatic was distributed equally between the carbonate phase and the organic/sulphide phases in the sediments. Ripley (1992) investigated sediments from Bermuda and reported that lead was associated with the carbonate phase in the sediments. For all of the stations the majority of the lead was removed from the sediment during the partial extraction process. This would indicate that the lead is adsorbed on the surface of the sediments, or associated with either the manganese/iron hydroxides or carbonates. From these reports it is clear that the lead association in sediments is partly dependent on the composition of the sediments, but where there are carbonates present some lead will be associated with it.

The association of lead with carbonates is not unexpected as the majority of lead is thought to be anthropogenic in nature from gasoline in vehicular emissions, and the exhausted lead predominantly (>90%) is in the form of an inorganic lead bromide/chloride complex (Finlayson-Pitts and Pitts, 1986), which readily forms a carbonate complex in the marine environment (Rosental *et al.*, 1986).

The results from this present study indicate that the release of lead from sediments in Bermuda occurs under both oxic and anoxic conditions. Balzer and Wefer (1981) present evidence for the dissolution of carbonate material under anoxic environments, which may lead to the release of lead associated with the carbonates. In oxic environments in Bermuda there may be release of lead from the sediments due to organic degradation, the mechanism of lead uptake into the organic phase of the sediments is discussed in the Harrington Sound section.

4.4.3.3 Summary

Dissolved lead concentrations are high relative to other studies of coastal areas, and are probably due to the low concentrations of suspended particulate material in the water column in Bermuda. The release of lead from the sediments appears minimal under both oxic and anoxic conditions for most of the areas in Bermuda. However the experimental simulations in this study indicate that there could be release from the more contaminated sediment in Bermuda. The mechanism for this is not fully understood. It is likely that there is mobilisation of the carbonate under anoxic conditions and this would release lead to the dissolved phase. The degradation of organic compounds in the sediment would lead to the release of lead associated with that material.

4.4.4 Manganese

Manganese, although particle reactive (Hunt, 1983), can also be subject to redox mediated mechanisms (Statham and Burton, 1986). These redox changes can be predominantly non-biological in nature, such as the distribution of manganese at reducing/oxic interfaces and photochemical reactions, or biologically mediated (Sunda and Huntsman, 1988).

4.4.4.1 Results

Data for the monthly concentrations of dissolved and particulate manganese can be seen in Figure 4.24. Dissolved manganese concentrations (Figure 4.24) are generally highest in St. George's and Hamilton Harbours. As with the other metals, the lowest concentrations of manganese are found at the Outer North Lagoon station (Fig. 4.24 h). Particulate bound concentrations of manganese are also high in the Harbour stations, although as was the case with the other metals, there is a high degree of variability within the data set.

The results for the concentrations of both total and labile manganese in the sediments are given in Figure 4.25. Generally the concentrations of manganese in sediments are similar in the Harbour station (Fig 4.25 a, e and f), and in Harrington Sound. For most of the stations, during most of the year, the majority of the manganese is released by the partial extraction method. However, the data for Harrington Sound reveals a greater proportion of the manganese is released after the total digestion during the summer period. For Hamilton Harbour at certain times of the year (Aug.-Dec.; Jul.-Oct.) there are higher proportions of labile manganese relative to the rest of the year.

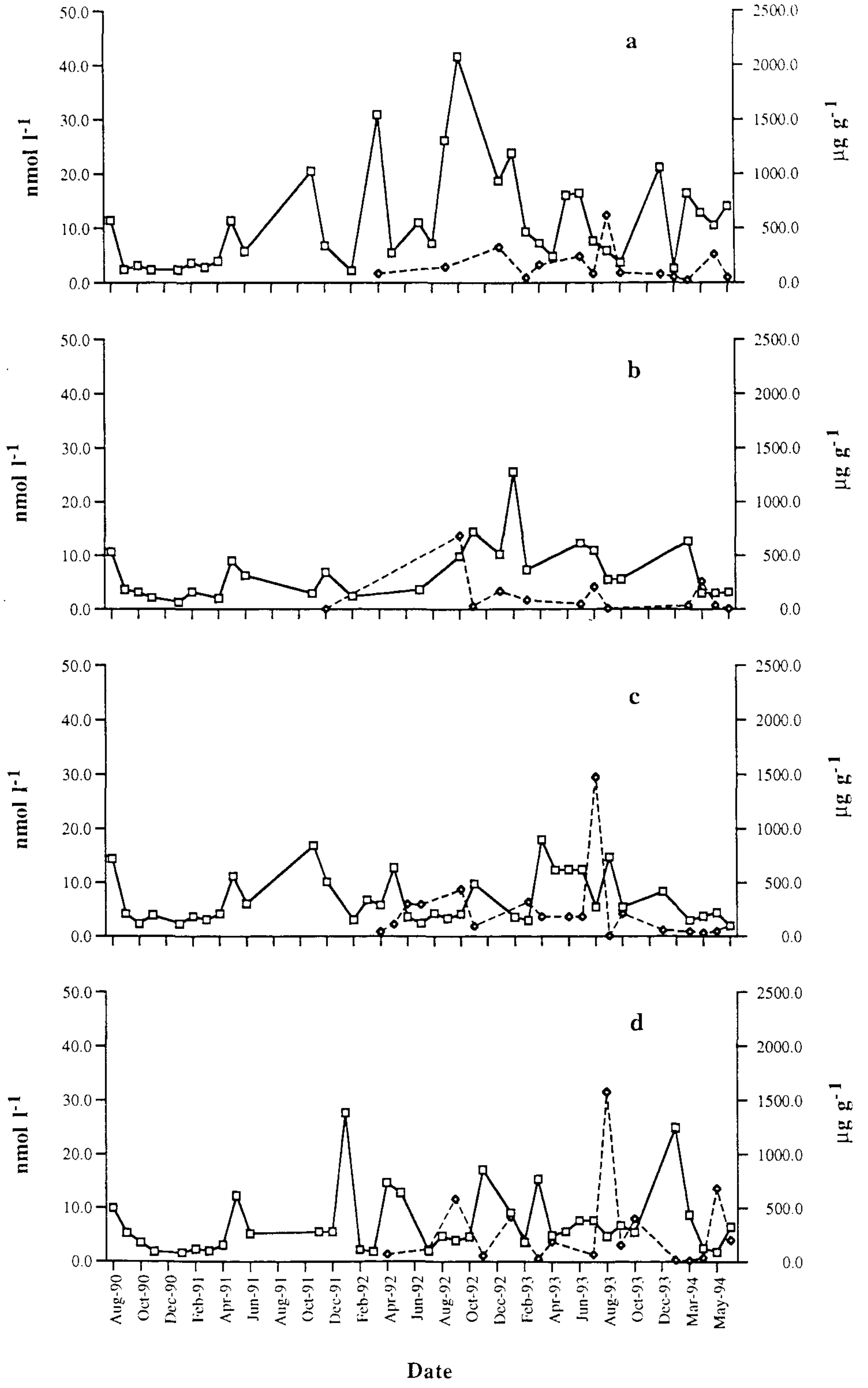

Figure 4.24.
Monthly distribution of dissolved manganese (solid line) and manganese associated with suspended particulate material (dashed line) in a) St. George's Harbour; b) Castle Harbour; c) Harrington Sound and d) Great Sound.

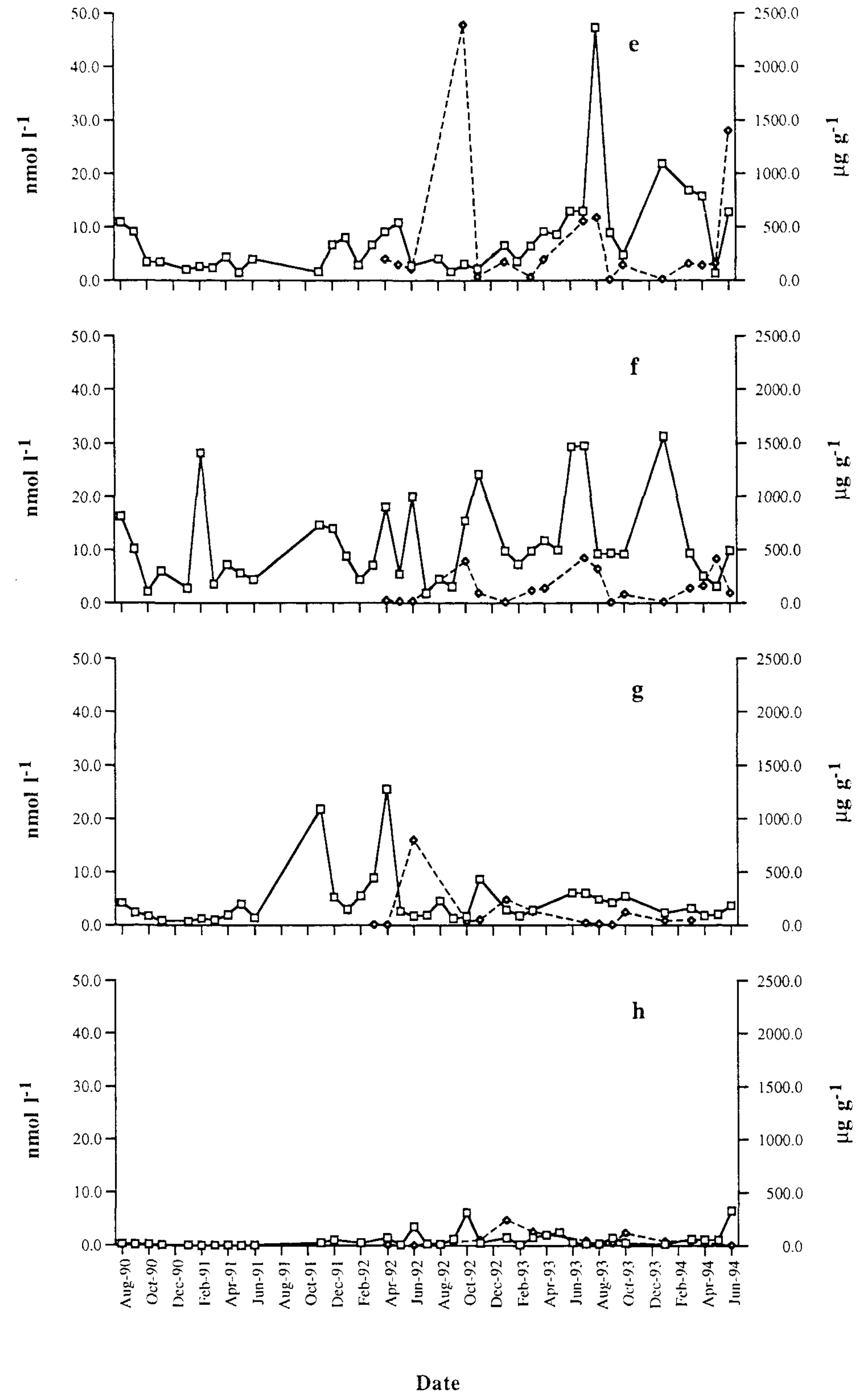

Figure 4.24 cont'd.
Monthly distribution of dissolved manganese (solid line) and manganese associated with suspended particulate material (dashed line) in e) Hamilton Harbour; f) Inner Hamilton Harbour; g) North Lagoon and h) Outer North Lagoon.

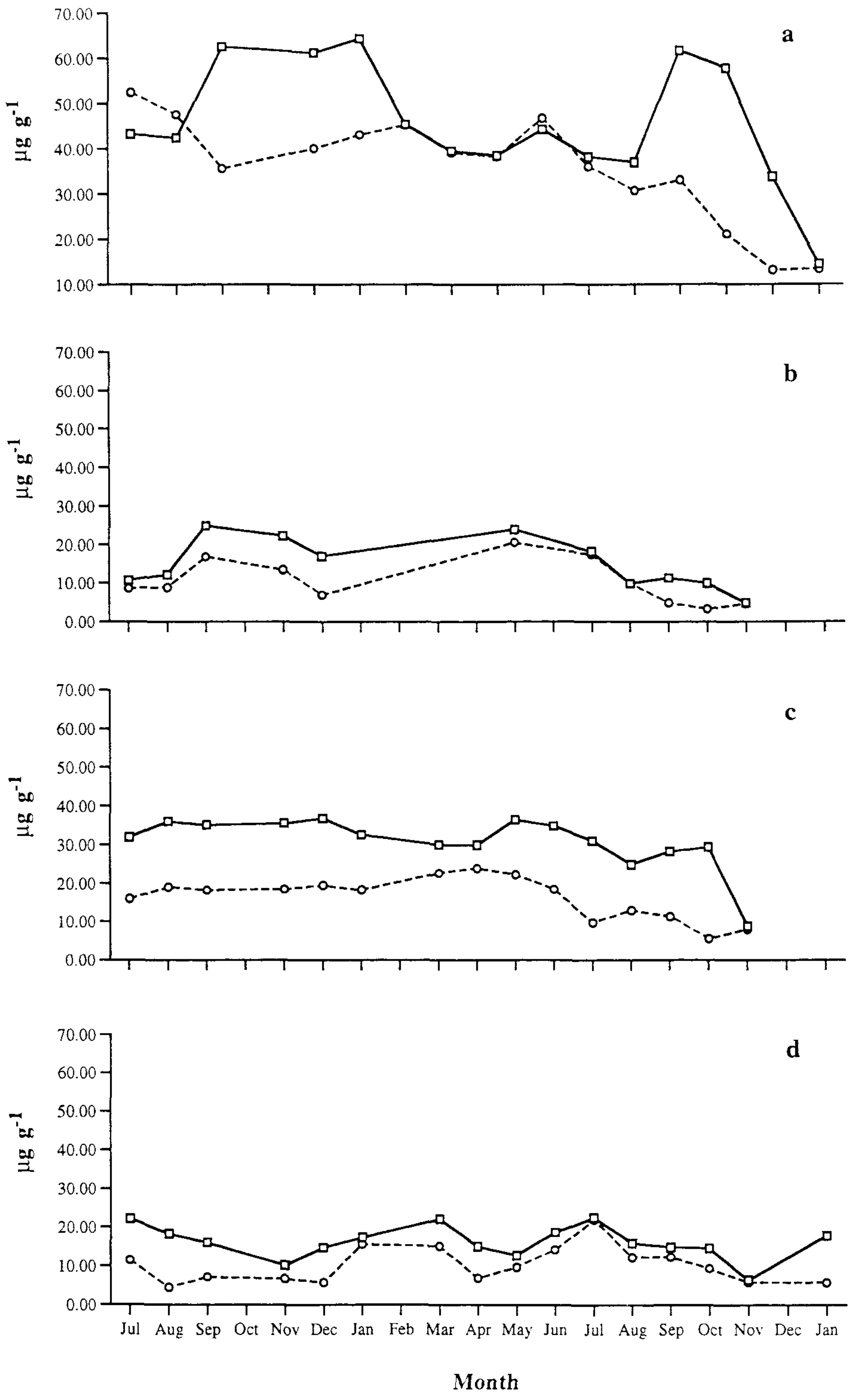

Figure 4.25.
Monthly distribution of total manganese (solid line) and partially bound manganese (dashed line) in sediment material from a) St. George's Harbour; b) Castle Harbour; c) Harrington Sound and d) Great Sound.

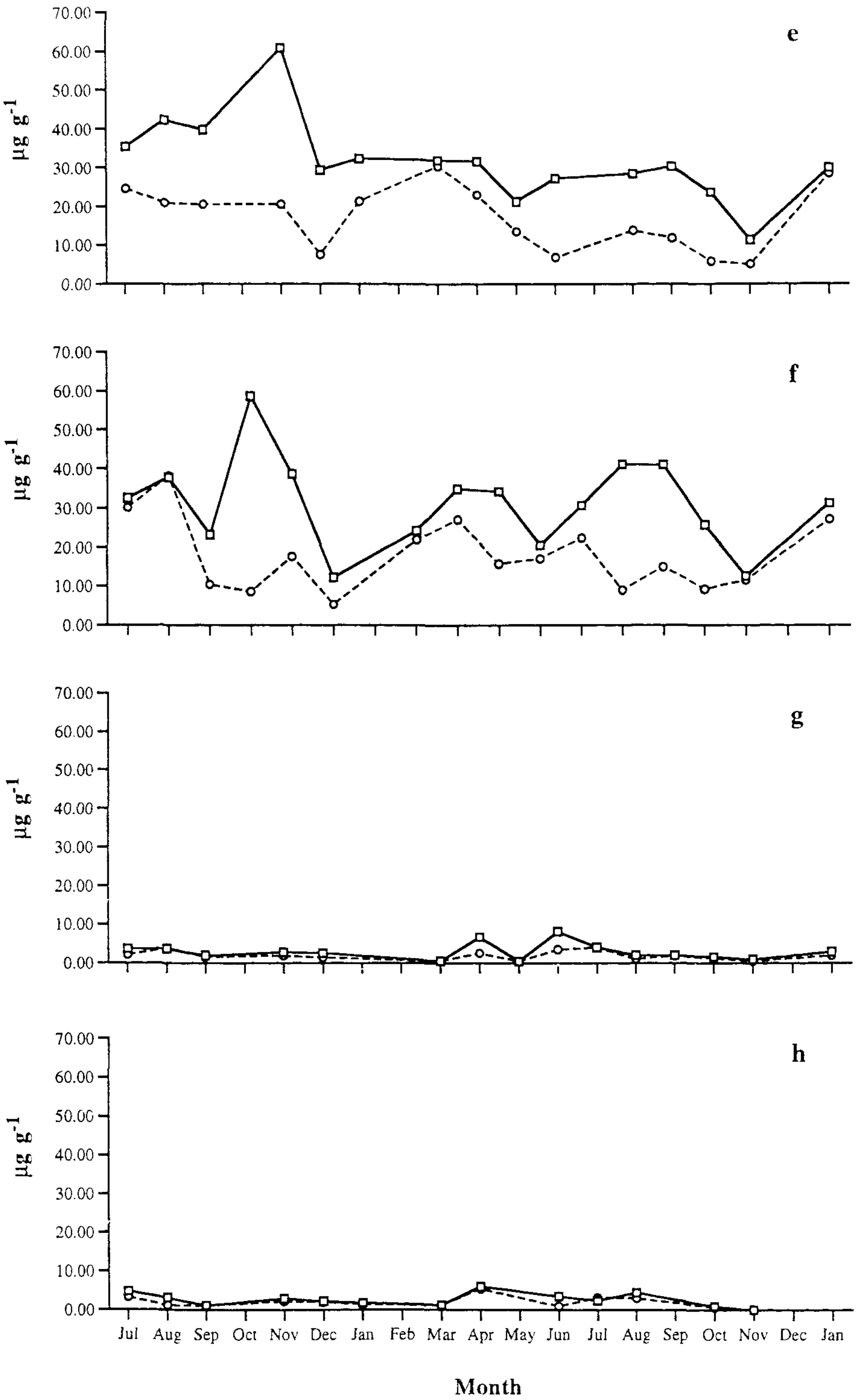

Figure 4.25 cont'd.
Monthly distribution of total manganese (solid line) and partially bound manganese (dashed line) in sediment material from e) Hamilton Harbour; f) Inner Hamilton Harbour; g) North Lagoon and h) Outer North Lagoon.

4.4.4.2 Discussion

The large variability in the data for manganese makes it difficult to interpret. The concentrations reported in this study are similar to those obtained in other similar studies in Bermuda. Jickells and Knap (1984) reported inshore water concentrations of manganese between 3.4 and 25 nmol l^{-1} at the same stations as used in this study. This large variability is typical of coastal data sets for manganese, for example Tappin *et al.* (1995) report highly variable manganese data for the North Sea area, and the presence of a seasonal cycle in the distribution of dissolved manganese. Part of the reason for the variability of the Bermuda data is probably the differing tidal states under which sampling was done as discussed earlier.

Manganese is known to be a redox sensitive element. However, the reduction of manganese (IV) is not only found to occur in reducing environments, or waters adjacent to reducing environments. There is evidence that the presence of reduced dissolved manganese (II) in oxygenated marine environments is a result of biological activity (Sunda and Huntsman, 1988). Sunda and Huntsman (1988) postulated that the reduced manganese found in the surface waters of the Sargasso Sea was the result of photoinhibition of the bacteria responsible for oxidising the manganese (II) to manganese (IV). Recently Matsunaga *et al.* (1995) have proposed that direct reduction of manganese can occur in marine surface waters as a result of the photo-decomposition of phytoplankton cells.

In this present study there is large variability in log K_d values for manganese (5.3±1.73). This is presumably due in part to its partition between dissolved and particulate phases being mediated predominantly by redox changes; Burton *et al.* (1993) suggest that reducing sediments in the North Sea are responsible for the introduction of dissolved manganese into that environment.

Manganese is associated predominantly with particulate material in oxic environments, physical processes at the stations are partly responsible for the large variability in the data. The sediments would release manganese that had undergone reduction to the soluble manganese (II) in the sub-surface sediments into the environment. This idea of reducing sediments in Bermuda was proposed to explain the presence of dissolved manganese in previous studies (Jickells and Knap, 1984). However since the waters around Bermuda (with the exception of Harrington Sound) are predominantly oxygenated, there would be little or no passive release from the surface of the sediments of this reduced manganese. Any reduction of manganese in the sediments would result in the migration of this soluble reduced manganese (II) to the surface of the sediments where oxidation would occur either at the sediment/water interface or in the water column above the sediments.

Some sedimentary release of dissolved manganese to Bermuda waters is supported by the differences between the stations for dissolved manganese. Harrington Sound is particularly noteworthy in this respect. There is a large concentration of particulate manganese associated with the sediments at this station, but low dissolved manganese concentrations in the water column. This station is the deepest of all of the stations and has no shipping activity. It can assumed that any manganese released from the sediments returns to the sediments following oxidation in the water column. The fact that his area has a period of anoxia also reduces the effect that organisms have through bioirrigation (Santschi *et al.*, 1990), as any such organisms would be killed during anoxic episodes.

Tessier *et al.* (1979) reported that the majority of the manganese in the river/estuarine sediments they studied was associated with the residual fraction (>50%) with the remainder being associated with the carbonates (13-28%) and the iron/manganese oxy-hydroxides (15-24%). Rosental *et al.* (1986) determined that for nearshore marine sediments (South Africa) up to 35% of the manganese was associated with the carbonates, readily reducible fraction and the iron/manganese oxy-hydroxides. A further 30% associated with the organic/sulphide fraction with the remainder was in the residual phase. These results contrast with data from Gerringa (1991) who determined that there was removal of dissolved manganese from the water column by the formation of carbonates which then fell to the sediments, and hence most of the manganese was associated with carbonates. Battison *et al.* (1993) report that the largest concentration of manganese (40%) was associated with the carbonate fraction in their study. It is very important to remember that for all of the other studies mentioned above which were concerned with any type of partial extraction method for metal/sediment associations, the sediments were siliclastic in nature. These other studies may indicate that if there were greater proportions of carbonate in the sediments there may have been more manganese associated with that fraction. There may be a saturation process with carbonate particles.

Wartel *et al.* (1990) report that manganese is associated with calcite in a solid solution according to the following equation

$${}_{x}\mathrm{Mn}^{2+} + \mathrm{CaCO}_{3(s)} \rightarrow \mathrm{Mn}_{x}\mathrm{Ca}_{1-x}\mathrm{CO}_{3(s)} + {}_{x}\mathrm{Ca}^{2+}$$

In another report Wartel *et al.* (1991) report that in the English Channel in the summer the concentration of particulate manganese increases due to a proliferation of coccolithophores whose calcite skeletons react with the dissolved manganese. It can be assumed that this bound manganese would fall to the sediments with deposition of coccoliths shed during growth, and following death. In Bermuda the sediments are dominated by carbonate material. There is a predominance of calcite producing organisms in the plankton (such as coccolithophores and foraminifera). These organisms could scavenge the manganese (II) from the water column and deposit it to the sediments. This is supported by the negative correlation of dissolved manganese and suspended particulate matter discussed earlier. Martin and Knauer (1983) report that manganese is readily bound to the surface of calcium carbonate particles that then fall to the sediments. Any manganese released to solution therefore may be bound to the carbonate material and other spm in the Bermuda environment.

McBride (1979) determined that the high initial uptake of manganese (II) ions at a carbonate surface was by adsorption, and this was followed by a lower uptake period during which nucleation of the manganese occurred. Prohic and Kniewald (1987) emphasised that carbonates have two modes of trace metal association: the first is the isomorphous substitution of calcium by metals such as manganese; the second is the association of the trace metals with the organic coatings on the carbonates. There is the potential for the release of manganese from Bermuda sediments to be limited due to the high calcite concentrations. The calcite could bind soluble manganese and prevent its release to the overlying water. When conditions are oxygenated there will be rapid removal of manganese from the water column. This could explain why the concentrations of manganese are low in the Bermuda inshore waters, relative to other areas, although it is has proved difficult to find studies that have determined the sediment, particulate and dissolved fractions of metals simultaneously.

The sediment data in this present study indicates that concentrations of manganese are high in the St. George's Harbour, the Hamilton Harbour stations and the Harrington Sound station. These are also the stations that show higher (but variable) concentrations of dissolved and particulate bound manganese. The partial extraction method resulted in the release of the majority of the manganese from the sediments, with an indication of seasonality for St. George's Harbour (Figure 4.25a).

It is note worthy that there is a relatively high proportion of the sediment trap material manganese that is in the non-labile form, this is in marked contrast to the sediment data from this area reported in this chapter. This supports the idea that the sediment material is repackaged by the biological component above the thermocline and as such is organically bound, or shielded by the organic matter. Another alternative is that the manganese is forming sulphides that are not released by the partial extraction technique. The formation of manganese sulphide complexes is supported by the presence of higher concentrations of manganese in Harrington Sound associated with the non-labile fraction in the sediments.

4.4.4.3 Summary

The release of manganese from sediments in Bermuda (as well as release from spm under anoxic conditions) is reported. Harrington Sound, with periodic anoxia, is the most important location for the release of large concentrations of dissolved manganese, with smaller areas of the Harbours also having potential as a source. The oxic waters of Bermuda result in rapid removal of most of this manganese back to particles and ultimately the sediments. Physical resuspension of the sediments by frequent shipping activity in the Harbours probably maintains the dissolved concentrations of manganese reported. The predominance of calcareous organisms in the Bermuda coastal waters (Pestana, 1995) is likely to have an affect on the manganese geochemistry by providing surfaces for the reactions described by Wartel *et al.* (1990a, b).

4.5 Temporal trends in metal data

The discussion above has focused mainly on the spatial distribution of metals in sediments and the water column. Seasonal trends in metal concentrations have been observed in some coastal water systems (e.g. manganese, Tappin *et al.*, 1995), and in this section the data is examined to see if similar trends are evident in the carbonate dominated sub-tropical system of Bermuda.

4.5.1 Cadmium

From the dissolved cadmium data in Figure 4.16., there is some evidence for temporal trends which are common to a large number of the Stations studied. There are increases in the concentration of dissolved cadmium in the January to March period for 1991, 1992 and 1993, for all stations, with the exception of the North Lagoon which implies a relationship between the release of cadmium from degrading phytoplankton at the sediment surface, and/or an increase in release of cadmium from reducing sediments as a result of higher bacterial processes due to higher breakdown of the increased concentrations of organic matter. From the analysis of chlorophyll at the Station (Appendix 5), the periods of increased dissolved cadmium are during or just following periods of higher chlorophyll a concentrations. This linkage is masked with the correlation analysis of the total data set. The sediment data shows no strong inter-station similarities, the high degradation of organic matter in the water column detailed in the Harrington Sound study implies a rapid release of cadmium form this falling material, and so there would be no increase in cadmium in sediment material.

It is not possible to see clear temporal changes in K_d values, as can be seen in Figure 4.26. Due to the high variability within the data it is difficult to see any pronounced seasonal trends in K_d values which is a reflection of the complexity of the system.

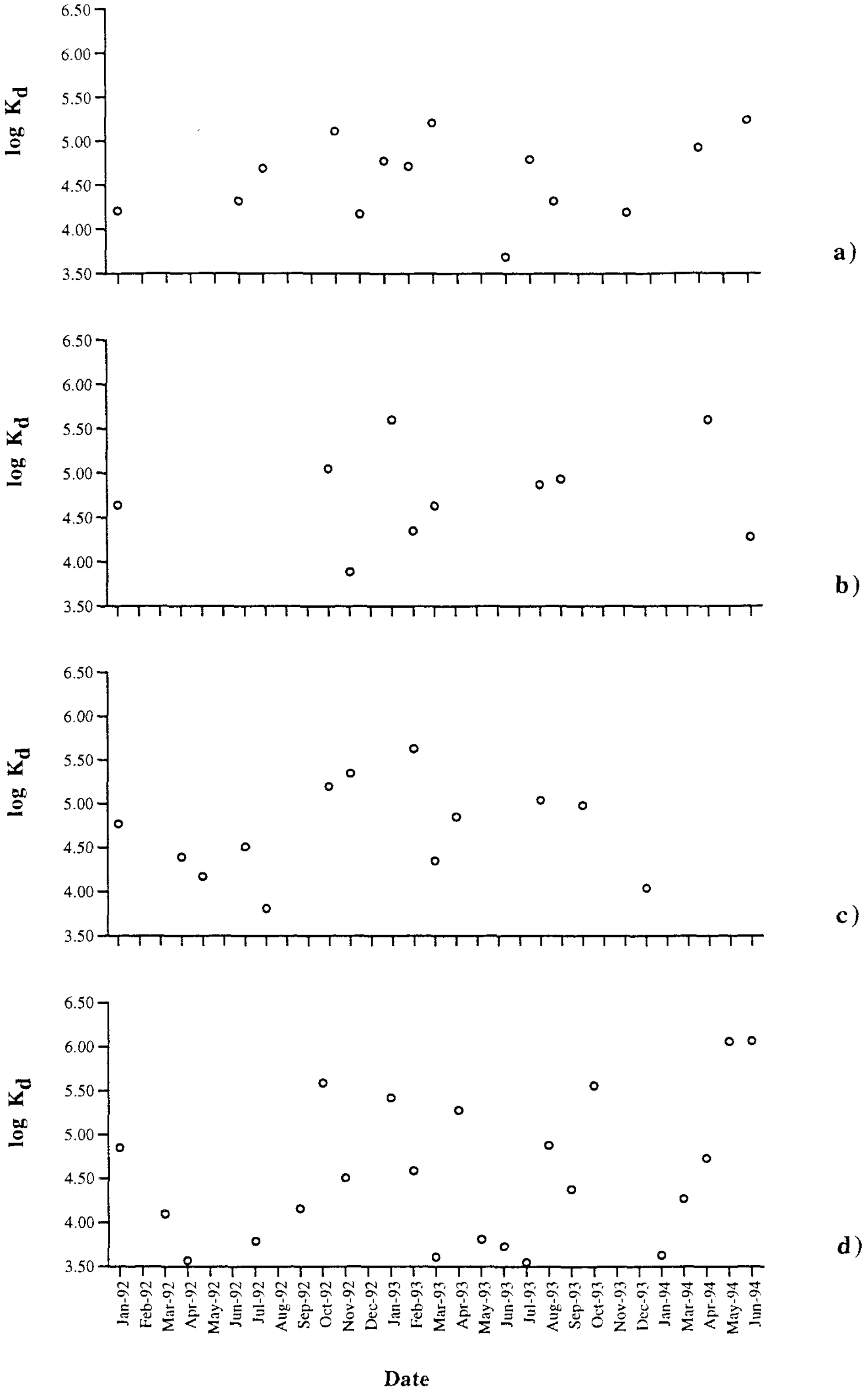

Figure 4.26
Monthly log K_d values for cadmium in the inshore waters. a)St George's Harbour, b)Castle Harbour, c) Harrington Sound and d) Great Sound.

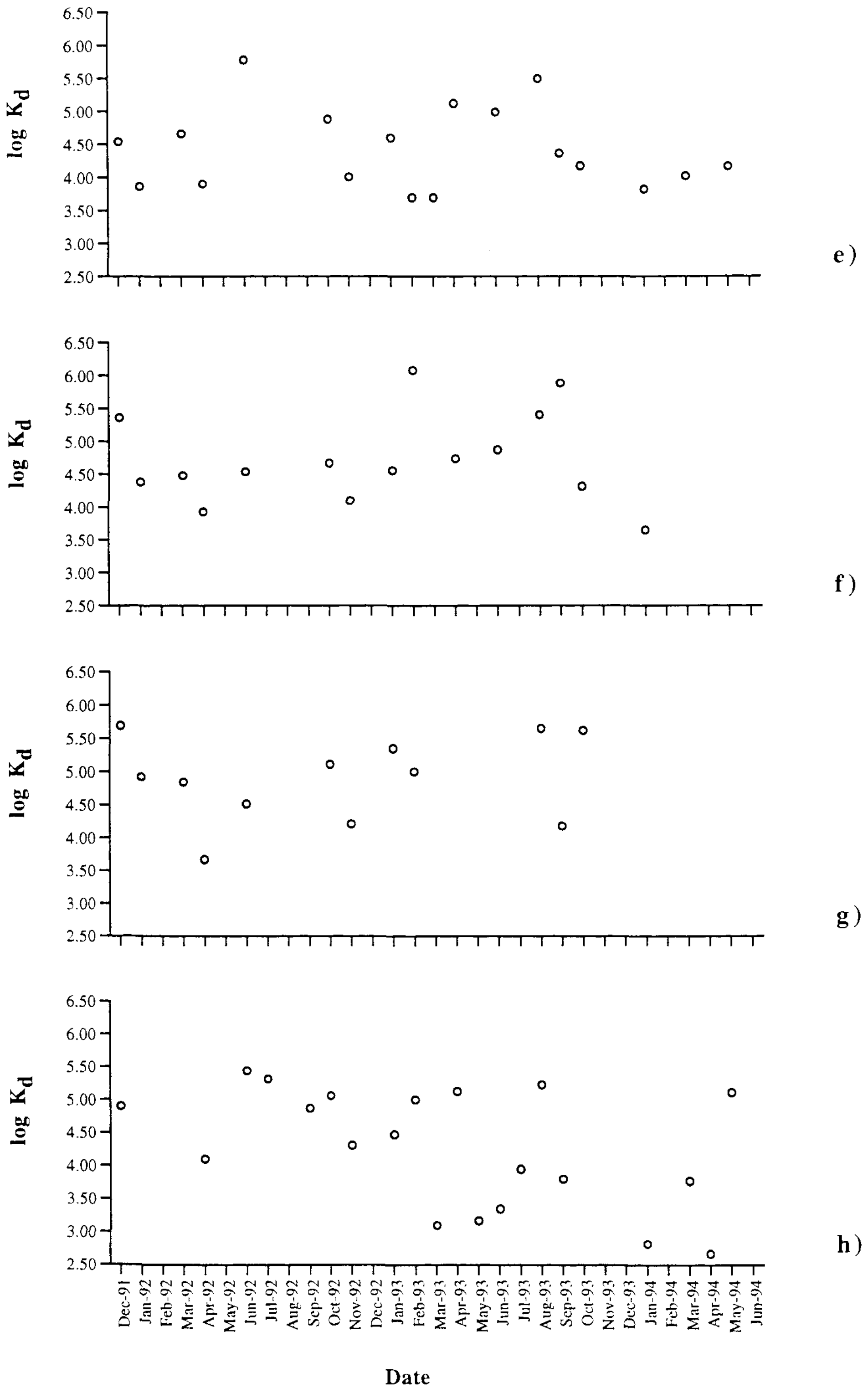

Figure 4.26
Monthly log K_d values for cadmium in the inshore waters. e)Hamilton Harbour, f) Inner Hamilton Harbour, g) North Lagoon and h) Outer North Lagoon.

4.5.2 Copper and nickel

From previous sections there is evidence that copper in the sediments of the inshore area is largely associated with organic material. An investigation of the changing association of copper within the sediments may reveal a seasonal aspect, if indeed the copper is tied to the biological system.

From the data in Figure 4.20, in St. George's Harbour there appears to be an increase in the concentration of copper associated with the labile phase in the sediments during the December to April period. After this time the concentration of copper associated with the labile phase decreases. This pattern is evident in the data from the Harrington Sound station (Figure 4.20c.); this distribution however is not so evident at other stations. The main reason for this behaviour at St. George's and Harrington Sound stations is the probable impact of shipping activity. St. George's during the winter has infrequent shipping activity (there are no cruise ships in Bermuda in winter but Hamilton has 2 large container ships each and every week of the year), and Harrington Sound has no shipping activity capable of disturbing the bottom sediments.

The change in association of copper from the less labile fraction of the sediments to the labile fraction of the sediments would be consistent with the degradation of the organic matter with which the copper is associated. There is the added complication with the Harrington Sound station that there is periodic anoxia during the summer. The shift to less available copper during the summer months at this station may be a result of binding of copper with sulphide, however the tank experiments indicate that this is not a strong overall factor in Bermuda.

The distribution of dissolved and particulate copper in the water column is more complicated. There appears to be a general trend towards more dissolved copper in the water column in the St. George's station (Figure 4.18a) in the winter months; this is particularly evident in 1993/94. Because of the complication of shipping activity this is not as evident in the Hamilton Harbour stations. From the K_d data in Figure 4.27 there is not any immediate trend evident, except for a general trend of increasing K_d in the May-August 1993 period, across all of the stations with the exception of Castle Harbour (Fig. 4.27b), which appears to reflect the onset of the cruise ship season with its associated sediment resuspension.

The distribution of nickel appears more complicated than that of copper. There are no distinct seasonal trends present in the data (Figure 4.19.).

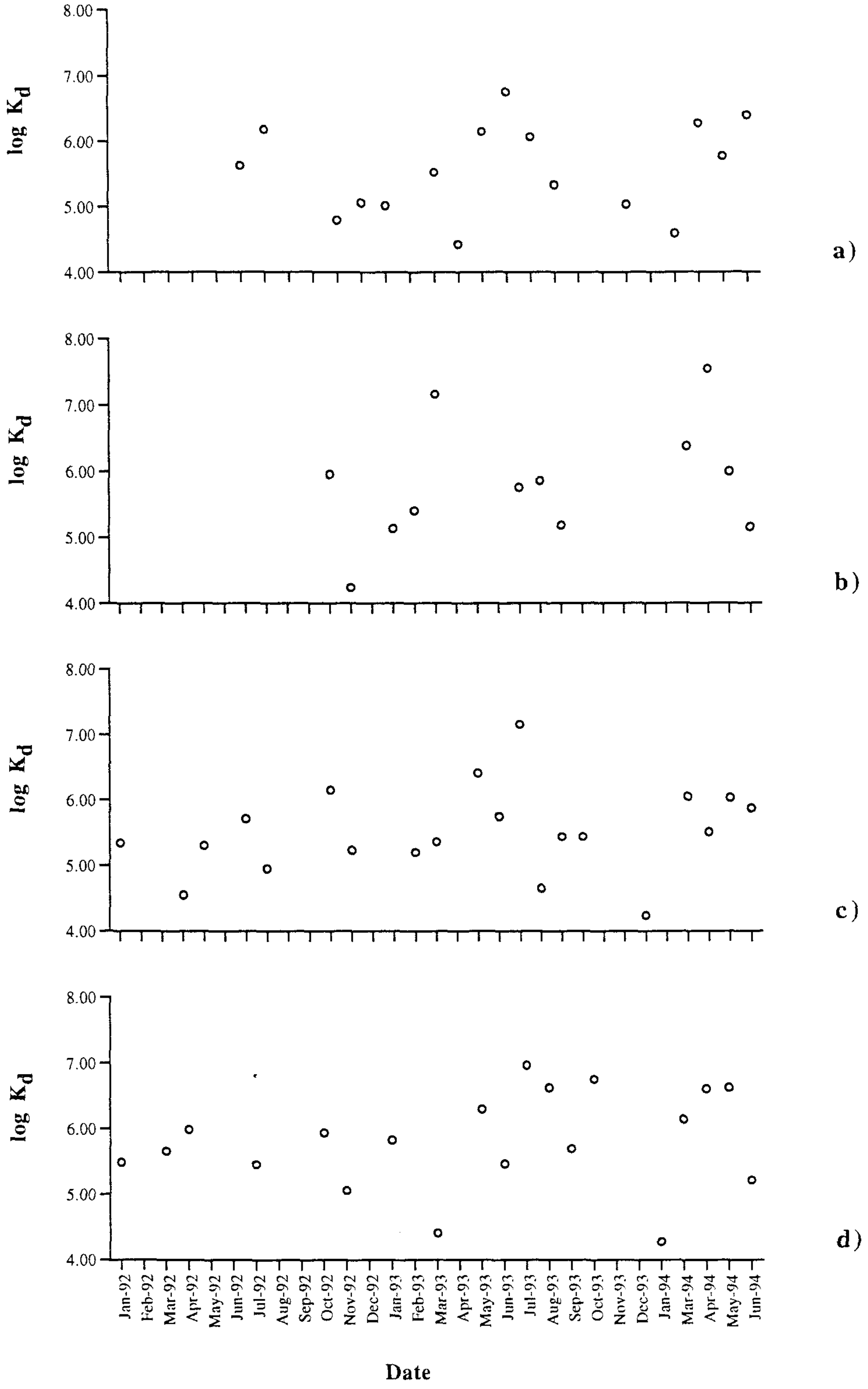

Figure 4.27
Monthly log K_d values for copper in the inshore waters. a)St George's Harbour, b)Castle Harbour, c) Harrington Sound and d) Great Sound.

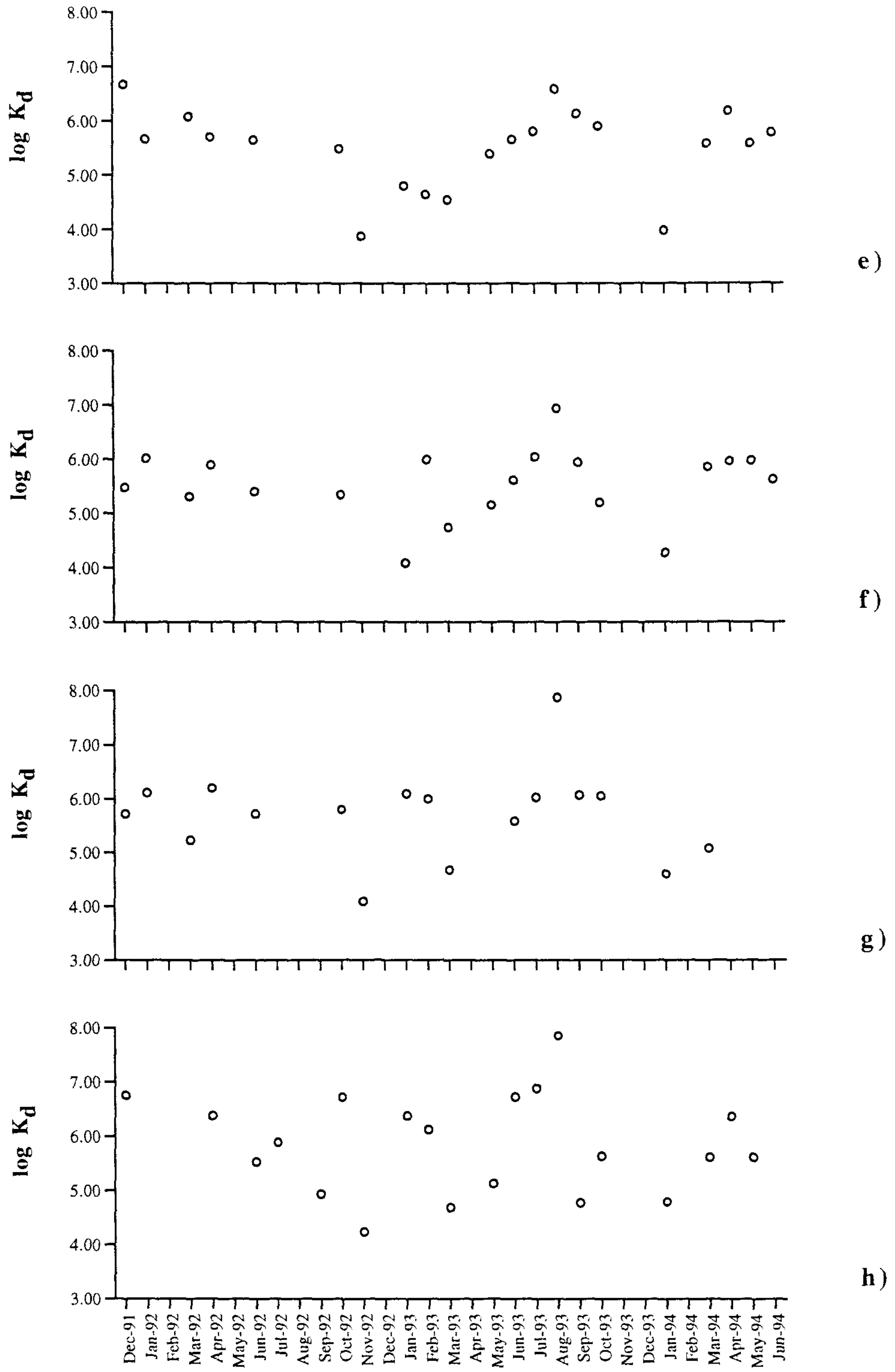

Figure 4.27 cont'd
Monthly log K_d values for copper in the inshore waters. e)Hamilton Harbour, f) Inner Hamilton Harbour, g) North Lagoon and h) Outer North Lagoon.

The data for the seasonal changes in K_d for nickel are shown in Figure 4.28. As with all of the plots of K_d there is a high degree of scatter in the data. There seems to be a general increase in K_d for the May-Sept. 1992 period and again in the June-Oct. 1993 period and again in the Apr.-Jun. 1994 period, this is particularly evident in Harrington Sound (c), Great Sound (d) and the Hamilton Harbour stations (e and f). This supports the idea that there is a removal of dissolved nickel and/or and increase in the particulate bound nickel. This could be caused by increased shipping activity during the summer months as was the case for the copper. This general lack of seasonal reactivity is in line with data from temperate coastal seas, and is consistent with the general unreactive nature of the element.

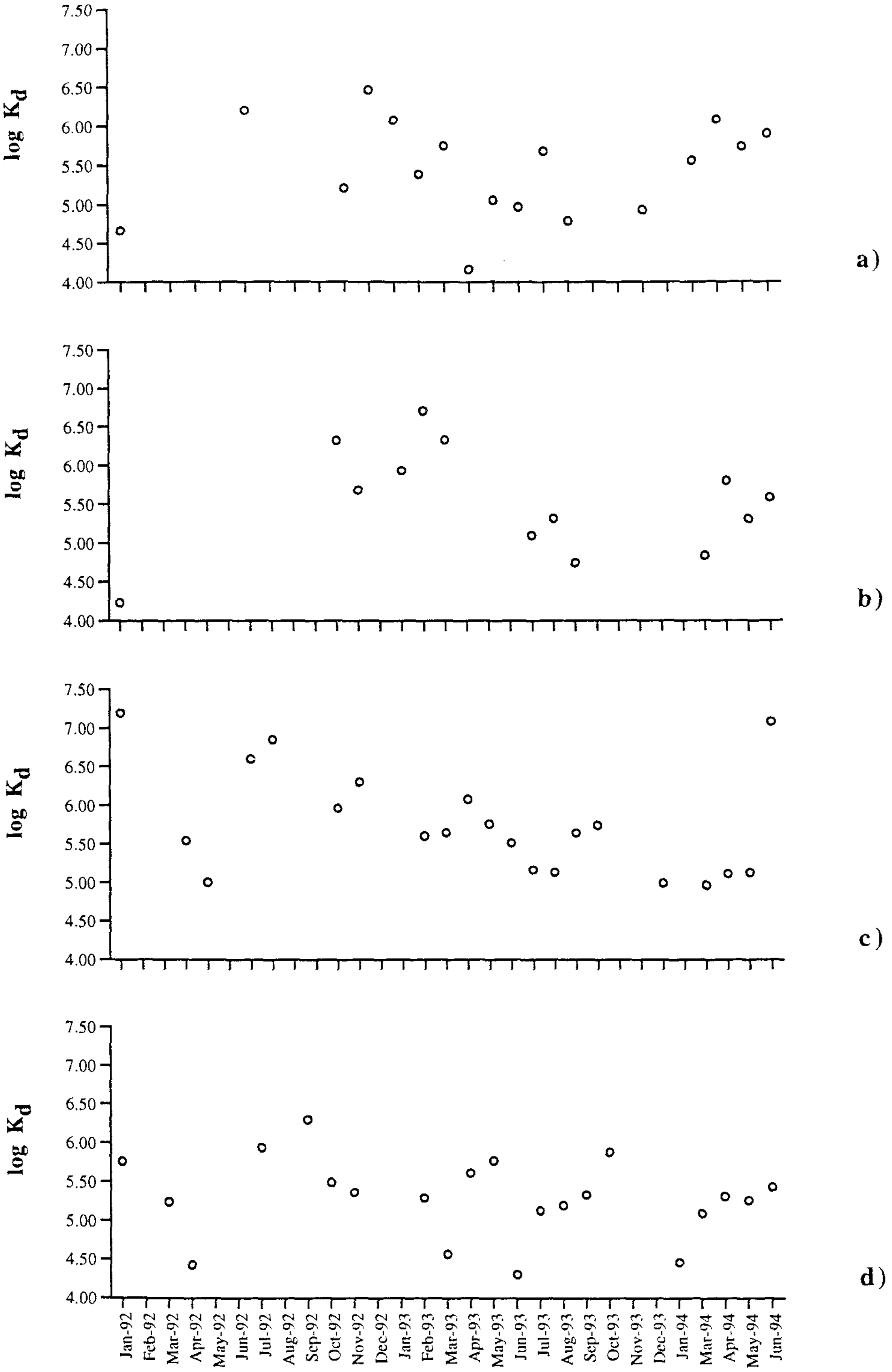

Figure 4.28
Monthly log K_d values for nickel in the inshore waters. a)St George's Harbour, b)Castle Harbour, c) Harrington Sound and d) Great Sound.

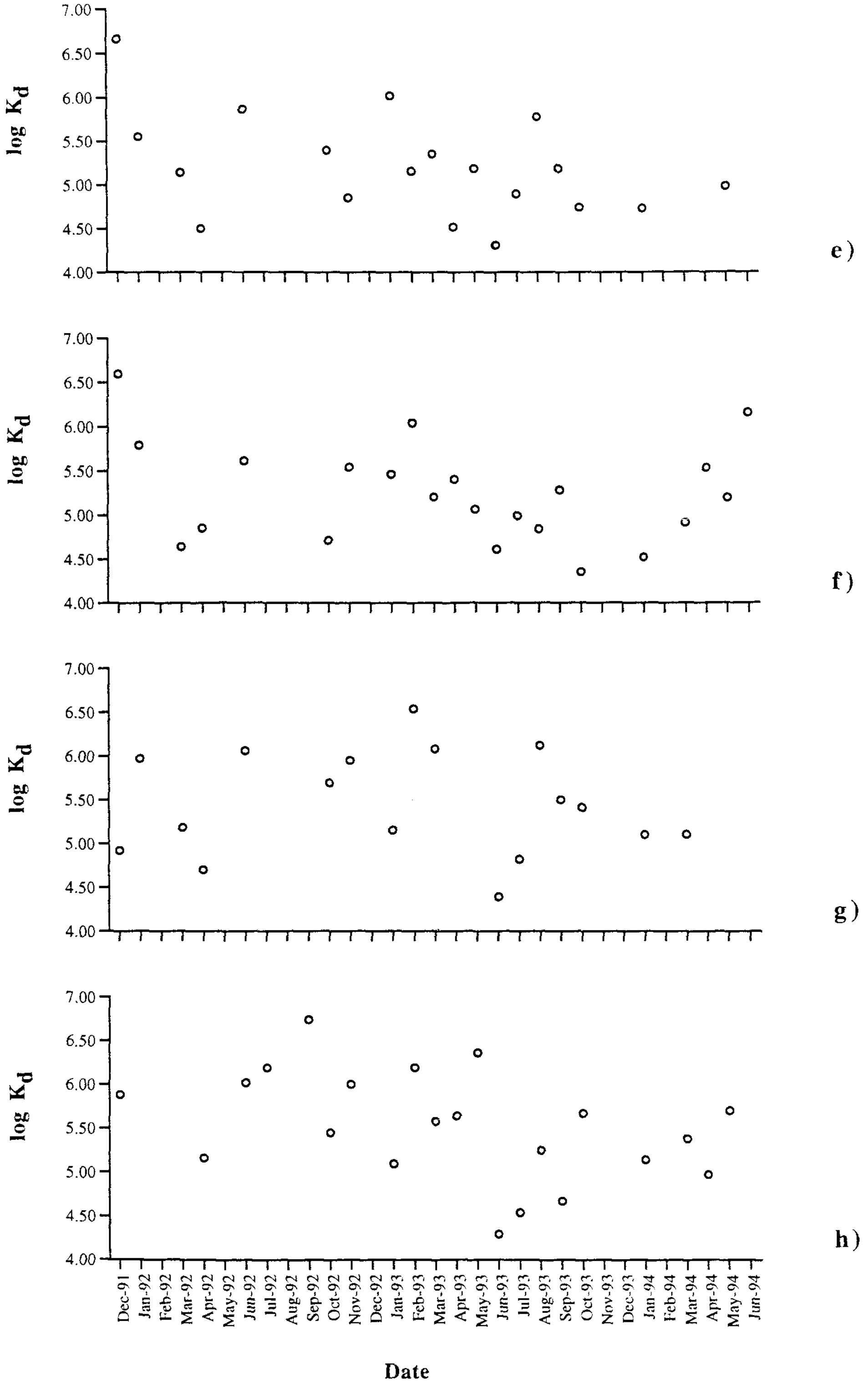

Figure 4.28 cont'd
Monthly log K_d values for nickel in the inshore waters. e)Hamilton Harbour, f) Inner Hamilton Harbour, g) North Lagoon and h) Outer North Lagoon.

4.5.3 Lead

The water column distribution of lead is thought to be more affected by changes in aeolian deposition and resuspension than by biological factors (Tappin et al, 1995). Dissolved and particulate lead in the Bermuda Coastal Zone show no apparent seasonal cycle for any of the stations studied. This is not unexpected as the majority of lead to the Bermuda Coastal Zone is derived from local anthropogenic lead, with very little from long range transport processes (Simmons and Knap, 1993). This lack of seasonal variability for dissolved lead was also found for coastal and estuarine waters of Southern England (Muller, 1996). Bermuda does not have a seasonal wet/dry cycle so there would be no one period of the year during which these run-off events would dominate over any other period. The sediment data presents (Figure 4.23) also show no strong seasonal pattern.

4.5.4 Manganese

Dissolved manganese has a peak in concentration at most of the stations in the late spring/early summer. This pattern of increase of dissolved (reduced) manganese in post-bloom periods is well documented (Dehairs *et al.*, 1989; Tappin *et al.*, 1995), and is explained by the large inputs of bloom material being decomposed and causing localised reducing conditions, resulting in the release of reduced manganese to the water column.

The K_d should therefore show obvious seasonal changes, but the monthly plots of K_d in Figure 4.29 show no such obvious trends between the stations and between the months. The station that might be expected to show the greatest changes would be Harrington Sound. From the study of the Station presented earlier it is evident that there is potential for the mobilisation of high concentrations of manganese from the sediments. There are decreases in the K_d of an order of magnitude during the late Autumn. This is probably due to a turn-over in the water column and the introduction of reduced manganese into the upper oxic water column. This high degree of scatter within the K_d values for manganese was also reported for the North Sea (Tappin *et al.*, 1995).

For all of the stations, with the exception of the Great Sound station, there is an increase of labile manganese in the March to May period. As with the cadmium discussed earlier this may be due to the influxes of organic material to the sediment following the spring bloom. In addition falling carbonate-rich plankton could be enriched with labile (carbonate bound) manganese, as was discussed for the Harrington

Sound data. The fact that there are no changes of association of other metals with this manganese change indicates that the adsorption of metals by the iron/manganese (oxy) hydroxides (Ciceri *et al.*, 1992) may not be as marked in this environment as in siliclastic environments.

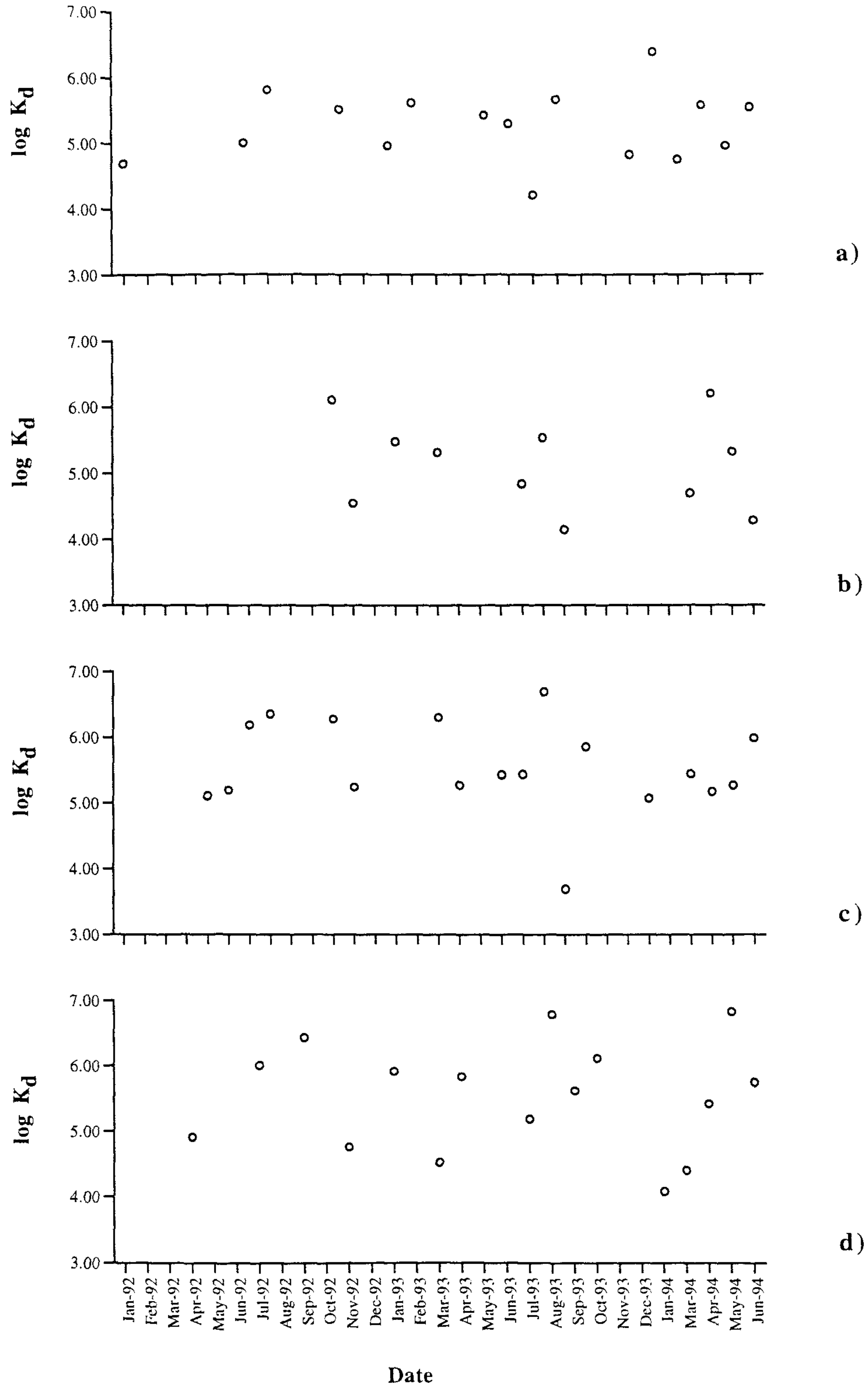

Figure 4.29
Monthly log K_d values for manganese in the inshore waters. a)St George's Harbour, b)Castle Harbour, c) Harrington Sound and d) Great Sound.

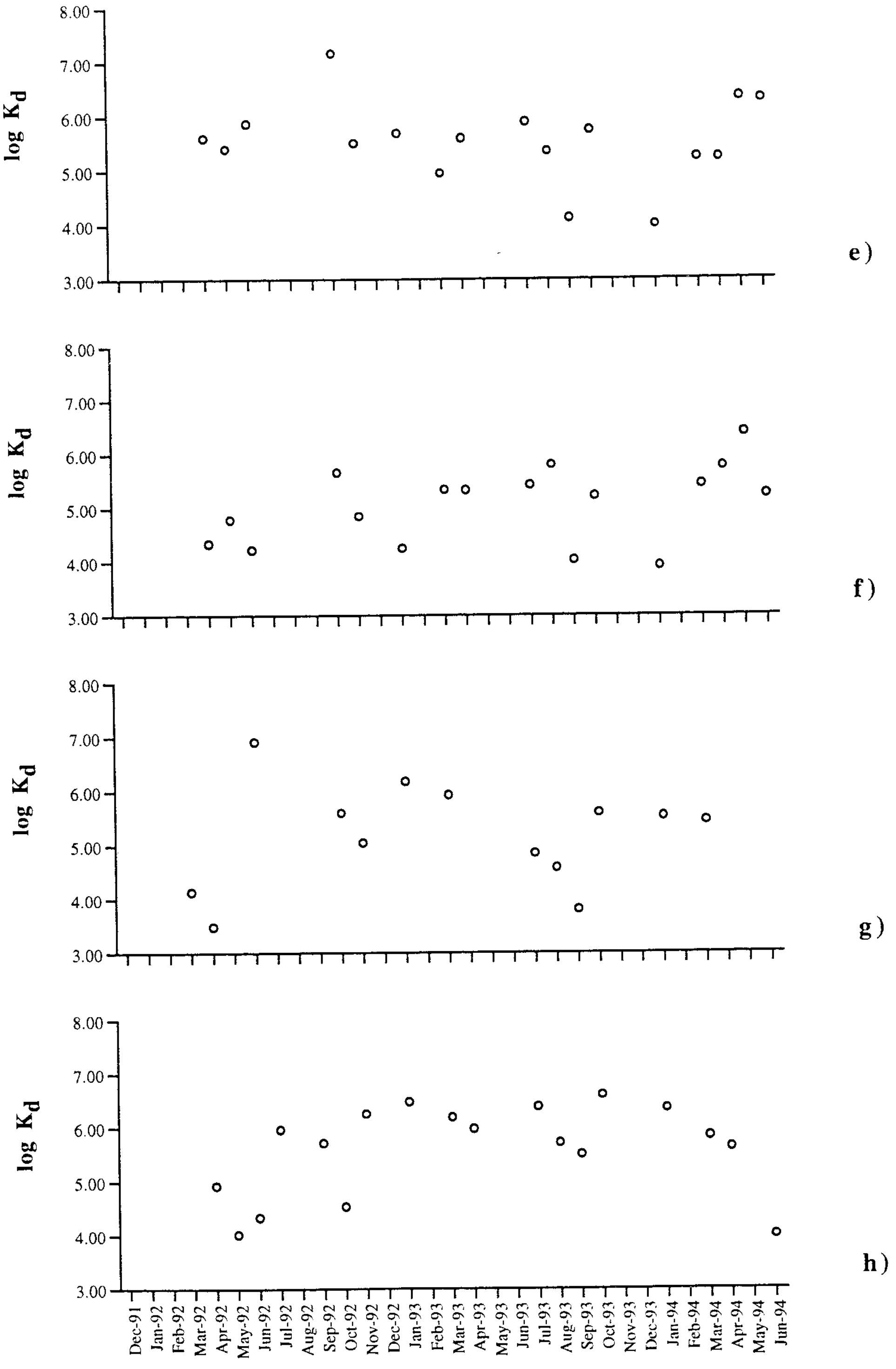

Figure 4.29 cont'd
Monthly log K_d values for manganese in the inshore waters. e)Hamilton Harbour, f) Inner Hamilton Harbour, g) North Lagoon and h) Outer North Lagoon.

4.5.5 Summary

The distributions of cadmium and manganese indicate some seasonal trend. The distribution of these elements appears to be tied into the seasonal phytoplankton bloom events. There are increases of dissolved cadmium in spring each year, due to the breakdown of organic material resulting from the phytoplankton blooms. The concentration of dissolved manganese increases in late spring/early summer, this is linked to the development of anoxic conditions in the sediment as a result of the bacterial degradation of the aforementioned phytoplankton material. There are increased concentrations of dissolved copper and nickel in the water column during the summer months and his may be related to the onset of shipping activity but it is not as resolved as the situation for cadmium and manganese. Lead does not show any evidence of seasonal trends.

CHAPTER 5

CHROMIUM CHEMISTRY IN THE SARGASSO SEA

5.1 Chromium chemistry in seawater

The chemical and physical controls of the distribution of trace metals in marine environments are complex. The investigation of those elements that exist in different redox states will allow a clearer understanding of the role of the form in which trace metal is present, in its geochemical cycling. Chromium is one element that occurs in at least two different redox states in natural waters (Elderfield, 1970; Hem, 1977; Rai *et al.*, 1989; Pettine *et al.*, 1991; Richard and Bourg, 1991): Chromium (III) and chromium(VI). A third redox species, Chromium (V) is unstable and is thought to be responsible for the toxic effects of chromium (Charlet and Manceau, 1992).

Chromium (III) is characterised by having 3d electrons, octahedrally coordinated with a high spin state, and typically forms strong, kinetically inert compounds (Murray *et al.*, 1983). Chromium (VI) is strongly acidic and forms oxo compounds, the main species being CrO_4^{2-} in oxygenated seawater. Chromium (VI) is thought to be more toxic than chromium (III) (Gendusa *et al.*, 1993)

Elderfield (1970) discussed the theoretical distribution of the two main species (III and VI), comparing experimental data with data obtained in oceanic environments. Elderfield suggested that the hexavalent form of chromium should be the dominant species. The following equation represents the proposed equilibrium:

$$\begin{gathered} Cr\ (III) <\text{---}> Cr\ (VI) + 3e^- \\ Cr(H_2O)_4OH_2{}^+ <\text{---}> CrO_4{}^{2-} + 6H^+ + 2H_2O + 3e^- \\ \log K = 65 \end{gathered} \qquad (5.1)$$

from equation 5.1, it follows that

$$\log [Cr(VI)/Cr(III)] = 6pH + 3pE - 65 \qquad (5.2)$$

From the paper by Elderfield, the pH of seawater is 8.1 and taking the pE as 12.1:

$$\log [Cr(VI)/Cr(III)] = 19.9 \qquad (5.3)$$

It is apparent from this that chromium (VI) is thermodynamically favoured in oceanic systems. The two coexisting species in equation 5.2 account for over 86% of the chromium found in seawater.

Since chromium (III) is found in some ocean samples, Hem (1977) proposed that a controlling species was chromite ($FeCr_2O_4$ (s)), formed from the interaction of chromium (III) and iron (III) hydroxide according to equation 5.4.

$$Fe(OH)_3\,_{(s)} + 2Cr(OH)_2{}^{+} + e^{-} = FeCr_2O_4 + 3H_2O + H^{+} \qquad (5.4)$$

If chromite alone was responsible for the solubility control of chromium (III) the solubility would be 10^{-10} M at pH 8.0 (Murray *et al.,* 1983). It is proposed that since chromium (III) is rapidly adsorbed onto surfaces, this reaction could proceed after the chromium (III) had absorbed onto the surface of the iron (III) hydroxide. Pettine *et al.*, (1992) proposed three candidates for the solubility control, chromite, Cr $(OH)_3$(s) and the mixed hydroxide $(Cr_xFe_{1-x})OH_3$ (s). From the same paper a review of the data from the environment indicates that the ratio $[Me_{ox}]/[Me_{red}]$ was in the range 1 - 20. This shows that the data reported for marine environments is extremely varied. Photochemical reactions may affect the distribution and speciation of chromium in the marine and freshwater environment. The photochemical oxidation of organic matter can produce iron (II) which can then reduce chromium (Pettine *et al.*, 1992; Kieber and Helz, 1992) or there may be direct oxidation of organic chromium species that then produce chromium (III) (Kaczynski and Kieber, 1993). The potential importance of reactions such as these is discussed in more detail in the discussion section of this chapter.

Although chromium (III) is less abundant in most of the oceanographic samples investigated than chromium (VI) (Jeandel and Minster, 1987, Elderfield, 1970, Pettine *et al.*, 1992), the presence of chromium (III) is an anomaly. Elderfield (1970) addressed this apparent anomaly and presented five possible explanations for it.

(i) The existing theoretical solubility constants available at the time of his paper were inapplicable to the marine environment.

(ii) Some equilibrium species (possibly organic in nature) were not considered.

(iii) The equilibrium between chromium (III) and chromium(VI) may not be attained and/or the equilibration rates are slow.

(iv) The real system is not in equilibrium with the atmosphere (although this is probably an insufficient explanation in itself).

(v) The samples are often filtered through a 0.45µm filter, there may be chromium(VI) bound to small particles, these may pass through the filter and this would bias the chromium (III) results.

Since this paper (Elderfield, 1970), there have been many theoretical and applied studies on chromium speciation (Rai *et al.*, 1987, Eary and Rai 1987, Pettine *et al.*, 1991, Grimaud and Michard, 1974, Jeandel and Minster, 1987), directed at understanding the anomalous behaviour of the chromium. It is easiest to address the anomaly in reference to the reasons put forward by Elderfield (1970):

(i) Rai *et al.* (1987) experimentally derived the hydrolysis constants for chromium (III) in seawater, concluding that the dominant species of chromium (III) was $Cr(OH)_3$, in contrast to Elderfield's (1970) hypothesis that the predominant seawater species was $Cr\ (OH)_2^+$. Furthermore Rai *et al.* (1987) discounted the importance of polynuclear species of chromium due to the natural low levels of chromium in the environment.

(ii) The importance of organic compounds to the redox states of chromium in natural seawater systems was first investigated by Nakayama *et al.* (1981a, 1981d.). They suggested that the previous methodology using iron (III) hydroxide complexation, developed by Cheucas and Riley (1966), and modified by Cranston and Murray (1978) (these methods will be discussed in more detail in a later chapter), was insensitive to the presence of organic bound species. They concluded that up to 65% of chromium (III) in seawater could be organically bound either with amino acids or some complexing groups on naturally occurring large organic molecules. Osaki *et al* (1983) also suggested that the iron (III) hydroxide method removed chromium complexed with glycine and tannic acid. Osaki *et al.* (1983) could not determine which organic bound chromium (III) species was responsible for the degree of organic complexation Nakayama *et al.* (1981d) had reported. Mackey (1983) investigated the organic complexes of various metals in seawater using High Performance Liquid Chromatography (HPLC), and found that metals such as copper were organically complexed, but reported no evidence for the complexation of chromium and cadmium. There are limitations to this method (such as the degree of polarity used in the eluant during the process) so this is not to say there are no possible organic complexes. Isshiki *et al.* (1989) suggested that the previous Nakayama *et al.* (1981d) work overestimated the percentage of organically bound chromium, since one of the reagents used was contaminate with chromium. A repeat of the experiment indicated that organic bound chromium (III) was a minor component in seawater (5-10%). Recent work concerning organically complexed chromium (Kaczynski and Kieber, 1993) found that the organic complexed chromium in open ocean waters was of the order of a few picograms l^{-1}, and was significantly less than 10% of the total chromium found.

(iii) Equilibration rates between chromium (III) and chromium (VI) were reported by Schroeder and Lee (1975). They determined a first order rate constant for the transformation of chromium(III) to chromium(VI) of $0.37 yr^{-1}$, for the direct oxidation with oxygen. Nakayama *et al.* (1981c.) investigated the involvement of manganese dioxide (Birnessite) in this reaction, and concluded that the manganese dioxide had a catalytic effect on the reaction. Eary and Rai (1987) later determined that although there was minimal oxidation of chromium (III) in the presence of oxygen, the oxidation occurred more rapidly in the presence of manganese dioxide and oxygen. Furthermore Eary and Rai (1987) found that the manganese dioxide was capable of oxidising the chromium (III) without the presence of oxygen. Recently Charlet and Manceau (1992) used a new Extended X-ray Absorption Fine structure Spectroscopy (EXAFS) technique. They suggested that the oxidative transformation of the chromium (III) occurred through the following process: Firstly, the chromium (III) is electrostatically attracted to the birnessite particles; chromium (III) diffuses into the birnessite lattice; electron transfer occurs between the chromium atoms and the manganese atoms via the oxo bridges; and finally chromium (VI) is released into solution.

(iv) At the time of Elderfield's paper the generally accepted pE of seawater was that suggested by Sillen (1965), which was 12.5 based on the redox couple O_2/H_2O. Breck (1974) suggested that the controlling influence was an O_2/H_2O_2, which would result in the pE of seawater being 8. However this is not important in this discussion as the pE of seawater would need to be as low as 5 to explain the chromium anomaly. Recent measurements of hydrogen peroxide in the ocean have revealed that concentrations can be high enough to lower the pE below 5, but these areas are thought to be localised (Zika *et al.*, 1985; Moore *et al.*, 1993)

(v) Chromium (VI) could be bound to small particles that pass through the filter used in sampling seawater thus biasing the data in favour of the chromium (III). Krauskopf (1956) determined that up to 47% of chromium (VI) would be absorbed onto iron (III) flocculant after 2 days. In a recent paper Regnier and Wollast (1993) determined most of the particulate bound chromium (amongst other metals) in estuarine waters, was in the smallest fraction (<4µm), although there were no data published regarding the species of the metals. In addition, co-precipitation of chromium (VI) with the iron (III) hydroxide has been suggested (Cranston and Murray, 1978, Nakayama *et al.*, 1981a). Cranston and Murray (1978) deduced, utilising radioisotope spikes of chromium species, that this did not occur. However this does not infer that there are no natural processes in seawater that can result in the formation of solid phase chromium (VI). These particular factors will be discussed at greater depth in a later section.

From the preceding discussion we have some idea of the complexity of the chemistry of chromium Pettine *et al.* (1991) summarised the issue: "Cycling (of chromium) is affected by complex and interrelated processes including chemical or photochemical redox transformations, precipitation/dissolution and absorption/desorption reactions as well as biological reactions".

We are left with a series of questions: What are the concentrations of chromium in an oligotrophic ocean water column such as the Sargasso Sea? What is the pattern of distribution between the chromium (III) and the chromium(VI)? Is there any evidence of sedimentary input of chromium into the water column? The importance of aeolian input for chromium has received little attention, however the Sargasso sea receives dust from two sources: the North American continental mass and North Africa (Duce *et al.*, 1991). This dust, as it sinks, could be an important contributor to chromium in surface, intermediate and ultimately deep water. How important is this dust? What is the relationship between the chromium, nutrients and oxygen in the water column? Is there any evidence of a photochemical or biological control over the speciation of chromium in the Sargasso Sea? The objectives of this study were to clarify several of these issues, through a detailed and careful examination of chromium speciation in the water column of the Sargasso Sea.

5.2 Determination of chromium (III) and chromium (VI) in seawater.

5.2.1 Review of analytical approaches.

The study of chromium in natural seawater systems is important, as it offers an insight into redox reactions occurring in the water column. Various methods have been used to determine the concentration of total chromium in natural seawater; the most commonly used methods are shown in Table 5.1, with detection limits as given in the original papers. Some of the methods collect the total chromium present; Subramanian (1988) complexed the total chromium with Ammonium Pyrolidinedithiocarbamate (APDC), followed by extraction of the organic complex into 4-methyl-2-pentanone (formerly known as Methyl Isobutyl Ketone), while Sherrell and Boyle (1988) used cobalt-APDC coprecipitation. Since determination of the species of chromium in seawater is often the aim of the study, methods must be used that enable the analyst to distinguish between the two dominant, naturally occurring species of chromium, (III) and (VI) (Elderfield, 1970)

The determination of the chromium species is commonly a two part process: (i) the separation and concentration of the species from seawater and, (ii) the subsequent determination of the species. One of the earliest, and presently most utilised, methods involves the coprecipitation of one or both of the chromium species with the iron species Fe (II) and Fe(III) (e.g. Cheucas and Riley, 1966; Fukai, 1967; Cranston and Murray, 1978; Nakayama *et al.*, 1981a; Cranston, 1983). Chromium (VI) is either reduced prior to the coprecipitation (Jeandel and Minster, 1984) or the coprecipitating agent used is iron (II) hydroxide which reduces chromium (VI) and thus oxidises the iron (II) to iron (III) hydroxide, leading to coprecipitation of chromium (III). The precipitate is collected by filtration and dissolved using hydrochloric acid, prior to its determination by graphite furnace atomic absorption spectroscopy. Chromium (III) can be determined by using the iron (III) hydroxide which should not collect the chromium (VI). Thus the difference between the total chromium (using iron (II) and iron (III) hydroxides) and the chromium (III) concentration, gives an estimate of the chromium (VI) concentration.

However, questions have arisen about the accuracy of the data obtained using this method (DeJong and Brinkman, 1978. Nakayama *et al.*, 1981a). The principal argument raised against this method centres around the possible adsorption of the chromium (VI) species onto the iron precipitate, leading to an overestimate of the

Author(s)	Technique	Detection Limit nmol l^{-1}
Cheucas and Riley. 1965.	Colourimetric	0.4
Fukai. 1967.	Coprecipitation Fe (III), reduce Cr (VI).	0.4
Elderfield. 1970.	As in Fukai.	0.4
Grimaud and Michard. 1974.	Coprecipitation Fe(III)/ion exchange.	0.8
Pankow *et al.* 1977.	Ion exchange resin.	1.0
Cranston and Murray. 1978.	Coprecipitation Fe(II)/Fe(III).	0.02
DeJong and Brinckman. 1978.	Aliquat 336.	0.2
Campbell and Yeats. 1981, 1984.	Alamine 336.	0.6
Mayazaki and Barnes. 1981.	Chelating resin for Cr(VI).	230
Nakayama *et al.* 1981	Coprecipitation Fe(III)/$Bi(OH)_3$	None given
Isozaki. 1983	Ion exchange (chelex resin)	None given
Murray *et al.* 1983.	Coprecipitation Fe(III).	0.02
Osaki *et al.* 1983.	APDC extraction and Coprecipitation.	None given
Jeandel and Minster. 1984, 1987.	Coprecipitation Fe (III)	0.1
Ahern *et al.* 1985.	Coprecipitation Fe(IIIP)	0.4
Harper and Riley. 1985.	Coprecipitation Fe(II) and Fe(III).	0.6
Sherrell and Boyle. 1988.	APDC/Co total Cr complexation.	None given
Subramanian. 1988.	APDC/MIBK total Cr complexation.	6
Isshiki *et al.* 1989.	Ion exchange resin.	0.08
Shah and Devi. 1990.	Ion exchange resin.	1.9
Lan *et al.* 1991.	Neutron Activation Analysis. (NAA)	0.6
Boussemart *et al.* 1992.	Cathodic Stripping Voltammetry. (CSV)	0.1
Elleouet *et al.* 1992.	Differential Pulse Voltammetry. (DPV)	0.4
Sperling *at al.* 1992.	Ion exchange resin.	1.9
Achterberg *et al.* 1994.	Silica separation and CSV.	0.1

Table 5.1 Review of the commonly used methods for the determination of chromium species in natural waters.

chromium (III) concentration. In a later paper, Harper and Riley (1985) discussed this problem and experimentally determined that this was not a significant source of error. Nakayama *et al.*(1981 a,b,c,d), in a series of papers suggested that the method does not take into account the possible role that organically bound chromium could have in the biogeochemistry of chromium. The authors suggest that organic bound chromium is being measured as either chromium (III), chromium (VI) or not at all. Nakayama *et al.* (1981c) proposed a method that enabled the distinction between chromium (III), chromium (VI) and organically bound chromium to be made. Chromium (VI) is complexed with bismuth oxide, and organically bound chromium (III) is oxidised using ammonium persulphate. As was discussed in the previous section, most of the reported organic bound chromium (III) was later reported to be the result of contamination of one of the reagents used in the method (Isshiki *et al.*, 1989).

Another approach to the determination of chromium species is use of methods which remove chromium (VI) species first, and then oxidise the chromium (III) to the (VI) species prior to their determination (De Jong and Brinkman, 1978; Campbell and Yeats, 1981, 1984; Huang and Pang, 1989). Organic agents which have been used are tri-n-octylamine (Campbell and Yeats, 1981), or tri-n-alkyl ammonium chloride (De Jong and Brinkman, 1978). The chromium (III) species are oxidised using persulphate compounds, and the difference between the chromium (VI) and the total chromium is taken as the concentration of chromium (III). The main drawbacks with this method are that it is very time consuming and there is a potential for greater contamination due to the increased number of steps involved.

More recently, several methods using ion exchange resins have been utilised to differentiate chromium species. Isshiki *et al.* (1989) used quinolin-8-ol to complex chromium (III), followed by collection on a macroporous resin. Chromium (VI) was reduced to chromium (III) using hydroxylamine to give a total chromium concentration. The method proved to be both precise and accurate and was applied to natural seawater samples. Shah and Devi (1990) used a poly-hydroxamic resin to preconcentrate chromium (III) followed by analysis using Flow Injection Atomic Spectroscopy (FIAS). Although they found the method suitable for the determination of chromium (III) in seawater samples, the method was very time consuming and only 80% of the chromium (III) was recovered even after long elution periods. Sperling *et al.* (1992) used an activated alumina column to sequentially separate the chromium species, but only natural freshwaters were considered. Rue *et al.*, (1997) use Chelex-100 resin to collect all the chromium (III) from collected seawater samples, the remaining seawater is then acidified and stored to allow the conversion of the chromium (VI) to chromium (III), which is then collected using Chelex-100.

Atomic absorption spectrophotometry (AAS) is the most commonly used method for determining chromium species after separation and/or concentration from the matrix. The graphite furnace technique (GFAAS) is normally used because of the availability of the instruments in trace metal laboratories, ease of use, and ability to determine metals at the µg/l range (Cranston and Murray, 1978; Campbell and Yeats, 1981,1984; Isshiki *et al.*, 1992.). Pyrolitically coated graphite tubes, equipped with L'Vov platforms are the most efficient type of tubes for the detection of low concentrations of chromium. Interferences can be decreased or sometimes eliminated by using a matrix modifier of $Mg(NO_3)_2$. Some researchers have used flame AAS, but this normally means that the samples have to be concentrated further due to the low concentrations of chromium found in natural waters (Sperling *et al.*, 1992).

Recently, the development of electrochemical techniques, such as Anodic Stripping Voltammetry (ASV) and Cathodic Stripping Voltammetry (CSV), have expanded the techniques available for studying the speciation of chromium in natural waters. It is possible to distinguish between the two main species of chromium present in seawater using CSV; this technique involves the collection of chromium (VI) from seawater after complexation with diethylene triamine pentaacetic acid (DPTA), onto a hanging mercury drop electrode (Boussemart *et al.*, 1992). Total chromium is determined after a period of UV oxidation to convert the chromium (III) to chromium (VI), chromium (VI) is determined in untreated samples and chromium (III) is calculated as the difference between the two results. As with all the previous methods, the samples have to be treated with the complexing agent (in this case the DPTA) immediately after collection to prevent changes in redox state of the chromium species during storage. An adaptation of this methodology has been used for the automatic shipboard determination of chromium species (Achterberg *et al.*, 1994). In this method chromium (III) was selectively removed from the seawater by its absorption onto a silica column. Both techniques, (UV oxidation and collection on silica columns) have proved to be effective for the determination of the separate chromium species in seawater. The detection limits of the procedure have been lowered to 1 pmol l^{-1} (Boussemart and Van Den Berg, 1994), while the method allows storage of the chromium (III) samples on the silica columns for long periods of time. Mugo and Orians (1993) have developed a method for measuring the concentration of chromium (III) and total chromium in seawater using electron capture detection gas chromatography.

For this Sargasso Sea study, a modified version of the Cranston and Murray (1978) method was used because of its relative ease of use and the availability of the necessary analytical equipment.

5.2.2 Determination of chromium in sediment trap material

The deep Ocean Flux Programme (OFP) began in 1978 and was primarily concerned with the collection of particles to analyse for organic carbon to try and tie in surface events (such as phytoplankton blooms) with the export of organic carbon associated with the particulate matter to the seabed (Deuser and Ross, 1980; Deuser, 1986). The traps used in this programme are based on the PARFLUX mark II described in detail by Honjo *et al.* (1980). The traps are open at a depth of 3200m and collect material for periods of up to 2 months. The collection pot is closed after a chosen time period, the traps are recovered and the sealed sample removed. The traps are poisoned with sodium azide to prevent bacterial growth.

The material from these traps has been analysed for other elements such as trace metals (Jickells *et al.*, 1984) and the isotopes of nitrogen (Altabet and Deuser, 1985). The data from these studies appears to show a tight coupling between upper ocean events and the production of rapidly falling particulate material that falls to the deep sea within a period of 30-60 days (Deuser *et al.*, 1981, Deuser 1986).

This work is not without controversy, and discussion of this controversy is presented later. A soon to be published paper (Siegel and Deuser, pers. comm. D. Siegel) will discuss the idea that the traps do not represent processes occurring in the ocean directly above the trap but could represent particulate material production many hundreds of miles away from the trap location. With these caveats in mind some useful data may be obtained by the analysis of chromium in trap material, as this material represents a potential removal pathway of chromium from the water column for the NW Atlantic area (not necessarily the Hydrostation S site, or the more removed OFP sampling area which is now located close to the BATS station, when the point of Siegel is taken into account).

The samples of sediment trap material were digested in Teflon bombs using a mixture of nitric and hydrofluoric acid, full details of this digestion can be found in Section 5.2.7.

5.2.3 Preparation of reagents for dissolved chromium analysis

5.2.3.1 0.01M Iron (III) hydroxide solution

0.39 g of high purity (99.997%) ammonium iron (II) sulphate hexahydrate (Aldrich chemicals) was dissolved in a liter of Milli-Q water. Iso-thermally distilled ammonium hydroxide solution (see Section 3.3.2.1) was added to bring the pH of the solution within 8-8.5. The solution was shaken for 24 hours to complete the oxidation of the iron (II) to iron (III). This solution is reportedly stable for one month (Harper and Riley, 1985), but it was prepared fresh before each cruise and was checked by GFAAS for chromium contamination[1].

5.2.3.2 Iron (II) hydroxide solution

This solution was prepared in the same way as the iron (III) solution above but was used immediately after the ammonium hydroxide was added. A green precipitate is formed and this is used. This was prepared when needed, since it is stable for approximately 10 minutes; after this time oxidation to iron (III) occurs.

5.2.3.3 5% Hydrochloric acid

ULTREX hydrochloric acid (Baker Chemicals) was diluted to form a 5% solution with Milli-Q water.

5.2.4 Separation of the iron precipitate from solution

In the original method used by Cranston and Murray (1978), the chromium/iron precipitate was removed from the sample of seawater using membrane filters. There are a variety of filters that could be used for this and analysis of the total chromium content of a variety of filters was performed. Nuclepore filters are normally employed in the study of particulate trace metals in seawater, and due to their availability three other filter types were also analysed for total chromium per filter (see Table 5.2); glass fiber,

---

[1] On two occasions when the check was performed there were unacceptably high concentrations of chromium in this solution. This was found to be a result of contaminated disposable pipette tips, this was rectified by making certain that only tips that had gone through the cleaning process in section 3.1 were used

nylon and Zefluor (Teflon coated). All the filters were soaked in a solution of 10% ULTREX nitric Acid for at least a week, followed by at least one week in 1% ULTREX nitric Acid, the filters were rinsed with Q-water to remove any residual acid before use. The filters were dissolved in 50% nitric acid. The Nuclepore filters required the use of Teflon Bombs for the dissolution of the filter as did the Teflon coated filters. Once the filters were dissolved, the solutions were diluted and determination of chromium was performed according to the protocol in section (5.2.4).

Type of Filter	**Total Cr (nmoles/filter)**
Glass Fiber (GF/F)	980 ± 450
Nuclepore (0.4µm)	310 ±100
Nylon (0.45µm)	70 ± 30
Zefluor(0.5µm) (Teflon)	130 ± 110

Table 5.2. Concentration of total chromium in commonly used laboratory filters.

An analysis of the efficiency of the filters to collect the iron/chromium complex was performed. Seawater samples were collected and stripped of chromium, by the addition of 10ml of the iron (II) hydroxide solution (section (5.2.2.2). The precipitate was allowed to settle and the seawater was decanted into a clean glass bottle, this was repeated twice. The stripped seawater was spiked with chromium (III) to yield a solution containing 2 µmol/l of chromium. Aliquots of the spiked solution were treated with the iron (III) hydroxide solution (5.2.2.1) and filtered through the cleaned filters. The precipitate on the filters was dissolved in 5% hydrochloric acid, and the resulting solution analysed by GFAAS (see section 5.2.4). The data can be seen in Table 5.3

Type of Filter	**Chromium recovery (%)**
Glass Fiber (GF/F)	Did not determine
Nuclepore (0.4µm)	138 ± 21
Nylon (0.45µm)	51 ± 12
Zefluor (0.5µm) (Teflon)	38 ± 27

Table 5.3. Recovery data for spiked seawater using available filters (not corrected for blanks)

From the data shown in Table 5.2 it was not necessary to analyse the recovery of chromium for the glass fiber filters as the total chromium in the filter contaminated the sample. The Nuclepore filters have been shown to be contaminated by chromium in other studies (Statham Pers. comm.), the data presented here supports this. The greater than 100% recovery for the chromium using the Nuclepore filters is presumably contamination from the filter, which was present even under the less aggressive hydrochloric acid treatment. The nylon and Teflon filters had the lowest concentrations of chromium of the filters studied, although their ability to collect the precipitate is unacceptable. The filters both showed degradation under the cleaning treatment. The nylon filter appeared to degrade and the 10% acid bath had a milky appearance, and the filter was translucent in part; this probably resulted in the precipitated iron/chromium complex passing through the filter. The Zefluor filter appeared to degrade in the acid bath, resulting in a separation of the Teflon layer from the filter support; as was the case with the nylon filter this probably reduced the efficiency of the collection of the precipitate.

Due to the large variations in blank determinations and in the recovery data, it was decided that some alternative method should be developed for the collection of the precipitated chromium. Centrifugation was chosen as an avenue of investigation, as a benefit was that if 50ml centrifuge tubes are used, a sample can be collected, precipitated with either the iron (II) or the iron (III) and centrifuged in the same tubes. This has the potential to reduce the contamination involved with chromium determination because the transfers are reduced. The tubes are readily available and they are easily cleaned to the protocol used for the equipment used in the concentration of trace metals in seawater (see section 3.1.2).

The efficiency of the centrifugation method as a form of precipitate collection was performed. Aliquots of seawater stripped of chromium by complexation with iron (II), as described earlier were produced. The first set of samples (A) were spiked with 10 nmol/l chromium (III) and 10 nmol/l chromium (VI), the second set (B) was spiked with 1 nmol l^{-1} of each of the chromium species. Blanks were determined for the experiment by the analysis of the stripped seawater that was used. The experiment was performed in triplicate and the results can be seen in Table 5.4

	A 10 nmol l^{-1} Cr(III) +10 nM Cr(VI)	% recovery	B 1 nmol l· Cr (III) + 1 nM Cr (VI)	% recovery	Blank (nM)
Fe (II)	21.34 ± 2.61	106.7	2.07 ± 0.15	103.5	0.06±0.01
Fe(III)	9.59 ± 1.21	95.9	0.95 ± 0.04	95	0.01±0.01

Table 5.4. Efficiency test for modified method, and blank data for stripped seawater (n=3, data ±1 std. dev., data not blank corrected).

From this experiment it can be seen that the recoveries using the centrifugation method are good. The stripping of the seawater using the iron (II) is shown to be an efficient method of producing chromium free seawater. The iron (II) solution is extracting both species of chromium whereas the iron (III) appears to be only removing the reduced chromium (III).

5.2.5 Determination of GFAAS conditions

The analysis of the chromium solution from the pre-concentration step by atomic absorption spectroscopy may not be as simple as the analysis of standards prepared in a simple dilute acid solution. The presence of chloride from the hydrochloric acid and the large amount of iron present from the iron hydroxide solutions may both interfere with the analysis of the samples. These can result in matrix interferences or molecular absorption of the signal that the source lamp is emitting and may not be due to the presence of the chromium; such a spectral interference is generally called background absorption (Perkin Elmer Corp., 1985). The signals produced by this interference can be reduced by the use of a deuterium arc background corrector. The second type of interference are termed non spectral interferences, and can be put into two groups; the first is a solute-volatalisation which takes place at the platform-sample interface, the second is a vapour phase interference that occurs once the sample has volatalised. One common method of eliminating this type of interference is the use of a standard addition technique. In this method the standard is added to the sample to be analysed, this will result in the standard being affected by any matrix affects that can result in non-spectral interference.

Harper and Riley (1985) determined that there was no interference with the determination of chromium from either the iron solution or the hydrochloric acid, using a Perkin Elmer 2280 atomic absorption spectrophotometer with a model HGA 400 graphite furnace, and using pyro-coated tubes. The centrifugation method could lead to small amounts of salt being introduced to the final hydrochloric acid solution, this could interfere with the analysis of the chromium by GFAAS, as a result of this all analysis of samples was performed using the method of standard additions, and depression/enhancement of the chromium signal would be accounted for.

Rubio *et al.* (1992) suggest that, for most samples, pyrolitically coated platform tubes give the best results for the analysis of chromium by GFAAS. There are different furnace programmes given in the literature, and so the best method for the instrument available was determined experimentally. The programmes used in the analysis of chromium by GFAAS in the literature are shown in Table 5.5.

	Temp	Ramp	Hold	Temp	Ramp	Hold	Temp	Ramp	Hold
Dry	140	5	15	140	10	25	140	10	10
Char	1650	10	20	1200	20	5	1200	10	20
Cool	20	3	3	20	3	3	20	3	3
Atom	2500	0	3	2630	0	3	2500	0	3
Clean	2600	2	3	2700	2	3	2600	2	3
Prog.	**A**			**B**			**C**		

Table 5.5. Reported GFAAS programmes for the determination of chromium (Source: A - Perkin Elmer Corp. B - Harper and Riley (1985). C - Rubio *et al.* (1992))

A test solution of 380 nmol l^{-1} was prepared in Q-water from a stock standard from Perkin Elmer. The solution was preserved using 1% nitric acid. 20 μl of standard were injected into the furnace using the auto-sampler.

Programme A. Absorbance = 0.231±0.003
Programme B. Absorbance = 0.233±0.004
Programme C. Absorbance = 0.201±0.007

There is no significant difference between the absorbance reading obtained using programme A and that from Programme B. Since the atomization temperature is less in Programme A, this was the programme chosen since the lower atomization temperature extends the life of the graphite tubes.

The linear range of the method is important and this must be checked for the potential concentration range that will be used in the determination of the chromium. For this, chromium (VI) standards of differing concentrations were made and analysed using the atomization Programme determined above. The results are given in Figure 5.1. The data was plotted using Cricket Graph and the equation for the line of best fit was generated using that programme. The curve appears to be linear upto a concentration of 200 nmol l^{-1}, and then as is usually the case the line begins to curve, but the line of best fit shown in Figure 5.1 is very good.

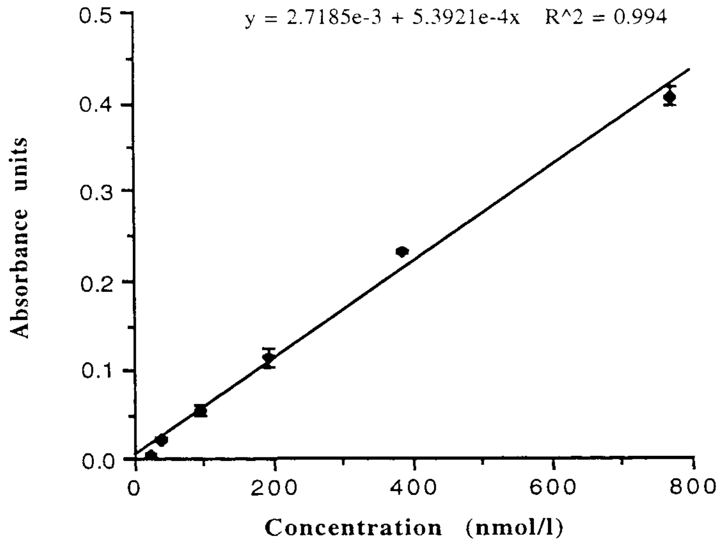

Figure 5.1. Graph of concentration versus absorbance for chromium determination by GFAAS (n=3)

Clearly from Figure 5.1 the linear range for this method is good for concentrations up to 769 nmol l^{-1}.

A check on the recovery of spikes added to seawater samples was done. This was performed by spiking previously stripped seawater, as outlined earlier, and then processing this spiked seawater along with the samples. This procedure provided a check from batch to batch of samples for the recovery of the chromium species, even though data for the recovery experiments outlined earlier indicate that this should not be a problem.

Certified reference material available for the independent assessment of accuracy for this method was used (NASS 2). The reported value for total chromium in NASS 2 certified reference material 3.36 ± 0.19 nmol l^{-1}; this water is collected at a depth of 1300m in the Sargasso Sea, and is unfiltered and acidified. The acidification would result in a total chromium value being obtained on analysis; when chromium (III) plus chromium (VI) concentrations are determined in this study the data is comparable to these certified concentrations (see Table 5.6). Contamination of the samples from the Niskin samplers and the CTD array was evaluated by collecting samples from the surface water at the station by hand. This involved passing the inverted centrifuge tubes below the surface microlayer and then turning the tubes to allow them to fill. The chromium content of samples collected at the surface were within 5% of those collected from surface waters using the Niskin bottles and therefore the cleaned Niskin bottles and the CTD array are producing minimal contamination.

5.2.6 Optimised procedure for the determination of chromium species in seawater.

Six 50ml samples of seawater were collected into previously cleaned (see section 3.1) and weighed 50ml low density polyethylene (LDPE) centrifuge tubes, directly from the Niskin bottles on the CTD rosette. The tubes were rinsed three times with aliquots of the seawater, and then filled to a set 50ml mark and capped. After two sets of triplicate samples from each depth were collected, the capped tubes were taken into the laboratory on the ship. The samples to be analysed for chromium (III) were treated with 0.5ml of iron (III), capped and shaken. The samples for total chromium were treated with 0.5 ml of the freshly prepared iron (II) precipitate, capped and shaken. This total procedure was completed as quickly as possible to avoid redox changes in the samples (usually within 1 hour of sample collection).

The samples were weighed in the shore laboratory to determine the exact amount of sample in each tube. The addition of the iron solution produces an addition of 0.51g this represents approximately 1% of the sample weight, and as such is a negligible factor in the determination of the final weight of sample. The centrifuge bottles were shaken on a mechanical shaker for at least an hour and then centrifuged using a table top centrifuge (approx. 5000 rpm for 15 minutes). After centrifugation the seawater was decanted off, and the bottles left on a bench in a clean room environment to evaporate any residual moisture. The precipitates were dissolved in 0.5ml of 5% hydrochloric acid. The samples were stable in this form and subsequently analysed using GFAAS. This represents a concentration factor of 100. Samples of the discarded seawater were collected and processed a second time with iron (III) to determine if all of the chromium was collected with the first extraction. There was no detectable chromium present in any of these re-analysed samples, this indicates that there is complete removal of chromium from the samples with one extraction. General analytical performance criteria are shown in Table 5.6.

	Precision	Detection limit	NASS 2	Determined
Chromium (III)	2.73±0.11	0.01		
Total Cr	4.27±0.44	0.02	3.36±0.19	3.17±0.2

Table 5.6. Precision (500m sample, n=5,±1 standard deviation), detection limit (3 * std. dev. on blank) and the certified NASS-2 total chromium and measured concentration (all data nmol l^{-1})

5.2.7 Analysis of deep ocean sediment trap material.

Samples of trap material from the Ocean Flux Program (OFP) run from the Woods Hole Oceanographic Institute (WHOI) were provided by Dr. Maureen Conti. These samples represented the samples for the periods shown in Table 5.6 below, and represent samples for the whole of the experimental period of this study. The samples are collected at 3200m. The trap material is the <37μm fraction and generally 1-1.5 mg of material were used for the analysis. The sediment material was digested using a mixture of hydrofluoric acid and concentrated nitric acid (both Ultrex grade) in Teflon digestion bombs. The method used was similar to that used for the sediment samples from the inshore waters study, outlined in Section 3.4.2, with the difference that hydrofluoric acid was used The samples were diluted to 2 ml with Q-water and analysed using GFAAS, quality control was performed by analysing MESS certified reference material. Date for blank values and recovery as well as precision for the extraction of chromium for the reference material is shown in Table 5.7. There was insufficient material to perform replicate analysis on the samples, but replicate analyses were performed on the certified reference material.

Date	Duration	Total Flux	<37μm Flux
Aug. 13th 1994	16	39.81	26.63
Oct. 12th 1994	13	33.39	22.09
Dec. 30th 1994	18	26.44	17.03
Feb 4th 1995	15	35.85	22.99
Mar 6th 1995	15	82.52	39.08
May 2nd 1995	14	44.13	24.43
Jul. 3rd 1995	15	41.19	25.43
Aug. 19th 1995	15	34.16	22.12
Oct. 5th 1995	13	32.70	23.72

Table 5.7. Sample data for OFP samples of sediment trap material (duration = days, Flux = mgm^{-2}d^{-1}).

	Certified value	Measured value	Recovery %	Blank	Detection limit
MESS 1	71±11	66.7±2.0	94±3	0.89	0.6

Table 5.8. Certified value (μg g^{-1}), measured value(μg g^{-1}),, % Recovery, blank value and detection limits, for the analysis of chromium in certified sediment reference material (for all n=5, detection limit is 3 * std. dev. on the blank, blank and detection limit in μg g^{-1})

5.2.8 Sampling programme for dissolved chromium

Samples were collected at Hydrostation S on a total of five occasions over a 17 month period, covering the four seasons, and an additional sample was taken during the phytoplankton bloom. The nutrient data was taken at the BATS station as part of the core data for that programme, oxygen and salinity data were determined at the Hydrostation S site. The stations are 40 kilometres apart and it is likely that the chromium concentrations are not different between the stations. The samples for chromium analysis were collected at the Hydrostation S site and not BATS because there was not enough time to collect extra samples at BATS, and to enable processing of the chromium samples quickly, the alternative would be 5 day sampling trips as part of the BATS programme. The dates and other information regarding the sampling is shown in Table 5.9. below.

Chromium sampling date	Number of samples	Maximum depth of cast (m)	Chl. a samples (to 250m)	BATS sampling date
16/11/94	24	2600	Yes	1/12/94
14/1/95	24	2600	Yes	12/1/95
16/6/95	24	2600	Yes	14/6/95
29/9/95	24	2600	Yes	13/10/94
28/3/96	24	2600	Yes	29/3/96

Table 5.9. Sampling data for chromium samples taken at Hydrostation S, and supporting nutrient samples from BATS.

5.2.9 Collection and analysis of samples for ancillary data

5.2.9.1 Oxygen Samples

Oxygen samples were collected in duplicate from the CTD rosette as the first sample from the bottles. The samples were fixed using Winkler reagents following the standard protocol of Strickland and Parsons (1974) as modified according to the JGOFS protocol (IOC, 1994). Samples were analysed either on-board ship or back in the laboratory within 24 hours. An oxygen auto-titrator (Metrohm 655 Dosimat burette and Metrohm 665 Dosimat titrator with AST computer data analysis programme) was used for the determination of oxygen. The detection limit for this analysis is 0.5 μmol kg^{-1}.

5.2.9.2 Salinity samples

Salinity samples are collected into 250ml borosilicate glass bottles and analysed according to the method given in Section 3.6.1.

5.2.9.3 Nutrient samples

Reactive phosphorus, nitrite, nitrate and reactive silicate were determined using an AA II auto analyser, as described in the JGOFS manual (UNESCO, 1994). Data for precision and detection limits for these analyses can be seen in Table 5.10.

	Precision	Detection limit
Phosphorus	±0.01	0.03
Nitrite	±0.001	0.01
Nitrate	±0.001	0.01
Reactive silicate	±0.01	0.03

Table 5.10. Precision and detection limit data for the analysis of nutrients by auto analyser (all data µmol l^{-1}).

5.3 Hydrodynamic and biogeochemical conditions at Hydrostation S

The Sargasso Sea represents one of the most studied areas of the world's deep oligotrophic ocean areas. Starting with work by Stommel and colleagues in 1954, at Hydrostation S as it is now known (formerly the Panulirus site), there have been measurements made of depth, temperature, salinity and oxygen at three-weekly intervals. Intermittent studies concerned with the chemical and biological nature of the area have also been performed (Menzel and Ryther, 1960, 1961; Jenkins, 1977,1982; Jenkins and Goldman, 1985). A basic sampling programme (salinity, oxygen and temperature) continues, and in 1990 was joined by the Joint Global Ocean Flux Study (JGOFS) site which is to the south east of the Hydrostation S site.

Hydrostation S is located at 32°10'N and 64°30W, in the western return flow of the Northern Atlantic sub-tropical gyre, within the subtropical frontal zone which lies between 26°N and 32°N (Halliwell *et al.*, 1994). To the north of the area the water masses are subject to strong seasonality. It is in this area north of Bermuda that the so called 18°C mode water is formed by winter convective processes (Talley and Rayner, 1982). This mode water is found at the Hydrostation site and is water that has a distinctive temperature/salinity signature. It is thought that the climatic conditions during formation of this water are the major controlling aspect of the specific signature (Ebbesmeyer and Lindstrom, 1986). To the south of the Hydrostation site is the oligotrophic, permanently stratified water of the sub-tropical convergence zone: here the nutrient rich 18°C water remains below the euphotic zone for most of the year (Malone *et al.*, 1993). The seasonal and main thermoclines are separated by a thinning wedge of this 18°C water, a schematic of this is shown in Figure 5.2 (Halliwell *et al.*, 1994, as modified to this form by Bates, 1995). The 18°C water is centred around 300m. Below this point and reaching to approximately 800m is the main thermocline water. The main thermocline water is identified by having a salinity between 36.4 and 36.1 and a temperature that quickly falls from 17°C to 7°C. At a depth of 800-900m there is a layer of water that is low in oxygen and has increased concentrations of nutrients. This is recognised and classified as dilute Antarctic Intermediate Water (AIW). Below this depth the identification of water mass origins becomes less straightforward. The general term for water that lies between 1100m and the bottom of the ocean (around 4000m at Hydrostation S) is North Atlantic Deep Water (NADW). NADW has been sub-divided into four water masses: Mediterranean water 1100m-1300m,

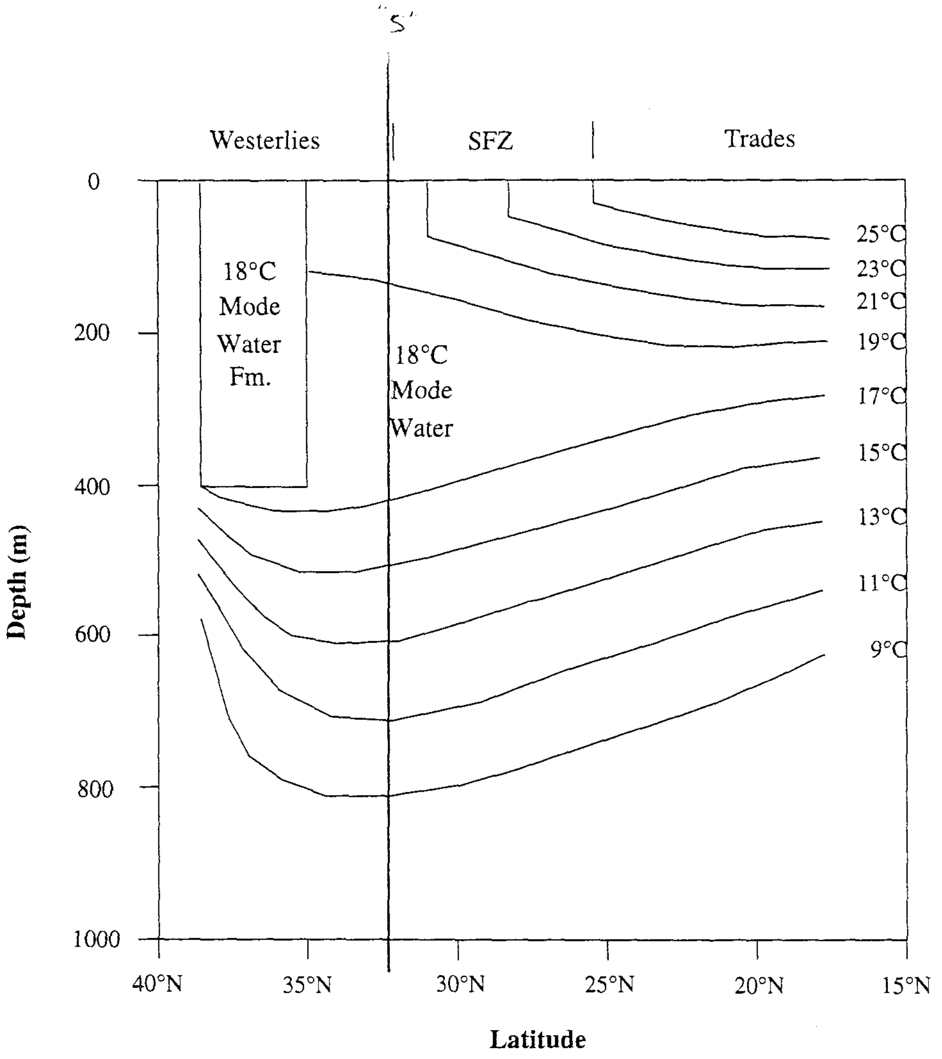

Figure 5.2. Schematic of water masses at Hydrostation S. (Halliwell et al. 1994)

Labrador seawater 1500m-2000m, Iceland-Scotland overflow water 2800m-3200m and below this is Denmark Strait water (Wright and Knap, 1983), the depths in between these points are gradients between the water masses.

In general there is a very marked seasonal cycle in the properties of the upper water column. Winter convection brings nutrients to the surface waters, which results in a bloom of phytoplankton forming. A shallow seasonal thermocline at around 40m is formed and nutrient concentrations drop concomitant with a increase in primary production. With lower temperatures and higher winds in the autumn the seasonal thermocline begins to erode until the winter conditions lead to a mixed water column in the upper 200m. This cycle is variable in time and intensity (Menzel and Ryther, 1960, 1961) and a similar pattern is found at the JGOFS Bermuda site (Michaels et al. 1994). This brief overview is a simplification of the cycles occurring in the upper waters at the Hydrostation S site: more attention will be given in the discussion of the data at the end of this chapter.

5.4 Results

All of the chromium data can be found in Appendix 4. A general outline of the data is given for the first month of sampling after that only differences between months are outlined.

5.4.1 Chromium in the upper water column (0-500m)

5.4.1.1 November 1994

Salinity and temperature data can be seen in Figure 5.3a. The Figure indicates that the upper 75m of the water mass was mixed, exhibiting isohaline and isothermal conditions. Below this surface layer the water column exhibits characteristics of the 18°C water, as discussed in section 5.3. Below 400m the main thermocline begins, and temperature and salinity start to decrease relative to the 18°C water conditions.

Nitrate and nitrite distribution through the water column are shown in Figure 5.3c. Nitrate is depleted (relative to greater depths) in the upper 100m of the profile and increases as one progresses down the water column. Nitrite concentrations are below the limits of detection at all depths (0.03 nmol l^{-1}).

Phosphate and silicate distribution can be seen in Figure 5.3b. Phosphate shows a pronounced peak at 30m, then falls below detection limits at 80m to 200m where concentrations increase through the remainder of the 18°C water into the main thermocline water. The peak in phosphate at 30m is probably contamination (BATS group, pers. comm.) Silicate shows a gradual increase from around 1 μmol l^{-1} in the surface waters to a concentration of 3.5 μmol l^{-1} at the beginning of the main thermocline water.

Both chromium (VI) and chromium (III) are presented together with the apparent oxygen utilisation (AOU) in Figures 5.3d and 5.3e. This provides a visual way of checking whether the degree of oxygen saturation could have an impact on the equilibrium between the two chromium species studied, as has been previously noted (Murray *et al.*, 1983). The AOU data reveals that the water column is supersaturated with respect to oxygen in the upper 100m, below which there is a sharp drop at the start of the 18°C water where the AOU is approximately -30 μmol l^{-1}. There is a further increase in the AOU as the main thermocline begins.

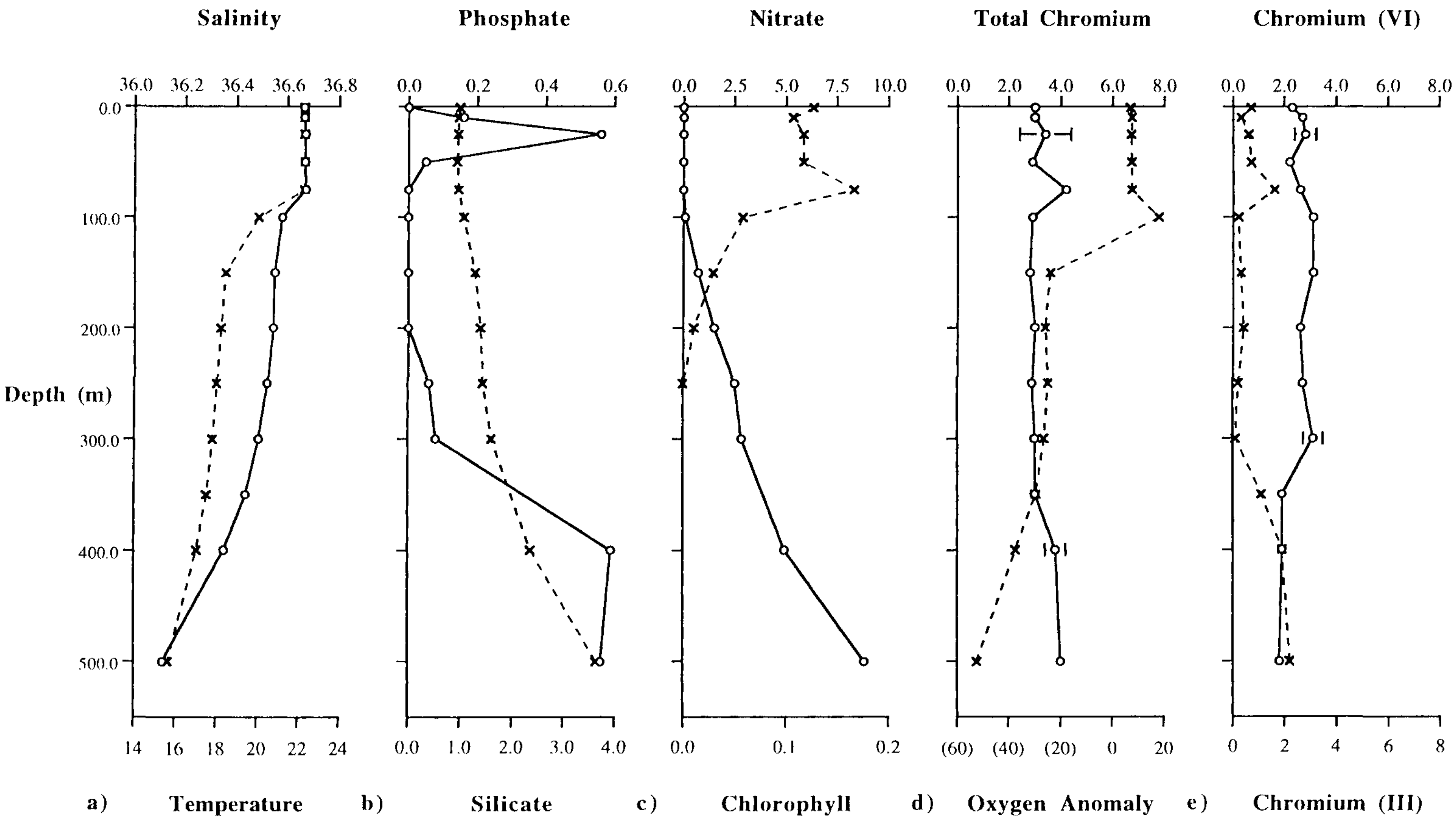

Figure 5.3 Physical and chemical parameters for the upper water column: November 1994. **a)** Salinity (solid) and Temperature (°C) (dashed) **b)** Phosphate (solid) and Silicate (dashed) (μmol kg^{-1}) **c)** Nitrate (solid) (μmol kg^{-1}) and chlorophyll (dashed) (μg kg^{-1}) **d)** Chromium (solid) (nmol l^{-1}) and Oxygen anomaly % (dashed) (saturation (-ve)=undersaturated) **e)** Chromium (VI) (solid) and Chromium (III) (dashed) (nmol l^{-1}, ±s.dev, n=3).

The chromium (VI) profile (Fig. 5.3e) reveals that this species of chromium is evenly distributed through the upper 100m of the water column. This even distribution continues through the 18°C water. At the start of the main thermocline water (400m), the chromium (VI) undergoes a small but significant decrease and is constant then down to 500m.

Chromium (III) concentrations (Fig. 5.3e) are significantly lower than the chromium (VI) in the upper 50m of the profile; 0.6 ± 0.2 nmol l^{-1} compared to 2.5±0.3 nmol l^{-1}. There is a spike in the chromium (III) concentration at 75m, then the concentration of the chromium (III) decreases and remains consistently low (0.2 ± 0.1 nmol l^{-1}) throughout the 18°C water. The concentration of chromium (III) increases in the main thermocline water.

5.4.1.2 January 1995

The temperature at the surface of the water column is markedly cooler than in the November samples (20° compared to 22°). Nitrite peaks at 0.045 µmol l^{-1} at a depth of 150m and then remains constant through the remainder of the upper profile. Phosphate (Fig. 5.4b) has a detectable presence in the upper 20m of the water column, then falls below the limit of detection between 25m and 75m.

The AOU pictured in Figure 5.4d reveals that the upper 75m of the water column is supersaturated, but unlike the November situation there is no peak in saturation at 100m, instead there is a increase in the AOU. This is a result of the well mixed state of these waters and indicates that the station is not undergoing a strong phytoplankton bloom, as the photosynthetic induced maximum that is found at 100m in the November profile is not present. The degree of supersaturation in the 18°C water is not as marked as it was in the November samples, even as one approaches the main thermocline waters.

Chromium (VI) (Fig. 5.4e) has a significant surface depletion when compared to the November sample period; 1.7 nmol l^{-1} compared to 2.6 ± 0.33 nmol l^{-1}. The concentration of chromium (VI) shows a peak concentration of 2.8 nmol l^{-1} at a depth of 75m. Below 150m the concentration shows a higher variability, but no significant difference, from the November profile (1.7 ± 0.5 nmol l^{-1} and 2.4 ± 0.6 nmol l^{-1} respectively).

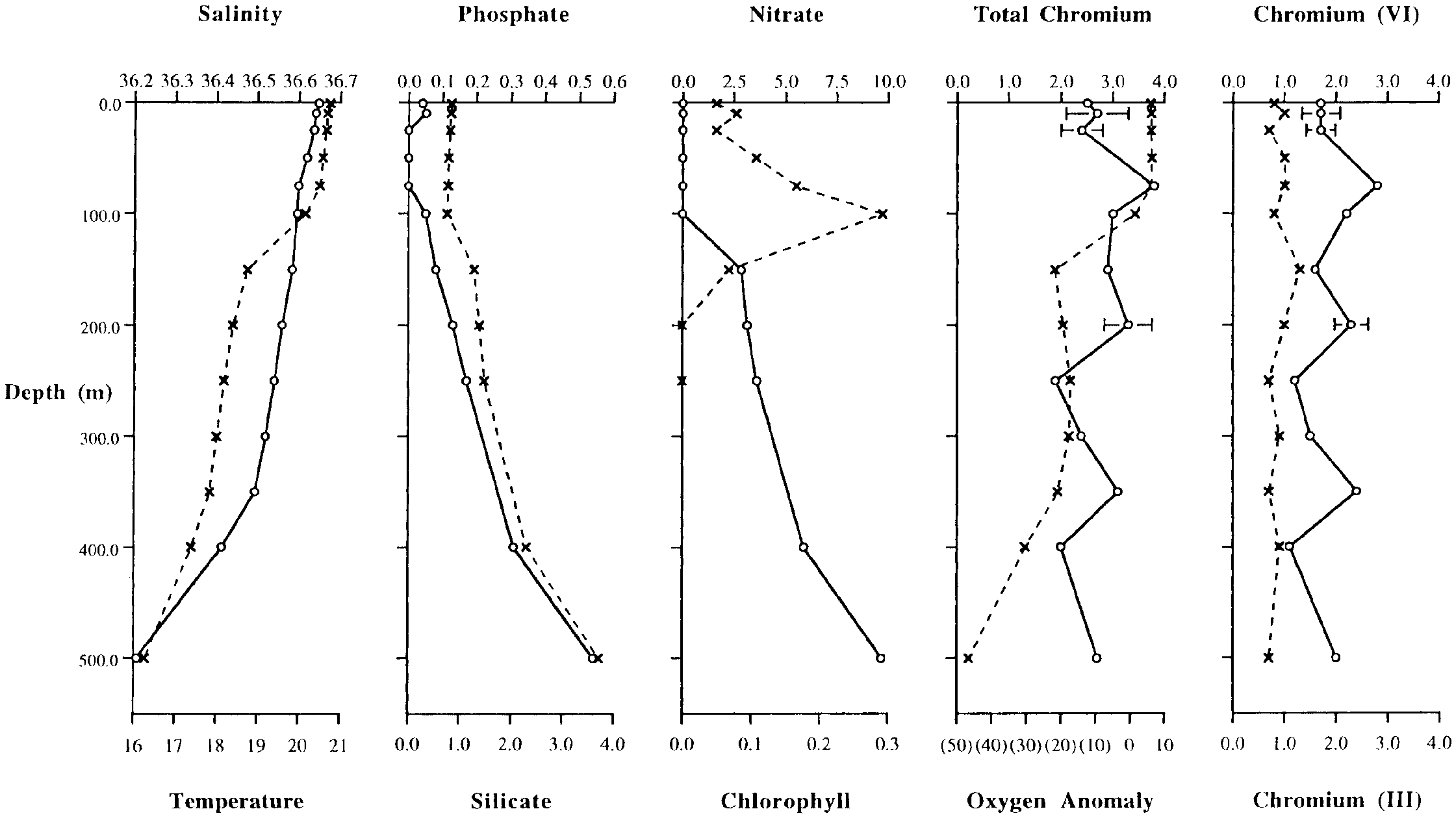

Figure 5.4 Physical and chemical parameters for the upper water column: January 1995. **a)** Salinity (solid) and Temperature (°C) (dashed) **b)** Phosphate (solid) and Silicate (dashed) (μmol kg^{-1}) **c)** Nitrate (solid) (μmol kg^{-1}) and chlorophyll (dashed) (μg kg^{-1}) **d)** Chromium (solid) (nmol l^{-1}) and Oxygen anomaly % (dashed) (saturation (-ve)=undersaturated) **e)** Chromium (VI) (solid) and Chromium (III) (dashed) (nmol l^{-1}, ±s.dev, n=3).

Chromium (III) in the upper 100m shows very little variation at 0.8 ± 0.1 nmol l^{-1} (Fig. 5.4e). There is a peak in concentration at 150m which coincides with the point at which the AOU rapidly increases. Between 200m and 500m the concentration of chromium (III) exhibits little variation, with a mean concentration of 0.8 nmol l^{-1}.

5.4.1.3 June 1995

Profiles for temperature and salinity reveal that the water is thermally stratified (Fig. 5.5a): evidence for this comes from the high temperatures throughout the surface 50m. There is evidence for an input of rainwater to the surface as the salinity here and down to 10m is lower than the remainder of the upper 50m. Surface temperatures are higher than the November and January conditions: this of course is expected due to the high atmospheric temperatures and insolation at this time of year.

The concentrations of nitrate are lower in the 18°C water and the main thermocline waters than both of the previous months. There is a spike in nitrite at 100m but this is thought to be experimental error (P. Countway pers. comm.), but this could be due a release from phytoplankton.

As was the case in the previous months there are spikes of phosphate present in the upper 50m of the profile (Fig. 5.5c), these are thought to be the result of contamination (P. Countway, pers. comm.). Increasing concentrations of phosphate are evident as one enters the bottom of the surface mixed layer (150m) and increasing through the 18°C water to the main thermocline. The concentrations of phosphate in the upper profile are lower than those found for this area in the January study, this is also evident for the silicate concentrations. Overall the June profile indicates that there has been a depletion of all the nutrients in the upper water column.

The AOU profile found in Figure 5.5d reveals that there is supersaturation in the upper 80m, a drop into undersaturated conditions at 100m then a gradual decline in the oxygen concentration through the remainder of the water column. The degree of supersaturation exhibited in the upper 80m is higher than that found in January and of the same order as the November samples.

The average chromium (VI) concentration (Fig. 5.5c) is higher in the upper 75m than at either of the previous months; 3.3 ± 0.6 nmol l^{-1} against 2.5 ± 0.3 nmol l^{-1} for November and 2.0 ± 0.6 nmol l^{-1} for January. There is a significant increase at

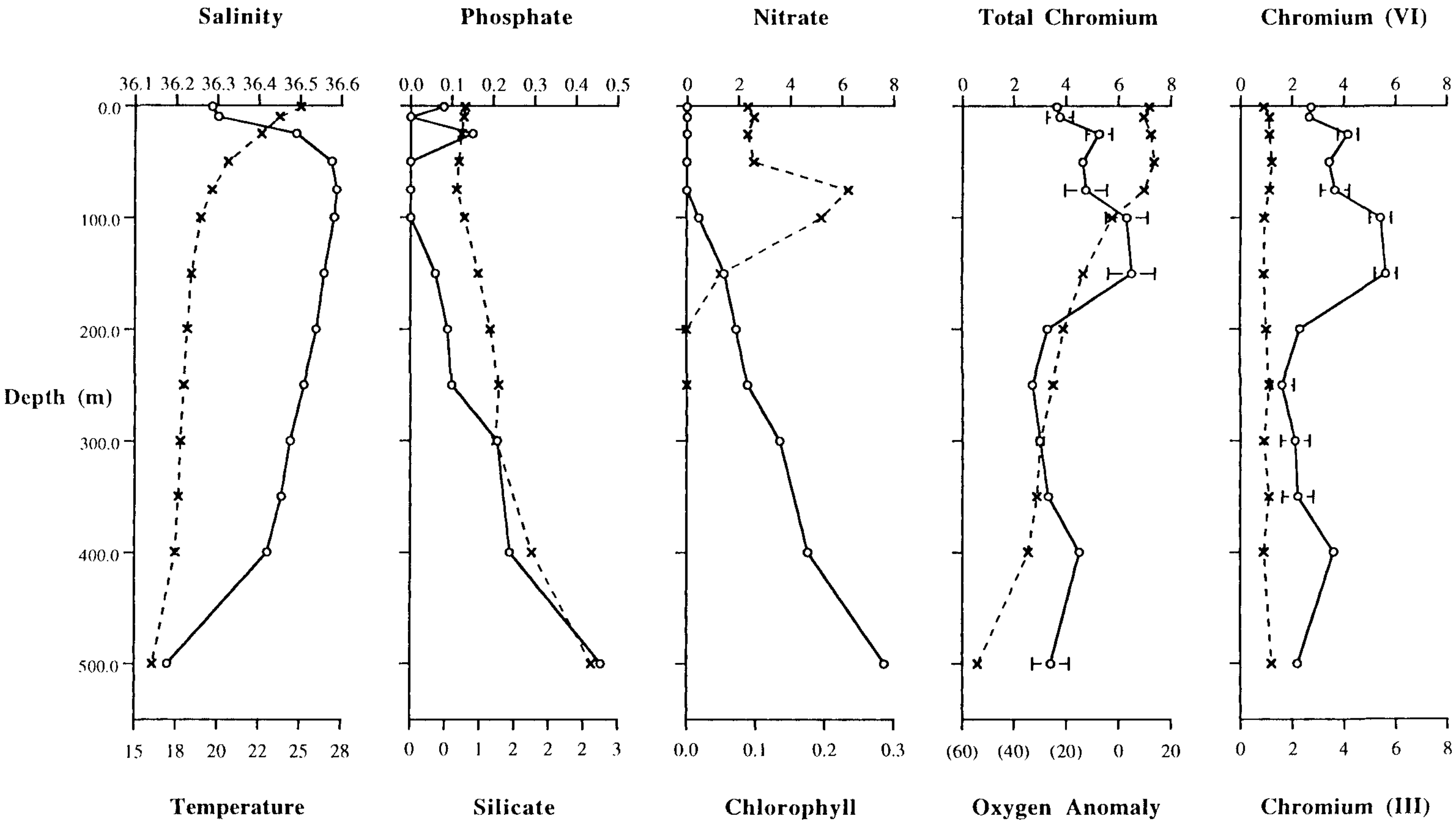

Figure 5.5 Physical and chemical parameters for the upper water column: June 1995. **a)** Salinity (solid) and Temperature (°C) (dashed) **b)** Phosphate and Silicate (dashed) (μmol kg^{-1}) **c)** Nitrate (solid) (μmol kg^{-1}) and chlorophyll (dashed) (μg kg^{-1}) **d)** Chromium (solid) (nmol l^{-1}) and Oxygen anomaly % (dashed) **e)** Chromium (VI) (solid) and Chromium (III) (dashed) (nmol l^{-1}, ±s.dev, n=3).

the base of the mixed layer and then the chromium concentration decreases to values found in the 18°C water for the previous sample periods.

There is no significant difference between the concentrations of chromium (III) in the upper 75m between June, January, and November (1.1 ± 0.1 nmol l^{-1}, 0.9 ± 0.1 nmol l^{-1} and 0.8 ± 0.5 nmol l^{-1} respectively). As was the case for the January samples the concentrations of chromium (III), in June, in the 18°C water (150-300m) are significantly higher than the concentrations for that water mass in November (1.0 ± 0.1 nmol l^{-1} and 0.3 ± 0.1 nmol l^{-1} respectively). The concentrations of chromium (III) in the upper part of the main thermocline water exhibits no significant difference from the previous months.

5.4.1.4 September 1995

Around this sampling period there was an unusually large amount of hurricane activity. Hurricane Felix passed directly over Bermuda on the 14th of August, hurricane Luis passed close but not directly over Bermuda on the 9th of September and hurricane Marilyn came close to Bermuda (100 miles) on the 18th of September. This season had the highest number of named storms in the last 30 years (National Hurricane Centre). This may have an effect on the data profiles and will be discussed where relevant at the end of this chapter.

The upper water column is warmer than the June samples due to the higher insolation during the later summer months (Fig. 5.6a). The hurricane passage, even though it probably cooled the surface waters and brought cooler water from deeper depths to the surface, appears to have had no lasting effect on the temperature profile. It is interesting that the salinity is almost constant through to the top of the main thermocline water. The surface salinity (to 75m) is lower than the surface salinity in both November and January but higher than the freshwater impacted June water. This is in most part due to mixing of the lower salinity water from about 100m depth, indicating that there may have been mixing to this depth, combined with inputs of freshwater from rain events associated with the hurricanes.

Phosphate is below detection in the upper 75m of the water column (Fig. 5.6b). Below this depth concentrations increase through the water column. Silicate exhibits a markedly different profile than was previously found. The surface concentrations are significantly lower than in the previous sample (upper 75m around 0.25 µmol l^{-1} compared 1.0 µmol l^{-1} for the other months) and there is a generally lower value for silicate down the whole of the water column.

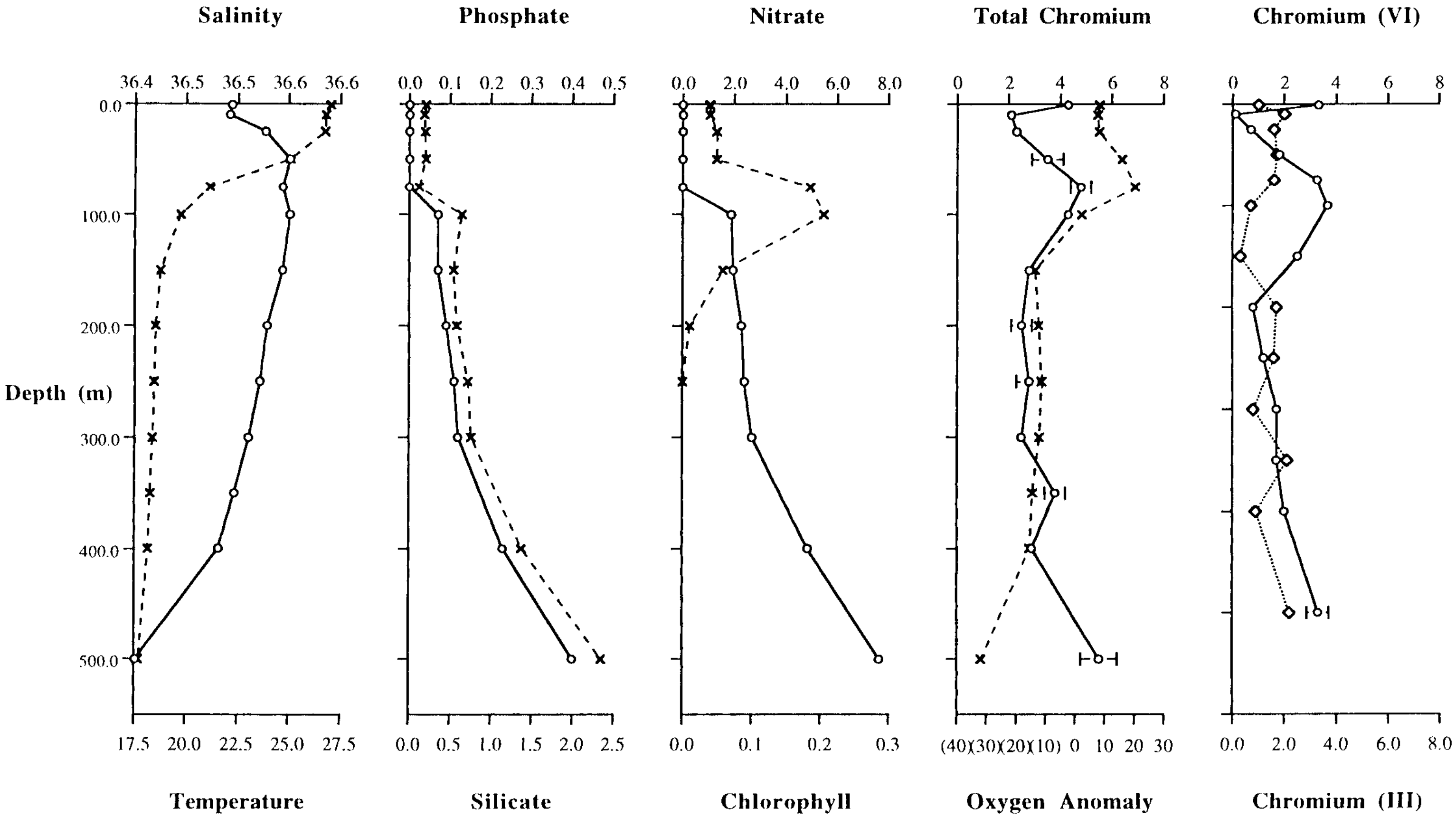

Figure 5.6 Physical and chemical parameters for the upper water column: September 1995. **a)** Salinity (solid) and Temperature (°C) (dashed) **b)** Phosphate (solid) and Silicate (dashed) (μmol kg^{-1}) **c)** Nitrate (solid) (μmol kg^{-1}) and chlorophyll (dashed) (μg kg^{-1}) **d)** Chromium (solid) (nmol l^{-1}) and Oxygen anomaly % (dashed) (saturation (-ve)=undersaturated) **e)** Chromium (VI) (solid) and Chromium (III) (dashed) (nmol l^{-1}, ±s.dev, n=3).

The only differences in chromium (VI) distribution from previous months is that chromium (VI) (Fig. 5.6e) shows a very dramatic drop at the 10m depth; to below the limit of detection. The concentration of chromium (VI) for the 18°C water is not significantly different from the other months, with the exception of November which had a higher chromium (VI) concentration (2.9 ± 0.3 nmol l^{-1} compared to 1.1 ± 0.7 nmol l^{-1}).

Chromium (III) for September (Fig. 5.6e) show significantly higher concentrations for the upper 75m, 1.6 ± 0.3 nmol l^{-1}, compared to 0.8 ± 0.5 nmol l^{-1} for November, 0.9 ± 0.1 nmol l^{-1} for January and 1.1±0.1 nmol l^{-1} for June. With the exception of the November samples there is no significant difference between the 150m-300m water. The data for November was significantly lower ($P<0.05$), although the degree of variability in the data was high (1.1 ± 0.7 nmol l^{-1}). The main thermocline water values were similar to the previous months, 1.7 ± 0.7 nmol l^{-1}.

5.4.2 Bacteria and *Trichodesmium* counts from the Bermuda Atlantic time series (BATS) study station

Because of the potential for bacterially mediated reduction of chromium (Smillie *et al.*, 1980), Figure 5.7a gives the bacterial numbers for the four months studied. From this one can see that the highest numbers of bacteria are found in the month of June 1995, with the lowest being found in September 1995. The profiles indicate that in general the highest bacteria numbers are located at a depth of 60m. Numbers are only reported down to a depth of 250m, there are counts lower down but the numbers are very low, generally less than $0.4 * 10^5$ cells per ml. The *Trichodesmium* abundance combined for 1994 and 1995 can be seen in Figure 5.7b. This data is provided by the BATS group and K. Elardo and K. Gundersen in particular.

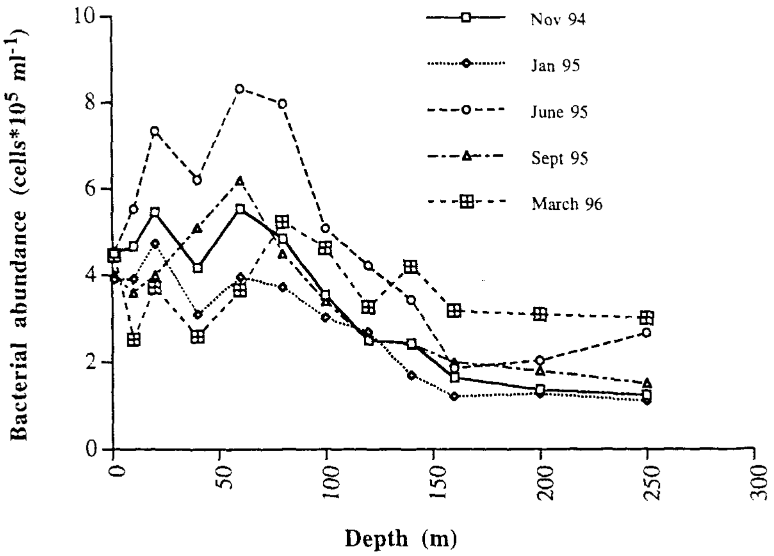

Figure 5.7a Total bacteria numbers versus depth at the BATS study station for the months of this study.

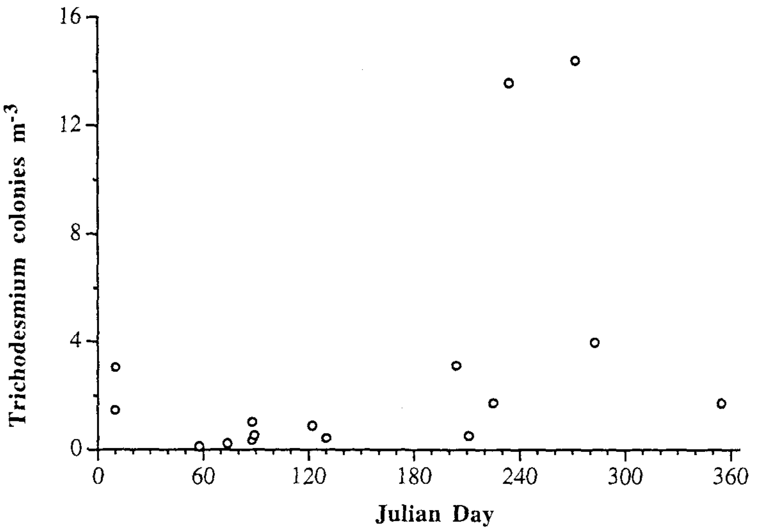

Figure 5.7b Number of Trichodesmium colonies in surface waters in 1994 and 1995 combined

5.4.3 Chromium in the deeper water column (600m-2600m)

The main thermocline water is found from 500m to around 800m, and in this depth range temperatures decrease from 17°C to 7°C, and the salinity changes from 36.4 to 36.1. The next water mass encountered is not identified in terms of a particular temperature salinity signature but a low oxygen, and high nutrient concentrations: this is the AIW. From the discussion in section 5.2 on the general hydrodynamics of the area, the water below the AIW (1200m-3000m) is generally classed as NADW, but there is debate as to the source of the water mass. In this discussion the term NADW will be used.

5.4.3.1 November 1994

Below 600m all of the profiles for each of the four months look very similar and vary in accordance with the discussion above. Salinity, temperature and the nutrient profiles for November, are shown in Figures 5.8a, 5.8b and 5.8c. As before, the profile distribution of the two chromium species are shown with that of the AOU (Figs. 5.8d and 5.8e). From the profiles it is evident that chromium (VI) remains at a fairly consistent concentration of 2.6 ± 0.2 nmol l^{-1} throughout the profile below 600m. Chromium (III) has a spike in concentration at the top of the zone with the oxygen minima, at a depth of 600m, after which it decreases to the 1000m depth level and then remains constant to the bottom of the profile. There are no chromium (III) data available for this month at the 2200m and 2600m depths due to experimental error. The concentration in the deeper waters below 1000m is constant with depth (1.5 ± 0.4 nmol l^{-1}), as was the case for the chromium (VI).

5.4.3.2 January 1995

The data for the profiles for January are shown in Figure 5.9.

The chromium species profiles for this month (Figures 5.9d and 5.9e) show a change from the previous month. There is a maximum concentration of chromium (VI) at a depth of 800m and throughout the area of the oxygen minima there is an increase in this species. Concentrations of chromium (VI) are in the same range as in the previous month for the depths below 1000m (2.1 ± 0.7 nmol l^{-1}). Chromium (III) differs from the previous month in that there is no pronounced peak at the oxygen minima and concentrations are generally the same throughout the profile from a depth of 600m (1 ± 0.3 nmol l^{-1}).

5.4.3.3 June 1995

The plots of data for June are shown in Figure 5.10.

The chromium data (Figs. 5.10d and 5.10e) is more like the data from November rather than January. There is an increase in the chromium (III) at the top of the AIW and, like the November samples, there is no concomitant decrease in the chromium (VI). However the concentrations of chromium (III) are higher at this point than in the November samples. Below the 1000m depth the concentrations of chromium (III) and chromium (VI) are not different from those of the previous months, 1.2 ± 0.3 and 2.9 ± 0.4 nmol l^{-1} respectively.

5.4.3.4 September 1995

The data for September is shown in Figure 5.11.

Like the January profile, chromium (VI) (Fig 5.11d) exhibits a maximum concentration at the depth that the AOU is greatest, at 800m. There is a dip at a depth of 600m and following the maximum at 800m there is a decrease and the lower water mass has a chromium (VI) concentration similar to that found for these depths in the previous months, 2.2 ± 1.2 nmol l^{-1}, although there is obviously more variability in this months data. The chromium (III) has a minimum at 700m and increases as the oxygen minima decreases. The deeper water concentrations are in agreement with data from previous months (0.9 ± 0.4 nmol l^{-1}).

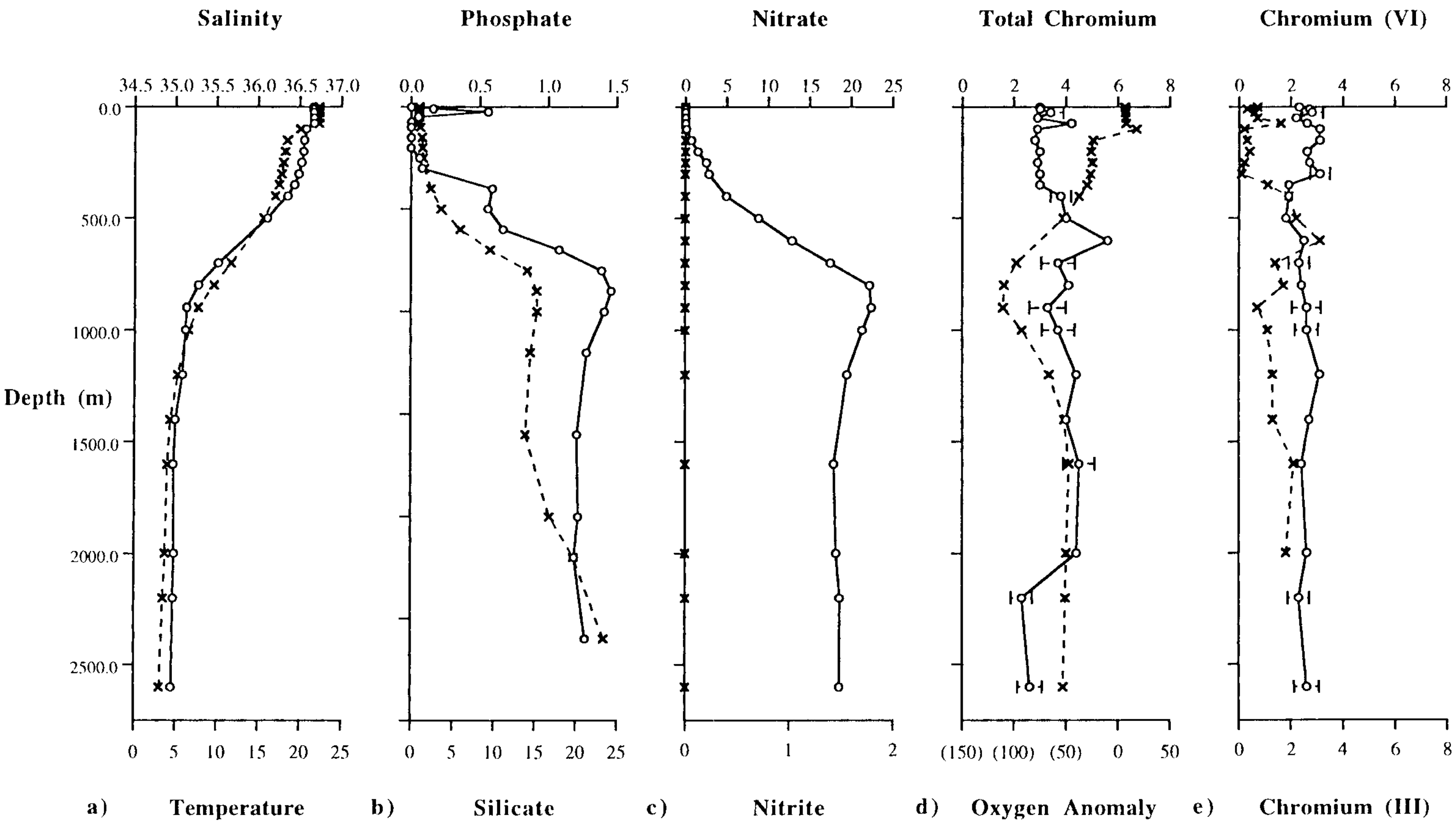

Figure 5.8 Physical and chemical parameters for the water column: November 1994. **a**) Salinity (solid) and Temperature (°C) (dashed) **b**) Phosphate (solid) and Silicate (dashed) (μmol kg^{-1}) **c**) Nitrate (solid) and Nitrate (dashed) (μmol kg^{-1}) **d**) Chromium (solid) (nmol l^{-1}) and Oxygen anomaly % (dashed) (saturation (-ve)=undersaturated) **e**) Chromium (VI) (solid) and Chromium (III) (dashed) (nmol l^{-1}, ±s.dev, n=3).

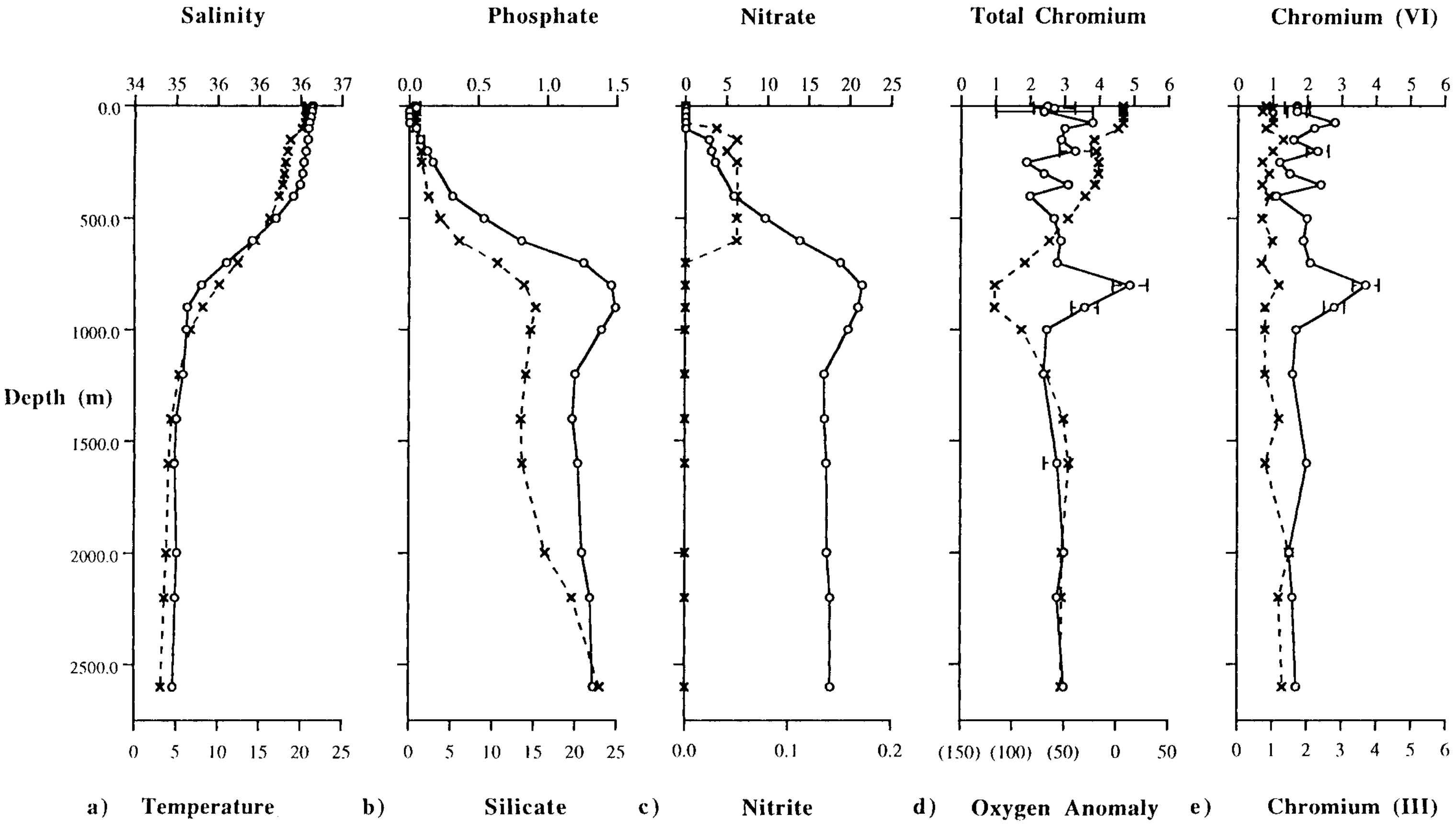

Figure 5.9 Physical and chemical parameters for the water column: January 1995. **a)** Salinity (solid) and Temperature (°C) (dashed) **b)** Phosphate (solid) and Silicate (dashed) (µmol kg^{-1}) **c)** Nitrate (solid) and Nitrate (dashed) (µmol kg^{-1}) **d)** Chromium (solid) (nmol l^{-1}) and Oxygen anomaly % (dashed) (saturation (-ve)=undersaturated) **e)** Chromium (VI) (solid) and Chromium (III) (dashed) (nmol l^{-1}, ±s.dev, n=3).

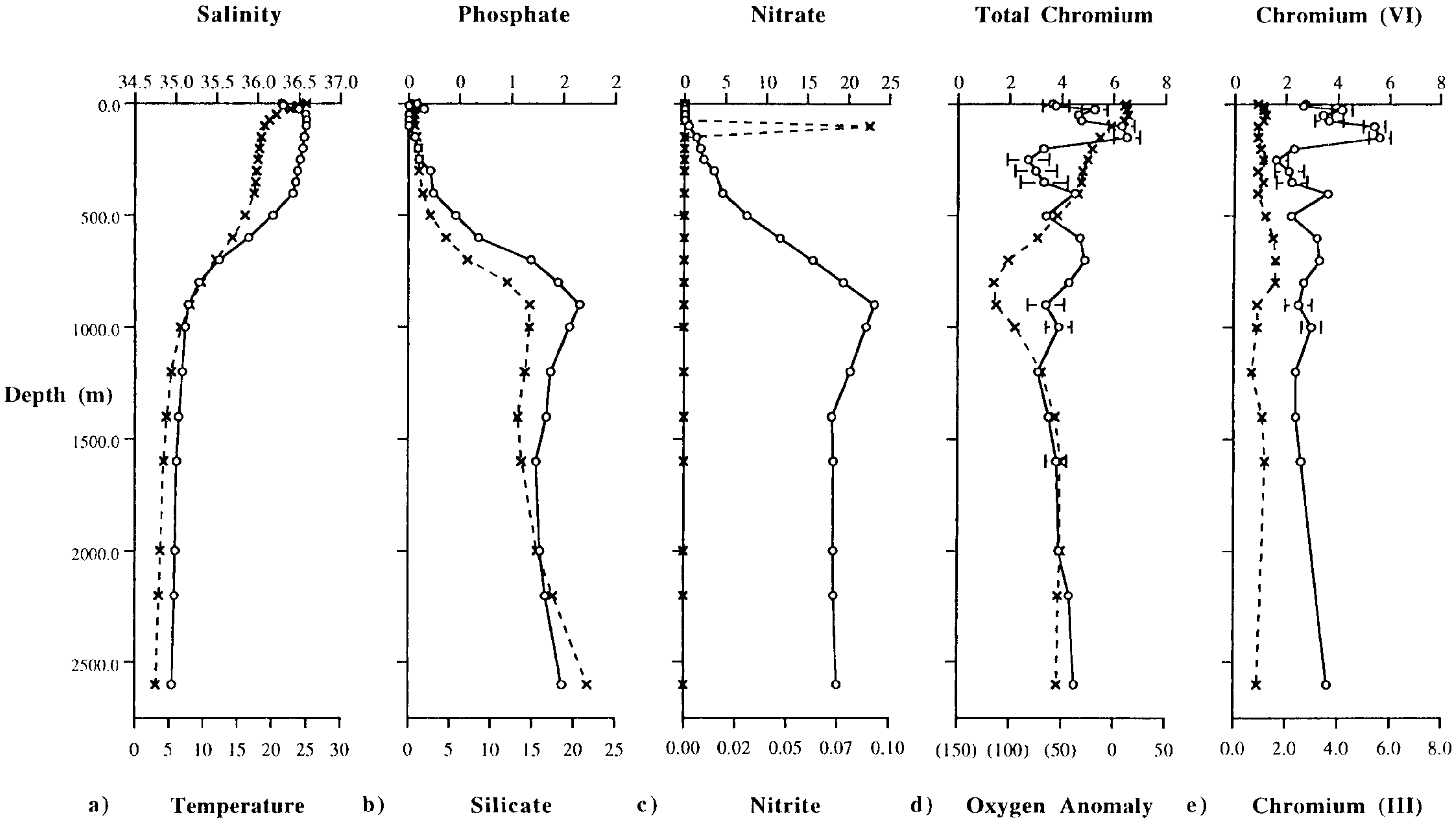

Figure 5.10 Physical and chemical parameters for the water column: June 1995. **a)** Salinity (solid) and Temperature (°C) (dashed) **b)** Phosphate (solid) and Silicate (dashed) (μmol kg^{-1}) **c)** Nitrate (solid) and Nitrate (dashed) (μmol kg^{-1}) **d)** Chromium (solid) (nmol l^{-1}) and Oxygen anomaly % (dashed) (saturation (-ve)=undersaturated) **e)** Chromium (VI) (solid) and Chromium (III) (dashed) (nmol l^{-1}, ±s.dev, n=3).

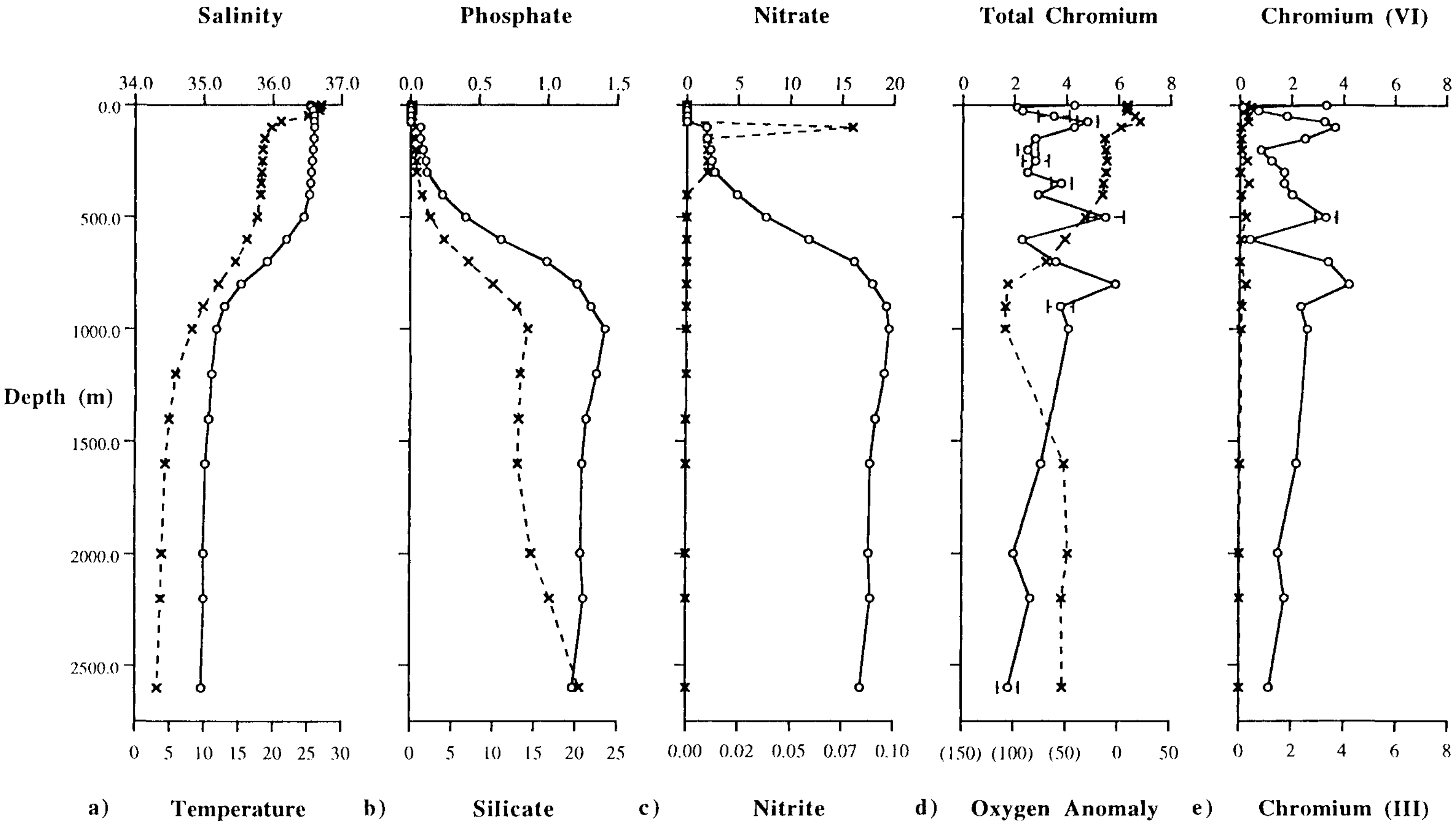

Figure 5.11 Physical and chemical parameters for the water column: September 1995. **a)** Salinity (solid) and Temperature (°C) (dashed) **b)** Phosphate (solid) and Silicate (dashed) (μmol kg^{-1}) **c)** Nitrate (solid) and Nitrate (dashed) (μmol kg^{-1}) **d)** Chromium (solid) (nmol l^{-1}) and Oxygen anomaly % (dashed) (saturation (-ve)=undersaturated) **e)** Chromium (VI) (solid) and Chromium (III) (dashed) (nmol l^{-1}, ±s.dev, n=3).

5.4.4 March 1996-Bloom conditions

Since the spring phytoplankton bloom was missed in 1995 an attempt was made in 1996 to sample at a time during the bloom. Bloom cruise sampling as part of the BATS program is more frequent, every 5 days, in an attempt to sample during or close to the bloom period. Samples were taken at Hydrostation S and also at the BATS station for the nutrients down to 250m; samples for chromium analysis were collected down to 600m at Hydrostation S.

From the salinity and temperature values shown in Figure 5.12a it is obvious that the upper 100m is well mixed with no sign of stratification. Phosphate concentrations shown in Figure 5.12b are similar to concentrations found in the other months. The pronounced peak in nitrate at 160m is not found in any of the other monthly samples except the January samples The chromium profiles shown in Figures 5.12d and e are very different to any of the other profiles shown. There is a slight decrease in the chromium (VI) down to 100m that corresponds to a large increase (over the other months) in chromium (III) that is not present in any of the other months studied. Both chromium (III) and chromium (VI) increase dramatically at a depth of 150m; the concentration of chromium (VI) is twice that found in any other month at this depth, and the chromium (III) is increased five fold over the concentrations normally encountered at this depth. Below this depth the concentration of chromium (III) are similar to those found in the previous months, but the concentration of chromium (VI) is generally lower than the other months, with the exception of January 1995 which has similar concentrations.

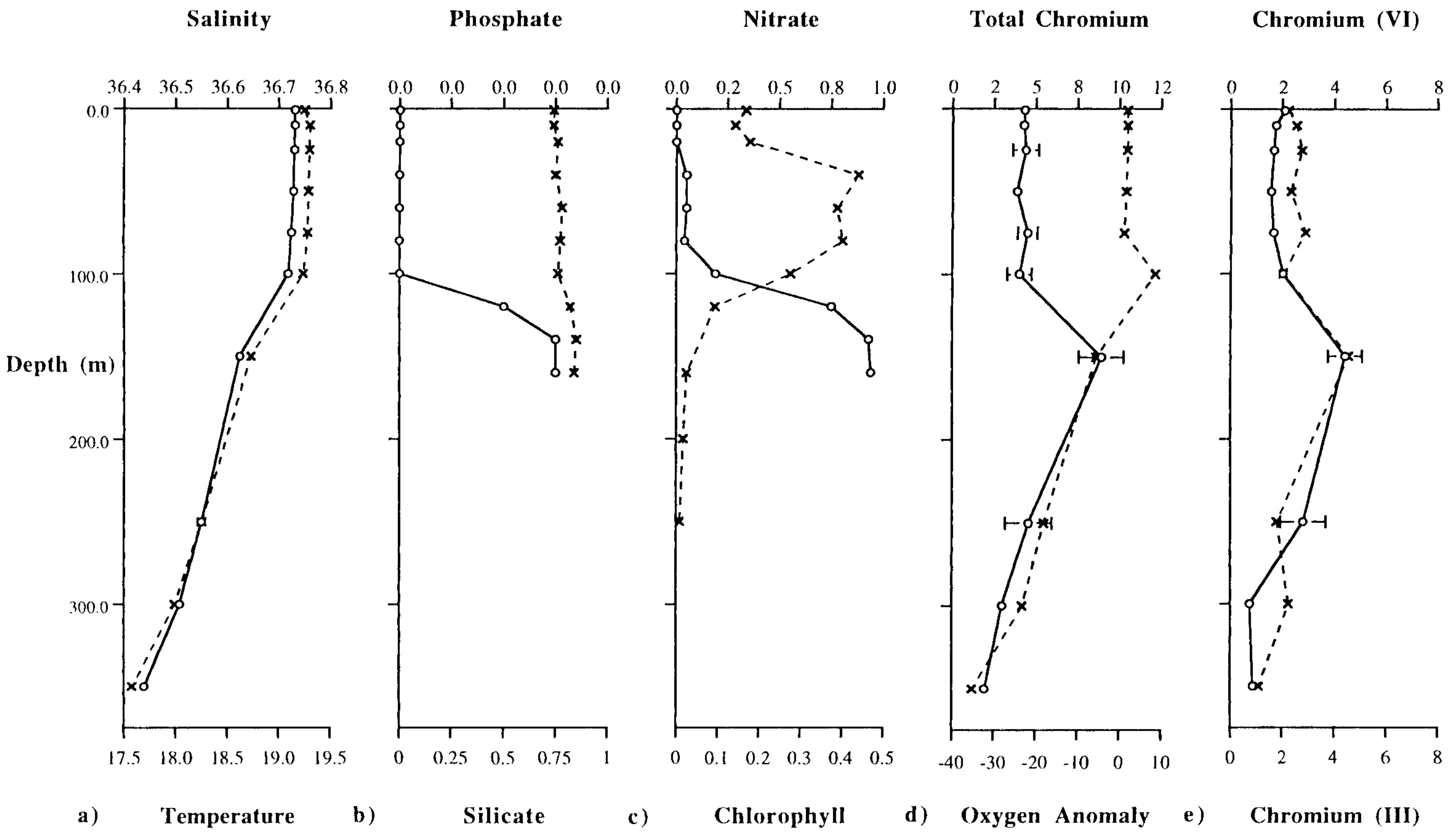

Figure 5.12 Physical and chemical parameters for the upper water column: March 1996. **a)** Salinity (solid) and Temperature (°C) (dashed) **b)** Phosphate (solid) and Silicate (dashed) (μmol kg^{-1}) **c)** Nitrate (solid) (μmol kg^{-1}) and Chlorophyll (dashed) (μg l^{-1}) **d)** Chromium (solid) (nmol l^{-1}) and Oxygen anomaly % (dashed) (saturation (-ve)=undersaturated) **e)** Chromium (VI) (solid) and Chromium (III) (dashed) (nmol l^{-1}, ±s.dev, n=3).

5.4.5 Chromium in sediment trap material

The data for the chromium in the sediment trap material is presented in Figure 5.12.

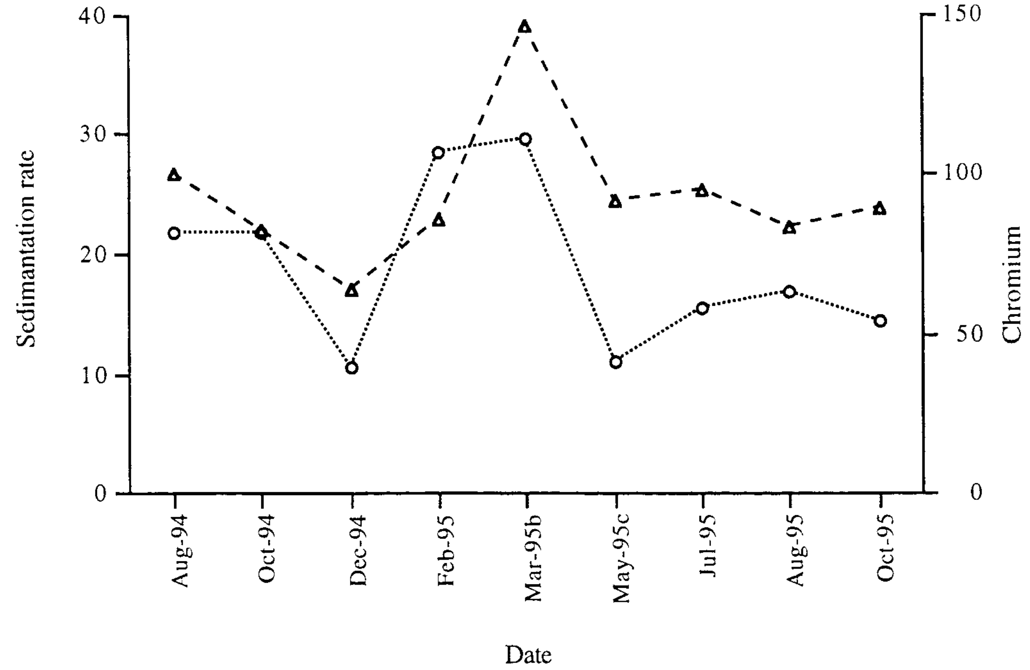

Figure 5.13. Concentration of total chromium in sediment trap material (---o---, µg/g) and vertical mass flux (---Δ---, mg $m^{-2}d^{-1}$).

The data indicates that during the time of maximum deposition of sedimentary material there is a high concentration of chromium associated with that material; this is especially evident in the Mar-95 sample. The high concentration of chromium associated with the material in the Feb-95 sample is somewhat anomalous. It can be assumed that the chromium associated with the sediment trap material was originally particle reactive chromium (III).

5.5 Discussion

There are very few studies that have investigated the distribution of chromium in open ocean environments and these, along with data for other marine environments are presented in Table 5.11.

Author(s) and Year	Region	Total Cr	Cr (VI)	Cr(III)
Fukai, 1967	Mediterranean Sea	4.4-8.3		
Grimaud & Michard, 1974	Pacific Ocean	6.7-7.5		
Cranston & Murray, 1978	Pacific-upper	2.4±0.7	2±0.4	0.2±0.1
	Pacific-lower	3.1±0.5	2.8±0.7	0.04±0.04
Murray *et al.*, 1983	E. Pacific		3.0	0.5-1.0
Cranston, 1983	NE Pacific	2.2±0.4		0.08±0.08
Campbell and Yeats, 1984	NW Atlantic	3.3-5.2		
Jeandel and Minster, 1987	Mediterranean Sea	2.6-3.4		
	Atlantic	2.8±0.2		0.1-1.6
	S. Pacific	3.6		0.05-0.08
Sherrell and Boyle, 1988	Mediterranean Sea	3.9		
	Sargasso Sea	2.9		
Achterberg *et al.*, 1994	Mediterranean Sea	2.1-3.2	2.2-2.7	0.4-0.9
Van Den Berg *et al.*, 1994	Mediterranean Sea		3 - 4	<0.2-1.5
Abu-Saba and Flegal, 1995	San Francisco Bay (salinity >21 only)	1.9-2.2	1.7-2.2	<003-0.2
Rue *et al.*, 1996	N. Pacific	2.0-4.38	1.78-4.38	0-0.73
This Study, 1996	Sargasso Sea	1.8-8.9	0.2-5.4	<0.01-4.5
	Bloom	1.7-8.9	0.2-4.4	0.7-4.5
	Non-Bloom	2.5-8	2.6-5	0.6-3

Table 5.11. Previously published chromium data for marine environments (all data expressed in nmol l^{-1}).

By comparison with data in Table 5.11 it can be seen that results presented here for the Sargasso Sea water column are not greatly different from earlier high quality data. The early data of Fukai (1967) and Grimaud and Michard (1974) are significantly higher than the other work and, as is the case for such early work on trace metals in the open ocean, probably result from contamination of samples. The data from the present study in the table is the range for the whole data over the whole water column and Time period (n=106). The only data for the Sargasso Sea area that is published are for surface samples of total chromium in the work by Sherrell and Boyle (1988), who found concentrations of 2.9 nmol l^{-1}, comparable with the total chromium concentrations in the upper 500m in this study (3.2±0.8).

5.5.1 Potential sources of chromium

There are a variety of processes which may control the distribution and speciation of chromium in the water column of the Sargasso Sea. Isopycnal transport from shelf zones has been proposed as a source of chromium in other locales such as the Atlantic near of the Straits of Gibraltar (Jeandel and Minster, 1987) and off the west coast of the United States (Murray *et al.*, 1983). It is however unlikely that for the upper waters of the Sargasso Sea, isopycnal transport is a major source. The nearest continental shelf is the eastern continental shelf of the U.S. (700km from Bermuda): transport from this area is effectively blocked by the presence of the Gulf Stream. The deeper water concentrations of chromium are probably the result of mixing of water masses with preformed concentrations of chromium (Broecker and Peng, 1982). It is, important to point out that there may be inputs into this region of the water column by falling particles that have associated chromium. This down column transport of particulate material can be rapid: Knappertsbusch and Brummer (1995) estimate that falling coccolithophores in the North Atlantic have settling velocities between 137m and 163m per day.

Riverine input of materials is thought to be unimportant in the Sargasso Sea area. There are no rivers on Bermuda and although Bermuda may provide inputs of contaminants that may influence waters as far as Hydrostation S, there are no major pollutant sources of chromium on the island (Chapter 2).

As was discussed in Chapter 1, the other major transport route for materials to this area is the atmosphere, through wet and dry deposition. The long range transport of lead to the Sargasso Sea has been documented (Boyle *et al.*, 1986; Veron *et al.*, 1993), as well as other metals to the same area (Jickells *et al.*, 1984) and it is expected that there will be transport of chromium to this area by the same process. Duce *et al.* (1976) reported depositional concentrations of 9 ng Cr $cm^{-2}yr^{-1}$ to the sea surface in samples from Bermuda and Buat-Menard and Chesselet (1979) reported fluxes of 14ng $cm^{-2}yr^{-1}$ for the sea surface of the tropical North Atlantic (data modified by Chester, 1990). More recent determinations of fluxes of chromium in rainwater for Bermuda were calculated as 127 $\mu g\ m^{-2}yr^{-1}$ (Tom Church, pers. comm.) these are very similar to the earlier results of Duce (1976) (90 μg $m^{-2}yr^{-1}$) and Buat-Menard and Chesselet (1979) (140 μg $m^{-2}yr^{-1}$).

Applying a similar approach to that of Jickells *et al.* (1994) for total chromium, instead of aluminium and manganese, produces a residence time of 2.2 years for the upper 100m of the water column.[1] The concentration of total chromium at the 1m depth for September is significantly higher than that of the three previous months in which samples were taken: 4.3 ± 0.3 nmol l^{-1} compared to 3±0.3 nmol l^{-1} for November, 2.5 ± 0.1 nmol l^{-1} in January and 3.6 ± 0.2 nmol l^{-1} for June. This increase in September surface input may be due to deposition associated with the hurricane. As a result of the anomalous chromium data for this period the concentrations are not used for the calculation of the residence time of chromium in the upper water column. This value of 2.2 years is obviously much lower than the mean ocean residence time (MORT) of 11000 years, given by Martin and Whitfield (1983), which represents the whole water column not just the upper 100m.

During periods of stratification the chromium will probably be recycled through the mixed layer and chromium will be exported from surface waters by particle adsorption or by biological uptake and repackaging, and vertical transport to deep water. Turn-over of the water column at the end of the summer will result in mixing with deeper water masses that have lower chromium concentrations.

There is no increase in the concentrations of chromium with depth; this implies that the sediments are not a source of chromium into this part of the water column, or that the recycling from particle phases is not very strong. The seabed at Hydrostation S is around 3300m and it is possible that if the bed is a source of chromium, as was argued by Jeandel and Minster (1987), the sampling programme here did not go deep enough to detect this potential source.

---

[1] Mean concentrations at 1m: 3.4 nmol l^{-1}, 50m: 3.7 nmol l^{-1} and 100m: 4.1 nmol l^{-1}, calculated from the four collection dates. Atmospheric inputs of 1.7 μmol m^{-2} yr^{-1} (Duce *et al.*, 1976) used in calculation, and 10% solubility of chromium from particles used (Chester and Murphy, 1988). Average of data used for calculation.

5.5.2 Potential processes of chromium reduction

As was discussed in section 5.1, the existence of reduced chromium species in oxygenated seawater is an anomaly. This work confirms the presence of chromium (III) in the oligotrophic Sargasso Sea. There are, hypotheses that can be explored to explain this new data.

Cutter (1992) advanced the idea that the control of reduced species in oxic environments is controlled by two processes; the production of the reduced species and the slow oxidation of that species to the more stable oxic form. It has been proposed that there is direct reduction of chromium (VI) by reducing species in seawater, one of which is hydrogen sulphide. The direct reduction of chromium (VI) by bacterially produced hydrogen sulphide was investigated by Smillie *et al.* (1981), who found such reduction does occur in shallow coastal areas with high organic input and effluent containing chromium (VI). Pettine and Millero (1994) performed laboratory experiments in oxic and anoxic sodium chloride media. Direct reduction did occur but only under conditions of anoxia or in oxic conditions with high (mM-μM) concentrations of hydrogen sulphide. Work by Cutter and Krahforst (1988) and later by Knoery and Cutter (1994) determined that the natural concentrations of sulphide in oxic seawater was <1.5 nmol l^{-1}, insufficient for direct reduction. Iron (II) has been demonstrated to reduce chromium (VI) under natural conditions (Shroeder and Lee, 1974), however the oxidation of iron (II) is rapid (with oxygen), and with the naturally occurring concentrations of iron (II) there is little direct evidence for chromium (VI) reduction.

Kieber and Helz (1992) suggest that the photoproduction of iron (II) can result in the reduction of chromium (VI), however their data is for freshwater systems and under neutral conditions. A later paper by Kaczynski and Kieber (1993) supported the idea of photoproduction of Cr (III) in natural waters including some marine environments. The reduction may be tied into the photodegredation of an organic chromium species, although a later paper produced evidence to show very low concentrations of organic bound chromium in natural marine waters (Kaczinski and Kieber, 1994). Earlier work by Waite and Morel (1984) found no evidence for the photoreduction of iron (III) in natural seawater samples.

Alternative and possibly linked routes for the reduction of chromium in surface waters have invoked a photochemically induced reduction pathway. It is known that photochemical reduction of manganese can occur in natural waters and is thought to be microbiologically mediated (Sunda and Huntsman, 1988). Bacteria are thought to be responsible for the oxidation of the thermodynamically unstable manganese (II). Spokes and Liss (1995) investigated the role that organic matter had in the reduction of manganese (IV) to manganese (II). They found that humic acid in marine systems was itself a reducing agent. In the same paper the reduction of iron (III) to soluble iron (II) was discussed: there was no evidence for the direct reduction of iron (III) via photochemical reactions. However they suggested that phytoplankton exudates may be responsible for the existence of reduced iron species in oxic marine environments.

The role of photochemistry in this study is not obvious. There is no significant depletion of chromium (VI) for any of the months, between the surface samples and those at 50m, with the exception of chromium (VI) in the samples from January. One would have expected monthly variations in the degree of surface depletion due to the increased insolation during the summer months. This is not to imply that this reaction may not be an important one in the case of chromium in Sargasso Sea waters. Sunda and Huntsman (1988) found that there was a diel cycle in the production of reduced manganese species in oceanic waters. The samples collected for chromium in this present study were collected around mid-day, if as is the case for manganese there is a photo-inhibition process in the reduction of chromium, it is possible that the chromium could be oxidised by the time the samples were collected. However this is unlikely as it is known that the oxidation of chromium (III) to chromium (VI) is slow in open ocean waters (Pettine *et al.*, 1991), any reduced chromium produced by during such reactions would presumably still be present; this may account for some of the reduced chromium present, but more work is needed to verify if such a control process is present.

Unlike previous studies (Murray *et al.*, 1983; Campbell and Yeats, 1984; Jeandel and Minster, 1987) there appears to be no correlation between total dissolved chromium and dissolved silicon (e.g. r^2 = -0.02 for September, r^2 = 0.013 for November). The correlations with the other nutrients, nitrate and phosphate, also show no significant relationship. It is important to note that the Sargasso Sea area is different from the majority of the other locations studied, as it is the most oligotrophic and is dominated in surface waters by foraminifera and coccolithophores as opposed to diatoms.

The sample data for September may better indicate possible controlling factors for chromium inter-conversions in the surface waters, as the distribution and speciation of chromium in the upper water column was very different from that of the previous months. The hurricanes that had passed must have led to a change that affected the reduction rate of chromium (VI) to chromium (III). At first it was thought that the passage of the hurricanes may have produced a bloom event, due to storm mixing and injection of nutrients into the upper water column, and some factor associated with such an event triggered the reduction of the chromium (VI) to chromium (III). However, the nutrient profiles in Figures 5.6b and 5.6c do not show any introduction of deep water nutrients into the upper 60m of the water column, and indeed it appears that the mixing occurred only in the upper 60m. The silica appears to be depleted in the upper 100m; this may be indicative of a diatom bloom event. There was, however, no evidence for such a bloom from the pigment data for that month (BATS group. pers comm.), so the decreased silica may be an experimental artifact. Bacterial numbers were collected in the upper 250m of the profile and analysed by the BATS group (Fig. 5.6). These do not indicate any large increase over previous months, indeed the data for June show higher numbers of bacteria than in the September data.

In September 1995 the highest numbers of the cyanobacterium *Trichodesmium* that had ever been measured in the Sargasso Sea (unpublished data; period 1991-1995; K. Orcutt pers. comm.) were observed. This species is colonial and has large numbers of associated diatoms and bacterioplankton. It is thought that these cyanobacteria may be an important component of the productivity of the sub-tropical gyre, since they are known nitrogen fixers (Dugdale *et al.* 1961, 1964; Carpenter, 1983; Karl *et al.*, 1992). There is limited evidence that these cyanobacteria (or organisms associated with them) are capable of reducing trace metals: Jones *et al.* (1986) reported the apparent reduction of iron during a *Trichodesmium* bloom in Australia and other metals show increases in biological availability during such events (Jones, 1992). This reduction of trace metals is apparently mediated by the production of organic compounds by the cyanobacteria and presumably the subsequent oxidation of these organic compounds by bacterial catalysis. Turley and Mackie (1995) determined that there was an export of cyanobacteria and bacteria to the deeper water associated with falling particles and these would presumably be still capable of reducing chromium in the water column. Hence it is possible that the cyanobacteria in the Sargasso Sea may have a role in the reduction of chromium (VI), and probably other metals.

The samples taken during the spring phytoplankton bloom offer an important insight into the possible controlling factors for the presence of the reduced chromium (III) in the oxygenated surface waters of the Sargasso Sea. The increase in chromium (III) in the surface 100m during the bloom and the associated decrease in chromium (VI) implies that the chromium (VI) is undergoing a reduction process. The oxygenated conditions present in these upper waters at this time do not imply that there is the likelihood of direct chemical reduction. The spike in the concentration of both species of chromium at the 150m depth indicates a probable association of the chromium with some component that is being recycled to the dissolved form at this depth. Since the samples taken in this study are unfiltered there is no way to determine if concentrations measured at this depth are associated with particulate matter. The reduction of the chromium (VI) to the chromium (III) species is discussed in more detail later.

The increase in chromium (III) cannot be explained by greater inputs of chromium (III) into the area at this time. The events that bring Saharan dust to the Sargasso Sea are predominantly during the summer (Prospero, 1968), and the chromium (III) measured here must be chromium that is being reduced *in-situ* as there are no increased inputs from a possible dust source. The chromium may be coming from rain events that are transporting chromium from the Atlantic coast of N. America (during the winter months the weather systems impacting Bermuda are from the west, and during the summer from the east), if this were the case elevated chromium (III) should be found in the samples from both November and January. However, both scenarios would additionally need to assume that the chromium present in rain, or released from particles is in reduced form.

The data for the sediment trap analysis supports the hypothesis that during the bloom conditions in the upper water column there is increased association of chromium with the particulate matter (predominantly phytoplankton, zooplankton and they faecal pellets of the zooplankton). This may be passive adsorption of particle reactive chromium (III); a direct uptake by phytoplankton of the chromium (VI) which is detoxified by conversion to chromium (III); or a direct uptake of particulate chromium (III), perhaps in association with bacteria or cyanobacteria by the zooplankton that then repackage the material into more rapidly falling faecal pellets (Bruland and Silver, 1981; Urrere and Knauer, 1981; Lee and Fisher, 1994) The high chromium signal associated with the trap material during a high verticle flux period indicates one or more of these processes is occurring.

Cranston and Murray (1978) reported that the mean life for chromium (III) in oxic waters was of the order of 6-20 days. Van Der Wiejden and Reith (1982) pointed out that this was in the presence of manganese oxide which they concluded had a catalytic effect on the oxidation reaction, and in open ocean environments the manganese dioxide is at too low a concentration to have this effect. Pettine *et al.* (1991) estimated that the half life of chromium (III) under natural seawater conditions is 45 days. It is possible that there are organic complexes of chromium (III) formed that are resistant to oxidation. This stability could be due to the shielding of the complexed chromium from oxygen, or the chromium (III) could be present in colloids that then aggregate and fall from the water column.

The uptake of chromium (VI) by phytoplankton and the subsequent reduction of that chromium to the less toxic chromium (III) as a protection mechanism is not easy to justify. There is evidence that although chromium (VI) is toxic to phytoplankton in freshwater systems this toxicity is negligible in seawater, up to a concentration of 1.9 μmol l^{-1} (Frey *et al.* 1983). Therefore there would be no ecological benefit to have this detoxification mechanism as it would need cellular energy for the reduction. A more likely explanation for the reduction process occurring would be that phytoplankton are able to use chromium (VI) as an electron acceptor in some cellular chemical reactions, although this idea is purely speculative at this stage.

The apparent correlation of chromium with dissolved silicon in other areas of the globe deserves further comment. The diatom populations in other areas could be responsible for taking in the chromium (VI). It is known that chromium (VI) is able to cross biological membranes (Nieboer and Jusys, 1988), once in the organisms it could be reduced to chromium (III) and then be released as the diatoms fall and are remineralised in the water column. This could result in chromium increases over those preformed concentrations found in the deep waters.

5.5.3 Conclusions

In conclusion it appears that the upper water column concentration of total chromium is maintained by inputs of new chromium arriving via aeolian transport. This chromium is cycled through the upper water column during the stratified period and is strongly linked to biological cycling. Some export of chromium may occur by the formation of refractory DOC/chromium colloidal associations that possibly form aggregates that fall through the thermocline, as well as export in association with background sinking particulate matter. Certain factors, particularly during bloom events, can dramatically shift the speciation of chromium towards the reduced chromium (III). This shift appears to be due to reduction of the chromium by organisms such as *Trichodesmium*, bacteria, phytoplankton or other unidentified biological agents. The sinking phytoplankton material, and zooplankton faecal pellets scavenge chromium from the water column (presumably particle reactive chromium (III)) and remove it from the upper water column. Some of this material is remineralised and remains in the upper 250m of the water column. Some is associated with sinking particulate matter which is removed from the upper water column to the deeper ocean.

There is evidence for some lateral advection of chromium into the study area, there are increases in the overall concentrations of chromium at a depth around 100-150m in both the bloom samples and the June samples. There is no evidence to support an increase at this depth from rain input as rain would presumably have a direct impact on the upper water column concentrations of chromium only. There is one additional source of chromium to this depth. The calculation of residence time for chromium in the Sargasso Sea assumed a 10% dissolution of chromium from the particles in rainwater. It is not improbable to assume that during bloom events, biological factors such as increased zooplankton feeding could increase the dissolution of chromium from the particles in the rainwater. Unfortunately the data presented in this study allows no further testing of this hypothesis.

5.6 Future work

The ideas put forward to explain the presence of reduced chromium in the oxygenated surface waters of the Sargasso Sea obviously necessitate further work. It would be interesting to perform laboratory experiments to determine the rate of reduction of chromium (VI) with different concentrations of DOC, with and without the presence of bacteria. Light and dark experiments need to be performed to determine if there is periodicity in the production of reduced chromium species. These laboratory studies should be followed up by studies at sea. The importance of particulate bound chromium in the speciation of chromium needs to be investigated further. Is the majority of chromium (III) that is being measured in these samples actually particle bound chromium?

At present there is ongoing work with the DOC group at BBSR looking at DOC in the Ross Sea, a diatom dominated system. Samples for chromium analysis are being collected for analysis. Presently Tom Church (University of Delaware) and Maureen Conti (Woods Hole Oceanographic Institute) are starting a study in Bermuda concerned with the atmospheric input of trace metals and their subsequent transport to the seafloor, hopefully it will be possible to include the determination of chromium and its speciation in these samples. Laboratory studies are needed to further study the dissolution rate of chromium from particles deposited in rainwater, and the chromium species involved. This will be performed along with the joint work with Tom Church and Maureen Conti.

Chapter 6

Conclusions

This summary of findings will be presented in two sections in the same way that the work has been handled. The first section will discuss the conclusions regarding trace metal chemistry in the coastal zone, and the second section will present the conclusions obtained for the study of chromium in the Sargasso Sea. At the end of these sections some suggestions are proposed for further research.

6.1 Trace metals in the Bermuda coastal zone

The first objective of this work was to determine the occurrence and geochemical behaviour of the trace metals lead, cadmium, copper, nickel and manganese in the coastal waters and carbonate sediments of Bermuda. A summary of this data with comparable data from earlier work in Bermuda (Jickells and Knap, 1984) and some comparison data from Tobago (Rajkumar and Persad, 1994) can be found in Table 6.1 for dissolved metals and Table 6.2 for metals in sediments. Tobago is one of the few places for which there are reported trace metals data in both the water column and sediments, the population is similar to Bermuda (50,000) and the main industry is tourism. This study is one of the few that could be found that have an environment and infrastructure similar to Bermuda. The data quality `in these reports however may not be as high as some of that available for other areas (e.g. Tappin et al., 1995), but is useful as a comparison of the state of the contamination of the Bermuda coastal zone relative to other similar areas.

From Table 6.1 it can be seen that the concentrations of cadmium in Bermuda have increased since 1984, but are markedly lower than those found in Tobago. Concentrations of copper are of the same order as that found in 1984. Tobago has higher concentrations of dissolved copper, the clean station has higher concentrations than those found in Bermuda, although there appears to be a detection limit problem with copper for the Tobago data (minimum copper measured was 7.9 nmol l^{-1}). Nickel was not reported in the earlier study and is not reported for Tobago. Lead in Bermuda is markedly lower in the present study than that measured in 1984, although lead was sampled only once in this earlier study. The concentrations of lead in the waters off Tobago are higher than those found in the Bermuda coastal zone (the detection limit for lead appears to be high, 2.4 nmol l^{-1}). Concentrations of dissolved manganese are similar to the earlier data from Bermuda for Harrington Sound and Hamilton Harbour, but the manganese concentrations reported for the North Lagoon show a decrease over the earlier study.

	Station	Cd nmol l^{-1}	Cd range	Cu nmol l^{-1}	Cu range	Ni nmol l^{-1}	Ni range	Pb nmol l^{-1}	Pb range	Mn nmol l^{-1}	Mn range
This Study Water	Harrington Sound	0.2±0.1	0-0.6	5.3±5.4	0.5-30.5	4.1±3.9	0.03-14.9	0.8±0.5	0.2-1.9	6.8±4.7	1.9-18.1
	Inn. Hamilton Harbour	0.3±0.3	0-1.8	11.2±12.5	0.5-66.9	4.8±3.7	1.0-20.4	1.6±0.9	0.1-3.5	10.9±7.8	2.1-31.3
	Outer North Lagoon	0.1±0.2	0-1.0	1.2±1.7	0-6.3	2.8±2.1	.1-8.4	0.3±0.3	0-1.0	0.7±0.6	0-2.5
Jickells and Knap (1984)											
Water	Harrington Sound	0.06±0.04		6.3±2.2		Not reported		1.45 1 datum		9.5±4.1	
	Inn. Hamilton Harbour	0.1±.02		26.8±9.0		Not reported		5.8 1 datum		24.8±21.4	
	Outer North Lagoon	0.04±0.03		3.1±1.4		Not reported		0.72 1 datum		3.5±2.4	
Rajkumar and Persad (1994)											
Water	Contaminated	3.9	0.5-10	16.5	7.9-52.4			3.4	2.4-8.6		
	Clean	2.0	0.5-5.8	16.8	7.9-62.9			2.7	2.4-4.1		

Table 6.1 Comparison of data for dissolved trace metals from this study, Jickells and Knap (1984) and data from Tobago (Rajkumar and Persad, 1994)

Source		**Cd $\mu g\ g^{-1}$**	**Cd range**	**Cu $\mu g\ g^{-1}$**	**Cu range**	**Ni $\mu g\ g^{-1}$**	**Ni range**	**Pb $\mu g\ g^{-1}$**	**Pb range**	**Mn $\mu g\ g^{-1}$**	**Mn range**
This study Sediments	Harrington Sound	0.19±0.1	0.04-0.39	13.83±6.3	4.63-26.3	3.98±1.83	2.13-9.44	28.21±11.31	6.87-40.9	32.25±3.5	24.8-36.3
	Inn. Hamilton Harbour	0.18±0.13	0.06-0.44	27.28±16.32	7.51-70.3	3.2±1.71	0.43-5.24	40.84±22.85	9.52-87.2	30.25±11.79	10.6-58.6
	Outer North Lagoon	0.01±0.01	0.003-0.01	0.51±0.65	0.01-1.91	0.18±0.26	0.01-0.87	0.69±1.08	0.01-1.33	2.86±1.78	0.01-5.99
Jickells and Knap (1984) Sediments											
	Harrington Sound	<1.2	1 datum	12.0	1 datum	<5	1 datum	31	1 datum	34	1 datum
	Inn. Hamilton Harbour	<3	1 datum	46	23-545	<12.5	1 datum	80	46-110	39	38-45
	Outer North Lagoon	<1.2	1 datum	<2.5	1 datum	<5	1 datum	<5	1 datum	<7	
Rajkumar and Persad (1994)											
	Contaminated	1.17	0.32-2.09	6.85	0.43-16.0			7.22	0.3-20.9		
	Clean	0.27	0.09-0.54	0.58	0.06-2.82			2.93	0.3-14.3		

Figure 6.2 Comparison of sediment data for this study, Jickells and Knap, Bermuda (1984) and Tobago (Rajkumar and Persad, 1994)

From Table 6.2 the problems of adequate sensitivity in the earlier study are evident; the detection limits are high for all of the metals. The result of this is that there is no cadmium and nickel for all stations in this study, and no data for metals at the North Lagoon station. For the remaining stations the data in this present report are of the same order as the earlier Jickells and Knap report. There is no reported data for nickel and manganese for Tobago. The data that is available for Tobago shows that both stations are higher with respect to cadmium. The concentrations of copper in the sediments for the contaminated station in Tobago are similar to the data from Bermuda, data for the clean site is similar to the North Lagoon in Bermuda. Concentrations of lead in the sediments are higher in Bermuda in both Harrington Sound and Hamilton Harbour compared to the contaminated site in Tobago.

The findings for the study of the processes affecting the distribution of trace metals in the coastal zone are best summarised in the form of a diagram, (Figure 6.1) where the size of the arrow represents the relative importance of that process, and the direction indicates whether the process is a source or a sink for trace metals relative to the water column.

The sediments have been suggested as a sources for most of the metals, either through the microbial breakdown of the organic material present, and/or the liberation from binding sites on the sediments that are capable of holding metals (Santschi *et al.*, 1990). The latter are likely to be substitution reactions at sites on the calcium carbonate such as those outlined for manganese on carbonate particles in Chapter 4. The tank incubation experiments outlined in Chapter 4 revealed that the sediments are a potential source of copper, cadmium and nickel under oxic conditions, and a sink for these metals under anoxic conditions. The situation for lead is more complex; there is a release under oxic conditions from contaminated sediments whereas sediments from a clean environment were a sink for lead. Under anoxic conditions lead was removed from the dissolved phase to the sediments in clean sediments, but those sediments with higher lead levels still released lead to the dissolved phase. Manganese is removed from the dissolved phase under oxic conditions, even to sediments that were high in total manganese, indicating that the sediments have a high capacity for manganese. Under anoxic conditions manganese concentrations increased in the dissolved phase.

With the exception of St. George's Harbour the sources of cadmium in the coastal zone appear to be diffuse, with the major factor influencing concentrations being exchange with offshore Sargasso Sea water. For St. George's Harbour the sediments are proposed as a source of dissolved cadmium; there is probably a source of cadmium in the harbour due to a dumping/construction project on the North side of the Harbour.

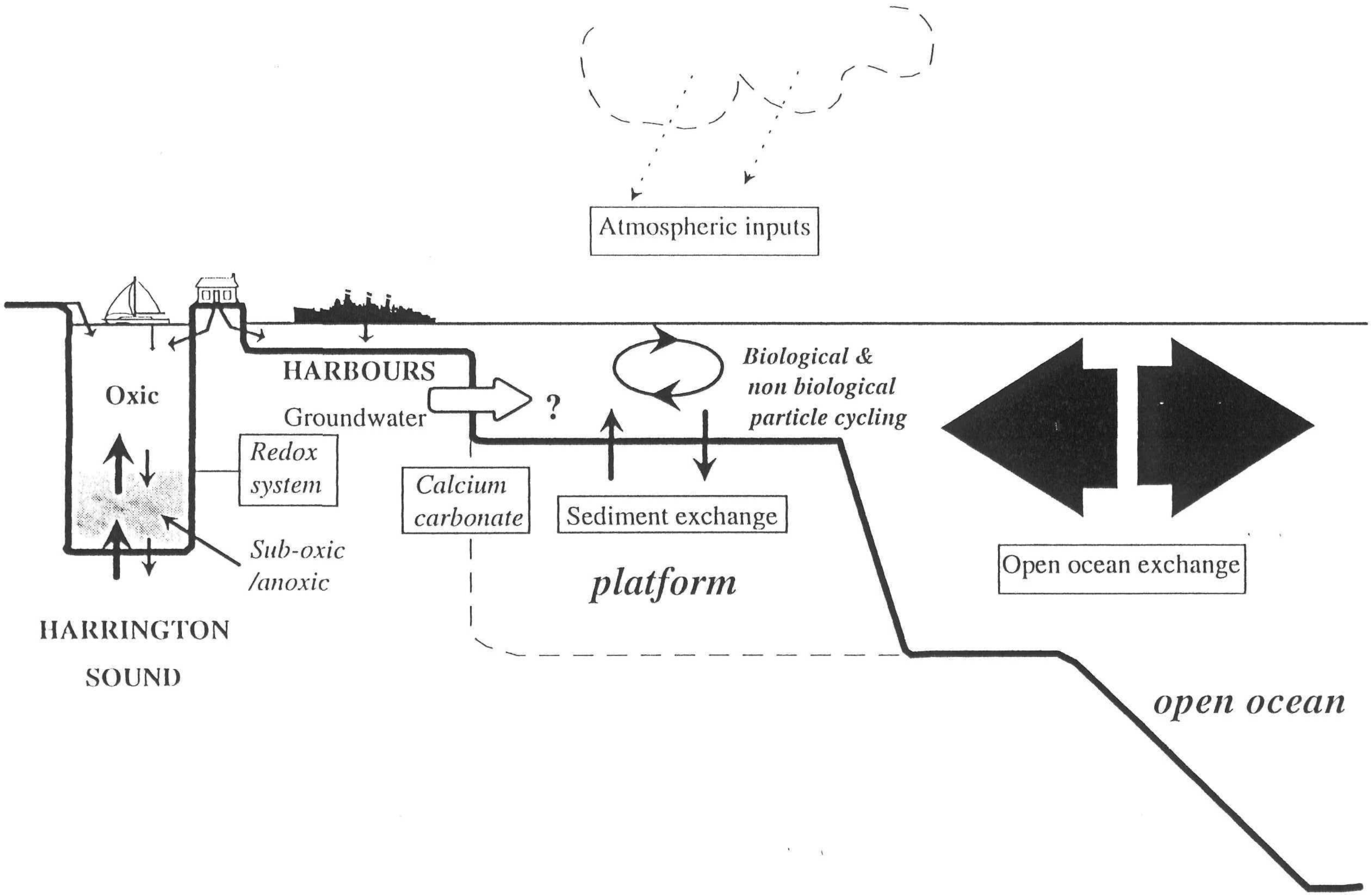

Figure 6.1 Principle inputs and pathways influencing metals in the Bermuda system.

The release of cadmium from sediments is thought to be via the breakdown of organic matter (Gerringa, 1990), the determination of cadmium association in sediment (Chapter 4) indicates that cadmium is in the organic fraction in Bermuda sediments.

For copper it is likely that the main source is the widespread use of copper based anti-fouling paints on boats and buoys in Bermuda waters. Previously published data have shown high tributyl tin (TBT) concentrations in the Bermuda coastal zone (Stebbing et al., 1990). This compound was banned in Bermuda prior to the start of this study, and the replacement paints use copper as a biocidal agent. It can be envisaged that the high number of pleasure craft in Bermuda will result in ever increasing concentrations of copper to the inshore waters. As was discussed earlier in this section the copper found in the water column and in sediments in this study is not higher than those previously found (Jickells and Knap, 1984), although there is a wide range of scatter in both of these studies. Release of copper from sediments is thought to be via the breakdown of organic matter (Kerner and Geisler, 1995) under oxic conditions, there is no evidence from the Harrington Sound study for an increase of copper release from the sediments (Section 4.3) under anoxic conditions. Nickel is thought to be similar to copper in geochemical nature (Burton and Statham, 1990). Nickel appears to have diverse sources in Bermuda, with an even distribution of the metal between all the inshore stations. The data for the Harrington Sound study indicates that runoff during rain events maybe a significant transport route for this metal to the inshore waters.

The sediments are a likely sink for lead in Bermuda, in much the same way as in other areas (Tappin *et al.*, 1995); lead is highly particle reactive and is scavenged from the water column onto particles (Lambert *et al.*, 1991). The relatively high dissolved lead concentration in the water column probably reflects the low concentration of suspended particulate material found in the Bermuda coastal zone. The investigation of the phase association indicated that lead was predominantly associated with the carbonate material in the sediments. The data from the Harrington Sound study (Section 4.3) produced evidence for the removal of lead from the water column not only on the surface of particles but with organic material, this can lead to a release of that associated lead during the degradation of the organic matter in sediments.

The data for manganese indicate that, like cadmium and nickel, there are diffuse sources of this metal to the inshore waters. The results for the tank incubation experiments and the study of Harrington Sound have indicated that the sediments are an important source of dissolved manganese under anoxic conditions, as has been observed for other shelf systems (Tappin et al., 1995). The data for the tank experiments also showed that the sediments have a high capacity for manganese, with, e.g., uptake from the water column into the relatively contaminated sediments of St. George's Harbour under oxic conditions. Calcium carbonate is known to have an important role in the removal of manganese from the water column (Prohic and Kniewald, 1987; Wartel et al., 1990b), and Bermudan coastal waters are rich in carbonate particles (Pestana, 1993).

No clear seasonal patterns in the distribution and behaviour of the studied trace metals in the Bermuda coastal zone were evident. This is probably due not only to the small data base reported here, but also the importance of a number of superimposed factors in Bermuda waters, including the physical disturbance of the sediments by shipping activity and the low productivity of the area of the coastal zone. The high degree of shipping activity results in an almost weekly (daily during May-October) mixing of the sediments, this would reduce the potential for the formation of reducing zones in sediments, and, the subsequent release of redox sensitive metals from those sediments. The oligotrophic nature of the coastal water and open ocean around Bermuda, the source of the flushing water for the platform, decreases the impact of biological factors in the biogeochemical behaviour of trace metals. To have a clearer view of any seasonal changes in metal concentrations, a much larger data base is needed, which will require the application of the next generation of high data output, automated underway and buoy based instruments (Merlivat and Brault, 1995; Achterberg and Van Den Berg, 1996).

The work performed during this study will be used in the development of the proposed "clean water act" from the Bermuda Government. The intention is that increased understanding of the processes that affect the release or uptake of metals from sediments can be used to help identify potential pollution problems from any increased inputs of trace metals to the coastal zone. Mr. Rod Johnson a physical oceanographer working for the BATS programme has developed a tidal model for the Bermuda platform. It is hoped that data from this study can be used within the framework of this model to determine the distribution of contaminants, such as trace metals and organic compounds, once introduced to the Bermuda coastal zone.

The work presented here indicates how important large system perturbations such as tidal exchange and sediment disturbance can be in the distribution of metals in the Bermuda coastal zone. The oligotrophic nature of the waters in Bermuda produce results that are unexpected, such as higher concentrations of dissolved lead in the water column due to the lack of particles in the water column that would normally scavenge this metal.

6.1.1 Further studies

It would be useful to have an expanded data base of distribution coefficient data to allow a better resolution of seasonal factors. The constant resuspension of sediments, due to shipping, in most of the stations of this study makes it difficult to interpret the suspended particulate/water column distribution of metals. Further work in Harrington Sound and Castle Harbour, areas with little resuspension due to shipping, could provide a better data base to answer the question of how seasonal factors affect the geochemistry of trace metals. Additional work must be performed to elucidate the reaction between carbonate grains and metal adsorption, this will most likely be best started in the laboratory before any further environmental investigation.

The role of biological processes in the distribution of metals in Bermuda is still poorly understood. The importance of phytoplankton in the speciation and binding of metals need elucidation, both here and most other areas (Sunda, 1989). The work on the distribution and speciation of chromium in the Sargasso Sea presented in this report has highlighted the potential importance of such factors.

The role of groundwater as a source of trace metals to the Bermuda coastal zone is not understood. There are thought to be inputs of groundwater to significant areas of the coastal zone, although there are no reliable estimates of the volumes involved. This groundwater is known to be contaminated with trace metals (Simmons, 1985), and it is a potential source of metals. Groundwater inputs were not studied in detail in this report because there was no direct evidence for inputs of groundwater to the study sites in this work, and there is a lack of information on fluxes of groundwater to the surrounding coastal waters. However, work is ongoing to determine the importance of this groundwater input as one of the factors affecting alkalinity in the inshore waters (Bates, pers. comm.), and results of this work will provide the potential for estimating the volume exchanges of groundwater with seawater.

6.2 Chromium speciation in the Sargasso Sea

Concentrations of total chromium in the upper water column (0-500m) are comparable to previously published work, 2-3 nmol l^{-1} (with the exception of June 1995), compared to 2.9 nmol l^{-1} for the Sargasso Sea reported by Sherrell and Boyle (1988). These concentrations are consistent between months (with the exception of June). There were high concentrations of reduced chromium found during bloom periods and immediately following storm events, possibly indicating atmospheric input and also biological modification of chromium speciation. The concentrations of total chromium in the deeper water column is generally of the order of 4 nmol l^{-1}, there is no published data for this area for comparison.

Thermodynamic calculations imply that there should be no chromium (III) in the oxic seawater (Elderfield, 1970). It is the presence of chromium (III) in oxic seawater reported by other workers (Elderfield, 1970; Murray *et al.*, 1983; Acterberg *et al.*, 1994; Van Den Berg *et al.*, 1994) that provided the stimulus for this study. As in other areas there were detectable (0.03 nmol l^{-1}) concentration of chromium (III) in the water column of the Sargasso Sea. Concentrations of chromium (III) were generally well above these detection limits. There are differences in the relative proportions of chromium (III) and chromium (VI) in the upper water column from month to month. In the deeper waters there is always more chromium (VI) than chromium (III), although there is always some detectable level of chromium (III).

The chromium data presented here represents the first seasonal study of chromium speciation for any open ocean site. The data indicates that the role of biological processes, either direct or indirect, is important in the reduction of chromium (VI) to chromium (III). The main source of chromium appears to be aeolian (Buat-Menard and Chesselet, 1979; Church pers. comm.), and estimates for the fluxes of chromium in rain and dust can account for the concentrations of chromium found in the surface waters of the Sargasso Sea.

The relatively invariant nature of the chromium distribution in the deeper waters of the Sargasso Sea suggests that the concentrations here are preformed i.e. they represent quasi steady state concentrations resulting from insitu recycling and scavenging processes superimposed on deep ocean mass transport.

There is evidence for advection of chromium into this area, and this may be important at depths below the surface waters (but not deep waters >500m). Storm and hurricane activity appear to affect the distribution of chromium between the reduced and oxidised species, although the mechanism for these changes is not currently clear. Data from an annual study of sediment trap material showed a higher concentration of chromium in material thought to be associated with bloom events in the upper water column, and not with falling material thought to have derived from dust events.

In summary it is probable that chromium in the Sargasso Sea is derived from both aeolian inputs and advective transport. Biological processes appear to be the major controlling factor for the relative distribution between the oxic and reduced species.

6.2.1 Future work

Work is ongoing to determine what group or groups of organisms are responsible for the reduction of chromium (VI) to the reduced chromium (III). Presently the work is focusing on the importance of bacterial processes in this reaction. It is intended that in the near future work can be performed using phytoplankton and the cyanobacterium *Trichodesmium* to determine the importance of these groups in the chemistry of chromium.

Samples are being collected during this year's bloom period to see if the behaviour reported in this study is consistent between years. To expand on the sediment trap work reported in this study, samples are being collected in time sequence traps on a continual basis to determine if there is a consistent relationship between deep sea concentrations of chromium in sinking material, and the biological processes in surface waters.

APPENDICES

Appendix 1.1

St.Georges

date	nmol l^{-1} Ni	nmol l^{-1} Cu	nmol l^{-1} Cd	nmol l^{-1} Pb	nmol l^{-1} Mn	µg g^{-1} Ni	µg g^{-1} Cu	µg g^{-1} Cd	µg g^{-1}	µg g^{-1} Mn	Log Kd Ni	Log Kd Cu	log Kd Cd	log Kd Pb	log Kd Mn
Aug-90	1.17	3.59	0.29	0.10	11.40										
Sep-90	6.20	5.76	0.48	0.19	2.40										
Oct-90	5.80	7.08	0.59	0.13	3.10										
Nov-90	6.05	2.99	0.36	0.15	2.30										
Jan-91	12.81	4.38	0.73	0.32	2.30										
Feb-91	2.73	9.19	1.68	0.56	3.60										
Mar-91	3.64	3.46	2.33	0.12	2.80										
Apr-91	0.66	5.13	0.47	0.08	3.90										
May-91	3.40	5.63	0.08	0.11	11.30										
Jun-91	2.17	6.92	0.15	0.14	5.70										
Nov-91	2.26	18.61	0.62	0.53	20.39										
Dec-91	24.49	12.25	0.18	0.49	6.74	861.82	272.23	3.08			5.78	5.54	5.18		
Feb-92	1.87	3.78	0.44	0.77	2.18										
Apr-92	5.38	1.29	0.11	0.87	30.80					83.23					4.69
May-92	1.98	0.81	1.41	0.92	5.46										
Jul-92	5.72	0.87	0.14	0.81	10.90										
Aug-92	1.23	2.21	0.21	0.27	7.20										
Sep-92	1.03	1.01	0.16	0.20	26.10										
Oct-92	3.07	1.12	1.05	1.12	41.50		105.27	5.83	980.83	1431.67		6.17	4.69	6.63	5.80
Jan-93	3.78	6.74	0.36	0.83	18.60	35.17	26.16	5.25	169.26	324.89	5.20	4.79	5.11	5.99	5.50
Feb-93	2.18	8.12	0.89	1.16	23.70	365.74	57.93	1.48	27.94		6.46	5.05	4.17	5.07	
Mar-93	3.77	6.27	0.56	0.84	9.30	261.21	40.48	3.74	100.20	45.69	6.07	5.01	4.77	5.76	4.95
Apr-93	7.14	10.80	0.23	2.05	7.25	97.54	0.00	1.33	44.77	163.49	5.37		4.71	5.02	5.61
May-93	7.26	11.59	0.13	1.66	4.77	235.81	242.03	0.00	75.41		5.74	5.52		5.34	
Jun-93	6.03	4.82	0.12	2.20	16.00	5.15	8.14	0.00	16.57		4.16	4.42		4.56	
Jul-93	8.38	1.26	0.66	3.14	16.40	54.20	109.48	0.00	51.34	239.36	5.04	6.14		4.90	5.42
Aug-93	8.52	0.22	0.89	1.30	7.60	45.26	77.39	0.49	0.00	81.98	4.96	6.74	3.69		5.29
Sep-93	15.50	5.22	0.53	1.25	5.82	424.74	378.62	3.64	339.79	5.07	5.67	6.06	4.79	6.12	4.20
Oct-93	8.52	4.01	0.89	1.30	3.64	29.96	54.67	2.10	50.99	88.83	4.78	5.33	4.32	5.28	5.65
Jan-94	6.98	11.33	1.25	0.72	21.11	34.18	77.01	2.16	120.28	75.28	4.92	5.03	4.19	5.91	4.81
Feb-94	2.74	10.39	1.51	0.29	2.55				169.26	324.89				6.45	6.37
Mar-94	4.91	28.80	1.78	2.08	16.40	101.61	71.52	0.00	174.32	50.06	5.55	4.59		5.61	4.74

Apr-94	2.21	4.52	0.77	0.52	12.80	151.92	523.78	7.23	548.37	258.27	6.07	6.26	4.92	6.71	5.56
May-94	3.21	1.96	0.63	2.34	10.48	101.61	71.52	0.00	174.32	49.98	5.73	5.76		5.56	4.94
Jun-94	3.25	3.79	0.38	1.55	14	151.92	573.78	7.23	548.37	258.25	5.90	6.38	5.23	6.23	5.53

Appendix 1.2

Castle Harbour

Date	nmol l^{-1} Ni	nmol l^{-1} Cu	nmol l^{-1} Cd	nmol l^{-1} Pb	nmol l^{-1} Mn	µg g^{-1} Ni	µg g^{-1} Cu	µg g^{-1} Cd	µg g^{-1} Pb	µg g^{-1} Mn	log Kd Ni	Log Kd Cu	log Kd Cd	log Kd Pb	Log Kd Mn
Aug-90	2.20	2.93	0.12	0.80	10.60										
Sep-90	5.02	2.05	0.08	1.10	3.60										
Oct-90	1.50	7.52	0.12	0.60	3.10										
Nov-90	5.35	2.08	0.06	1.00	2.10										
Jan-91	4.71	1.48	0.13	0.50	1.30										
Feb-91	7.52	4.26	0.80	0.44	3.20										
Apr-91	6.71	0.69	0.15	0.40	2.00										
May-91	2.05	2.49	0.07	0.50	9.00										
Jun-91	1.51	2.83	0.10	0.50	6.20										
Nov-91	0.96	4.88	0.26	0.51	2.91										
Dec-91	3.15	0.42	0.09	1.82	6.81	3.15		0.42		0.06	4.23		4.64		2.22
Feb-92	3.56	1.89	0.61	0.63	2.37										
Jul-92	10.09	0.40	0.50	0.84	3.60										
Oct-92	5.37	1.15	0.17	0.34	9.83	657.30	64.99	2.09	75.73	681.64	6.32	5.95	5.05	6.03	6.10
Nov-92	11.40	18.73	1.33	1.26	14.40	321.55	20.67	1.16	11.42	27.47	5.68	4.24	3.89	4.64	4.54
Jan-93	4.48	2.36	0.27	0.69	10.20	222.16	20.28	12.16	188.24	166.62	5.93	5.13	5.60	6.12	5.47
Feb-93	3.08	2.60	0.44	0.68	25.50	938.63	41.89	1.11	13.44		6.71	5.40	4.35	4.98	
Mar-93	3.20	1.69	0.23	0.49	7.30	401.07	1535.82	1.10	169.05	82.13	6.33	7.16	4.63	6.22	5.31
Jul-93	12.90	0.31	0.19	1.30	12.23	92.40	11.20	0.00	1.71	45.74	5.09	5.75		3.80	4.83
Aug-93	5.45	0.80	0.09	0.58	10.92	65.09	36.10	0.73	21.56	203.50	5.31	5.85	4.87	5.25	5.53
Sep-93	8.01	2.63	0.10	0.97	5.46	25.76	25.13	0.95	21.99	4.12	4.74	5.18	4.93	5.04	4.14
Oct-93	5.45	3.10	0.09	0.58	5.54										
Mar-94	6.52	0.35	0.21	0.46	12.64	26.04	52.09	0.00	200.76	34.18	4.83	6.37		6.32	4.69
Apr-94	4.11	0.24	0.16	0.55	2.95	151.92	523.78	7.23	548.37	258.27	5.80	7.54	5.60	6.68	6.20
May-94	2.20	0.83	0.60	0.39	2.98	26.04	52.09	0.00	200.76	34.18	5.30	5.99		6.40	5.32
Jun-94	0.92	2.24	0.08	0.59	3.15	20.75	20.06	0.17	73.13	3.29	5.58	5.15	4.28	5.78	4.28

Appendix 1.3

Harrington Sound

Date	nmol l^{-1} Ni	nmol l^{-1} Cu	nmol l^{-1} Cd	nmol l^{-1} Pb	nmol l^{-1} Mn	μg g^{-1} Ni	μg g^{-1} Cu	μg g^{-1} Cd	μg g^{-1} Pb	μg g^{-1} Mn	log Kd Ni	log Kd Cu	log Kd Cd	log Kd Pb	Log Kd Mn
Aug-90	6.81	3.24	0.06	0.80	14.40										
Sep-90	4.13	3.78	0.06	1.00	4.20										
Oct-90	9.50	2.64	0.06	0.80	2.30										
Nov-90	13.70	4.03	0.05	1.10	3.90										
Jan-91	4.20	2.74	0.14	1.90	2.30										
Feb-91	0.09	9.38	0.17	0.90	3.70										
Mar-91	3.73	3.49	0.20	0.90	3.10										
Apr-91	2.68	2.68	0.07	0.60	4.20										
May-91	3.18	5.70	0.07	0.60	11.20										
Jun-91	5.11	4.06	0.07	0.70	6.10										
Nov-91	1.85	5.19	0.23	1.58	16.90										
Dec-91	0.46	6.36	0.09	0.55	10.15	417.07	88.91	0.59			7.19	5.34	4.77		
Jan-92	2.56	1.95	0.25	1.40	3.03										
Mar-92	2.83	7.56	0.33	0.34	6.76	57.47	16.98	0.92	22.28		5.54	4.55	4.39	5.50	
Apr-92	1.43	3.34	0.12	0.42	5.80	8.35	42.00	0.20	33.80	41.33	5.00	5.30	4.17	5.59	5.11
May-92	0.03	0.94	0.36	0.54	12.74					111.75					5.20
Jun-92	1.72	0.31	0.12	0.43	3.60	403.92	10.20	0.44	70.20	299.00	6.60	5.71	4.51	5.90	6.18
Jul-92	0.97	2.17	0.56	0.47	2.40	403.92	12.41	0.41	66.76	294.74	6.85	4.95	3.81	5.84	6.35
Aug-92	2.49	3.65	0.29	0.17	4.30										
Sep-92	5.72	9.30	0.27	1.52	3.34										
Oct-92	2.50	3.65	0.29	0.53	4.19	134.01	327.04	5.18	408.48	437.49	5.96	6.15	5.20	6.57	6.28
Nov-92	1.50	4.70	0.10	0.20	9.80	175.08	50.87	2.50	37.03	94.10	6.30	5.23	5.35	5.95	5.24
Feb-93	2.28	3.21	0.03	0.21	3.60	53.90	32.69	1.45	29.91		5.60	5.20	5.63	5.84	
Mar-93	3.43	2.95	0.18	1.04	2.94	87.10	42.79	0.45	128.37	320.37	5.64	5.36	4.35	5.78	6.30
Apr-93	9.80	4.79	0.19	1.84	18.05	692.14	0.00	1.51	35.63	182.95	6.08		4.85	4.97	5.27
May-93	13.58	10.20	0.20	1.72	12.40	461.21	1680.96	0.00	83.11		5.76	6.41		5.37	
Jun-93	1.60	1.56	0.10	1.02	12.44	30.07	55.33	0.00	35.28	182.95	5.51	5.75		5.22	5.43
Jul-93	3.58	0.06	0.04	1.01	12.43	30.07	55.33	0.00	35.28	182.95	5.16	7.16		5.23	5.43
Aug-93	5.30	10.20	0.09	0.85	5.46	42.10	28.67	1.12	66.07	1475.41	5.13	4.65	5.04	5.57	6.69

Sep-93	14.91	12.53	0.00	1.32	14.82	383.64	220.51	14.34	369.30	4.03	5.64	5.44		6.13	3.69
Oct-93	2.49	3.65	0.29	0.17	5.46	80.75	64.08	3.13	69.29	209.94	5.74	5.44	4.98	6.29	5.85
Jan-94	3.95	30.48	0.24	0.79	8.30	22.87	33.56	0.30	55.24	53.75	4.99	4.24	4.04	5.53	5.07
Mar-94	1.48	0.87	0.11	0.53	2.98	7.93	61.46	0.00	79.30	44.81	4.96	6.05		5.86	5.44
Apr-94	2.21	0.50	0.21	0.22	3.74	16.79	10.27	0.00	142.34	30.24	5.11	5.51		6.49	5.17
May-94	0.99	0.90	0.22	0.53	4.40	7.93	61.46	0.00	79.30	44.80	5.13	6.03		5.86	5.27
Jul-94	0.80	7.21	0.08	0.55	1.93	559.56	342.21	0.00	474.47	100.80	7.08	5.87		6.62	5.98

Appendix 1.4

Great Sound

Date	nmol l^{-1} Ni	nmol l^{-1} Cu	nmol l^{-1} Cd	nmol l^{-1} Pb	nmol l^{-1} Mn	µg g^{-1} Ni	µg g^{-1} Cu	µg g^{-1} Cd	µg g^{-1} Pb	µg g^{-1} Mn	log Kd Ni	Log Kd Cu	Log Kd Cd	Log Kd Pb	Log Kd Mn
Aug-90	1.68	3.68	0.06	1.70	9.90										
Sep-90	5.64	3.75	0.07	1.40	5.30										
Oct-90	3.85	2.85	0.08	1.10	3.52										
Nov-90	5.23	3.59	0.12	2.30	1.80										
Jan-91	3.28	3.24	0.09	1.30	1.60										
Feb-91	3.07	14.32	0.18	1.25	2.32										
Mar-91	13.09	5.16	0.24	1.60	2.00										
Apr-91	6.24	3.56	0.09	0.80	3.10										
May-91	4.92	4.75	0.05	0.70	12.30										
Jun-91	2.24	5.48	0.10	1.00	5.20										
Nov-91	1.54	5.04	0.36	0.45	5.50										
Dec-91	2.08	0.48	0.18	1.23	5.52	420.89	151.31	29.71			6.54	6.70	6.17		
Jan-92	1.91	2.53	0.16	1.17	27.64	65.87	49.06	1.28	33.09		5.77	5.48	4.86	5.14	
Feb-92	1.53	2.36	0.09	1.01	2.18										
Mar-92	3.40	1.48	0.07	1.06	1.80	35.10	43.09	0.10	15.82		5.24	5.66	4.10	4.86	
Apr-92	4.42	0.78	0.19	1.33	14.60	6.94	48.14	0.13	16.03	65.83	4.43	5.99	3.78	4.76	4.91
May-92	1.57	0.70	0.08	0.53	12.74					802.20					6.06
Jul-92	2.84	0.32	0.39	1.66	2.00	82.52	5.85	0.27	32.84	152.31	5.69	5.45	3.79	4.98	6.14
Aug-92	3.88	5.45	0.20	1.20	4.69										
Sep-92	1.53	10.32	0.44	1.98	3.90										
Oct-92	5.83	3.30	0.10	0.85	4.55	105.85	188.55	4.33	234.85	580.72	5.49	5.95	5.59	6.13	6.37
Nov-92	12.08	5.04	0.44	1.51	17.10	163.20	3.71	1.61	17.74	53.93	5.36	4.06	4.51	4.75	4.76
Jan-93	3.95	3.97	0.12	1.21	9.10	164.55	170.31	3.58	167.67	414.46	5.85	5.83	5.42	5.83	5.92
Feb-93	4.21	2.83	0.18	1.25	3.60	48.58	0.00	0.78	33.19		5.29		4.59	5.11	
Mar-93	3.96	3.98	0.13	1.20	15.40	8.56	6.55	0.00	20.43	28.67	4.57	4.41		4.91	4.53
Apr-93	4.87	3.21	0.10	1.40	4.86	115.59	0.00	2.15	45.32	185.64	5.61		5.28	5.19	5.84
May-93	13.60	6.20	0.11	2.17	5.63	470.06	779.37	0.00	79.99		5.77	6.30		5.25	
Jun-93	5.45	0.94	0.05	1.45	7.64	0.00	83.16	0.43	11.68			6.14	4.86	4.59	
Jul-93	3.76	0.09	0.05	1.45	7.66	29.50	53.09	0.00	4.85	185.64	5.13	6.97		4.21	5.64
Aug-93	5.11	0.13	0.09	0.87	4.73	47.85	35.57	0.77	40.94	1576.19	5.20	6.65	4.89	5.36	6.78
Sep-93	6.98	2.68	0.53	1.30	6.73	56.24	85.07	1.42	56.95	4.30	5.14	5.70	4.37	5.32	4.07

Oct-93	5.11	0.61	0.09	0.87	5.46	229.58	221.25	3.70	123.12	398.06	5.88	6.76	5.57	5.84	6.12
Jan-94	7.84	31.00	0.27	0.77	24.92	13.14	37.50	0.13	84.41	16.75	4.46	4.28	3.63	5.72	4.09
Mar-94	2.82	0.53	0.12	0.48	8.72	20.45	47.75	0.25	98.80	12.32	5.09	6.15	4.27	6.00	4.41
Apr-94	2.58	0.42	0.12	0.41	2.55	72.30	139.27	31.96	494.67	681.89	5.68	6.72	6.37	6.77	6.69
May-94	6.84	0.51	0.25	1.29	1.82	20.45	47.75	0.25	98.80	12.32	4.71	6.17	3.95	5.57	5.09
Jun-94	0.67	3.84	0.07	0.67	6.50	72.30	139.27	31.96	494.67	681.86	6.26	5.76	6.61	6.55	6.28

Appendix 1.2

Castle Harbour

Date	nmol l^{-1} Ni	nmol l^{-1} Cu	nmol l^{-1} Cd	nmol l^{-1} Pb	nmol l^{-1} Mn	$\mu g\ g^{-1}$ Ni	$\mu g\ g^{-1}$ Cu	$\mu g\ g^{-1}$ Cd	$\mu g\ g^{-1}$ Pb	$\mu g\ g^{-1}$ Mn	log Kd Ni	Log Kd Cu	log Kd Cd	log Kd Pb	Log Kd Mn
Aug-90	2.20	2.93	0.12	0.80	10.60										
Sep-90	5.02	2.05	0.08	1.10	3.60										
Oct-90	1.50	7.52	0.12	0.60	3.10										
Nov-90	5.35	2.08	0.06	1.00	2.10										
Jan-91	4.71	1.48	0.13	0.50	1.30										
Feb-91	7.52	4.26	0.80	0.44	3.20										
Apr-91	6.71	0.69	0.15	0.40	2.00										
May-91	2.05	2.49	0.07	0.50	9.00										
Jun-91	1.51	2.83	0.10	0.50	6.20										
Nov-91	0.96	4.88	0.26	0.51	2.91										
Dec-91	3.15	0.42	0.09	1.82	6.81	3.15		0.42		0.06	4.23		4.64		2.22
Feb-92	3.56	1.89	0.61	0.63	2.37										
Jul-92	10.09	0.40	0.50	0.84	3.60										
Oct-92	5.37	1.15	0.17	0.34	9.83	657.30	64.99	2.09	75.73	681.64	6.32	5.95	5.05	6.03	6.10
Nov-92	11.40	18.73	1.33	1.26	14.40	321.55	20.67	1.16	11.42	27.47	5.68	4.24	3.89	4.64	4.54
Jan-93	4.48	2.36	0.27	0.69	10.20	222.16	20.28	12.16	188.24	166.62	5.93	5.13	5.60	6.12	5.47
Feb-93	3.08	2.60	0.44	0.68	25.50	938.63	41.89	1.11	13.44		6.71	5.40	4.35	4.98	
Mar-93	3.20	1.69	0.23	0.49	7.30	401.07	1535.82	1.10	169.05	82.13	6.33	7.16	4.63	6.22	5.31
Jul-93	12.90	0.31	0.19	1.30	12.23	92.40	11.20	0.00	1.71	45.74	5.09	5.75		3.80	4.83
Aug-93	5.45	0.80	0.09	0.58	10.92	65.09	36.10	0.73	21.56	203.50	5.31	5.85	4.87	5.25	5.53
Sep-93	8.01	2.63	0.10	0.97	5.46	25.76	25.13	0.95	21.99	4.12	4.74	5.18	4.93	5.04	4.14
Oct-93	5.45	3.10	0.09	0.58	5.54										
Mar-94	6.52	0.35	0.21	0.46	12.64	26.04	52.09	0.00	200.76	34.18	4.83	6.37		6.32	4.69
Apr-94	4.11	0.24	0.16	0.55	2.95	151.92	523.78	7.23	548.37	258.27	5.80	7.54	5.60	6.68	6.20
May-94	2.20	0.83	0.60	0.39	2.98	26.04	52.09	0.00	200.76	34.18	5.30	5.99		6.40	5.32
Jun-94	0.92	2.24	0.08	0.59	3.15	20.75	20.06	0.17	73.13	3.29	5.58	5.15	4.28	5.78	4.28

Appendix 1.3

Harrington Sound

Date	nmol l^{-1} Ni	nmol l^{-1} Cu	nmol l^{-1} Cd	nmol l^{-1} Pb	nmol l^{-1} Mn	μg g^{-1} Ni	μg g^{-1} Cu	μg g^{-1} Cd	μg g^{-1} Pb	μg g^{-1} Mn	log Kd Ni	log Kd Cu	log Kd Cd	log Kd Pb	Log Kd Mn
Aug-90	6.81	3.24	0.06	0.80	14.40										
Sep-90	4.13	3.78	0.06	1.00	4.20										
Oct-90	9.50	2.64	0.06	0.80	2.30										
Nov-90	13.70	4.03	0.05	1.10	3.90										
Jan-91	4.20	2.74	0.14	1.90	2.30										
Feb-91	0.09	9.38	0.17	0.90	3.70										
Mar-91	3.73	3.49	0.20	0.90	3.10										
Apr-91	2.68	2.68	0.07	0.60	4.20										
May-91	3.18	5.70	0.07	0.60	11.20										
Jun-91	5.11	4.06	0.07	0.70	6.10										
Nov-91	1.85	5.19	0.23	1.58	16.90										
Dec-91	0.46	6.36	0.09	0.55	10.15	417.07	88.91	0.59			7.19	5.34	4.77		
Jan-92	2.56	1.95	0.25	1.40	3.03										
Mar-92	2.83	7.56	0.33	0.34	6.76	57.47	16.98	0.92	22.28		5.54	4.55	4.39	5.50	
Apr-92	1.43	3.34	0.12	0.42	5.80	8.35	42.00	0.20	33.80	41.33	5.00	5.30	4.17	5.59	5.11
May-92	0.03	0.94	0.36	0.54	12.74					111.75					5.20
Jun-92	1.72	0.31	0.12	0.43	3.60	403.92	10.20	0.44	70.20	299.00	6.60	5.71	4.51	5.90	6.18
Jul-92	0.97	2.17	0.56	0.47	2.40	403.92	12.41	0.41	66.76	294.74	6.85	4.95	3.81	5.84	6.35
Aug-92	2.49	3.65	0.29	0.17	4.30										
Sep-92	5.72	9.30	0.27	1.52	3.34										
Oct-92	2.50	3.65	0.29	0.53	4.19	134.01	327.04	5.18	408.48	437.49	5.96	6.15	5.20	6.57	6.28
Nov-92	1.50	4.70	0.10	0.20	9.80	175.08	50.87	2.50	37.03	94.10	6.30	5.23	5.35	5.95	5.24
Feb-93	2.28	3.21	0.03	0.21	3.60	53.90	32.69	1.45	29.91		5.60	5.20	5.63	5.84	
Mar-93	3.43	2.95	0.18	1.04	2.94	87.10	42.79	0.45	128.37	320.37	5.64	5.36	4.35	5.78	6.30
Apr-93	9.80	4.79	0.19	1.84	18.05	692.14	0.00	1.51	35.63	182.95	6.08		4.85	4.97	5.27
May-93	13.58	10.20	0.20	1.72	12.40	461.21	1680.96	0.00	83.11		5.76	6.41		5.37	
Jun-93	1.60	1.56	0.10	1.02	12.44	30.07	55.33	0.00	35.28	182.95	5.51	5.75		5.22	5.43
Jul-93	3.58	0.06	0.04	1.01	12.43	30.07	55.33	0.00	35.28	182.95	5.16	7.16		5.23	5.43
Aug-93	5.30	10.20	0.09	0.85	5.46	42.10	28.67	1.12	66.07	1475.41	5.13	4.65	5.04	5.57	6.69

Sep-93	14.91	12.53	0.00	1.32	14.82	383.64	220.51	14.34	369.30	4.03	5.64	5.44		6.13	3.69
Oct-93	2.49	3.65	0.29	0.17	5.46	80.75	64.08	3.13	69.29	209.94	5.74	5.44	4.98	6.29	5.85
Jan-94	3.95	30.48	0.24	0.79	8.30	22.87	33.56	0.30	55.24	53.75	4.99	4.24	4.04	5.53	5.07
Mar-94	1.48	0.87	0.11	0.53	2.98	7.93	61.46	0.00	79.30	44.81	4.96	6.05		5.86	5.44
Apr-94	2.21	0.50	0.21	0.22	3.74	16.79	10.27	0.00	142.34	30.24	5.11	5.51		6.49	5.17
May-94	0.99	0.90	0.22	0.53	4.40	7.93	61.46	0.00	79.30	44.80	5.13	6.03		5.86	5.27
Jul-94	0.80	7.21	0.08	0.55	1.93	559.56	342.21	0.00	474.47	100.80	7.08	5.87		6.62	5.98

Appendix 1.4

Great Sound

Date	nmol l^{-1} Ni	nmol l^{-1} Cu	nmol l^{-1} Cd	nmol l^{-1} Pb	nmol l^{-1} Mn	µg g^{-1} Ni	µg g^{-1} Cu	µg g^{-1} Cd	µg g^{-1} Pb	µg g^{-1} Mn	log Kd Ni	Log Kd Cu	Log Kd Cd	Log Kd Pb	Log Kd Mn
Aug-90	1.68	3.68	0.06	1.70	9.90										
Sep-90	5.64	3.75	0.07	1.40	5.30										
Oct-90	3.85	2.85	0.08	1.10	3.52										
Nov-90	5.23	3.59	0.12	2.30	1.80										
Jan-91	3.28	3.24	0.09	1.30	1.60										
Feb-91	3.07	14.32	0.18	1.25	2.32										
Mar-91	13.09	5.16	0.24	1.60	2.00										
Apr-91	6.24	3.56	0.09	0.80	3.10										
May-91	4.92	4.75	0.05	0.70	12.30										
Jun-91	2.24	5.48	0.10	1.00	5.20										
Nov-91	1.54	5.04	0.36	0.45	5.50										
Dec-91	2.08	0.48	0.18	1.23	5.52	420.89	151.31	29.71			6.54	6.70	6.17		
Jan-92	1.91	2.53	0.16	1.17	27.64	65.87	49.06	1.28	33.09		5.77	5.48	4.86	5.14	
Feb-92	1.53	2.36	0.09	1.01	2.18										
Mar-92	3.40	1.48	0.07	1.06	1.80	35.10	43.09	0.10	15.82		5.24	5.66	4.10	4.86	
Apr-92	4.42	0.78	0.19	1.33	14.60	6.94	48.14	0.13	16.03	65.83	4.43	5.99	3.78	4.76	4.91
May-92	1.57	0.70	0.08	0.53	12.74					802.20					6.06
Jul-92	2.84	0.32	0.39	1.66	2.00	82.52	5.85	0.27	32.84	152.31	5.69	5.45	3.79	4.98	6.14
Aug-92	3.88	5.45	0.20	1.20	4.69										
Sep-92	1.53	10.32	0.44	1.98	3.90										
Oct-92	5.83	3.30	0.10	0.85	4.55	105.85	188.55	4.33	234.85	580.72	5.49	5.95	5.59	6.13	6.37
Nov-92	12.08	5.04	0.44	1.51	17.10	163.20	3.71	1.61	17.74	53.93	5.36	4.06	4.51	4.75	4.76
Jan-93	3.95	3.97	0.12	1.21	9.10	164.55	170.31	3.58	167.67	414.46	5.85	5.83	5.42	5.83	5.92
Feb-93	4.21	2.83	0.18	1.25	3.60	48.58	0.00	0.78	33.19		5.29		4.59	5.11	
Mar-93	3.96	3.98	0.13	1.20	15.40	8.56	6.55	0.00	20.43	28.67	4.57	4.41		4.91	4.53
Apr-93	4.87	3.21	0.10	1.40	4.86	115.59	0.00	2.15	45.32	185.64	5.61		5.28	5.19	5.84
May-93	13.60	6.20	0.11	2.17	5.63	470.06	779.37	0.00	79.99		5.77	6.30		5.25	
Jun-93	5.45	0.94	0.05	1.45	7.64	0.00	83.16	0.43	11.68			6.14	4.86	4.59	
Jul-93	3.76	0.09	0.05	1.45	7.66	29.50	53.09	0.00	4.85	185.64	5.13	6.97		4.21	5.64
Aug-93	5.11	0.13	0.09	0.87	4.73	47.85	35.57	0.77	40.94	1576.19	5.20	6.65	4.89	5.36	6.78
Sep-93	6.98	2.68	0.53	1.30	6.73	56.24	85.07	1.42	56.95	4.30	5.14	5.70	4.37	5.32	4.07

Oct-93	5.11	0.61	0.09	0.87	5.46	229.58	221.25	3.70	123.12	398.06	5.88	6.76	5.57	5.84	6.12
Jan-94	7.84	31.00	0.27	0.77	24.92	13.14	37.50	0.13	84.41	16.75	4.46	4.28	3.63	5.72	4.09
Mar-94	2.82	0.53	0.12	0.48	8.72	20.45	47.75	0.25	98.80	12.32	5.09	6.15	4.27	6.00	4.41
Apr-94	2.58	0.42	0.12	0.41	2.55	72.30	139.27	31.96	494.67	681.89	5.68	6.72	6.37	6.77	6.69
May-94	6.84	0.51	0.25	1.29	1.82	20.45	47.75	0.25	98.80	12.32	4.71	6.17	3.95	5.57	5.09
Jun-94	0.67	3.84	0.07	0.67	6.50	72.30	139.27	31.96	494.67	681.86	6.26	5.76	6.61	6.55	6.28

Appendix 1.5

Outer Hamilton Harbour

Date	nmol l^{-1} Ni	nmol l^{-1} Cu	nmol l^{-1} Cd	nmol l^{-1} Pb	nmol l^{-1} Mn	µg g^{-1} Ni	µg g^{-1} Cu	µg g^{-1} Cd	µg g^{-1} Pb	µg g^{-1} Mn	Log Kd Ni	Log Kd Cu	Log Kd Cd	Log Kd Pb	Log Kd Mn
Aug-90	4.14	9.85	0.06	1.50	10.90										
Sep-90	4.14	10.04	0.07	2.50	9.10										
Oct-90	2.21	12.46	0.12	1.00	3.40										
Nov-90	13.50	10.29	0.17	2.50	3.50										
Jan-91	2.54	7.87	0.10	2.30	2.10										
Feb-91	3.24	10.86	0.62	1.79	2.65										
Mar-91	13.34	7.62	0.14	1.50	2.40										
Apr-91	6.55	10.10	0.06	1.00	4.40										
May-91	3.70	14.26	0.07	1.50	1.51										
Jun-91	2.59	14.29	0.08	1.50	4.00										
Nov-91	2.39	7.24	0.44	0.69	1.64										
Dec-91	2.06	0.73	0.18	1.05	6.73	546.05	213.73	0.70			6.66	6.67	4.54		
Jan-92	2.22	1.03	0.43	1.20	8.00	46.58	30.05	0.35	31.22		5.55	5.66	3.86	5.10	
Feb-92	1.87	7.24	0.27	1.79	2.91										
Mar-92	1.87	1.08	0.08	0.85	6.68	15.17	80.53	0.42	31.35		5.14	6.07	4.66	5.25	
Apr-92	2.13	1.32	0.09	1.11	9.10	3.93	42.15	0.08	5.58	200.16	4.50	5.70	3.90	4.39	5.60
May-92	1.71	1.86	0.08	1.07	10.92					152.31					5.40
Jun-92	2.80	1.44	0.07	0.84	2.79	118.02	40.11	4.90	106.26	111.76	5.86	5.64	5.77	5.78	5.86
Aug-92	3.98	4.75	0.22	2.02	4.15										
Sep-92	1.87	2.23	0.04	0.81	1.70										
Oct-92	7.77	1.73	0.25	0.53	3.09	110.80	33.42	2.08	139.60	2392.51	5.39	5.48	4.87	6.10	7.15
Nov-92	9.68	35.09	0.36	2.33	2.20	39.78	16.42	0.40	55.01	38.05	4.85	3.87	4.00	5.06	5.50
Jan-93	3.07	10.17	0.12	1.56	6.60	182.56	41.00	0.53	63.53	175.00	6.01	4.80	4.59	5.29	5.68
Feb-93	3.46	6.28	0.62	1.16	3.60	28.89	17.33	0.34	36.00		5.15	4.64	3.69	5.18	
Mar-93	3.06	10.66	0.11	1.57	6.44	40.36	23.29	0.06	55.21	31.48	5.35	4.54	3.69	5.23	4.95
Apr-93	8.47	7.25	0.19	3.12	9.18	16.39	0.00	2.74	68.71	196.16	4.52		5.11	5.03	5.59
May-93	9.60	10.17	0.21	2.73	8.57	85.27	154.50	0.00	37.12		5.18	5.38		4.82	
Jun-93	8.19	2.99	0.04	2.80	12.95	9.73	83.16	0.43	29.56		4.31	5.64	4.98	4.71	
Jul-93	8.19	2.99	0.04	2.80	12.92	37.20	118.25	0.00	116.68	552.80	4.89	5.79		5.30	5.89
Aug-93	2.65	0.52	0.09	2.61	47.32	91.77	121.08	3.01	56.16	588.43	5.77	6.56	5.48	5.02	5.35
Sep-93	9.88	3.28	0.62	0.40	8.92	88.31	267.56	1.59	127.96	6.51	5.18	6.11	4.36	6.19	4.12

Oct-93	9.81	2.28	0.53	2.61	4.73	31.36	111.76	0.88	43.07	143.79	4.74	5.89	4.17	4.90	5.74
Jan-94	3.41	27.22	0.27	0.66	21.84	10.85	16.69	0.20	131.75	11.98	4.73	3.98	3.82	5.98	4.00
Mar-94	2.19	1.33	0.18	1.02	16.88	0.00	30.51	0.21	103.85	158.91		5.56	4.02	5.69	5.23
Apr-94	2.40	1.67	0.10	0.45	15.76	0.00	153.39	0.00	164.20	142.06		6.16		6.25	5.22
May-94	1.87	1.29	0.13	0.63	1.33	10.54	30.51	0.21	103.85	158.79	4.98	5.57	4.16	5.90	6.34
Jun-94	0.94	19.83	0.09	1.36	12.74	0.00	721.49	0.00	77.23	1399.32		5.76		5.44	6.30

Appendix 1.6

Inner Hamilton Harbour

Date	nmol l^{-1} Ni	nmol l^{-1} Cu	nmol l^{-1} Cd	nmol l^{-1} Pb	nmol l^{-1} Mn	μg g^{-1} Ni	μg g^{-1} Cu	μg g^{-1} Cd	μg g^{-1} Pb	μg g^{-1} Mn	Log Kd Ni	Log Kd Cu	Log Kd Cd	Log Kd Pb	Log Kd Mn
Aug-90	4.13	13.13	0.09	1.70	16.30										
Sep-90	3.98	14.70	0.09	0.47	10.20										
Oct-90	3.77	6.80	0.04	1.50	2.10										
Nov-90	3.51	10.29	0.08	0.38	6.00										
Jan-91	2.56	5.35	0.10	0.39	2.80										
Feb-91	2.04	21.87	0.36	0.41	28.20										
Mar-91	4.24	8.06	0.10	1.60	3.50										
Apr-91	5.43	13.06	0.11	1.70	7.20										
May-91	3.16	18.35	0.08	1.60	5.60										
Jun-91	2.06	18.29	0.06	1.60	4.40										
Nov-91	1.47	17.15	0.53	0.92	14.60										
Dec-91	1.93	0.82	0.18	0.52	13.95	438.31	15.31	4.56			6.59	5.47	5.36		
Jan-92	1.91	1.08	0.47	1.17	8.72	68.57	70.59	1.27	117.96		5.79	6.01	4.38	5.69	
Feb-92	1.02	5.19	1.78	1.30	4.36										
Mar-92	3.38	1.67	0.09	0.54	7.03	8.62	21.02	0.30	24.26		4.64	5.30	4.48	5.34	
Apr-92	1.95	1.63	0.08	1.25	18.00	8.01	81.11	0.08	22.09	21.85	4.85	5.89	3.93	4.93	4.34
May-92	2.23	2.91	0.10	1.18	5.46										4.78
Jun-92	3.00	1.53	0.16	0.13	20.00	71.06	24.14	0.62	74.46	18.11	5.61	5.39	4.54	6.44	4.22
Jul-92	6.47	1.53	0.16	0.13	1.80										
Aug-92	5.14	12.49	0.22	0.92	4.50										
Sep-92	2.50	13.38	0.18	1.49	3.10										
Oct-92	3.78	0.94	0.39	2.28	15.47	11.47	13.18	2.07	84.83	392.51	4.71	5.34	4.67	5.25	5.66
Nov-92	7.85	66.88	0.89	2.47	24.20	160.36		1.26	95.84	94.88	5.54		4.10	5.27	4.85
Jan-93	4.91	17.97	0.16	2.01	9.80	82.40	13.60	0.65	200.20	9.48	5.46	4.08	4.56	5.68	4.25
Feb-93	3.51	6.12	0.27	2.70	7.30	224.04	377.19	36.30	432.02		6.04	5.99	6.08	5.89	
Mar-93	4.90	17.96	0.15	2.00	9.80	45.07	61.76	0.00	98.77	116.75	5.20	4.73		5.38	5.34
Apr-93	9.45	22.54	0.39	3.50	11.73	138.78	0.00	2.41	93.91	139.05	5.40		4.74	5.11	5.33
May-93	12.77	27.30	0.09	2.74	9.97	85.21	245.97	0.00	82.71		5.06	5.15		5.16	
Jun-93	6.12	2.99	0.06	3.19	29.31	14.52	75.64	0.50	52.06		4.61	5.60	4.87	4.90	
Jul-93	6.12	2.99	0.06	3.19	29.49	35.50	204.09	0.00	283.56	422.83	4.99	6.03		5.63	5.42
Aug-93	7.16	0.46	0.05	2.99	9.21	28.78	245.57	1.51	73.35	321.08	4.84	6.93	5.40	5.07	5.80

Sep-93	7.25	3.12	0.01	3.14	9.28	81.38	167.03	0.85	216.88	5.29	5.28	5.93	5.88	5.52	4.02
Oct-93	20.44	6.12	0.53	2.99	9.10	26.78	59.99	1.22	87.38	80.95	4.35	5.19	4.31	5.15	5.21
Jan-94	4.43	24.71	0.44	0.67	31.28	8.67	28.59	0.23	38.61	13.96	4.52	4.26	3.65	5.44	3.91
Mar-94	3.56	1.53	0.29	0.94	9.28	16.90	68.18	0.00	97.34	136.50	4.91	5.85		5.70	5.43
Apr-94	3.56	1.49	0.09	1.63	5.06	71.22	83.57	0.00	122.65	161.73	5.53	5.95		5.56	5.76
May-94	5.65	3.56	0.13	0.80	3.09	51.05	205.92	0.00	293.99	412.21	5.19	5.96		6.25	6.39
Jun-94	4.90	17.97	0.15	2.00	9.79	410.37	481.53	0.00	70.67	93.21	6.15	5.62		5.23	5.24

Appendix 1.7

Inner N.Lagoon

Date	nmol l^{-1} Ni	nmol l^{-1} Cu	nmol l^{-1} Cd	nmol l^{-1} Pb	nmol l^{-1} Mn	$\mu g\ g^{-1}$ Ni	$\mu g\ g^{-1}$ Cu	$\mu g\ g^{-1}$ Cd	$\mu g\ g^{-1}$ Pb	$\mu g\ g^{-1}$ Mn	Log Kd Ni	Log Kd Cu	Log Kd Cd	Log Kd Pb	Log Kd Mn
Aug-90	1.83	2.20	0.08	1.20	4.20										
Sep-90	2.77	2.14	0.04	1.20	2.40										
Oct-90	1.61	6.23	0.12	0.60	1.70										
Nov-90	2.04	1.86	0.04	0.80	0.90										
Jan-91	2.08	3.05	0.31	0.10	0.80										
Feb-91	3.58	6.70	0.03	1.40	1.30										
Mar-91	2.17	1.89	0.13	0.80	1.00										
Apr-91	4.54	2.05	0.09	0.60	2.00										
May-91	3.88	2.90	0.04	0.70	4.00										
Jun-91	2.43	3.34	0.06	0.20	1.40										
Nov-91	1.19	4.72	0.18	0.28	21.80										
Dec-91	1.72	0.62	0.09	0.64	5.30	8.34	20.06	4.85			4.92	5.71	5.69		
Jan-92	1.32	0.40	0.09	0.31	2.92	72.45	32.72	0.80	26.43		5.97	6.11	4.92	5.62	
Feb-92	2.21	2.20	0.27	0.77	5.50										
Mar-92	2.45	0.91	0.06	0.53	8.92	21.55	9.62	0.50	13.60	6.84	5.18	5.22	4.84	5.09	4.14
Apr-92	4.64	0.61	0.10	0.40	25.50	13.75	61.58	0.05	24.45	4.31	4.70	6.20	3.67	5.47	3.49
May-92	1.31	4.64	0.18	0.59	2.65										
Jun-92	2.62	0.44	0.13	0.43	1.80	174.88	14.23	0.47	8.58	802.20	6.06	5.71	4.51	4.98	6.91
Jul-92	2.90	1.42	0.53	0.48	1.92										
Aug-92	3.73	0.94	0.13	0.33	4.60										
Sep-92	3.04	12.08	0.38	0.86	1.31										
Oct-92	1.08	0.90	0.09	0.20	1.64	31.18	36.01	1.30	84.08	35.59	5.69	5.80	5.11	6.31	5.60
Nov-92	5.86	15.11	0.44	1.09	8.70	307.36	11.69	0.82	24.23	53.72	5.95	4.09	4.21	5.03	5.05
Jan-93	9.20	0.20	0.18	0.85	2.90	75.59	15.69	4.56	34.35	242.14	5.15	6.09	5.35	5.29	6.18
Feb-93	1.45	4.25	0.18	0.58	1.80	291.69	268.26	2.02	239.17		6.54	6.00	5.00	6.30	
Mar-93	1.63	0.98	0.17	0.85	2.80	116.06	2.96	0.00	24.90	130.41	6.08	4.68		5.15	5.93
Jun-93	8.35	0.79	0.05	1.16	6.05	12.05	19.45	0.00	1.87		4.39	5.59		3.89	
Jul-93	8.35	0.79	0.05	1.16	6.01	32.20	52.47	0.00	14.87	23.48	4.82	6.02		4.79	4.85
Aug-93	2.04	0.11	0.09	0.68	4.84	159.94	522.48	4.44	649.55	10.14	6.12	7.87	5.65	6.67	4.58
Sep-93	9.71	1.22	2.40	0.82	4.19	181.97	90.99	4.04	118.28	1.46	5.50	6.07	4.18	5.84	3.80
Oct-93	7.16	1.05	0.09	0.68	5.46	108.93	74.27	4.13	399.40	120.48	5.41	6.05	5.62	6.46	5.60

Jan-94	3.41	24.23	0.18	0.61	2.37	25.16	60.95	0.00	102.07	44.51	5.10	4.60		5.91	5.53
Mar-94	2.38	0.73	0.14	1.15	3.16	17.71	5.64	0.00	64.25	48.80	5.10	5.08		5.43	5.45
Apr-94	2.56	0.34	0.42	0.99	1.82										
May-94	1.86	0.43	0.20	0.29	2.04										
Jun-94	1.09	2.20	0.11	0.78	3.64										

Appendix 1.8

Outer N. Lagoon

Date	nmol l^{-1} Ni	nmol l^{-1} Cu	nmol l^{-1} Cd	nmol l^{-1} Pb	nmol l^{-1} Mn	µg g^{-1} Ni	µg g^{-1} Cu	µg g^{-1} Cd	µg g^{-1} Pb	µg g^{-1} Mn	Log Kd Ni	Log Kd Cu	Log Kd Cd	Log Kd Pb	Log Kd Mn
Aug-90	0.14	1.64	0.09	0.10	3.20										
Sep-90	2.10	3.56	0.03	0.10	2.10										
Oct-90	3.63	1.54	0.04	0.40	2.10										
Nov-90	0.18	3.34	0.08	0.43	1.20										
Jan-91	5.17	2.11	0.11	0.00	1.00										
Feb-91	3.75	2.23	0.01	0.00	0.40										
Mar-91	3.72	0.82	0.06	0.70	0.70										
Apr-91	3.34	1.01	0.05	0.60	1.10										
May-91	2.24	0.19	0.05	0.50	0.40										
Jun-91	1.91	1.13	0.06	0.20	1.40										
Nov-91	1.30	4.25	0.09	0.11	5.50										
Dec-91	1.63	0.09	0.09	0.64	3.64	4.06	44.78	9.62			4.63	6.90	5.98		
Feb-92	1.12	0.79	0.03	0.31	0.52										
Apr-92	1.61	0.40	0.12	1.01	1.46	53.33	54.99	0.17	4.28	7.31	5.75	6.33	4.09	4.31	4.96
May-92	2.17	0.42	0.05	0.02	2.18					1.24					4.02
Jun-92	1.91	0.29	0.02	0.00	3.60	118.10	6.25	0.62	10.28	4.31	6.02	5.53	5.44		4.34
Jul-92	1.91	0.29	0.02	0.00	0.36										
Aug-92	1.24	0.62	0.08	0.17	0.29										
Sep-92	0.41	2.14	0.07	0.96	1.25										
Oct-92	1.85	0.11	0.10	0.59	6.19	47.36	53.71	1.03	69.68	11.78	5.64	6.88	4.97	5.76	4.54
Nov-92	5.25	10.70	0.36	0.49	5.50	212.80	13.56	0.99	37.53	16.13	5.84	4.30	4.39	5.57	4.73
Jan-93	10.41	0.02	0.14	0.62	1.50	193.80	10.66	4.93	19.48	466.00	5.50	6.92	5.50	5.18	6.75
Feb-93	3.17	3.23	0.18	0.19	1.80	95.84	0.00	2.57	0.00		5.71		5.11		
Mar-93	5.20	0.95	0.14	0.62	1.54	35.85	1.57	0.00	39.00	522.10	5.07	4.42		5.48	6.79
Apr-93	6.68	5.54	0.08	0.12	2.02	0.00	0.00	21.99	469.31	103.59			6.39	7.28	5.97
May-93	7.78	6.27	0.12	0.19	2.50	187.22	56.29	0.00	0.00		5.61	5.15			
Jun-93	10.41	0.02	0.12	0.58	0.62	21.69	14.02	0.39	0.00		4.55	7.04	4.46		
Jul-93	10.22	0.11	0.02	0.68	0.36	20.60	23.60	0.00	0.00	103.54	4.54	6.53			6.71
Aug-93	3.92	0.03	0.06	0.39	6.04	58.90	172.46	0.85	122.05	9.58	5.41	7.94	5.08	6.18	4.46
Sep-93	8.35	4.12	0.98	0.82	1.46	14.04	6.02	0.17	5.18	0.52	4.46	4.36	3.19	4.48	3.81
Oct-93	3.92	2.65	0.00	0.39	0.55	118.54	56.52	2.36	41.61	40.82	5.71	5.53		5.72	6.13

Jan-94	3.07	15.58	0.27	0.90	1.44	41.18	37.73	1.57	54.39	49.36	5.36	4.58	4.72	5.46	5.80
Mar-94	1.25	0.22	0.03	0.20	4.44	62.37	0.00	22.87	0.00	0.00	5.93		6.83		
Apr-94	0.99	0.35	0.38	0.20	1.16										
May-94	2.13	0.24	0.20	0.16	1.09	62.37	6.24	2.87	0.00	0.00	5.70	5.61	5.11		
Jun-94	1.08	1.54	0.03	0.83	6.55					0.36					

Appendix 2 Correlation data for the dissolved metals data base

2.1 St. George's

Correlation Matrix for Variables: $X_1 \dots X_{11}$

	Nickel	Copper	Cadmium	Lead	Mangane...	chloroph...	Tempera...	Nitrate
Nickel	1							
Copper	-.121	1						
Cadmium	-.27	.339	1					
Lead	.121	.45	-.058	1				
Manganese	.044	.259	-.047	.156	1			
chlorophyll	.542	-.296	.282	-.005	-.336	1		
Temperat...	.569	-.455	-.563	.034	.036	.317	1	
Nitrate	-.184	-.023	.089	-.197	.431	-.177	-.289	1
phosphate	-.195	-.172	.499	-.513	-.379	.201	-.292	-.154
salinity	.089	-.256	-.241	.133	.165	-.079	.176	.039
part mat...	-.011	-.316	-.587	-.085	-.098	-.126	.297	-.26

Correlation Matrix for Variables: $X_1 \dots X_{11}$

	phosphate	salinity	part mat...
phosphate	1		
salinity	-.538	1	
part material	.039	-3.31E-4	1

2.2 Castle Harbour.

Correlation Matrix for Variables: $X_1 \dots X_{11}$

	Nickel	Copper	Cadmium	Lead	Mangane...	Chloroph...	Tempera...	Nitrate
Nickel	1							
Copper	.291	1						
Cadmium	.388	.811	1					
Lead	.791	.496	.5	1				
Manganese	.293	.108	.329	.214	1			
Chlorophyll	.186	-.233	-.344	.086	-.319	1		
Temperat...	.258	-.092	-.472	.273	-.45	.481	1	
Nitrate	-.416	-2.77E-4	.188	-.209	-.392	-.101	-.418	1
Phosphate	-.044	-.171	-.197	-.311	.018	-.125	-.101	.176
Salinity	.463	-.188	.202	.241	.281	.138	-.029	-.276
susp mat...	.648	.233	.256	.818	.039	.01	.365	-.092

Correlation Matrix for Variables: $X_1 \dots X_{11}$

	Phosphate	Salinity	susp ma...
Phosphate	1		
Salinity	-.234	1	
susp material	-.26	.158	1

2.3 Harrington Sound

Correlation Matrix for Variables: $X_1 \dots X_{11}$

	Nickel	Copper	Cadmium	Lead	Mangane...	Chloroph...	Tempera...	Nitrate
Nickel	1							
Copper	.216	1						
Cadmium	.269	.273	1					
Lead	.838	.137	.166	1				
Manganese	.638	.115	.152	.698	1			
Chlorophyll	-.035	.086	.379	-.323	-.176	1		
Temperat...	-.025	-.217	.005	.06	.027	.461	1	
Nitrate	-.246	-.418	-.251	-.003	-.047	-.376	-.101	1
Phosphate	.104	-.256	.641	-.021	.067	.555	.228	-.237
Salinity	.18	-.131	.034	.088	.29	.268	.726	-.282
Susp mat...	-.293	-.187	.064	-.331	.068	-.237	-.034	.003

Correlation Matrix for Variables: X_1 ... X_{11}

	Phosphate	Salinity	Susp ma...
Phosphate	1		
Salinity	.201	1	
Susp material	.24	.367	1

2.4 Great Sound

Correlation Matrix for Variables: X_1 ... X_{11}

	Nickel	Copper	Cadmium	Lead	Mangane...	Chloroph...	Tempera...	Nitrate
Nickel	1							
Copper	.298	1						
Cadmium	.423	.241	1					
Lead	.671	-.114	.182	1				
Manganese	-.007	.523	.29	-.052	1			
Chlorophyll	.11	-.244	.321	.035	-.267	1		
Temperat...	.053	-.337	-.137	-.007	-.605	.55	1	
Nitrate	-.147	.683	.074	-.285	.808	-.226	-.562	1
Phosphate	.01	-.247	.058	.106	-.087	.588	.24	-.283
Salinity	.255	-.375	-.161	.256	-.174	.385	.573	-.346
Susp mat...	.009	.02	.339	.106	.685	-.401	-.543	.269

Correlation Matrix for Variables: X_1 ... X_{11}

	Phosphate	Salinity	Susp ma...
Phosphate	1		
Salinity	.349	1	
Susp material	-.26	-.106	1

2.5 Outer Hamilton Harbour

Correlation Matrix for Variables: X_1 ... X_{11}

	Nickel	Copper	Cadmiu	Lead	Mangane...	Chloroph...	Tempera...	Nitrate
Nickel	1							
Copper	.138	1						
Cadmiu	.417	.062	1					
Lead	.519	-.08	-.104	1				
Manganese	-.264	-.055	-.258	.005	1			
Chlorophyll	.372	-.264	.377	.123	.334	1		
Temperat...	.083	-.383	-.412	.074	.216	.205	1	
Nitrate	-.025	.142	.053	.091	-.135	-.207	-.674	1
Phosphate	.393	-.248	.443	-.052	-.108	.358	.186	-.38
Salinity	.511	-.063	-.004	.298	-.314	-.018	.201	-.242
Susp mat...	-.241	.129	-.28	-.251	-.391	-.34	-.242	.09

Correlation Matrix for Variables: X_1 ... X_{11}

	Phosphate	Salinity	Susp ma...
Phosphate	1		
Salinity	.226	1	
Susp material	-.065	.301	1

2.6 Inner Hamilton Harbour

Correlation Matrix for Variables: X_1 ... X_{11}

	Nickel	Copper	Cadmium	Lead	Mangane...	Chloroph...	Tempera...	Nitrate
Nickel	1							
Copper	.226	1						
Cadmium	-.148	.234	1					
Lead	.571	.13	-.231	1				
Manganese	-.045	.402	-.081	.024	1			
Chlorophyll	.633	-.178	.017	.212	-.207	1		
Temperat...	.421	-.176	-.38	.493	-.029	.274	1	
Nitrate	-.392	-.07	.276	-.373	-.101	-.4	-.332	1
Phosphate	.171	.007	-.033	.359	-.068	-.034	.345	-.004
Salinity	.425	.091	-.11	.508	.174	.203	.405	-.352
Susp mat...	-.425	.058	.799	-.258	.009	-.134	-.372	.12

Correlation Matrix for Variables: X_1 ... X_{11}

	Phosphate	Salinity	Susp ma...
Phosphate	1		
Salinity	.49	1	
Susp material	-.107	.016	1

2.7 Inner North Lagoon

Correlation Matrix for Variables: X_1 ... X_{11}

	Nickel	Copper	Cadmium	Lead	Mangane...	Chloroph...	Tempera...	Phosphate
Nickel	1							
Copper	.117	1						
Cadmium	.073	.613	1					
Lead	.505	.122	.368	1				
Manganese	.366	-.113	.011	-.101	1			
Chlorophyll	-.021	-.312	-.367	-.009	.009	1		
Temperat...	.628	-.166	-.311	.463	.005	.017	1	
Phosphate	.179	-.225	-.106	-.17	.066	.732	-.222	1
Natrate	-.174	-.007	.162	-.138	-.087	-.023	-.099	-.006
Salinity	-.188	.131	-.049	-.017	-.502	.214	.42	-.09
Susp mat...	.205	.027	.329	-.019	.829	-.187	-.017	-.146

Correlation Matrix for Variables: X_1 ... X_{11}

	Natrate	Salinity	Susp ma...
Natrate	1		
Salinity	.155	1	
Susp material	.276	-.267	1

2.8 Outer North Lagoon

Correlation Matrix for Variables: X_1 ... X_{11}

	Nickel	Copper	Cadmium	Lead	Mangane...	Chloroph...	Tempera...	Nitrate
Nickel	1							
Copper	.129	1						
Cadmium	.353	.341	1					
Lead	.513	-.233	.482	1				
Manganese	-.047	-.157	.002	.272	1			
Chlorophyll	.194	-.041	.266	.304	-.118	1		
Temperat...	.109	-.31	.217	.242	-.044	.416	1	
Nitrate	-.283	-.197	-.159	-.412	-.198	-.114	.036	1
Phosphate	.331	.262	-.019	-.178	.177	-.097	.026	-.046
Salinity	.264	.296	-.256	-.077	.195	-.572	-.383	-.397
Susp mat...	-.561	-.495	-.276	-.223	-.066	.032	.196	.602

Correlation Matrix for Variables: X_1 ... X_{11}

	Phosphate	Salinity	Susp ma...
Phosphate	1		
Salinity	.464	1	
Susp matter	-.336	-.54	1

Appendix 3 Trace metals in Bermuda sediments: Total and labile (all $\mu g\ g^{-1}$)

3.1 St. George's Harbour

Date	Total Pb	Partial Pb	% partial	Total Mn	Partial Mn	% partial	Total Cu	Partial Cu	% partial	Total Ni	Partial Ni	% partial Ni
Jul	76.60	34.82	45.46	43.25	52.44	121.25	30.26	8.53	28.17	10.14	0.63	6.23
Aug	57.68	53.66	93.03	42.41	47.49	111.98	19.72	8.54	43.30	3.97	0.65	16.30
Sep	70.00	33.6	48.00	62.4	35.56	56.99	26.36	7.57	28.70	5.09	1.40	27.56
Nov	40.18	34.67	86.29	61.12	39.92	65.31	13.83	7.4	53.51	0.88	0.43	48.41
Dec	43.52	40.43	92.90	45.02	43.00	95.52	16.55	7.69	46.50	3.42	0.88	25.69
Jan	47.49	40.47	85.22	45.31	45.14	99.62	12.96	7.471	57.65	5.7	0.14	2.46
Mar	31.98	22.68	70.92	39.4	39	98.98	21.61	13.68	63.30	2.99	0.78	26.09
Apr	48.99	46.6	95.12	38.38	38.13	99.34	23.57	13.83	58.68	3.41	0.71	20.82
May	70.66	68.3	96.66	44.14	46.62	105.62	24.59	8.59	34.93	2.85	0.7	24.56
Jun	71.13	70.03	98.45	38.06	35.95	94.46	19.08	7.59	39.78	3.69	0.24	6.50
Jul	37.36	25.8	69.06	36.88	30.65	83.11	26	6.16	23.69	3.52	0.77	21.88
Aug	55.38	46.1	83.24	61.48	32.93	53.56	27.49	13.68	49.76	1.7	0.268	15.76
Sep	53.20	52.5	98.68	57.56	21.11	36.67	57.4	3.47	6.04	4.86	0.784	16.13
Oct	44.21	40.32	91.20	36.24	13.148	36.28	20.56	10.68	51.92	3.96	1.939	48.92
Nov	136.44	64.522	47.28	14.447	13.383	92.64	28.7	8.07	28.15	4.89	1.453	29.71

3.2 Castle Harbour

Date	Total Pb	Partial Pb	% partial	Total Mn	Partial Mn	% partial	Total Cu	Partial Cu	% partial	Total Ni	Partial Ni	% partial
Jul	5.49	5.40	98.36	10.70	8.63	80.65	1.47	0.69	46.60	1.02	0.00	0.00
Aug	7.74	6.32	81.65	12.11	8.83	72.91	1.21	1.13	93.06	1.12	0.47	41.61
Sep	12.34	7.00	56.73	24.72	16.70	67.56	2.44	0.69	28.40	3.11	0.52	16.78
Nov	13.81	6.40	46.34	22.12	13.36	60.38	1.28	0.47	36.33	0.32	0.17	53.13
Dec	6.27	3.17	50.56	10.32	6.87	66.57	1.89	0.29	15.08	1.32	0.97	73.71
May	19.04	5.90	30.99	23.77	20.42	85.91	3.18	1.00	31.45	1.44	0.78	54.17
Jul	11.83	6.68	56.47	18.01	17.14	95.17	1.79	0.52	29.05	0.70	0.65	92.86
Aug	8.28	7.70	93.00	9.80	9.80	100.05	1.69	0.23	13.61	0.50	0.31	62.00
Sep	6.87	1.43	20.82	11.20	4.81	42.95	0.32	0.18	56.25	1.78		0.00
Oct	6.23	4.82	77.34	7.98	3.28	41.09	1.24	0.39	31.37	1.23	1.07	86.89
Nov	5.24	5.50	105.04	4.83	4.58	94.76	3.49	2.03	58.24	1.76	0.16	8.98

3.3 Harrington Sound

Date	Total Pb	Partial Pb	% partial	Total Mn	Partial Mn	% partial	Total Cu	Partial Cu	% partial	Total Ni	Partial Ni	% partial
Jul	40.94	12.23	29.88	31.87	15.92	49.95	26.02	1.90	7.30	4.31	0.57	13.16
Aug	18.17	12.00	66.04	36.05	18.95	52.57	4.63	0.75	16.20	2.87	0.46	15.96
Sep	24.14	14.74	61.06	35.15	18.21	51.81	7.59	1.41	18.55	4.24	1.10	25.85
Nov	40.00	12.00	30.00	35.62	18.45	51.80	5.50	0.88	16.04	9.44	1.04	10.99
Dec	23.25	18.56	79.81	36.25	19.44	53.62	15.24	1.13	7.44	3.26	0.79	24.14
Jan	33.93	25.42	74.92	32.55	18.23	56.00	7.46	6.48	86.89	5.61	0.18	3.14
Mar	32.98	16.36	49.61	29.98	22.63	75.48	13.36	2.71	20.28	2.13	0.44	20.66
Apr	34.31	30.09	87.70	29.90	23.86	79.78	14.39	4.18	29.05	2.53	0.49	19.37
May	48.67	15.70	32.26	36.52	22.23	60.87	14.14	2.79	19.73	3.08	0.97	31.49
Jun	27.95	21.24	75.99	34.89	18.45	52.88	11.86	0.71	5.99	2.35	1.02	43.40
Jul	27.31	21.44	78.51	31.03	9.76	31.45	15.49	2.30	14.85	3.65	1.32	36.16
Aug	13.58	12.80	94.26	24.80	12.93	52.14	14.35	1.61	11.22	2.56	0.19	7.42
Sep	6.87	3.69	53.71	28.16	11.29	40.09	26.32	1.69	6.42	4.32	0.87	20.23
Oct	34.26	27.20	79.40	32.22	15.54	48.22	15.26	3.43	22.44	4.25	1.45	34.16
Nov	16.77	15.27	91.04	28.82	8.03	27.86	15.86	1.01	6.39	5.09	1.06	20.82

3.4 Great Sound

Date	Total Pb	Partial Pb	% partial	Total Mn	Partial Mn	% partial	Total Cu	Partial Cu	% partial	Total Ni	Partial Ni	% partial
Jul	13.80	11.82	85.66	22.20	11.50	51.80	3.08	2.77	89.87	1.33	0.50	37.82
Aug	16.95	8.00	47.20	18.31	4.46	24.36	2.15	0.97	45.26	1.21	0.39	32.48
Sep	17.47	10.57	60.50	16.10	7.20	44.69	3.08	1.28	41.66	3.26	0.90	27.70
Nov	10.00	9.60	96.00	10.26	6.76	65.88	2.00	0.81	40.70	0.98	0.60	61.53
Dec	9.99	7.68	76.90	9.36	5.74	61.30	2.97	0.62	20.81	1.13	0.61	54.16
Jan	13.31	9.65	72.50	17.37	15.62	89.90	2.01	0.74	36.57	0.47	0.23	48.72
Mar	11.38	11.02	96.84	22.18	15.20	68.53	5.26	1.13	21.48	0.20	0.10	49.00
Apr	11.67	10.86	93.06	15.05	6.90	45.85	3.41	0.44	12.90	0.10	0.10	100.00
May	9.99	6.20	62.06	12.77	9.71	76.04	2.97	0.93	31.31	0.64	0.23	35.94
Jun	11.21	10.90	97.23	18.74	14.18	75.67	1.50	0.64	42.67	1.22	0.88	71.95
Jul	13.46	12.44	92.42	22.51	22.00	97.73	4.48	0.90	20.09	1.24	0.66	53.23
Aug	7.30	6.31	86.44	15.92	12.28	77.15	6.55	1.25	19.07	1.46	0.30	20.55
Sep	10.96	3.14	28.65	14.86	12.31	82.84	3.58	1.31	36.64	2.01	0.62	31.00
Oct	7.77	6.10	78.52	14.26	9.40	65.94	3.05	1.86	60.82	1.96	0.63	32.19
Nov	7.55	6.96	92.19	6.41	5.80	90.51	3.87	1.04	26.73	1.13	0.55	48.36
Jan	5.58	5.17	92.67	17.87	5.76	32.23	2.47	0.89	36.09	0.59	0.41	70.77

3.5 Outer Hamilton Harbour

Date	Total Pb	Partial Pb	% partial	Total Mn	Partial Mn	% partial	Total Cu	Partial Cu	% partial	Total Ni	Partial Ni	% partial
Jul	90.15	74.02	82.11	35.37	24.58	69.49	51.59	20.22	39.20	3.00	1.33	44.33
Aug	43.43	28.88	66.50	42.33	20.89	49.35	49.83	15.27	30.65	5.87	0.53	8.98
Sep	29.95	24.32	81.20	39.73	20.46	51.50	36.10	8.61	23.84	3.57	1.18	32.94
Nov	46.31	38.55	83.24	60.66	20.54	33.86	43.04	8.51	19.76	7.27	0.81	11.20
Dec	33.26	24.84	74.68	28.65	7.56	26.37	22.55	3.72	16.48	3.26	1.01	30.88
Jan	35.85	21.02	58.63	32.17	21.16	65.76	22.19	12.57	56.65	5.52	1.08	19.55
Mar	54.77	36.76	67.12	31.72	30.17	95.10	37.31	19.09	51.17	3.69	0.45	12.20
Apr	25.03	10.11	40.39	31.48	22.85	72.58	39.14	33.28	85.03	4.66	0.92	19.74
May	28.46	25.92	91.08	21.07	13.41	63.64	19.91	7.47	37.52	1.26	0.77	61.11
Jun	27.56	18.90	68.57	27.04	6.81	25.18	10.30	4.93	47.86	3.86	0.67	17.36
Aug	20.70	18.36	88.70	28.23	13.69	48.49	69.76	18.21	26.10	4.77	0.91	19.08
Sep	10.24	6.18	60.35	30.06	11.76	39.12	5.84	5.09	87.13	3.50	1.00	28.63
Oct	44.53	40.22	90.32	23.55	5.81	24.66	32.16	17.09	53.13	2.95	1.97	66.61
Nov	30.29	29.47	97.31	11.29	5.00	44.29	30.91	10.29	33.29	3.00	1.54	51.23
Jan	98.02	94.20	96.10	29.80	28.30	94.97	71.88	18.37	25.56	5.49	0.78	14.22

3.6 Inner Hamilton Harbour

Date	Total Pb	Partial Pb	% partial	Total Mn	Partial Mn	% partial	Total Cu	Partial Cu	% partial	Total Ni	Partial Ni	% partial
Jul	85.92	53.40	62.15	32.51	30.10	92.59	34.62	3.37	9.72	4.61	0.66	14.23
Aug	37.47	20.45	54.57	37.76	38.12	100.95	38.90	4.26	10.96	4.76	0.18	3.70
Sep	28.17	25.00	88.75	23.18	10.39	44.82	11.56	3.34	28.89	1.99	0.51	25.83
Nov	26.80	20.36	75.97	58.62	8.54	14.57	7.51	0.74	9.80	1.77	0.56	31.53
Dec	44.24	37.63	85.07	23.26	17.57	75.57		1.64			0.57	
Jan	19.40	20.01	103.14	12.18	5.26	43.15	16.40	6.43	39.20	2.35	0.48	20.34
Mar	27.44	25.31	92.24	24.17	21.84	90.37	13.83	11.75	84.96	0.43	0.40	93.02
Apr	7.71	2.83	36.71	34.85	26.98	77.42	31.15	4.47	14.35	2.80	1.43	51.07
May	15.55	14.10	90.68	34.17	15.71	45.98	13.43	3.16	23.53	1.55	0.43	27.74
Jun	56.82	52.03	91.57	20.43	16.98	83.11	19.24	14.58	75.78	1.12	1.21	108.04
Jul	51.68	47.53	91.97	30.55			30.39	6.14	20.20	4.30	0.61	14.19
Aug	37.13	28.36	76.38	41.02	8.94	21.79	23.08	5.65	24.49	5.90	0.58	9.83
Sep	9.52	6.18	64.92	41.00	14.90	36.34	70.31	6.86	9.76	5.24		0.00
Oct	35.56	30.05	84.51	28.56	9.20	32.19		2.27			1.52	
Nov	49.78	5.67	11.39	10.57	11.52	108.96	33.74	2.83	8.39	4.51	1.10	24.32
Jan	87.16	67.46	77.39	31.25	27.09	86.69	39.24	4.59	11.69	3.43	0.65	18.90

3.7 Inner North Lagoon

Date	Total Pb	Partial Pb	% partial	Total Mn	Partial Mn	% partial	Total Cu	Partial Cu	% partial	Total Ni	Partial Ni	% partial
Jul	4.01	2.71	67.58	3.60	2.12	58.89	1.31	0.88	66.95	0.49	0.43	87.76
Aug	3.23	2.60	80.50	3.66	3.82	104.37	0.22	0.21	95.45	0.36	0.00	0.00
Sep	1.90	1.68	88.42	1.90	1.61	84.47	0.00	0.43		2.99	0.00	0.00
Nov	1.66	1.57	94.58	2.76	1.88	68.22	0.40	0.10	25.75	0.00	0.27	
Dec	0.97	0.86	88.75		1.42			0.20			0.00	
Mar	1.34	1.29	96.27	0.52	0.49	94.23	0.16	0.17	106.25	0.00	0.00	
Apr	4.36	3.62	83.03	6.66	2.55	38.33	0.82	0.17	20.73	0.23	0.25	108.70
May	1.41	1.30	92.20	0.42	0.46	109.52	0.14	0.18	128.57	0.00	0.35	
Jun	6.57	5.20	79.15	8.10	3.44	42.47	1.63	0.58	35.58	1.24	1.20	96.77
Jul	4.65	4.36	93.76	4.05	5.35	132.10	0.89	0.40	44.94	0.00	0.23	
Aug	1.15	1.05	91.30	2.04	1.08	52.94	0.80	0.19	23.75	0.10	0.10	100.00
Sep	0.00	0.00		2.04		0.00	0.80	0.00	0.00	0.00		
Oct	2.00	1.91	95.30		0.12			2.73			0.86	
Nov	1.52	1.47	96.71	0.00	0.00		0.88	0.55	62.33	0.61	0.59	96.38
Jan	0.35	0.18	49.72	2.86	1.91	66.78	0.93	0.52	56.48	0.35	0.26	72.73

3.8 Outer North Lagoon

Date	Total Pb	Partial Pb	% partial	Total Mn	Partial Mn	% partial	Total Cu	Partial Cu	% partial	Total Ni	Partial Ni	% partial
Jul	1.33	1.11	83.46	4.76	3.24	68.07	0.22	0.27	122.27	0.35	0.25	70.57
Aug	0.90	0.73	81.11	3.15	1.19	37.78	0.03	0.04	133.33	0.21	0.00	0.00
Sep	0.00	0.06		1.12	1.13	100.89	0.00	2.87		0.87	0.00	0.00
Nov	0.25	0.10	40.00	2.97	2.23	74.92	0.29	0.20	68.97	0.00	0.10	
Dec		0.00			1.97			0.03			0.00	
Jan	0.01	0.00	0.00	1.84	1.45	78.64	0.15	0.40	266.67	0.00	0.10	
Mar	0.05	0.00	0.00	1.23	1.15	93.50	0.00	0.05		0.00	0.00	
Apr	0.00	0.00		5.99	5.41	90.38	0.00	0.00		0.14	0.15	107.14
Jun	3.50	2.20	62.86	3.50	0.94	26.86	1.30	0.30	23.08	0.00	1.08	
Jul	0.29	0.25	86.21	2.40	3.18	132.50	1.07	0.23	21.50	0.00	0.26	
Aug		0.05		4.52	3.03	67.04	0.60	0.17	28.33	0.09	0.00	0.00
Oct		0.95			0.06			2.85			0.19	
Nov	0.62	0.53	84.94	0.00	0.00		1.91	1.89	99.06	0.37	0.00	0.00

Appendix 4 Data set for chromium in the Sargasso sea

4.1 November 1994

Depth (m)	Cr (VI) nmol l^{-1}	s.d Cr (VI) nmol l^{-1}	Total Cr nmol l^{-1}	s.d. Cr nmol l^{-1}	Cr (III) nmol l^{-1}	s.d. Cr (III) nmol l^{-1}	Temp °C	Salinity	O_2 µmol kg^{-1}	O_2 Anom µmol kg^{-1}	NO_3 µmol kg^{-1}	NO_2 µmol kg^{-1}	PO_4 µmol kg^{-1}	SiO_4 µmol kg^{-1}
1	2.30	0.17	3.00	0.22	0.70	0.04	22.30	36.66	215.24	6.80	0.00	0.00	0.00	0.99
10	2.70	0.33	3.00	0.37	0.30	0.04	22.31	36.66	215.81	7.38	0.00	0.00	0.16	0.97
25	2.80	0.41	3.40	0.50	0.60	0.18	22.31	36.67	215.59	7.17	0.00	0.00	0.56	0.96
50	2.20	0.23	2.90	0.30	0.70	0.12	22.31	36.67	215.72	7.30	0.00	0.00	0.05	0.94
75	2.60	0.06	4.20	0.10	1.60	0.22	22.30	36.67	215.89	7.43	0.00	0.00	0.00	0.97
100	3.10	0.05	2.90	0.05	0.20	0.00	20.08	36.58	234.67	17.81	0.09	0.00	0.00	1.07
150	3.10	0.22	2.80	0.20	0.30	0.02	18.47	36.55	199.20	-24.11	0.72	0.00	0.00	1.29
200	2.60	0.17	3.00	0.20	0.40	0.05	18.24	36.54	198.24	-26.05	1.50	0.00	0.00	1.39
250	2.70	0.33	2.90	0.35	0.20	0.03	18.02	36.52	200.40	-24.82	2.52	0.00	0.06	1.44
300	3.10	0.38	3.00	0.37	0.10	0.00	17.81	36.49	199.70	-26.46	2.85	0.00	0.08	1.61
350	1.90	0.09	3.00	0.15	1.10	0.01	17.53	36.44	197.83	-29.65				
400	1.90	0.20	3.80	0.40	1.90	0.23	17.06	36.35	192.12	-37.52	4.95	0.00	0.59	2.37
500	1.80	0.14	4.00	0.30	2.20	0.68	15.67	36.11	183.78	-52.46	8.83	0.00	0.56	3.64
600	2.50	0.16	5.60	0.35	3.10	0.43					12.85	0.00	0.67	5.96
700	2.30	0.40	3.70	0.64	1.40	0.08	11.73	35.52	159.02	-97.91	17.48	0.00	1.08	9.58
800	2.40	0.03	4.10	0.05	1.70	0.23	9.62	35.27	159.34	-109.88	22.21	0.00	1.39	14.11
900	2.60	0.55	3.30	0.70	0.70	0.00	7.73	35.14	170.52	-110.59	22.40	0.00	1.46	15.26
1000	2.60	0.44	3.70	0.63	1.10	0.02	6.56	35.12	196.36	-92.38	21.31	0.00	1.41	15.31
1200	3.10	0.14	4.40	0.20	1.30	0.03	5.27	35.08	231.49	-66.24	19.46	0.00	1.28	14.48
1400	2.70	0.15	4.00	0.22	1.30	0.11	4.37	35.00	252.64	-51.78				
1600	2.40	0.33	4.50	0.61	2.10	0.58	4.03	34.98	259.76	-47.22	17.89	0.00	1.21	13.88
2000	2.60	0.12	4.40	0.20	1.80	0.04	3.76	34.99	259.23	-49.77	18.17	0.00	1.22	16.80
2200	2.30	0.41	2.30	0.41			3.53	34.97	260.10	-50.72	18.60	0.00	1.19	19.74
2600	2.60	0.47	2.60	0.47			3.10	34.95	261.22	-52.92	18.56	0.00	1.27	23.40

4.2 January 1995

Depth (m)	Cr (VI) nmol l^{-1}	s.d Cr (VI) nmol l^{-1}	Total Cr nmol l^{-1}	s.d. Cr nmol l^{-1}	Cr (III) nmol l^{-1}	s.d. Cr (III) nmol l^{-1}	Temp ℃	Salinity	O_2 µmol kg^{-1}	O_2 Anom µmol kg^{-1}	NO_3 µmol kg^{-1}	NO_2 µmol kg^{-1}	PO_4 µmol kg^{-1}	SiO_4 µmol kg^{-1}
1	1.70	0.07	2.50	0.11	0.80	0.13	20.75	36.65	220.20	6.02	0.00	0.00	0.04	0.83
10	1.70	0.37	2.70	0.60	1.00	0.15	20.68	36.64	220.33	6.23	0.00	0.00	0.05	0.82
25	1.70	0.28	2.40	1.40	0.70		20.66	36.64	220.55	6.13	0.00	0.00	0.00	0.81
50					1.00	0.03	20.58	36.62	221.11	6.36	0.00	0.00	0.00	0.78
75	2.80	0.10	3.80	0.14	1.00	0.03	20.51	36.60	221.46	6.15	0.00	0.00	0.00	0.77
100	2.20	0.12	3.00	0.16	0.80	0.03	20.16	36.60	218.22	1.41	0.00	0.03	0.05	0.75
150	1.60	0.07	2.90	0.12	1.30	0.09	18.75	36.58	200.30	-21.69	2.87	0.05	0.08	1.28
200	2.30	0.32	3.30	0.46	1.00	0.09	18.40	36.56	203.99	-19.43	3.14	0.04	0.13	1.38
250	1.20	0.01	1.90	0.02	0.70	0.07	18.19	36.54	207.55	-17.27	3.61	0.05	0.17	1.48
300	1.50	0.02	2.40	0.03	0.90	0.16	18.00	36.52	207.23	-17.64				
350	2.40	0.01	3.10	0.01	0.70	0.19	17.84	36.50	203.36	-20.93				
400	1.10	0.09	2.00	0.16	0.90	0.06	17.40	36.41	197.39	-30.31	5.90	0.05	0.31	2.31
500	2.00	0.08	2.70	0.11	0.70	0.09	16.26	36.21	186.88	-46.54	9.69	0.05	0.54	3.71
600	1.90	0.01	2.90	0.02	1.00	0.30	14.52	35.92	177.11	-64.50	13.93	0.05	0.81	6.01
700	2.10	0.06	2.80	0.08	0.70	0.06	12.38	35.60	165.20	-88.08	18.88	0.00	1.26	10.62
800	3.70	0.38	4.90	0.50	1.20	0.00	10.14	35.31	149.13	-116.90	21.52	0.00	1.46	13.82
900	2.80	0.30	3.60	0.38	0.80	0.07	8.21	35.14	160.88	-117.10	21.04	0.00	1.49	15.26
1000	1.70	0.14	2.50	0.21	0.80	0.13	6.68	35.13	196.75	-91.01	19.80	0.00	1.39	14.63
1200	1.60	0.17	2.40	0.26	0.80	0.01	5.37	35.08	228.97	-67.84	16.90	0.00	1.20	14.05
1400					1.20	0.14	4.41	35.00	253.86	-50.78	16.97	0.00	1.18	13.46
1600	2.00	0.27	2.80	0.38	0.80	0.06	4.10	34.98	259.94	-45.77	17.20	0.00	1.22	13.61
2000	1.50	0.05	3.00	0.09	1.50	0.06	3.90	35.01	255.58	-52.27	17.26	0.00	1.25	16.41
2200	1.60	0.01	2.80	0.01	1.20	0.05	3.63	34.99	257.23	-52.33	17.66	0.00	1.31	19.61
2600	1.70	0.14	3.00	0.25	1.30	0.08	3.19	34.96	260.83	-52.70	17.68	0.00	1.33	22.97

4.3 June 1995

Depth (m)	Cr (VI) nmol l^{-1}	s.d Cr (VI) nmol l^{-1}	Total Cr nmol l^{-1}	s.d. Cr nmol l^{-1}	Cr (III) nmol l^{-1}	s.d. Cr (III) nmol l^{-1}	Temp °C	Salinity	O_2 µmol kg^{-1}	O_2 Anom µmol kg^{-1}	NO_3 µmol kg^{-1}	NO_2 µmol kg^{-1}	PO_4 µmol kg^{-1}	SiO_4 µmol kg^{-1}
1	2.74	0.15	3.64	0.20	0.90	0.30	25.03	36.29	211.33	11.66	0.00	0.00	0.08	0.79
10	2.65	0.35	3.75	0.50	1.10	0.30	23.75	36.30	213.47	9.55	0.00	0.00	0.00	0.77
25	4.15	0.40	5.25	0.50	1.10	0.10	22.67	36.49	219.74	12.32	0.00	0.00	0.15	0.74
50	3.42	0.22	4.62	0.30	1.20	0.20	20.64	36.58	228.26	13.56	0.00	0.00	0.00	0.70
75	3.64	0.55	4.74	0.20	1.10	0.10	19.65	36.59	228.25	9.71	0.00	0.00	0.00	0.67
100	5.40	0.42	6.30	0.50	0.90	0.10	18.99	36.58	218.59	-2.57	0.47	0.09	0.00	0.78
150	5.60	0.43	6.50	0.50	0.90	0.20	18.41	36.56	210.08	-13.46	1.45	0.00	0.06	0.98
200	2.30	0.21	3.30	0.30	1.00	0.10	18.18	36.54	203.63	-20.93	1.91	0.00	0.09	1.16
250	1.60	0.47	2.70	0.80	1.10	0.10	17.96	36.51	200.40	-25.12	2.34	0.00	0.10	1.28
300	2.10	0.56	3.00	0.80	0.90	0.10	17.76	36.48	196.44	-29.98	3.59	0.00	0.21	1.24
350	2.21	0.60	3.31	0.90	1.10	0.20	17.64	36.46	195.65	-31.32				
400	3.60	0.24	4.50	0.30	0.90	0.10	17.45	36.42	193.21	-34.60	4.67	0.00	0.24	1.76
500	2.20	0.13	3.40	0.20	1.20	0.20	16.09	36.18	180.09	-54.12	7.64	0.00	0.46	2.62
600	3.20	0.07	4.70	0.10	1.50	0.30	14.28	35.88	170.01	-73.18	11.67	0.00	0.68	4.57
700	3.30	0.13	4.90	0.20	1.60	0.20	11.83	35.53	154.93	-101.39	15.69	0.00	1.19	7.20
800	2.70	0.13	4.30	0.20	1.60	0.20	9.74	35.28	153.38	-115.17	19.43	0.00	1.45	12.00
900	2.50	0.51	3.40	0.70	0.90	0.10	8.07	35.15	165.92	-112.98	23.23	0.00	1.66	14.69
1000	3.00	0.38	3.90	0.50	0.90	0.10	6.68	35.11	193.23	-94.76	22.18	0.00	1.56	14.67
1200	2.40	0.12	3.10	0.15	0.70	0.10	5.30	35.07	228.14	-69.39	20.24	0.00	1.38	14.14
1400	2.40	0.17	3.50	0.25	1.10	0.20	4.61	35.03	246.30	-56.25	18.03	0.00	1.34	13.28
1600	2.60	0.26	3.80	0.40	1.20	0.20	4.20	35.01	254.46	-51.17	18.25	0.00	1.24	13.75
2000			3.90	0.20			3.71	34.99	258.14	-51.19	18.25	0.00	1.28	15.64
2200			4.30	0.30			3.51	34.98	257.75	-53.19	18.30	0.00	1.33	17.57
2600	3.60	0.16	4.50	0.20	0.90	0.10	3.07	34.95	260.18	-54.17	18.69	0.00	1.49	21.70

4.4 September 1995

Depth (m)	Cr (VI) nmol l^{-1}	s.d Cr (VI) nmol l^{-1}	Total Cr nmol l^{-1}	s.d. Cr nmol l^{-1}	Cr (III) nmol l^{-1}	s.d. Cr (III) nmol l^{-1}	Temp °C	Salinity	O_2 µM	O_2 Anom µmol kg^{-1}	NO_3 µmol kg^{-1}	NO_2 µmol kg^{-1}	PO_4 µmol kg^{-1}	SiO_4 µmol kg^{-1}
1	3.32	0.23	4.30	0.30	1.00	0.20	27.01	36.54	201.34	8.31	0.00	0.00	0.00	0.20
10	0.10	0.01	2.10	0.10	2.00	0.40	26.77	36.54	201.41	7.64	0.00	0.00	0.00	0.18
25	0.70	0.30	2.30	0.30	1.60	0.20	26.74	36.58	201.93	8.12	0.00	0.00	0.00	0.19
50	1.80	0.30	3.50	0.60	1.70	0.30	25.06	36.60	214.94	15.85	0.00	0.00	0.00	0.20
75	3.24	0.27	4.80	0.40	1.60	0.30	21.14	36.59	233.08	20.26	0.00	0.00	0.00	0.12
100	3.65	0.17	4.30	0.20	0.70	0.05	19.75	36.60	220.37	2.25	1.88	0.08	0.07	0.64
150	2.50	0.18	2.80	0.20	0.30	0.04	18.77	36.59	208.57	-13.48	1.94	0.01	0.07	0.54
200	0.80	0.13	2.50	0.40	1.70	0.06	18.52	36.58	210.78	-12.29	2.27	0.01	0.09	0.58
250	1.20	0.21	2.80	0.50	1.60	0.26	18.45	36.57	212.04	-11.35	2.39	0.01	0.11	0.72
300	1.70	0.20	2.50	0.30	0.80	0.01	18.37	36.56	211.68	-12.05	2.69	0.01	0.12	0.76
350	1.70	0.18	3.80	0.40	2.10	0.33	18.26	36.55	209.81	-14.39				
400	2.00	0.14	2.90	0.20	0.90	0.04	18.16	36.53	209.28	-15.37	4.84	0.00	0.23	1.38
500	3.30	0.42	5.50	0.70	2.20	0.23	17.69	36.45	194.87	-31.85	7.63	0.00	0.40	2.35
600	0.40	0.02	2.30	0.10	1.90	0.05	16.25	36.20	182.18	-51.25	11.77	0.00	0.66	4.09
700	3.40	0.01	3.60	0.01	0.20	0.01	14.53	35.92	172.54	-69.37	16.14	0.00	0.99	7.02
800	4.20	0.21	5.90	0.30	1.70	0.24	12.02	35.54	149.24	-106.04	17.94	0.00	1.21	10.02
900	2.35	0.31	3.80	0.50	1.45	0.09	9.85	35.30	159.86	-107.98	19.31	0.00	1.31	12.89
1000	2.60	0.19	4.10	0.35	1.50	0.07	8.21	35.18	169.49	-108.52	19.56	0.00	1.41	14.23
1200							5.83	35.10	214.77		19.09	0.00	1.35	13.33
1400							4.94	35.07	239.26		18.29	0.00	1.28	13.19
1600	2.20	0.15	3.05	0.20	0.85	0.03	4.38	35.02	252.64	-51.67	17.77	0.00	1.25	13.06
2000	1.50	0.08	2.00	0.10	0.50	0.02	3.88	35.00	260.23	-47.84	17.61	0.00	1.24	14.71
2200	1.75	0.07	2.65	0.10	0.90	0.02	3.73	35.00	255.32	-53.88	17.79	0.00	1.26	16.91
2600	1.15	0.26	1.80	0.40	0.65	0.01	3.22	34.96	260.18	-53.03	16.82	0.00	1.18	20.49

4.5 March 1996 Bloom Cruise

Depth (m)	Cr (VI) nmol l^{-1}	s.d Cr (VI)	Total Cr nmol l^{-1}	s.d. Cr nmol l^{-1}	Cr (III) nmol l^{-1}	s.d. Cr (III) nmol l^{-1}	Temp °C	Salinity	O_2 µmol kg^{-1}	O_2 Anom µmol kg^{-1}	NO_3 µmol kg^{-1}	NO_2 µmol kg^{-1}	PO_4 µmol kg^{-1}	SiO_4 µmol kg^{-1}
1	2.08	0.21	4.30	0.44	2.22	0.56	19.25	36.73	221.70	1.90	0.00	0.00	0.00	0.74
10	1.73	0.18	4.27	0.44	2.54	0.14	19.30	36.73	221.57	1.88	0.00	0.00	0.00	0.74
25	1.65	0.29	4.39	0.78	2.73	0.11	19.30	36.73	221.57	1.87	0.00	0.00	0.00	0.76
50	1.55	0.10	3.87	0.24	2.32	0.15	19.28	36.73	221.35	1.60	0.05	0.01	0.00	0.75
75	1.64	0.21	4.51	0.59	2.87	0.13	19.28	36.72	220.91	1.13	0.05	0.01	0.00	0.78
100	2.01	0.36	4.04	0.73	2.03	0.83	19.23	36.72	228.57	8.61	0.04	0.01	0.00	0.77
150	4.42	0.66	8.96	1.33	4.54	0.03	18.73	36.62	216.64	-5.51	0.19	0.04	0.00	0.76
250	2.81	0.86	4.60	1.42	1.79	0.20	18.25	36.55	206.24	-17.98	0.75	0.02	0.02	0.82
300	0.76	0.09	3.01	0.36	2.25	0.05	17.99	36.51	202.28	-23.10	0.93	0.04	0.03	0.85
350	0.87	0.13	1.97	0.30	1.10	0.00	17.58	36.44	192.05	-35.19	0.94	0.07	0.03	0.84
400	1.48	0.20	2.39	0.33	0.90	0.05	16.80	36.30	186.64	-44.21	1.34	0.02	0.04	0.90
600	1.62	0.05	2.31	0.08	0.69	0.00	13.64	35.79	168.44	-78.06	2.30	0.01	0.09	1.10
1000	0.23	0.03	1.68	0.20	1.45	0.01	6.68	35.15	202.96	-84.94	8.83	0.00	0.56	3.64

REFERENCES

Abu-Saba, K.E. and A.R. Flegal. (1995) Chromium in San Francisco Bay: Superposition of geochemical processes causes complex spatial distributions of redox species. *Marine Chemistry* 49: 189-199.

Achterberg, E.P. and C.M.G. Van Den Berg. (1994) Automated Voltametric system for shipboard determination of metal speciation in sea water. *Analytica Chimica Acta* 284: 463-471.

Achterberg, E.P. and C.M.G. Van Den Berg. (1996) Automated monitoring of Ni, Cu and Zn in the Irish Sea. *Marine Pollution Bulletin* 32: 471-479.

Alldredge, A.L., C.C. Gotschalk, and S. MacIntyre. (1987) Evidence for sustained residence of macrocrustacean fecal pellets in surface waters off Southern California. *Deep-Sea Research* 34: 1641-1652.

Altabet, M.A. and W.G. Deuser. (1985) Seasonal variations in the natural abundance of ^{15}N in particles sinking to the deep Sargasso Sea. *Nature* 315: 218-219.

Amdurer, M., D.M. Adler, and P.H. Santschi. (1982) Radiotracer studies of trace metal behaviour in mesocosms: advantages and limitations. In *Marine mesocosms, biological and chemical research in experimental ecosystems*, ed. G.D. Grice and M.R. Reeve. 81-96. New York: Springer Verlag.

Backstrum, K. and L. Danielsson. (1990) A mechanised continuous flow system for the concentration and determination of Co, Cu, Ni, Pb, Cd and Fe in seawater using graphite furnace atomic absorption. *Marine Chemistry* 29: 33-46.

Bacon, M.P. and R.F. Anderson. (1982) Distribution of thorium isotopes between dissolved and particulate forms in the deep sea. *Journal of Geophysical Research* 87: 2045-2056.

Baffi, F., A.M. Cardinale, and R. Bruzzone. (1992) Pre-concentration of chromium, copper and manganese from seawater on pre-treated solid materials for determination by AAS. *Analytica Chimica Acta* 270 (1): 79-86.

Balistrieri, L., P.G. Brewer, and J.W. Murray. (1981) Scavenging residence times of trace metals and surface chemistry of sinking particles in the deep ocean. *Deep Sea Research* 28A: 101-121.

Balls, P.W. (1988) The control of trace metal concentrations in coastal seawater through partitioning onto suspended particulate matter. *Netherlands Journal of Sea Research* 22: 213-218.

Balls, P.W. (1989) Trend monitoring of dissolved trace metals in coastal seawater. A waste of effort? *Marine Pollution Bulletin* 20: 546-548.

Balls, P.W. (1990) Distribution and composition of suspended particulate material in the Clyde estuary and associated sea locks. *Estuarine, Coastal and Shelf Science* 30: 475-487.

Balls, P.W. and G. Topping. (1987) The influence of inputs to the Firth of Forth on the concentrations of trace metals in coastal waters. *Environmental Pollution* 45: 159-172.

Balzer, W. and G. Wefer. (1981) Dissolution of carbonate minerals in a subtropical shallow marine environment. *Marine Chemistry* 10: 545-558.

Barbeau, K. and R. Wollast. (1994) microautoradiography (with combined liquid scintillation) applied to the study of trace metal uptake by suspended particles: Initial results using ^{63}Ni as a tracer. *Limnology and oceanography* 39 (5): 1211-1222.

Barnes, J.A. and B. Von. Bodungen. (1978) The Bermuda Marine Environment. Vol. 2. Special Publication 17. Bermuda Biological Station.

Bates, N.R. (1995) Investigation of the physical and biological controls of the oceanic CO_2 system in the Sargasso Sea. Ph.D. Thesis, Southampton.

Battison, G.A., R. Gerbasi, S. Degetto, and G. Sbrignadello. (1993) Heavy metal speciation in coastal sediments using total-reflection X-ray fluorescence spectrometry. *Spectrochimica Acta* 48B: 217-221.

Buat-Menard, P. and R. Chesselet. (1979) Variable influence of the atmospheric flux on the trace metal chemistry of oceanic suspended matter. *Earth and Planetary Science Letters.* 42: 399-411.

Benoit, G., S.D. Oktay-Marshall, A. Cantu, E.M. Hood, C.H. Coleman, M.O. Corapcioglu, and P.H. Santschi. (1994) Partitioning between filter-retained particles, colloids and solution in six Texas estuaries. *Marine Chemistry* 45: 307-336.

Berner, R.A. (1971) Principles of chemical sedimentology. New York: McGraw Hill.

Bigelow, H.B. (1905) The shoal-water deposits of the Bermuda banks. *Proceedings American Academy Arts and Science.* 40: 557-592.

Blain, S., P. Appriou, and H. Handel. (1991) Column preconcentration of trace metals from seawater with macroporous resins impregnated with lipophilic tetraaza macrocycles. *Analyst* 116: 815-820.

Bodungen, B.V., T.D. Jickells, S.R. Smith, J.A.D. Ward, and G.B. Hillier. (1982) The Bermuda Marine Environment: Vol. 3. Vol. 18. B.B.S.R. Special publication,

Boothman, W.S. *Characterization of trace metal association with polluted marine sediments by selective extractions.* American Society for Testing and Materials, 1988. p 81-92 STP 976.

Borg, H. and P. Jonsson. (1996) Large scale metal distribution in Baltic Sea sediments. *Marine Pollution Bulletin* 32: 8-21.

Boulegue, J. (1983) Trace metals (Fe, Cu, Zn and Cd) in anoxic environments. In *Trace metals in seawater*, 563-579 ed. C.S. Wong, E. Boyle, K. W. Bruland, J.D. Burton, and E.D. Goldberg. Plenum Press.

Boussemart, M. and C.M.G. Van Den. Berg. (1994) Preconcentration of Chromium (III) from sea-water by adsorption on silica and voltammetric determination. *Analyst* 119: 1349-1353.

Boussemart, M., C.M.G. Van Den Berg, and M. Ghaddaf. (1992) The determination of Chromium speciation in seawater using cathodic stripping voltammetry. *Analytica Chimica Acta* 262: 103-115.

Boyle, E.A., F. Sclater and J.M. Edmond. (1976) On the marine geochemistry of cadmium. Nature 263: 42-44.

Boyle, E. and S. Huested. (1983) Aspects of the surface distributions of Cu, Ni, Cd, and Pb in the N. Atlantic and N Pacific. In *Trace metals in seawater*, ed. C.S. Wong, E. Boyle, K. W. Bruland, J.D. Burton, and E.D. Goldberg. Plenum Press.

Boyle, E.A., S.D. Chapnick, G.T. Shen, and M.P. Bacon. (1986) Temporal variability of lead in the western north atlantic. *Journal of Geophysical Research* 91: 8573-8593.

Boyle, E.A. and J.M. Edmond. (1977) Determination of Cu, Ni and Cd in seawater by APDC chelate coprecipitation and flameless Atomic Absorption Spectroscopy. *Analytica Chimica Acta* 91 (2): 189-197.

Boyle, E.A., S.S. Huested, and S.P. Jones. (1981) On the distribution of Cu, Ni, Cd in the surface waters of the North Atlantic and North Pacific Ocean. *Journal of geophysical research.* 86 (C9): 8048-8066.

Breck, W.G. (1974) Redox levels in the sea. In *The Sea*, 895. Vol 5. Wiley-Interscience. New York.

Broecker, W.S. and T.H. Peng. (1982) Tracers in the Sea. Lamont-Doherty Geological Observatory. Edigio Press.

Bruegmann, L., L.G. Danielsson, B. Magnusson, and S. Westerlund. (1985) Lead in the North Sea and North East Atlantic ocean. *Marine Chemistry* 16: 47-60.

Bruland, K.W. (1983) Oceanographic distributions of Cadmium, zinc, nickel and copper in the North Pacific. *Earth and Planetary Science Letters* 47: 176-198.

Bruland, K.W., J.R. Donat, and D.A. Hutchins. (1991) Interactive influences if bioactive trace metals on biological production in oceanic waters. *Limnology and Oceanography* 36: 1555-1577.

Bruland, K.W. and R.P. Franks. (1983) Mn, Ni, Cu, Zn and Cd in the Western north atlantic In *Trace metals in seawater*, ed. C.S. Wong, E. Boyle, K. W. Bruland, J.D. Burton, and E.D. Goldberg. Plenum Press.

Bruland, K.W., R.P. Franks, G.A. Knauer, and J.H. Martin. (1979) Sampling and analytical methods fro the determination of Cu, Cd, Zn and Ni at the nanogram per litre level in seawater. *Analytica Chimica Acta* 105: 233-245.

Bruland, K.W. and M.W. Silver. (1981) Sinking rates of fecal pellets from gelatinous zooplankton (Salps, Pteropods, Doliolids). *Marine Biology* 63: 295-300.

Bryan, G.W. (1976) Heavy metal contamination in the sea. In *Marine Pollution*, ed. R. Johnston. 185-290. New York: Academic Press.

Buessler, K.O., A.F. Michaels, D.A. Siegel, and A.H. Knap. (1994) Three dimensional time-dependent approach to calibrating sediment trap fluxes. *Global Geochemical Cycles* 8: 179-193.

Burns, K.A., M.G. Ehrhardt, J. MacPherson, J.A. Tierney, G. Kananen, and D. Connelly. (1990) Organic and trace metal contaminants in sediments, seawater and organisms from two Bermudan harbours. *Journal of Experimental Marine Biology and Ecology* 138: 9-34.

Burton, J.D., M. Althaus, G.E. Millward, A.W. Morris, P.J. Statham, A.D. Tappin, and A. Turner. (1993) Processes influencing the fate of trace metals in the North Sea. *Philosophical Transactions of the Royal Society of London.* 343 (A): 557-568.

Burton, J.D., W.A. Maher, and P.J. Statham. (1983) Some recent measurements of trace metals in atlantic ocean waters. In *Trace metals in seawater*, ed. C.S. Wong, E. Boyle, K. W. Bruland, J.D. Burton, and E.D. Goldberg. Plenum press.

Burton, J.D. and P.J. Statham. (1986) Trace metals in Seawater. In *Heavy metals in the marine environment.*, ed. R. Furness and P. Rainbow. Boca Raton, Florida: CRC Press.

Calmono, W., W. Ahlf, and J-C. Bening. (1992) Chemical mobility and bioavailability of sediment-bound heavy metals influenced by salinity. *Hydrobiologia* 235/236: 605-610.

Campbell, J.A. and P.A. Yeats. (1981) Dissolved chromium in the NW Atlantic Ocean. *Earth and Planetary Science letters.* 53: 427-433.

Campbell, J.A. and P.A. Yeats. (1984) Dissolved chromium in the St. Lawrence estuary. *Estuarine and Coastal Shelf Science* 19: 513-522.

Carpenter, E.J. (1983) Physiology and ecology of marine planktonic Oscillataria (Trichodesmium). *Marine Biology Letters* 4: 69-85.

Charlet, L. and A. Manceau. (1992) In Situ Characterization of Heavy Metal Surface Reactions - The Chromium Case. *International Journal of Environmental Analytical Chemistry* 46: 97-108.

Cherry, R.D., J.J.W. Higgo, and S.W. Fowler. (1978) Zooplankton fecal pellets and element residence times in the ocean. *Nature* 274 (5668): 246-248.

Chester, R. (1990) Marine Geochemistry. London: Unwin Hyman.

Chester, R., A. Thomas, F.J. Lin, A.S. Basaham and G. Jacinto. (1988) The solid state speciation of copper in surface water particulates and oceanic sediments. *Marine Chemistry* 24: 261-292.

Chester, R., A.S. Berry, and K.J.T. Murphy. (1991) The distributions of atmospheric trace metals and mineral aerosols over the Indian Ocean. *Marine Chemistry* 34: 261-290.

Chester, R. and M.J Hughes. (1967) A chemical technique for the separation of ferro-manganese minerals, carbonate minerals and adsorbed trace elements from pelagic sediments. *Chemical Geology* 2: 249-262.

Chester, R. and K.J.T. Murphy. (1988) Metals in the marine atmosphere. In *Heavy metals in the marine environment.*, ed. R. Furness and P. Rainbow. Boca Raton, Florida: CRC Press.

Cheucas, L. and J.P. Riley. (1966) The spectrophotometric determination of Chromium in seawater. *Analytica Chimica Acta* 35: 240-246.

Ciceri, G. , S. Maran, W. Martinotti, and G. Queriazza. (1992) Geochemical cycling of heavy metals in a marine coastal area: benthic flux determination from pore water profiles and in situ measurements using benthic chambers. *Hydrobiologia* 235/236: 501-517.

Clegg, S.L. and M. Whitfield. (1990) A generalised model for the scavenging of trace metals in the open ocean. 1. Particle cycling. *Deep Sea Research.* 37: 809-832.

Clegg, S.L. and M. Whitfield. (1991) A generalised model for the scavenging of trace metals in the open ocean 2. Particle cycling. *Deep Sea Research* 38: 91-120.

Corliss, J.B., J. Dymond, L.I. Gordon, J.M. Edmond, R.P. Von Herzen, R.D. Ballard, E. Green, D. Williams, A. Bainbridge, K. Crane, and T.M. Van Andel. (1979) Submarine thermal springs on the Galapagos rise. *Science* 203 (4385): 1073-1083.

Cornell, S., A. Rendell, and T.D. Jickells. (1995) Atmospheric inputs of dissolved organic nitrogen to the oceans. *Nature* 376 (6537): 243-246.

Cranston, R.E. (1983) Chromium in Cascadia basin, Northeast Pacific ocean. *Marine Chemistry* 13: 109-125.

Cranston, R.E. and J.W. Murray. (1978) The determination of Cr species in natural waters. *Analytica Chimica Acta* 99: 275-282.

Crecelius, E.A. (1980) The solubility of coal fly ash and marine aerosols in sea water. *Marine Chemistry* 8: 245-250.

Cross, F.A. and W.G. Sunda. (1985) The relationship between chemical speciation and bioavailability of trace metals to marine organisms: A review. In *International symposium on utilization of coastal ecosystem planning, pollution and production in* edited by N. Labish-Chao and W. Kirby-Smith, 169-182. Publisher: NOAA.

Cutter, G.A. (1992) Kinetic controls on metalloid speciation in seawater. *Marine Chemistry* 40: 65-80.

Cutter, G.A. and C.F. Krahforst. (1988) Sulphide in surface waters of the Western Atlantic Ocean. *Geophysical Research letters* 15: 1393-1396.

Davis, R.A. Jr. (1973) Principles of Oceanography. London: Addison-Wesley Publishing Co.

De Baar, J.W., P.M. Saager, R.F. Nolting, and J. Van Der. Meer. (1994) Cadmium versus phosphate in the world ocean. *Marine Chemistry* 46: 261-281.

De Jong, G.J. and U.A. Brinkman. (1978) Determination of Cr (III) and Cr (VI) in seawater by AAS. *Analytica Chimica Acta* 98: 243-250.

Dehairs, F., W. Baeyens, and D. Van Gansbeke. (1989) Tight coupling between enrichment of iron and manganese in North Sea suspended matter and sediment redox processes: Evidence for seasonal variability. *Estuarine, Coastal and Shelf Science* 29: 457-471.

Deuser, W.G. (1986) Seasonal and interannual variations in deep-water particle fluxes in the Sargasso Sea and their relation to surface hydrography. *Deep Sea Research* 33: 225-246.

Deuser, W.G. and E.H. Ross. (1980) Seasonal change in the flux of organic carbon to the deep Sargasso Sea. *Nature* 283: 364-365

Duce, R.A., G.L. Hoffman, B.J. Ray, I.S. Fletcher, G.T. Fashing, S.R. Piotrowitz, P.R. Walsh, E.J. Hoffman, J.M. Miller, and L.J. Hefter. (1976) Trace metals in the marine atmosphere: sources and fluxes. In *Marine Pollutant Transfer*, ed. H. Windom and R.A. Duce. 77-119. Lexington: Heath.

Duce, R.A., P.S. Liss, J.T. Merrill, E.L. Atlas, P. Buat-Menard, B.B. Hicks, J.M. Miller, J.M. Prospero, R. Arimoto, T.M. Church, W. Ellis, J.M. Galloway, L. Hansen, T.D. Jickells, A.H. Knap, K.H. Reinhardt, B. Schneider, A. Soudine, J.J. Tokos, S. Tsunogai, R. Wollast, and M. Zhou. (1991) The atmospheric input of trace species to the world ocean. *Global Biogeochemical Cycles* 5: 193-259.

Dugdale, R.C., J.J. Goering, and J.H. Ryther. (1964) High nitrogen fixation in the Sargasso Sea and Arabian Sea. *Limnology and Oceanography* 9: 507-510.

Dugdale, R.C., D.W. Menzel, and J.H. Ryther. (1961) Nitrogen fixation in the Sargasso Sea. *Deep Sea Research* 7: 297-300.

Dyrssen, D. and K. Kremling. (1990) Increasing hydrogen sulphide concentration and trace metals behaviour in anoxic Baltic waters. *Marine Chemistry* 30 : 193-204.

Eary, L.E. and D. Rai. (1987) Kinetics of chromium (III) oxidation to chromium (VI) by reaction with Manganese Dioxide. *Environmental Science and Technology* 21: 1187-1193.

Ebbesmeyer, C.C. and E.J. Lindstrom. (1986) Structure and origin of 18°C water observed during the POLYMODE local dynamics experiment. *Journal of Physical Oceanography* 16: 443-453.

Edmond, J.M., K.L. Von Damm, R.E. McDuff, and C.I. Measures. (1982) Chemistry of hot springs on the East Pacific rise and the effluent disposal. *Nature* 297: 187-191.

Elderfield, H. (1970) Chromium speciation in seawater. *Earth and Planetary Science Letters* 9: 10-16.

Elderfield, H. (1976) Hydrogenous material in marine sediments: excluding manganese nodules. In: Chemical Oceanography. eds. J.P. Riley and R. Chester. Vol 5. pp. 137-215. Academic Press. London.

Elderfield, H., N. Luedtke, R.J. McCaffrey, and M. Bender. (1981) Benthic flux studies in Narragansett Bay. *American Journal of Science* 281: 768-787.

Emerson, S., R.E. Cranston, and P.S. Liss. (1979) Redox species in a reducing Fjord: equilibrium and kinetic considerations. *Deep Sea Research* 26A: 859-878.

Emerson, S., R. Jahnke, and D. Heggie. (1984) Sediment-water exchange in shallow water estuarine sediments. *Journal of Marine Research* 42: 709-730.

Environment, Department of the. *Quality status of the North Sea.* Scientific and technical working group, 1987. HMSO 88pp.

Everaarts, J.M. (1989) Heavy metals (Cu, Zn, Cd, Pb) in sediment of the Java sea, estuarine and coastal areas of East Java and some deep sea areas. *Netherlands Journal of Sea Research* 23 (4): 403-413.

Fang, S., S. Xu, and S. Zhang. (1987) Fundamental and practical considerations in the design of on-line column preconcentration for flow-injection atomic spectrometric systems. *Analytica Chimica Acta* 200: 35-49.

Fang, Z., M. Sperling, and B. Welz. (1990) Flow injection on-line sorbent extraction preconcentration for graphite furnace AAS. *Journal of Atomic Spectrometry* 5: 639-646.

Fang, Z., Z. Zhu, S. Zhang, S. Xu, L. Guo, and L. Sun. (1988) On-line separation and preconcentration in flow-injection analysis. *Analytica Chimica Acta* 214: 41-55.

Finlayson-Pitts, B.J. and J.N. Jr. Finlayson. (1986) Atmospheric chemistry: fundamentals and experimental techniques. NY: John Wiley.

Fisher, N.S., C.V. Nolan, and S.W. Fowler. (1991) Scavenging and retention of metals by zooplankton faecal pellets and marine snow. *Deep Sea Research* 38 (10): 1261-1275.

Flegal, A.R., H. Maring, and S. Niemeyer. (1993) Anthopogenic lead in Antarctic seawater. *Nature* 6443: 242-244.

Forstner, V., W. Ahlf, and W. Calmano. (1989) Studies on the transfer of heavy metals between sedimentary phases with a multi-chamber device: combined effects of salinity and redox variation. *Marine Chemistry* 28: 145-158.

Francois, R. (1988) A study on the regulation on the concentrations of some trace metals (Rb, Sr, Zn, Pb, Cu, V, Cr, Ni, Mn and Mo) in Saanich Inlet, British Columbia, Canada. *Marine Geology* 83: 285-308.

Franklin, M.L. and J.W. Morse. (1982) The interaction of copper with the surface of calcite. *Ocean Science and Engineering* 7: 147-174.

Frey, B.E., F.G. Riedel, A.E. Bass, and L.F. Small. (1983) Sensitivity of estuarine phytoplankton to hexavalent chromium. *Estuarine Coastal and Shelf Science* 17: 181-187.

Fu, G. and H.E. Allen. (1992) Cadmium adsorption by oxic sediment. *Water Research* 26: 225-233.

Fukai, R. (1967) Valency state of chromium in seawater. *Nature* 213: 901.

Gaillard, J-F., H. Pauwels, and G. Michard. (1989) Chemical diagenesis in coastal marine sediments. *Oceanologica Acta* 12: 175-187.

Gendusa, T. C., T.L. Beitinger, and J.H. Rodgers. (1993) Toxicity of hexavalent Chromium from aqueous and sediment sources to Pimephales promelas and Ictalurus punctatus. *Bulletin of Environmental Contamination and Toxicology* 50: 144-151.

German, C.R., B.A. Barriero, N.C. Higgs, T.A. Nelson, and M.R. Palmer. (1995) Seawater-matasomatism in hydrothermal sediments (Escanaba Trough, NE Pacific). *Chemical Geology* 119 (1): 175-190.

Gerringa, L.G.A. (1991) Availability of Cu, Cd, Ni, Pb, Zn, Fe and Mn in marine sediment slurries under anaerobic conditions and at 20% air saturation. *Netherlands Journal of Sea Research*: 145-156.

Gerringa, L.J.A. (1990) Aerobic degradation of organic matter and the mobility of Cu, Cd, Ni, Pb, Zn, Fe and Mn in marine sediment slurries. *Marine Chemistry* 29: 355-374.

Gerringa, L.J.A. and J.P. Cambon. (1991) The extractability of copper from marine sediment as a function of degradation of organic matter. *Netherlands Journal of Sea Research* 27: 157-163.

GESAMP. *The sea surface microlayer and its role in global change.* WMO GENEVA, 1995. Report Number 59.

Giani, M., M. Gabellini, D. Pellegrini, S. Constantini, E. Beccaloni, and R. Giordano. (1994) Concentration and partitioning of Hg, Cr and Pb in sediments of dredge and disposal sites of the N. Adriatic Sea. *Science of the Total Environment* 158: 97-112

Goldberg, E.D. (1975) Marine Pollution. In *Chemical Oceanography*, Vol. 3. ed. J.P. Riley and G. Skirrow. 39-89. London: Academic Press.

Goldberg, E.D., K. Minoru, K. Bertine, V. Hodge, M. Stallard, D. Martincic, N. Mikak, M. Branica, and J.K. Abaychi. (1988) Marine geochemistry - 2: Scavenging redox. *Applied Geochemistry* 3: 561-571.

Gonzalez-Davila, M. (1995) The role of plankton cells on the control of heavy metal concentration in seawater. *Marine Chemistry* 48: 215-236.

Government, Bermuda. (1994) *Bermuda Digest of Statistics.* Bermuda Government. Statistical Department

Grimaud, D. and G. Michard. (1974) Concentration du chrome dans deux profils de l'ocean Pacifique. *Marine Chemistry* 2: 229-237.

Gust, G., A.F. Michaels, R.J. Johnson, W.G. Deuser, and W. Bowles. (1994) Mooring line motions and sediment trap hydromechanics: insitu intercomparison of three common deployment designs. *Deep Sea Research* 41: 831-857.

Hall, I. (1991)*Cycling of trace metals in coastal waters: Biogeochemical processes involving suspended particles.* University of Southampton. M.Phil./Ph.D. upgrading report

Hall, I.R. (1993) Cycling of trace metals in coastal waters: Biogeochemical processes involving suspended particles. Ph.D., Southampton.

Hall, L.A. (1991) A preliminary investigation into the speciation of trace metals in sediments from the Gulf of Paria off the coast of Trinidad. *Environmental Intelligence* 17 (3): 437-447.

Halliwell, G.R., G. Peng, and D.B. Olson. (1994) Stability of the Sargasso Sea subtropical frontal zone. *Journal of Physical Oceanography* 24: 1166-1183.

Hansell, D.A. and J.A. Newton. (1994) Design and evaluation of a "swimmer" segregating particle interception trap. *Limnology and Oceanography* 39 (6): 1487-1495.

Harper, D. and J.P. Riley. *Determination of low concentrations of dissolved and particulate chromium in natural waters.* Water Research Council, 1985. Technical Report TR 215. University of Liverpool.

Hayward, S.J., V.H. Gomez, and W. Sterrer. (1981) Bermuda's Delicate Balance. Publisher: The Bermuda National Trust.

Hekinian, R., V. Renard, and J.L. Cheminee. (1983) Hydrothermal deposits on the East Pacific Rise near 13°N: Geological settling and distribution of active sulphide chimneys. In *Hydrothermal processes at seafloor spreading centers.*, ed. P.A. Rona, K. Bostrom, L. Laubier, and K.L. Smith Jr. 571-594. New York: Plenum Press.

Hem, J.D. (1977) Reaction of metal ions at surfaces of hydrous iron oxide. *Geochimica et Cosmochimica Acta* 41: 527-538.

Hirata, S. (1992) Trace Metals in Humic Substances of Coastal Sediments of the Seto Inland Sea, Japan. *Science of the Total Environment* 118: 325-333.

Hirner, A.V. (1992) Trace element speciation in soils and sediments using sequential chemical extraction methods. *International Journal of Environmental Analytical Chemistry* 46: 77-85.

Hoenig, M., E. Puskaric, P. Choisy, and M. Wartel. (1991) Direct determination of high and mid-volatile elements (Cd, Pb, Mn) in seawater by electrothermal atomic absorption spectroscopy: existing approaches and critical parameters. *Analusis* 19: 285-291.

Honeyman, B.D., L.S. Balistrieri, and J.W. Murray. (1988) Oceanic trace metals scavenging: the importance of particle concentration. *Deep Sea Research* 35: 227-246.

Honeyman, B.D. and P.H. Santschi. (1989) A brownian-pumping model for oceanic trace metal scavenging: evidence from Th isotopes. *Journal of Marine Research* 47: 951-992.

Honjo, S., J.F. Connell, and P.L. Sachs. (1980) Deep-Ocean sediment trap; design and function of PARFLUX Mark II. *Deep Sea Research* 27: 745-753.

Howard, A.G. and P.J. Statham. (1993) Inorganic trace analysis: Philosophy and practice. Chichester: John Wiley and Sons.

Huang, H. and X. Pang. (1989) The determination of different valence chromium in seawater. *Sinica Acta*: 57-60.

Humphris, S.E. (1978) Trace element mobility during hydrothermal alteration of oceanic basalts. *Geochimica et Cosmochimica Acta* 42: 127-136.

Hunt, C.D. (1983) Incorporation and deposition of manganese and other trace metals by flocculant organic matter in a controlled marine ecosystem. *Limnology and Oceanography* 28 (2): 302-308.

Huynh-Ngoc, L., N.E. Whitehead, M. Boussemart, and D. Calmet. (1989) Dissolved nickel and cobalt in the aquatic environment around Monaco. *Marine Chemistry* 26: 119-132.

Hydes, D.J., P.J. Statham, and J.D. Burton. (1986) A verticle profile of dissolved trace metals (Al, Cd, Cu, Mn, Ni) over the median valley of the mid-atlantic ridge 43°N: Implications for hydrothermal activity. *The Science of the Total Environment* 49: 133-145.

I.O.C. (1994) Protocols for the Joint Global Ocean Flux Study (JGOFS) core measurements. ed. Scientific Committee on Oceanic Research. Report #29. Publisher: UNESCO.

Isshiki, K., Y. Sohrin, H. Karatani, and E. Nakayama. (1989) Preconcentration of chromium(III) and chromium(VI) in sea water by complexation with quinolin-8-ol and adsorption on macroporous resin. *Analytica Chimica Acta* 224: 55-64.

James, R.H., P.J. Statham, N.H. Morley, and J.D. Burton. (1993) Aspects of the geochemistry of dissolved and particulate Cd, Cu, Ni, Co and Pb in the Dover Strait. *Oceanologica Acta* 16: 553-564.

Jeandel, C. and J.F. Minster. (1984) Isotope dilution measurement of inorganic chromium (III) and total chromium in seawater. *Marine Chemistry* 14: 347-364.

Jeandel, C. and J.F. Minster. (1987) Chromium behaviour in the ocean: global verses regional processes. *Global Biogeochemical Cycles* 1: 131-154.

Jenkins, W.J. (1977) Tritium-helium dating in the Sargasso Sea: A measurement of oxygen utilization rates. *Science* 196: 291-292.

Jenkins, W.J. (1982) Oxygen utilization rates in North Atlantic subtropical gyre and primary production in oligotrophic systems. *Nature* 300: 246-248.

Jenkins, W.J. and J.C. Goldman. (1985) Seasonal oxygen cycling and primary production in the Sargasso Sea. *Journal of Marine Research* 43: 465-491.

Jickells, T.D. (1986) Studies of trace elements in the Sargasso sea and the mid-atlantic Bight. Ph.D. Thesis. University of Southampton.

Jickells, T.D., W.G. Deuser, and R.A. Bellastock. (1990) Temporal variations in the concentrations of some particulate elements in the surface waters at the Sargasso Sea and their relationship to deep sea fluxes. *Marine Chemistry* 29: 203-219.

Jickells, T.D., W.G. Deuser, and A.H. Knap. (1984) The sedimentation rates of trace elements in the Sargasso Sea measured by sediment traps. *Deep Sea Research* 31: 1169-1178.

Jickells, T.D., A.H. Knap, and T.M. Church. (1984) Trace metals in Bermuda rainwater. *Journal of Geophysical Research* 89: 1423-1428.

Jickells, T.D., A.H. Knap, and S.R. Smith. (1986) Trace metals and nutrient fluxes through the Bermuda inshore waters. *Journal de Conseil International pour L'Exploration de la Mer* 186: 251-262.

Jickells, T.D., P.P. Newton, P. King, R.S. Lampitt, and C. Boutle. (1996) A comparison of sediment trap records of particle fluxes from 19 to 48°N in the Northeast Atlantic and their relation to surface water productivity. *Deep Sea Research* 43: 971-986.

Johnson, K.S., K.H. Coale, V.A. Elrod, and N.W. Tindale. (1994) Iron photochemistry in seawater from the Equatorial Pacific. *Marine Chemistry* 46 (4): 319-334.

Jones, C.J. and J.W. Murray. (1984) Nickel, cadmium and copper in the Northeast Pacific off the coast of Washington. *Limnology and Oceanography* 29 (4): 711-720.

Jones, G.B. (1992) Effect of Trichodesmium blooms on water quality in the Great Barrier Reef lagoon. In *Marine Pelagic Cyanobacteria: Trichodesmium and other diazotrophs*, ed. E.J. Carpenter, D. G. Capone, and J.G. Rueter.

Jones, G.B., F.G. Thomas, and C. Burdon-Jones. (1986) Influence of *Trichodesmium* blooms on cadmium and iron speciation in Great Barrier Reef lagoon waters. *Estuarine, Coastal and Shelf Science* 23: 387-401.

Kaczynski, S.E. and R.J. Kieber. (1993) Aqueous trivalent chromium photoproduction in natural waters. *Environmental Science and Technology* 27: 1572-1576.

Kaczynski, S.E. and R.J. Kieber. (1994) Hydrophobic C_{18} bound organic complexes of chromium and their potential impact on the geochemistry of chromium in natural waters. *Environmental Science and Technology* 28: 799-804.

Kantipuly, C., S. Katragadda, A. Chow, and H.D. Gesser. (1990) Chelating polymers and related supports for separating and preconcentration of trace metals. *Talanta* 37: 491-517.

Karl, D.M., R. Letelier, D.V. Hebel, D.F. Bird, and C.D. Winn. (1991) Trichodesmium blooms and new nitrogen in the North Pacific gyre. In *Marine Pelagic Cyanobacteria: Trichodesmium and other diazotrophs.*, ed. E.J. Carpenter, D.G. Capone, and J.G. Rueter. Kluwer Academic Press.

Kerner, M. and C.-D. Geisler. (1995) Dynamics of copper release during early aerobic degradation in aggregated seston from the Elbe estuary. *Marine Chemistry* 51: 133-144.

Kersten, M. and U. Forstner. (1987) Effect of sample pretreatment on the reliability of solid speciation data of heavy metals-Implications for the study of early diagenetic processes. *Marine Chemistry* 22: 299-312.

Kheboian, C. and C.F. Bauer. (1987) Accuracy of selective extraction procedures for metal speciation in model aquatic systems. *Analytical Chemistry* 59: 1417-1423.

Kieber, R.J. and G.R. Helz. (1992) Indirect photoreduction of chromium (VI). *Environmental Science and Technology* 26: 307-312.

King, J.N. and S. Fritz. (1985) Concentration of metal ions by complexation with Sodium Bis(2-hydroxyethyl) dithiocarbamate and sorption on XAD-4 resin. *Analytical Chemistry* 57: 1016-1020.

Kinrade, J.D. and L. Van Loon. (1974) Solvent extraction for use with atomic absorption spectroscopy. *Analytical Chemistry* 46: 1894-1898.

Klinkhammer, G.P. (1980) Observations of the distribution of manganese over the East Pacific Rise. *Chemical Geology*. 29: 211-226.

Knap, A.H., C.B. Cook, S.B. Cook, J.A.K. Simmons, R.J. Jones, and A.E. Murray. (1991) *Marine environmental studies to determine the impact of the mass burn incinerator proposed for Tynes Bay, Bermuda.* Bermuda Government. Ministry of Works and Engineering

Knappertsbusch, K-M. and G-J. A. Brummer. (1995) A sediment trap investigation of sinking coccolithophorids in the North Atlantic. *Deep Sea Research Oceanography Progress Series* 42: 1083-1109.

Knauer, G.A. and J.H. Martin. (1983) The cycle of living and dead particulate organic matter in the pelagic environment in relation to trace metals. In *Trace metals in sea water*, ed. C.S. Wong, E. Boyle, K.W. Bruland, J.D. Burton, and E.D. Goldberg. 447-465. New York and London: Plenum Press.

Knoery, J.R. and G.A. Cutter. (1994) Biogeochemistry of dissolved hydrogen sulphide species and carbonyl sulphide in the western North Atlantic Ocean. *Geochimica et Cosmochimica Acta* 58: 5421-5431.

Kozar, S., H. Bilinski, and M. Branica. (1992b) Adsorption of lead and cadmium ions on calcite in the Krka estuary. *Marine Chemistry* 40: 215-230.

Kozar, S., H. Bilinski, M. Branica, and M.J. Schwuger. (1992a) Adsorption of Cd(II) and Pb(II) on Bentonite Under Estuarine and Seawater Conditions. *Science Total Environment* 121: 203-216.

Krauskopf, K.B. (1956) Factors controlling the concentrations of thirteen rare metals in seawater. *Geochimica et Cosmochimica Acta* 9: 1-33.

Kremling, K. (1983a) Trace metal fronts in European shelf waters. *Nature* 303: 225-227.

Kremling, K. (1983b) The behaviour of Zn, Cd, Cu, Ni, Co, Fe and Mn in anoxic Baltic waters. *Marine Chemistry* 13: 87-108.

Kremling, K. and C. Pohl. (1989) Studies on the spatial and seasonal variability of dissolved Cd, Cu and Ni in N.Atlantic surface waters. *Marine Chemistry* 27: 43-60.

Krumgalz, B.S. and G. Fainshtein. (1989) Trace metal contents in certified reference sediments determined by nitric acid digestion and AAS. *Analytica Chimica Acta* 218: 335-340.

Kudo, I., H. Kokobun, and Matsunaga. (1996) Cadmium in the South West Pacific ocean: Two factors significantly affecting the Cadmium-phosphate relationship in the ocean. *Marine Chemistry* 54: 55-67.

Kumar, U.V. and G.S. Roonwal. (1987) Geochemical characteristics and selective leaching of transition elements in sediments from the central Pacific Ocean. *Indian Journal of Marine Science* 16: 77-85.

Lambert, C.E., A. Veron, P. Buat-Menard, M. Heyraud, F. Grousset, and W. Simpson. (1991) The role of large biogenic particles in the transport of atmospheric pollutant lead down the N. Atlantic sediments. *Oceanologica Acta* 14: 67-76.

Lange, G.J.De, G. Catalano, G.P. Klinkhammer, and G.W. III Luther. (1990) The interface between oxic seawater and the anoxic Bannock brine; it's sharpness and the consequences for the redox-related cycling on Mn and Ba. *Marine Chemistry* 31: 205-217.

Lapp, B. and W. Balzer. (1993) Early diagenesis of trace metals used as an indicator of past productivity changes in coastal sediments. *Geochimica et Cosmochimica Acta* 57 (19): 4639-4652.

Lee, B-G. and N. Fisher. (1994) Effects of zooplankton grazing on the release of elements from planktonic debris. *Marine Ecology Progress Series* 110: 271-281.

Lee, J.G., S.B. Roberts, and F.M.M. Morel. (1995) Cadmium: a nutrient for the marine diatom Thalassiosira weisseglii. *Limnology and Oceanography* 40: 1056-1063.

Lewis, B.L. and W.M. Landing. (1992) The investigation of dissolved and suspended-particulate trace metal fractionation in the Black sea. *Marine Chemistry* 40: 105-141.

Libes, S.M. (1992) An introduction to marine biogeochemistry. John Wiley.

Loring, D.H. and Rantala R.T.T. (1988) An intercalibration exercise for trace metals in marine sediments. *Marine Chemistry* 24: 13-28.

Loring, D.H. and R.T.T. Rantala. (1990)*Sediments and suspended particulate matter: Total and partial methods of digestion.* ICES. Report #9.

Lui, Z-S. and S-D. Huang. (1992) Determination of copper and cadmium in seawater by preconcentration and electrothermal atomic absorption spectroscopy. *Analytica Chimica Acta* 267: 31-37.

Lyons, Wm. B., P.B. Armstrong, and H.E. Gaudette. (1983) Trace metal concentrations and fluxes in Bermuda sediments. *Marine Pollution Bulletin* 14: 65-68.

Lyons, Wm.B., K.M. Wilson, and P.B. Armstrong. (1980) Trace metal pore water geochemistry of nearshore Bermuda carbonate sediments. *Oceanologica Acta* 3: 363-367.

MacDoanald, R.W., D.M. MacDoanald, M.C. O'Brien, and C. Gobeil. (1991) Accumulation of heavy metals (Pb, Zn, Cu, Cd), carbon and nitrogen in sediments from Strait of Georgia. B.C. Canada. *Marine Chemistry* 34: 109-135.

Mackey, D.J. (1983) Metal-organic complexes in seawater - An investigation of naturally occurring complexes of Cu, Zn, Fe, Mg, Ni, Cr, Mn, and Cd using HPLC with atomic fluorescence detection. *Marine Chemistry*: 169-180.

Magnusson, B. and S. Westerlund. (1981) Solvent extraction procedures combined with back-extraction for trace metals determinations by atomic absorption spectrometry. *Analytica Chimica Acta* 131: 63-72.

Malahoff, A. (1982) A comparison of the massive submarine polymettalic sulphides of the Galapagos Rift with some continental deposits. *Journal of the Marine Technology Society* 16: 39-45.

Malley, D.F. and K.H. Mills. (1992) Whole lake experimentation as a tool to assess ecosystem health, responses to stress and recovery: the Experimental Lakes Area experience. *Journal of Aquatic Ecosystem Health* 1: 159-174.

Malone, T.C., S.E. Pike, and D.J. Conley. (1993) Transient variations in phytoplankton productivity at the JGOFS Bermuda time series station. *Deep Sea Research* 40: 903-924.

Martin, J-M. and M. Whitfield. (1983) The significance of river input of chemical elements to the ocean. In *Trace metals in seawater*, ed. C.S. Wong, E. Boyle, K. W. Bruland, J.D. Burton, and E.D. Goldberg. Plenum Press.

Martin, J.H., S.E. Fitzwater, R.M. Gordon, C.N. Hunter, and S.J. Tanner. (1993) Iron, primary productivity and carbon-nitrogen flux studies during the JGOFS North Atlantic Bloom Experiment. In *JGOFS the North Atlantic Bloom Experiment*, ed. H.W. Ducklow and R.P. Harris. 115-134. 40.

Martin, J.M. (1970) The possible transport of trace metals via the moulted copepod exoskeletons. *Limnology and Oceanography* 15: 756-761.

Martin, J. M., M. H. Dai, and G. Cauwet. (1995) Significance of colloids in the biogeochemical cycling of organic carbon and trace metals in the Venice Lagoon (Italy). *Limnology and Oceanography* 40: 119-131.

Martin, J.M. and G.A. Knauer. (1983) VERTEX: Manganese transport with Calcium carbonate. *Deep Sea Research* 30: 411-425.

Martin, J.M., P. Nirel, and A.J. Thomas. (1987) Sequential extraction techniques: Promises and problems. *Marine Chemistry* 22: 313-341.

Martin, J.M. and A.J. Thomas. (1994) The global insignificance of telluric input of dissolved trace metals (Cd, Cu, Ni, and Zn) to ocean margins. *Marine Chemistry* 46: 165-178.

Martincik, D., Z. Kwokal, and M. Branica. (1990a) Distribution of Zn, Pb, Cd and Cu between different size fractions of sediments 1. The Limski Kanal (N.Adriatic Sea). *The Science of the Total Environment* 95: 201-215.

Martincik, D, Z. Kwokal, and M. Branica. (1990b) Distribution of Zn, Pb, Cd and Cu between different size fractions of sediments 2. The Krka river estuary and Kornati islands (Central Adriatic Sea). *The Science of the Total Environment* 95: 217-225.

Matsunaga, K., T. Ohyana, K. Kuma, Kudo, and Y. Suzuki. (1995) Photo-reduction of manganese dioxide in seawater by organic substances under ultraviolet or sunlight. *Water Research* 29: 757-759.

McBride, M.B. (1979) Chemisorption and precipitation of Mn^{2+} at $CaCO_3$ surfaces. *Soil Science Society of America Journal* 43: 693-698.

Measures, C.I., J.M. Edmond, and T.D. Jickells. (1986) Aluminium in the Northwest Atlantic. *Geochimica. Cosmochimica. Acta* 50: 1423-1429.

Menzel, D.W. and J.H. Ryther. (1960) The annual cycle of primary production in the Sargasso Sea off Bermuda. *Deep Sea Research* 6: 351-366.

Menzel, D.W. and J.H. Ryther. (1961) Annual variations in primary production of the Sargasso Sea off Bermuda. *Deep Sea Research* 7: 282-288.

Merlivat, L. and P. Brault. (1995) Carioca Buoy-carbon dioxide monitor. *Sea Technology* 36: 23-30.

Michaels, A.H., A.H. Knap, R.L. Dow, K. Gundersen, R.J. Johnson, J. Sorensen, A. Close, G.A. Knauer, S.E. Lohrenz, V.A. Asper, M. Tuel, and R. Bidigare. (1994) Seasonal patterns of ocean biogeochemistry at the U.S. JGOFS Bermuda Atlantic Time-series study site. *Deep Sea Research* 7: 1013-1038.

Midorikawa, T., E. Tanoue, and Y. Sugimura. (1992) Interaction Between Dissolved Organic Matter in Seawater and Copper. *Science Total Environment* 118: 499-507.

Millero, F.J. and D.J. Hawke. (1992) Ionic interactions of divalent metals in natural waters. *Marine Chemistry* 40: 19-48.

Milliman, J.D. (1991) Flux and fate of fluvial sediment and water in coastal seas. In *Ocean margin processes in global change*, ed. R.F.C. Mantoura, J.M. Martin, and R. Wollast. 69-89. Chichester: Wiley.

Millward, G.E. (1995) Processes affecting trace element speciation in estuaries: A review. *Analyst* 120: 609-614.

Monteny, F., M. Elskens, and W. Baeyens. (1993) The behaviour of copper and zinc in the Scheldt estuary. *Marine and estuarine gradients* 27: 279-286.

Moore, C.A., Farmer, C.T. and Zika, R.G. (1993) Influence of the Orinoco river on hydrogen peroxide distribution and production in the East Caribbean. *Journal of Geophysical Research* 98: 2289-2298.

Moran, S. and K.O. Buesseler. (1992) Short residence time of colloids in the upper ocean estimated from ^{238}U-^{234}Th disequillibria. *Nature* 355 (6392): 221-223.

Moran, S.B., P.A. Yeats, and P.W. Balls. (1996) On the role of colloids in trace metal solid-solution partitioning in continental shelf waters: a comparison of model results and field data. *Continental Shelf Research* 16: 397-408.

Morel, F.M.M., R.J.N. Hudson, and N.M. Price. (1991) Limitation of productivity by trace metals in the sea. *Limnology and oceanography* 36: 1742-1755.

Morley, N.H., P.J. Statham, and J.D. Burton. (1993) Dissolved trace metals in the Southwestern Indian Ocean. *Deep Sea Research* 40: 1043-1062.

Morris, B., J. Barnes, F. Brown, and J. Markham. (1977) *The Bermuda marine environment.* Bermuda Biological Station for Research. Special Publication 15.

Morse, J.W. (1986) The surface chemistry of calcium carbonate minerals in natural waters: An overview. *Marine Chemistry.* 20: 91-112.

Morse, J.W. (1994) Interactions of trace metals with authigenic sulfide minerals: implications for their bioavailability. *Marine Chemistry* 46: 1-6.

Morse, J.W. and F.T. Mackenzie. (1990) Geochemistry of sedimentary carbonates. Vol. 48. Developments in sedimentology. New York: Elsevier.

Mugo, R.K. and K.J. Orians. (1993) Seagoing method for the determination of chromium (III) and total chromium in sea water by electron capture detection gas chromatography. *Analytica Chimica Acta* 271: 1-9.

Muller, F.L. and D.R. Kessler. (1990) Kinetic approach to trace metal complexation in seawater: Application to zinc and cadmium. *Environmental Science and Technology* 24: 234-242.

Muller, F.L.L. (1996) Interactions of copper, lead and cadmium with the dissolved, colloidal and particulate components of estuarine and coastal waters. *Marine Chemistry* 52: 245-268.

Murray, J.W., B. Spell, and B. Paul. (1983) The contrasting geochemistry of Mn and Cr in the eastern tropical Pacific ocean. In *Trace metals in sea water*, ed. C.S. Wong, E. Boyle, K.W. Bruland, J.D. Burton, and E.D. Goldberg. 447-465. New York and London: Plenum Press.

Mykytiuk, A.P., D.S. Russell, and R.E. Sturgeon. (1980) Simultaneous determination of iron, cadmium, zinc, copper, nickel, lead and uranium in seawater by stable isotope dilution spark source mass spectrometry. *Analytical Chemistry* 52: 1281-1283.

Nakayama, E., T. Kuwamoto, H. Tokoro, and T. Fujinaga. (1981a) Dissolved state of chromium in seawater. *Nature (London)* 290: 768-770.

Nakayama, E., T. Kuwamoto, S. Tsurubo, and T. Fulinaga. (1981c) Chemical speciation of Chromium in seawater. Part 2. Effects of manganese oxides and reducible organic materials on the redox processes of Chromium. *Analytica Chimica Acta* 130: 401-404.

Nakayama, E., T. Kuwamoto, S. Tsurubo, and T. Fulinaga. (1981d) Chemical speciation of Chromium in seawater. Part 3. The determination of Chromium species. *Analytica Chimica Acta* 131: 247-254.

Nakayama, E., T. Kuwamoto, S. Tsurubo, H. Tokoro, and T. Fulinaga. (1981b) Chemical speciation of Chromium in seawater. Part 1. Effect of naturally occurring organic materials on the complex formation of Chromium (III). *Analytica Chimica Acta* 130: 289-294.

Neuman, A.C. (1965) Process of recent carbonate sedimentation in Harrington Sound, Bermuda. *Bulletin of Marine Science* 15: 987-1035.

Niebor, E. and A.A. Jusys, (1988) *Chromium in the natural and human environments.* Vol. 20. Advances in environmental sciences and technology. New York: Wiley-Interscience,

Nimmo, M., C.M.G. van den Berg, and J. Brown. (1989) The chemical speciation of dissolved Nickel, Copper, Vanadium and Iron in Liverpool Bay, Irish Sea. *Estuarine, Coastal and Shelf Science.* 29: 57-74.

Nirel, P.M.V. and F.M.M. Morel. (1990) Pitfalls of sequential extractions. *Water Research* 8: 1055-1056.

Noriki, S., N. Ishimori, K. Harada, and S. Tsunogai. (1985) Removal of trace metals from seawater during a phytoplankton bloom as studied with sediment traps in Funka Bay, Japan. *Marine Chemistry* 17: 75-89.

Oeztuerk, M. (1995) Trends of trace metals (Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb) distributions at the oxic-anoxic interface and in sulphidic water of the Drammensfjord. *Marine Chemistry* 48: 329-342.

Oh, J.R. (1991) Chemical speciation of dissolved nickel in Chinhae Bay. *Ocean Research* 13: 11-18.

Osaki, S., T. Osaki, N. Hirashima, and Y. Takashima. (1983) The effect of organic matter and colloidal particles on the determination of Chromium (VI) in natural waters. *Talanta.* 30 (7): 523-526.

Pai, S. (1988) Pre-concentration efficiency of Chelex-100 resin for heavy metals in seawater. Part II. Distribution of heavy metals on a Chelex-100 column and optimisation of the column efficiency by a plate simulation method. *Analytica Chimica Acta* 211: 271-280.

Pai, S., P. Whurg, and R. Lai. (1988) Pre-concentration efficiency of Chelex-100 resin for heavy metals in seawater. Part I. Effects of pH and salts on the distribution ratios of heavy metals. *Analytica Chimica Acta* 211: 257-270.

Patterson, C., D. Settle, and B. Glover. (1976) Analysis of lead in polluted coastal seawater. *Marine Chemistry* 4: 305-319.

Paulson, A.J., H.C Jr. Curl, and J.F. Gendron. (1994) Partitioning of copper in estuarine waters 1. Partitioning in a poisoned system. *Marine Chemistry* 45: 67-80.

Pederson, T.F., R.D. Waters, and R.W. MacDonald. (1989) On the natural enrichment of cadmium and molybdenum in the sediments of Uclulet Inlet, British Columbia. *Science of the Total Environment* 79: 125-139.

Perkin, Elmer. (1985)*Techniques in graphite furnace atomic absorption spectrophotometry.* Product Department.

Pestana, H.R. (1993)*Guide to the identification of carbonate grains and carbonate producing organisms.* Bermuda Biological Station for Research Inc. Special Publication 32.

Pettine, M., M Camusso, and W. Martinotti. (1992) Dissolved and particulate transport of arsenic and chromium in the Po River (Italy). *Science of the Total Environment* 119: 253-280.

Pettine, M., F.J. Millero, and T. LaNoce. (1991) Chromium (III) interactions in seawater through its oxidation kinetics. *Marine Chemistry* 34: 29-46.

Pettine, M., F.J. Millero, and R. Passino. (1994) Reduction of Chromium (VI) with hydrogen sulfide in NaCl media. *Marine Chemistry* 46: 335-344.

Piron, M., A. Pineau, and R.M. Mabele. (1990) Sediment, parameters and distribution of metals in fine sediments of the Loire estuary. *Water, Air and Soil Pollution* 50: 267-277.

Price, N.M. and M.M. Morel. (1990) Cadmium and Cobalt substitution for Zinc in a marine diatom. *Nature* 344: 658-661.

Prohic, E. and G. Kniewald. (1987) Heavy metals distribution in recent sediments of the Krka river estuary - An example of sequential extraction analysis. *Marine Chemistry* 22: 279-297.

Prospero, J.W. (1968) Atmospheric dust studies on Barbados. *Bulletin of the American Meteorological Society* 49: 645-652.

Rai, D., L.E. Eary, and J.M. Zachara. (1989) Environmental chemistry of Chromium. *Science of the Total Environment* 86: 15-23.

Rai, D., B.M. Sass, and D.A. Moore. (1987) Chromium (III) hydrolysis constants and solubility of chromium (III) hydroxide. *Inorganic Chemistry* 26: 345-349.

Rajkumar, W. and D. Persad. (1994) Heavy metals and petroleum hydrocarbons in nearshore areas of Tobago, West Indies. *Marine Pollution Bulletin* 28: 701-703.

Rapin, F., A. Tessier, P.G.C. Campbell, and R. Carignan. (1986) Potential artifacts in the determination of metal partitioning in sediments by a sequential extraction procedure. *Environmental Science and Technology* 20: 836-840.

Regnier, P. and R. Wollast. (1993) Distribution of trace metals in suspended matter of the Scheldt estuary. *Marine Chemistry* 43: 3-19.

Reynolds, C.S., G.P. Harris, and D.N. Gouldney. (1985) Comparison of carbon-specific growth rates and rates of cellular increase of phytoplankton in large limnetic enclosures. *Journal of Plankton Research.* 7: 791-820.

Richard, F.C. and A.C.M. Bourg. (1991) Aqueous Geochemistry of chromium: A review. *Water Research* 25: 807-817.

Rifaat, A.E., M.Kh. El-Sayed, A. Beltagy, M.A. Morsy, and A. Nawar. (1992) Geochemical predictive models of manganese, zinc, nickel, copper and cadmium in Nile shelf sediments. *Marine Geology* 108: 59-71.

Ripley, M. (1992) An investigation into trace metal associations within carbonate sediments from Bermuda inshore waters by sequential extraction. B.Sc., Southampton.

Riso, R.D., F. Quentel, and C. Madec. (1990) Distribution of some trace metals in well mixed and stratified areas of the western Brittany coastal waters. *Oceanologica Acta* 13: 475-479.

Rodger, G.K. and I.M. Davies. (1992) The recovery of a sewage sludge dumping ground: Trace metal geochemistry in the sediment. *Science of the Total Environment* 119: 57-75.

Rosental, R., G.A. Eagle, and M.J. Orren. (1986) Trace metal distribution in different chemical fractions of nearshore marine sediments. *Estuarine, Coastal and Shelf Science* 22: 303-324.

Rubio, R., A. Sahuquillo, G. Rauret, and P. Quevauviller. (1992) Determination of Chromium in Environmental and Biological Samples by Atomic Absorption Spectroscopy - A Review. *International Journal of Environmental Analytical Chemistry* 47: 99-128.

Rue, E.L., G.J. Smith, G.A. Cutter, and K.W. Bruland. (1997) The response of trace element redox couples to suboxic conditions in the water column. *Deep Sea Research* 44: 113-134.

Ruiz Pino, D. P., C. Jeandel, J. -P. Bethoux, and J. -F. Minister. (1990) Are the trace metal cycles balanced in the Mediterranean Sea? *Palaeogeography, Palaeoclimatology, and Palaeoecology* 82: 369-388.

Rule, J.H. and R.W. Alden. (1992) Partitioning of cadmium in geochemical fractions of anaerobic estuarine sediments. *Estuarine, Coastal and Shelf Science* 34: 487-499.

Salomons, W. and U. Foerstner. (1984) Metals in the hydrocycle. Berlin: Springer Verlag.

Santschi, P., P. Hohener, G. Benoit, and M. Buchholtz-Ten Brink. (1990) Chemical processes at the sediment-water interface. *Marine Chemistry* 30: 269-315.

Sanudo Wilhelmy, S.A. and A.R. Flegal. (1991) Trace element distributions in coastal waters along the US-Mexican boundary: relative contributions of natural processes vs. anthropogenic inputs. *Marine Chemistry* 33: 371-392.

Sanudo Wilhelmy, S.A. and A.R Flegal. (1996) Trace metal concentrations in the surf zone and in coastal waters off Baja California, Mexico. *Environmental Science and Technology* 30: 1575-1580.

Sawlan, J.J. and J.W. Murray. (1983) Trace metal remobilisation in the interstitial waters of red clays and hemipelagic marine sediments. *Earth and Planetary Science Letters* 64: 213-230.

Schaule, B.K. and C.C. Patterson. (1981) Lead concentrations in the North East Pacific. Evidence for global perturbations. *Earth and Planetary Science Letters* 54: 97-116.

Schaule, B.K. and C.C. Patterson, ed. (1983) *Perturbations in the natural lead depth profile in the Sargasso Sea by industrial lead.* Vol. 9. NATO conference series. NY: Plenum Press.

Schroeder, D.C. and G.F. Lee. (1975) Potential transformations of Chromium in natural waters. *Water, Air and Soil pollution.* 4: 355-365.

Secretariat, Ozone. (1993) Handbook for the Montreal Protocol on substances that deplete the ozone layer. UN.

Shah, A. and S. Devi. (1990) Determination of Chromium by on-line preconcentration on a poly (hydroxamic acid) resin in the flow injection AAS. *Analytica Chimica Acta* 236: 469-473.

Sherrell, R.M. and E.A. Boyle. (1988) Zinc, chromium, vanadium and iron in the Mediterranean sea. *Deep Sea Research* 35: 1319-1334.

Sherrell, R.M. and E.A. Boyle. (1992) The trace metal composition of suspended particles in the oceanic water column near Bermuda. *Earth and Planetary Science letters.* 111: 155-174.

Siegel, D.A., T.C. Granata, A.F. Michaels, and T.D. Dickey. (1990) Mesoscale eddy diffusion, particle sinking and the interpretation of sediment trap data. *Journal of Geophysical Research* 95 (C4): 5305-5311.

Sillen, L.G. (1961) The physical chemistry of seawater. In *International Oceanographic Conference in New York,* edited by M. Sears, American association for the advancement of science, 549-583.

Skwarzec, B., R. Bojanowski, and J. Bocacek. (1988) The determination of Cu, Pb, Cd and Zn in the southern Baltic water, suspension and sediments. *Oceanologia* 25: 75-85.

Smillie, R.H., K. Hunter, and M. Loutit. (1981) Reduction of chromium (VI) by bacterially produced Hydrogen Sulphide in a marine environment. *Water Research* 15: 1351-1354.

Sperling, M., S. Xu, and B. Welz. (1992) Determination of chromium (III) and chromium (VI) in water using flow injection on-line preconcentration with selective adsorption on activated alumina and Flame Atomic Absorption spectrometric determination. *Analytical Chemistry* 64: 3101-3108.

Spokes, L.J. and P.S. Liss. (1995) Photochemically induced redox reactions in seawater, I. Cations. *Marine Chemistry* 49: 201-213.

Statham, P.J. (1985) The determination of dissolved Mn and Cd in seawater at low nmol^{-1} concentrations by chelation and extraction followed by electrothermal AAS. *Analytica Chimica Acta* 169: 149-159.

Statham, P.J. and J.D. Burton. (1986) Dissolved manganese in the North Atlantic Ocean, 0-35°N. *Earth and Plan. Science.* 79: 55-65.

Statham, P.J., J.D. Burton, and D.J. Hydes. (1985) Cadmium and manganese in the Alboran Sea and adjacent N. Atlantic: geochemical implications for the Mediterranean. *Nature* 313 (6003): 565-567.

Statham, P.J. and R. Chester. (1988) Dissolution of manganese from marine atmospheric particulates into seawater and rainwater. *Geochimica et Cosmochimica Acta* 52: 2433-2437.

Statham, P.J., N.H. Morley, and J.D. Burton. *Transport of contaminants through the Dover strait: Trace metals and nutrients.* Fluxmanche, 1991. Interim report

Stebbing, A.R.D. (1985) Organotin and water quality-some lessons to be learned. *Marine Pollution Bulletin* 16: 383-390.

Strickland, J.D.H. and T.R. Parsons. (1972) A practical handbook of seawater analysis. Fisheries Research Board of Canada Bulletin #167.

Sturgeon, R.E. (1989) Graphite furnace atomic absorption analysis of marine samples for trace metals. *Spectrochimica Acta* 44B: 1209-1220.

Sturgeon, R.E., S.S. Berman, J.A.H. Desaulniers, and D.S. Russell. (1980) Pre-concentration of trace metals from seawater for determination by graphite furnace AAS. *Talanta* 27: 85-94.

Subramanian, K. (1988) Determination of Cr (III) and Cr (VI) by ammonium pyrrolidinecarbodithioate-methyl isobutly ketone furnace AAS. *Analytical Chemistry* 60: 11-15.

Sunda, W.G. and R.V. Gessner. (1989) The production of extracellular copper complexing ligands by marine and estuarine fungi. *Chemical Speciation and Bioavailability* 1: 65-70.

Sunda, W.G. and A.K. Hanson. (1987) Measurement of free cupric ion concentration in seawater by ligand competition technique involving copper sorption onto C_{18} SEP-PAK cartridges. *Limnology and Oceanography* 32: 537-551.

Sunda, W.G. and S.A. Huntsman. (1988) Effects of sunlight on redox cycles of manganese in the southwestern Sargasso sea. *Deep Sea Research* 35: 1297-1317.

Sunda, W.G. and S.A. Huntsman. (1990) Diel cycles in microbial manganese oxidation and manganese redox speciation coastal waters of the Bahama islands. *Limnology and Oceanography* 35: 325-338.

Symes, J.L. and D.R. Kester. (1985) Copper (II) interaction with carbonate species based on malachite solubility in perchlorate medium at the ionic strength of seawater. *Marine Chemistry* 16: 189-211.

Talley, L.D. and M.R. Raymer. (1982) Eighteen degree water variability. *Journal of Marine Research* 40: 757-775.

Tappin, A.D. (1988) Studies of trace metals in shelf waters of the British Isles. Ph.D. Thesis. University of Southampton.

Tappin, A.J., G.E. Millward, P.J. Statham, J.D. Burton, and A.W. Morris. (1995) Trace metals in the central and southern North Sea. *Estuarine and Coastal Shelf Science* 41: 275-323.

Tessier, A., P.G.C. Campbell, and M. Bisson. (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* 51: 844-851.

Topping, G. (1986) Quality of data: with special reference to the measurement of trace metals in marine samples. *Science of the Total Environment* 49: 9-25.

Turekian, K.K. (1977) The state of metals in the ocean. *Geochimica et Cosmochimica Acta* 41: 1131-1144.

Turley, C.M. and P.J. Mackie. (1995) Bacterial and cyanobacterial flux to the deep NE Atlantic on sedimenting particles. *Deep Sea Research* 42: 1453-1474.

Turner, A., G.E. Millward, A.J. Bale, and A.W. Morris. (1992) The solid-solution partitioning of trace metals in the Southern North Sea- in situ radiochemical experiments. *Continental Shelf Research* 12: 1311-1329.

Urrere, M.A. and G.A. Knauer. (1981) Zooplankton fecal pellet fluxes and the verticle transport of particulate organic material in the pelagic environment. *Journal of Plankton Research* 3: 369-387.

Valin, R.V. and J.W. Morse. (1982) An investigation of methods commonly used for the selective removal and characterisation of trace metals in sediments. *Marine Chemistry* 11: 535-564.

Van Den Berg, C.M.G. (1986) The determination of trace metals in seawater using cathodic stripping voltammetry. *The Science of the Total Environment* 49: 88-99.

Van Den Berg, C.M.G., M. Boussemart, K. Yokoi, T. Prartono, and L.A.M. Campos. (1994) Speciation of aluminium, chromium and titanium in the NW Mediterranean. *Marine Chemistry* 45: 267-282.

Van Der Weijden, C.H. and M. Reith. (1982) Chromium (III)-Chromium (VI) Interconversions in seawater. *Marine Chemistry* 11: 565-572.

Van Der Weijden, R.R. (1994) Sorption and sorption reversibility of Cd on Calcite under simulated riverine, estuarine and marine conditions. *Marine Chemistry* 47: 65-79

Van Geen, A. and E. Boyle. (1990) Automated preconcentration of trace metals from seawater and freshwater. *Analytical Chemistry* 62: 1705-1709.

Vermieren, K., C. Vandecasteele, and R. Dams. (1990) Determination of trace amounts of Cd, Pb, Cu and Zn in natural waters by ICP AES with thermospray nebulisation, after enrichment on Chelex-100. *Analyst* 115: 17-22.

Veron, A.J., T.M. Church, A.R. Flegal, C.C. Patterson, and Y. Erel. (1993) Response of lead cycling in the Sargasso sea to changes in tropospheric input. *Journal of Geophysical Research* 98 (C10): 18269-18276.

Waite, T.D. and M.M. Morel. (1984) Coulometric study of the redox dynamics of iron in seawater. *Analytical Chemistry* 56: 787-792.

Wangersky, B.J., S. Bradley Moran, R.J. Pett, D.E. Slauenwhite, and X. Zhou. (1989) Biological control of trace metal residence times: An experimental approach. *Marine Chemistry* 28: 215-226.

Wartel, M., M. Skiker, Y Auger, and A. Boughreit. (1990) Interaction of Mn(II) with carbonates in seawater: Assessment of the solubility product of $MnCO_3$ and Mn distribution coefficient between the liquid phase and $CaCO_3$ particles. *Marine Chemistry* 29: 99-117.

Wartel, M., M. Skiker, Y. Auger, A. Boughriet, E. Puskaric, and P. Guegueniat. (1991) Seasonal variation of Mn^{2+} adsorption on to calcareous surfaces in the English Channel, and its implication on the Mn distribution coefficient. In *Reactivity of chemical species in aquatic environments*, ed. M. Branica and G. Kniewald.

Wefer, G., R. Dawson, and G. Hempel. (1981)*The Harrington Sound Project.* Kiel University. BBSR Special Publication 19.

Wells, M.L. and E.D. Goldberg. (1991) Occurrence of small colloids in seawater. *Nature* 353: 342-344.

Wells, M.L. and E.D. Goldberg. (1992) Marine sub-micron particles. *Marine Chemistry* 40: 5-18.

Wen, L.S., M.C. Stordal, D. Tang, G.A. Gill, and P.H. Santschi. (1996) An untraclean cross-filtration technique for the study of the trace metal phase speciation in seawater. *Marine Chemistry* 55: 129-152.

Westerlund, S.F.G., L.G. Anderson, P.O.J. Hall, A. Iverfeldt, M.N. Rutgers van der Loeff, and B. Sundby. (1986) Benthic fluxes of Cadmium, Copper, Nickel, Zinc and Lead in the coastal environment. *Geochimica et Cosmochimica Acta* 50: 1289-1296.

Williams, M.R. (1995) Particulate trace metals in British coastal waters. Ph.D. Thesis. University of Plymouth.

Windom, H.L., R.G.Jr. Smith, and C. Rawlinson. (1989) Particulate trace metal composition and flux across the U.S continental shelf. *Marine Chemistry* 27: 283-297.

Wright, W.R. and A.H. Knap. *Hydrostation "S" off Bermuda in 1982.* UNESCO, 1983.

Zika, R. , Saltzman, E.S and Cooper, W.J. (1985) Hydrogen peroxide concentrations in the Peru upwelling area. *Marine Chemistry* 17:265-275.

Zwolsman, J.J.G., G.T.M. van Eck, and G. Burger. (1996) Spatial and temporal distribution of trace metals in sediments from the Scheldt estuary, South-west Netherlands. *Estuarine, Coastal and Shelf science* 43: 55-79.