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# MONITORING OF TRACE METAL BEHAVIOUR IN NATURAL WATERS

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**MONITORING OF TRACE METAL BEHAVIOUR IN NATURAL WATERS**

by

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in partial fulfilment for the degree of

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Faculty of Science

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## Abstract

An automated voltammetric dissolved trace metal monitor was developed and validated for *in situ* analysis of estuarine waters. The system was successfully applied to the determination of Ni concentrations during two studies in the Tamar Estuary.

The automated system used Adsorptive Cathodic Stripping Voltammetry (AdCSV) for trace metal analysis with a continuous flow sampling procedure and an on line UV digestion system to ensure complete breakdown of interfering and metal complexing organic ligands. Its application to the measurement of total dissolved Ni in the Tamar Estuary showed a high measuring frequency of up to 6 fully calibrated samples per hour and trace metal concentrations ranged between Ni ~10 nM to ~50 nM with a salinity gradient of between ~0 to ~25.

A procedure was developed to evaluate suspended particulate material (SPM) trace metal extraction efficiencies of using EDTA extraction solutions followed by analysis of metals using Inductively Coupled Plasma Mass Spectrometry. The use of EDTA allowed the determination of the easily exchangeable particulate metal fraction using well defined constraints with respect to the competition between EDTA and the particles. Optimum particle extraction time was 72 hours, using 0.05 M EDTA concentration and extractant : particle ratio of 200:1. The extraction procedure was applied to the study of particulate Zn, Ni, Cu, Mn and Mg composition of SPM collected from the Scheldt Estuary.

In addition, seasonal investigation of dissolved chemical speciation of Cu, Co, Ni and Zn in the Tamar estuary using AdCSV was undertaken. The results showed contrasting behaviour for these metals with a high seasonal variability of Zn and Co and a low seasonal variability for Cu and Ni. The low concentration of Zn and Co during summer months suggested that low river flow rates, low rainfall caused minimal sediment disturbance thereby reducing the contribution of Co and Zn enrich pore waters to the estuary. Furthermore, it was suggested that uptake of Zn and Cu by phytoplankton could have contributed to the lower concentrations of these elements during the summer survey. The electrochemically non labile fraction of dissolved Cu, Zn, Ni and Co exhibited highest values at high salinities and indicates the importance of organic complexation of these metals in the lower estuary. Furthermore, during the spring surveys elevated fractions of organically complexed Cu, Zn, and Ni were observed and it was suggested that seasonally enhanced levels of primary productivity could have lead to the complexation of these elements by algal exudates and break down products.

0.05 M EDTA extraction protocol was applied to the study of dissolved and particulate Zn, Cu, Co and Ni in the Scheldt estuary. Dissolved Co and Ni exhibited elevated

concentrations in the upper estuary, which were related to anthropogenic discharges into the estuary. It was possible to identify a relationship between particulate organic carbon and particulate Zn, Cu and Ni, which suggested that complexation of these elements by organic particulate material was an important factor in their dissolved/particulate partitioning.

Results of dissolved Cu natural complexing ligand titration experiments showed similar behaviour for  $Cu_L$  and  $K_{Cu_L}$  for the Tamar and Scheldt estuaries with high values at low salinity decreasing to low values at high salinity. The Scheldt generally exhibited higher values for  $K_{Cu_L}$  and  $Cu_L$  concentrations ( $K_{Cu_L} \sim 15.7$ ;  $Cu_L \sim 200 \text{ Cu neq l}^{-1}$ ;  $S = 1$ ) than the Tamar estuary ( $K_{Cu_L} \sim 14.0$ ;  $Cu_L \sim 170 \text{ Cu neq l}^{-1}$ ;  $S = 0$ ). It was suggested that anthropogenic inputs of nutrients in the Scheldt lead to enhanced levels of phytoplankton activity and complexation of Cu by algal exudates and break down products compared with the Tamar.

Total dissolved Ni and Co was undertaken on samples collected from the Atlantic Ocean using detection by AdCSV. The results indicated that Ni and Co exhibited contrasting behaviour in the oceanic waters compared with estuarine waters. The distribution of Co showed low concentrations (mean Co  $\sim 40 \text{ pM}$ ) in the Atlantic Ocean and elevated concentration associated with aeolian particulate inputs off the Northwest coast of Africa. In contrast, Ni was relatively homogeneously distributed over large parts of the Atlantic ( $2.4 \pm 0.7 \text{ nM}$ ). However, both Ni and Co exhibited conservative behaviour during mixing between the Brazilian Current with the Ni and Co enriched Falklands Current indicating the importance of physical water transport on trace metal distribution in oceanic systems.

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## **AUTHOR'S DECLARATION**

At no time during the registration for the degree of Doctor of Philosophy has the author been registered for any other University award.

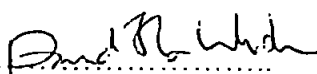
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All experimental and written work for this thesis not mentioned below was undertaken solely by D-J Whitworth. After participating in a research cruise on the Scheldt estuary Prof Wollast, kindly supplied data for organic carbon measurements, which were quoted in Chapter 4. In addition, Mr Bowie and Mr Woodward supplied data for Al, Fe, nitrite, ortho phosphate, silicate, salinity, temperature, coulter particle number and chlorophyll-a for the Atlantic Meridional Transects quoted in Chapter 5. After consultation with Dr Achterberg, Dr Nimmo, Prof. Worsfold, Ms Herzl, Dr Gledhill and Ms Braungardt three sections from this thesis were adapted and published in peer reviewed journals (see Publications below).

Relevant seminars and conferences were attended and in a number of cases work was presented; external institutions were visited for consultation purposes and several papers prepared for publication.

### **Publications**

Achterberg E.P., Braungardt C. and Whitworth D-J. (1998) Electrochemical monitor for near real-time determination of dissolved trace metals in marine waters. In: Sensors in Oceanography (ed. M. Varney), in press.

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Whitworth D-J., Achterberg E.P., Nimmo M. and Worsfold P.J. (1998) Validation and in-situ application of an automated dissolved nickel monitor for estuarine studies. *Analytica Chimica Acta* **371**: 235-246.

Whitworth D-J., Achterberg E.P., Herzl V., Nimmo M., Gledhill M. and Worsfold P.J., (1999) Development of a simple extraction procedure using ligand competition for biogeochemically available metals of estuarine suspended particulate matter. *Analytica Chimica Acta* **392**: 3-17.

### **Papers presented**

Whitworth D-J., Achterberg E.P., Nimmo M. and Worsfold P.J. (1996) A study of trace metals speciation in estuaries using high-resolution monitoring techniques. UK Oceanography. Bangor University. Conference proceedings.

Whitworth D-J., Nimmo M. and Achterberg E.P. (1997) Assessment of the bioavailable trace metal concentration of coastal marine sediments. British Petroleum Constancy report.

Whitworth D-J., Achterberg E.P., Nimmo M. and Worsfold P.J. (1997) Seasonal study of dissolved Ni, Cu, Zn and Co speciation in estuaries using adsorptive cathodic stripping voltammetry. Progress In Chemical Oceanography.

Whitworth D-J., Achterberg E.P., Nimmo M. and Worsfold P.J. (1997) High resolution in-situ measurements of chemical speciation of dissolved Ni and Co in the Tamar estuary. March Mor. Conference proceedings.

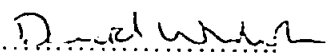
Whitworth D-J., Achterberg E.P., Nimmo M. and Worsfold P.J. (1998) Validation and in situ application of automated adsorptive cathodic stripping voltammetry (ACSV). Trace Metal Meetings, Zeneca.

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Bowie A.R., Whitworth D-J., Achterberg E.P., Worsfold P.J. and Mantoura F.R.C. (1998)  
Iron distributions along two Atlantic Meridional; Transects by flow injection –  
Chemiluminescence Analysis. UK Oceanography. Southampton Oceanography Centre.  
Conference proceedings.

Bowie A.R., Whitworth D-J., Achterberg E.P., Worsfold P.J. and Mantoura F.R.C. (1998)  
Iron biogeochemistry in seawater. SCOR Working group, 109. Royal Netherlands Academy  
of Arts and Sciences. Conference proceedings.

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# 1 Introduction

Figure 1.1 presents a broad overview of the earth surface aquatic environments and some of the inputs, transport mechanisms and sinks for trace metals. Factors responsible for inputs of trace metals into the biosphere include: eruption of volcanic material which can project large quantities of particulate metal into the environment; chemical and physical weathering of the terrestrial environment; and anthropogenic discharges. Inputs of trace metals can lead to enhanced trace metal concentrations in the aquatic environments. The transport of particulate and dissolved trace metals through the riverine environment can lead to enhanced concentrations of metals entering an estuarine system. In some estuarine environments, and particularly river delta systems internal estuarine processes (e.g. adsorption, complexation, flocculate, precipitation) can lead to the deposition of particulate trace metals and trace metals can become caught up in the internal cycle of estuarine systems. Consequently, estuaries act as a filter for metals and reduced levels of trace metals reach the coastal marine system. Processes affecting trace metal concentrations in coastal and shelf sea environments include aeolian deposition (wet and dry) of trace metals, uptake of metals by biota, the sinking of particulate metals, the mixing of open ocean surface water and the upwelling of deep ocean waters. Lowest trace metal concentrations can be observed in open ocean environments owing to uptake by phytoplankton, net deposition of particulate trace metals and low rates of trace metal inputs. Trace metals settling in the deep ocean can either become deposited or, as a result of oceanic currents, can become upwelled at continental shelf edges, and hence be recycled in the marine systems.

The main emphasis of this thesis is an investigation of processes affecting Co, Ni, Zn and Cu transport in the estuarine environment. In addition, the behaviour of Co and Ni was

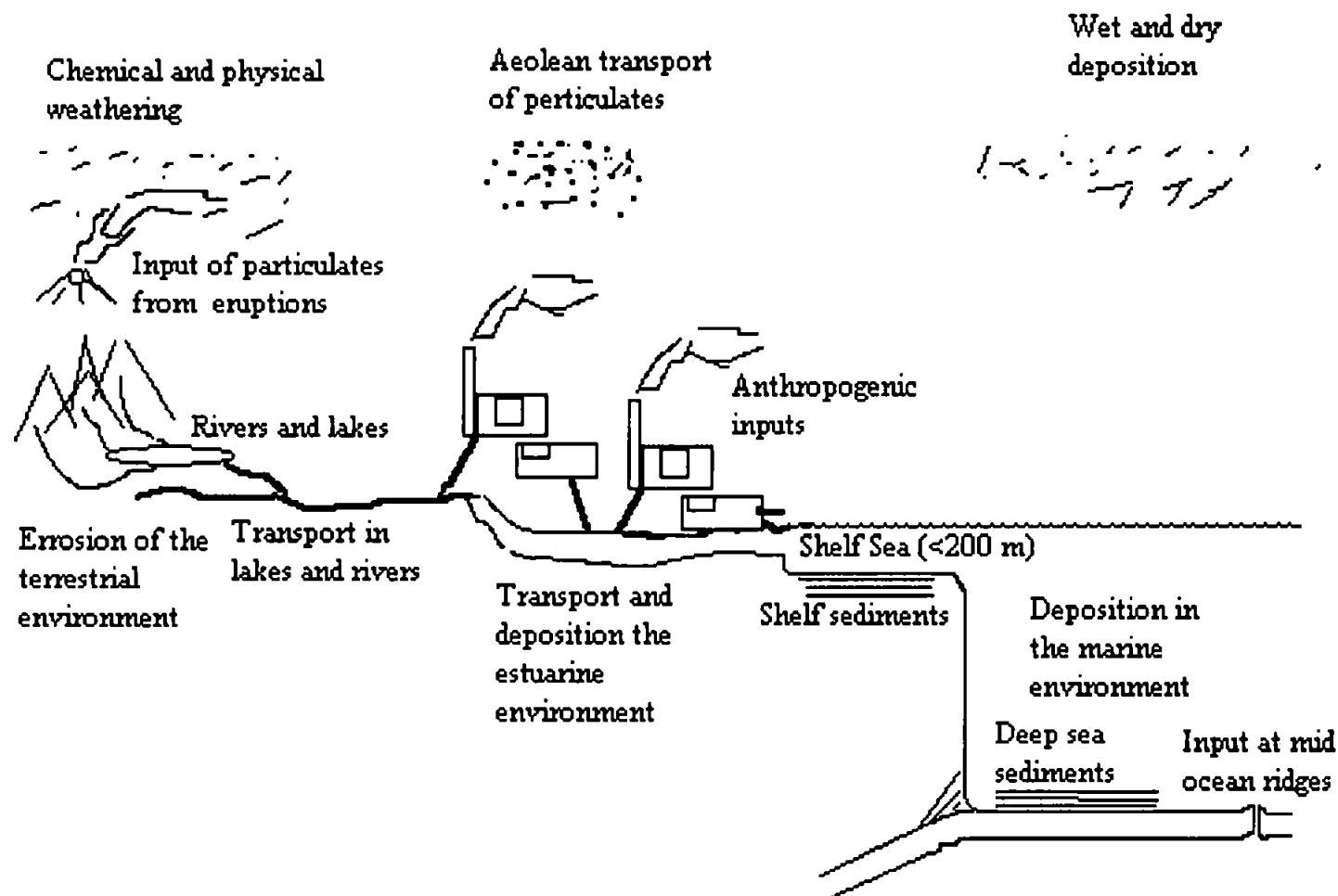


Figure 1.1 A schematic representation of some of inputs, transport mechanisms and sinks for trace metals in the aquatic environment.

investigated in surface open oceanic waters to assess the factors influencing their behaviour in this environment.

Rivers are one of the most important pathways for the transport of continental and anthropogenically derived material to the oceans. Estuaries form the interface between the rivers and the oceans. As estuaries are characterised by dynamic physico-chemical gradients, modifications of the distribution of trace metals between dissolved and particulate species may occur (Ackroyd *et al.*, 1986; Zwolsmann *et al.*, 1997; Elbaz-Poulichet *et al.*, 1996; Laslett and Balls, 1995; Paucot and Wollast, 1997). Defining estuarine biogeochemical pathways of trace metals requires an understanding of their distribution and hence their behaviour. Estuaries are governed by tidal action and by river flow. In the mixing zone of salt and fresh water, strong longitudinal gradients in physico-chemical parameters including, dissolved oxygen, salinity, pH, Eh and temperature develop. These master variables affect internal estuarine processes concerning trace metals (i.e. as adsorption/desorption; precipitation; coprecipitation; flocculation; sediment re-suspension).

The distribution of trace metals in estuaries has been extensively studied during the last two decades to assess the effect of anthropogenic inputs on these systems (e.g. Klinkhammer and Bender, 1981; Apte *et al.*, 1990) and for the development of realistic oceanic mass balances (Boyle *et al.*, 1982). The estuarine geochemistry of dissolved trace metals is controlled by a complex interplay of hydrodynamic factors, industrial and municipal wastewater discharges, natural inputs and biogeochemical processes (Millward, 1995; Regnier *et al.*, 1997; Zwolsman *et al.*, 1997; Campbell *et al.*, 1988). These factors yield large temporal and spatial variations in estuarine dissolved trace metals concentrations.

Elements such as Co, Ni, Zn and Cu exhibit contrasting behaviours in different estuaries and appear to be subject to more than one controlling process. The chemical form of Cu, Zn, Co and Ni may have a profound effect on their toxicity, solubility and particulate

adsorptive/desorptive characteristics. Zwolsman and Van Eck, (1993) observed that dissolved complexation of Zn and Cd by  $\text{Cl}^-$  in seawater enhanced their solubility (Pettersen *et al.*, 1997). Furthermore, it has been reported that in the presence of dissolved organic metal complexing ligands, organisms were able to tolerate enhanced concentrations of dissolved Cu (Paulson *et al.*, 1994a, b). Studies by Knauer *et al.*, 1982 have shown that dissolved Co can co-vary with dissolved Mn in estuarine and coastal waters and suggested that their geochemical behaviour were linked to co-precipitation of Co during the formation of Mn oxy/hydroxides in the low salinity zone (salinity = 0 to 10). Ni has been shown to exhibit conservative behaviour in the Rhone Estuary (France) during mixing between Ni enriched river water and Ni depleted seawater (Elbaz-Poulichet *et al.*, 1996). In contrast, Laslett and Balls, (1995) in a study of the Forth Estuary (Great Britain), revealed enrichment of Ni in the mid estuary during summer months, which was attributed to the remobilisation of Ni with Mn in an oxygen minimum zone.

Because of the transient variations in trace metal concentrations, high resolution monitoring techniques are required to enhance our understanding of the biogeochemical processes affecting the chemical constituent levels. Few analytical techniques have the ability to measure dissolved trace metals directly in estuarine waters. The difficulty lies in the highly variable water chemistry and interference from major ions (i.e.  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Cl}^-$ ), which are present at elevated concentrations. The trace metal concentrations may also exhibit strong gradients in estuaries. Many trace metals occur at enhanced levels in the freshwater end of an estuarine system (e.g.  $[\text{Zn}] = 269 \text{ nM}$  at in the Scheldt river; Zwolsman *et al.*, 1997) and at lower levels in the seawater end of the estuary (e.g.  $[\text{Zn}] = 15 \text{ nM}$  at salinity 35 in the Scheldt estuary; Zwolsman *et al.*, 1997). Many estuarine trace metal studies have been conducted using discrete sampling strategies followed by laboratory based analysis using flame or graphite furnace atomic absorption spectrometry (AAS) (Zwolsman *et al.*, 1997) or inductively coupled plasma mass spectrometry (Nickson *et al.*, 1995). These techniques often require dilution or matrix removal by means of

solvent or solid phase extraction in order to avoid analytical interferences associated with the enhanced concentration of easily ionisable ions present in estuarine waters (e.g.  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Cl}^-$ ). This approach limits the number of samples that can be processed due to the time required for the pre-treatment of samples prior to analysis. The discrete sampling approach followed by laboratory analysis involves a number of sample handling operations, which increases the potential for sample contamination.

Adsorptive Cathodic Stripping Voltammetric (AdCSV) methods were adopted for dissolved trace metal measurements throughout this study. Electrochemical techniques are capable of direct dissolved trace metal analysis at low concentrations without prior trace metal pre-concentration or matrix removal procedures (van den Berg, 1989). In addition, electrochemical methods are well suited for an automated measurement approach. A number of studies have been published for estuarine trace metal investigations using various electrochemical approaches. Zirino *et al.*, (1978), have reported on automated measurements of Cu and Zn in San Diego Bay using automated adsorptive anodic stripping voltammetry (AdASV). This approach was able to analyse up to 3 samples per hour, and calibration was performed hourly by the addition of an internal metal standard. A limitation of the use of AdASV is that in estuaries and seawater this technique is restricted to the determination of Cu, Pb, Cd and Zn (van den Berg, 1989). Other elements can be determined using this technique, but their seawater concentrations are too low for detection by AdASV, or the analysis is hampered by interferences. Van den Berg, (1991c) performed ship-board measurements of labile Cu and Zn in the Tamar estuary using on-line cathodic stripping chronopotentiometry (CSC). Furthermore, Wang *et al.*, (1995) have reported the remote determination of labile Cu in an estuarine system (San Diego Bay) using CSC with a gold fibre electrode. The method applied by Wang *et al.*, (1995) has a reported limit of detection of ca. 5 nM, and is therefore suitable for estuarine and coastal waters with enhanced metal levels, but not for more pristine waters. The analytical approaches for CSC utilised external calibration procedures for corroboration of the trace metal concentrations

in the estuarine samples. For this purpose, samples with known added metal standards were determined, often at the start and finish of the fieldwork. Due to the strong variations in the sample matrix, which is characteristic for estuarine systems, important changes in sensitivity of the analysis may consequently result in errors in the calculated sample concentration.

For estuarine and oceanic studies AdCSV was utilised in conjunction with the internal metal standard addition approach. This calibration method corrects for changes in sensitivity of the analysis associated with sample matrix variability and therefore each sample is fully quantified. Advantages of AdCSV include a high sensitivity (e.g. limit of detection for Ni = 0.1 nM) (Pihlar *et al.*, 1981), adaptability for automated usage and an ability to determine a wide range of trace metals in seawater (over 20 metals including Co, Cu, Ni, Zn, V, U and Fe) (van den Berg, 1989; van den Berg, 1991a, b).

Trace metal behaviour in estuaries is strongly influenced by suspended particulate material (SPM). Particle-water interactions of trace metals determine whether they are flushed from an estuary in the dissolved phase, or because of adsorption onto particles are retained within the internal cycle of the estuary (Morris *et al.*, 1986). In many estuaries removal of dissolved metal concentrations has been observed in the turbidity maximum zone (TMZ), which is an estuarine region with strongly enhanced SPM levels (e.g. > 600 mg l<sup>-1</sup> in Tamar estuary (U.K.), salinity 0.5-5 psu) (Ackroyd *et al.*, 1986; Grabemann *et al.*, 1997). Desorption of SPM bound metals (e.g. Zn (Ackroyd *et al.*, 1986), and Cd, Cu and Zn (Zwolsman *et al.*, 1997)) has been observed in higher salinity regions of estuaries and has been explained by an increases in major cation concentrations leading to competition for adsorption sites at the surface of SPM. Furthermore, mid estuarine enrichment in dissolved Zn, Cd and Cu has been reported owing to desorption of particulate metals from surface sites on SPM and complexation with e.g. Cl<sup>-</sup> and infusion of metal enriched interstitial waters (Ackroyd *et al.*, 1986; Zwolsman and Van Eck, 1993). Suspended particulate matter may consist of biological, organic and mineral phases (Buffle, 1988) and each of these

phases has a different affinity for trace metals. Studies involving the determination of trace metals in SPM and sediments often determine total metal concentrations. This approach does not provide information about the biogeochemical availability of the particulate matter associated trace metals. For soils and sediments, workers have employed sequential chemical extraction schemes in order to investigate trace metal association with organic and mineral phases in their particles. Commonly employed sequential extraction procedures for sediments include the 5 step scheme developed by Tessier *et al.*, (1979) and the 3 step BCR scheme (Queauvauviller *et al.*, 1997; Lopez-Sanchez *et al.*, 1998), and variations on these schemes (Campanella *et al.*, 1995; Kersten and Forstner, 1987). A large number of studies have been published employing the multi-step sequential extraction schemes on sediments (Szefer *et al.*, 1995; Kersten and Forstner, 1986; Weimin *et al.*, 1992) and soils (Gibson and Farmer, 1986; Shan and Bin, 1993; McGrath, 1996). The sequential extraction procedures have a number of disadvantages limiting their widespread use for studies into SPM associated trace metals. Firstly, the procedures often use 1 g of dry material, an amount that is often difficult to obtain for SPM by filtration of natural waters. Furthermore, parts of sequential extraction schemes suffer from re-adsorption of the extracted metal onto the residual phases remaining after each extraction step, and a limited specificity of the reagents for the targeted phases of the soil or sediment (Whalley and Grant, 1994, and Lead *et al.*, 1998). In addition, the procedures are labour-intensive and because of the numerous steps involved have enhanced associated errors and an enhanced risk of sample contamination. Hence, a novel SPM extraction methodology was developed during the experimental stage of this study. The methodology applied a ligand competition procedure to the investigation of non-lattice bound trace metals associated with SPM. The methodology used EDTA (ethylenediaminetetraacetic acid) as the added competing ligand. The use of EDTA for soil and sediment extraction procedures has been reported by other workers (McGrath, 1996; Ure *et al.*, 1993). However, little or no work appears to have been carried out using EDTA extraction for SPM associated metals. The

analytical procedure for SPM associated trace metals reported complemented the ligand competition techniques for determination of trace metal complexation by dissolved organic ligands in natural waters (Achterberg and van den Berg, 1997; Achterberg, 1993; Achterberg *et al.*, 1997).

This thesis is composed of six chapters, which are summarised below:

1. Chapter 2 contains an analytical characterisation of methodologies and protocols for (1) water collection, (2) analysis of dissolved Ni, Co, Cu and Zn by AdCSV, and (3) determination of particulate 0.05 M EDTA exchangeable Co, Ni, Co, Zn, Mn, Cu, Pb, Mg and Al.
2. Chapter 3 presents a study of the seasonal variability of dissolved Co, Ni, Zn and Cu in the Tamar Estuary.
3. Chapter 4 presents a study of the behaviour of dissolved and particulate Cu, Co, Zn and Ni during a winter survey of the Scheldt Estuary.
4. Chapter 5 presents a study of the distribution of Co and Ni in waters of the North and South Atlantic.
5. Chapters 6 gives an overview of Co, Ni, Zn and Cu behaviour in estuaries and contrasts processes affecting the behaviour of Ni and Co in oceanic and estuarine systems.

## 2 Methodology and Experimental

This chapter has been sub divided into three main sections. Section 2.1 (Sample collection and pre-treatment), describes the sample collection and pre-treatment procedures (e.g. filtration, acidification). Section 2.2 (Analysis of water samples), describes the measurement of pH, salinity, temperature and oxygen, in addition to the batch and automated measurements of Co, Ni, Cu and Zn by AdCSV. Section 2.3 (Analysis of SPM samples), details the development of a procedure to investigate the particulate Co, Ni, Zn, Cu, Mn, Pb, Al and Mg concentrations of estuarine SPM and their analysis by ICP-MS.

### 2.1 Sample collection and pre treatment

#### *2.1.1 Labware and sample bottles*

All reagents and wash solutions used during this study were made up in water purified by reverse osmosis (Milli-RO, Millipore) followed by ion-exchange (Milli-Q, Millipore). All labware and sample bottles (Nalgene) were composed of high density polyethylene (HDPE) and were thoroughly washed prior to use to minimise trace metal contamination. Reagent containers and sample bottles were soaked in 2% v:v Decon 90 for 24 hours, then washed with copious quantities of Milli-Q water and transferred to a 50% v:v HCl (AnalaR) bath and left for one week. They were subsequently rinsed with Milli-Q water and then placed into a 20% v:v HNO<sub>3</sub> (AnalaR) bath. After a further week the bottles were thoroughly washed in Milli-Q water and stored inside re-sealable polythene bags prior to use (Achterberg *et al.*, 1997).

The efficiency of the acid washing procedure was assessed by adding acidified Milli-Q water (ca pH 2, using quartz distilled HCl) to 5 washed containers which were then left over night at room temperature. The concentrations of Ni, Co, Cu and Zn in all sub aliquots of the Milli-Q water were below the limit of detection (Co < 0.004 nM; Ni < 0.1 nM; Cu < 0.2 nM and Zn < 0.5 nM) by Adsorptive Cathodic Stripping Voltammetry (AdCSV) and indicate that the acid washing procedure was satisfactory for trace metal studies.

### *2.1.2 Sampling protocols and pre-treatment*

#### **1 Water collection**

Discrete water samples were collected in 250 ml and 500 ml acid cleaned HDPE bottles. After 3 rinses with sample the bottles were filled to the brim and closed. The bottles were then stored in polythene bags and kept cool (ca 4 °C) prior to laboratory analysis at Plymouth University. For this study water and SPM samples were collected from the Tamar Estuary (United Kingdom (Chapter 3)), the Scheldt Estuary (Belgium (Chapter 4)) and the Atlantic Ocean (Chapter 5) specific details of sampling locations and methods can be found in Chapters 3, 4 and 5.

#### **2 Water filtration and collection of suspended particulate material (SPM)**

Cellulose nitrate filters (47 mm diameter, Whatman) were acid cleaned in 0.05 M HCl (quartz distilled) overnight prior to use. The vacuum filtration unit (500 ml polysulfone, Nalgene) was soaked in 2% v:v Decon 90 detergent overnight then transferred to a ~2 M HCl acid bath and left for 1 week. In order to ensure the wash procedure was adequate blank values of trace metals in Milli-Q water were determined by AdCSV after filtration. The results showed that the Co, Ni, Zn and Cu concentrations in the filtered Milli-Q water

were below the limit of detection by AdCSV. A vacuum hand-pump (Nalgene) was used to evacuate the filtration unit.

The concentration of SPM in water samples was determined by the weight of particulate material collected on a pre weighed 0.45  $\mu\text{m}$  porosity filter from a known volume (usually ~250 ml) of water sample. The filters were collected after filtration and then placed in a drying cabinet overnight at 45 °C preceding re weighing using a precision balance (5 decimal place, Sartorius) which was calibrated twice monthly. For SPM leaching studies the filters were subsequently stored at -17 °C.

### 3 Preservation of water samples by acidification using HCl

Samples intended for total dissolved trace metal studies were filtered (through 0.45  $\mu\text{m}$  porosity filters (see below)) and acidified to pH 2 using concentrated sub boiled HCl (1  $\mu\text{l}$  per 1 ml of sample) for storage. Measurement of total dissolved trace metals was normally conducted within 2 weeks of sampling. However, in the case of some samples longer time between sample collection (and acidification) and analysis of total dissolved metal concentrations was necessary. For example, owing to transport time, samples collected during the Atlantic Meridional Transects were not analysed until up to ~1 year after collection.

Experiments were undertaken to ensure that the preservation of samples using concentrated HCl prevented the precipitation of dissolved trace metals. Hence, filtered (through 0.45  $\mu\text{m}$  porosity filters) seawater was collected from the Southern North Sea (Belgium) in a 2.5 l acid washed HDPE bottle and acidified to pH ~2 using concentrated HCl (1 $\mu\text{l}$  per 1 ml of sample) during a cruise with the *Belgica* on 14-12-1996 (Chapter 5). Five initial measurements of total dissolved Co, Zn, Ni and Cu were performed within one week of collection and the water sample was analysed periodically for use as an internal laboratory

standard sea water sample ( $S = 34.52$ ). The results of subsequent analysis of the Southern North Sea internal laboratory standard seawater are presented in Table 2.a. These data show that analysis of total dissolved Co, Ni, Zn and Cu in the North Sea seawater sample gave comparable results when preserved with HCl for up to 1.5 years after the initial analysis.

Table 2.a Effect of storage time on the concentration of total dissolved Co, Ni, Zn, Cu when preserved in the presence of concentrated HCl (1 $\mu$ l per 1 ml of sample). Each reported value is based on at least 5 replicate measurements.

| Time (months) | Co (pM)       | Ni (nM)       | Zn (nM)        | Cu (nM)       |
|---------------|---------------|---------------|----------------|---------------|
| 0             | 459 $\pm$ 12  | 4.2 $\pm$ 0.3 | 10.1 $\pm$ 0.5 | 3.6 $\pm$ 0.2 |
| 6             | 456 $\pm$ 10  | 4.0 $\pm$ 0.5 | 9.4 $\pm$ 0.2  | 3.6 $\pm$ 0.4 |
| 12            | 452 $\pm$ 3.4 | 4.1 $\pm$ 0.1 | 9.2 $\pm$ 0.2  | 3.4 $\pm$ 0.3 |
| 18            | 454 $\pm$ 11  | 4.2 $\pm$ 0.7 | 9.2 $\pm$ 0.1  | 3.5 $\pm$ 0.2 |

#### 4 UV photo digestion of dissolved organic material

In order to avoid interferences during voltammetric total dissolved trace metal determinations, water samples were exposed to UV light for 4 hours. This approach breaks down surfactants, which interfere with the AdCSV method and also degrades metal complexing organic ligands thereby freeing bound metals. This was achieved by adding 30 ml of acidified sample (pH 2) into a thoroughly acid washed 35 ml quartz tube with a PTFE

cap. 60  $\mu\text{l}$  of  $\text{H}_2\text{O}_2$  (27 % v:v) was added to the samples in order to aid the decomposition of dissolved organic compounds (Achterberg and van den Berg, 1994a). The samples were exposed to UV light for ca 4 hours and the sample temperature was between 60 to 70  $^{\circ}\text{C}$ . UV-digestion was undertaken using an laboratory built system containing a 400 W medium pressure mercury vapour lamp (Photochemical Reactors).

## 2.2 Analysis of water samples

### 2.2.1 Measurement of aquatic master variables

#### 1 Salinity and conductivity

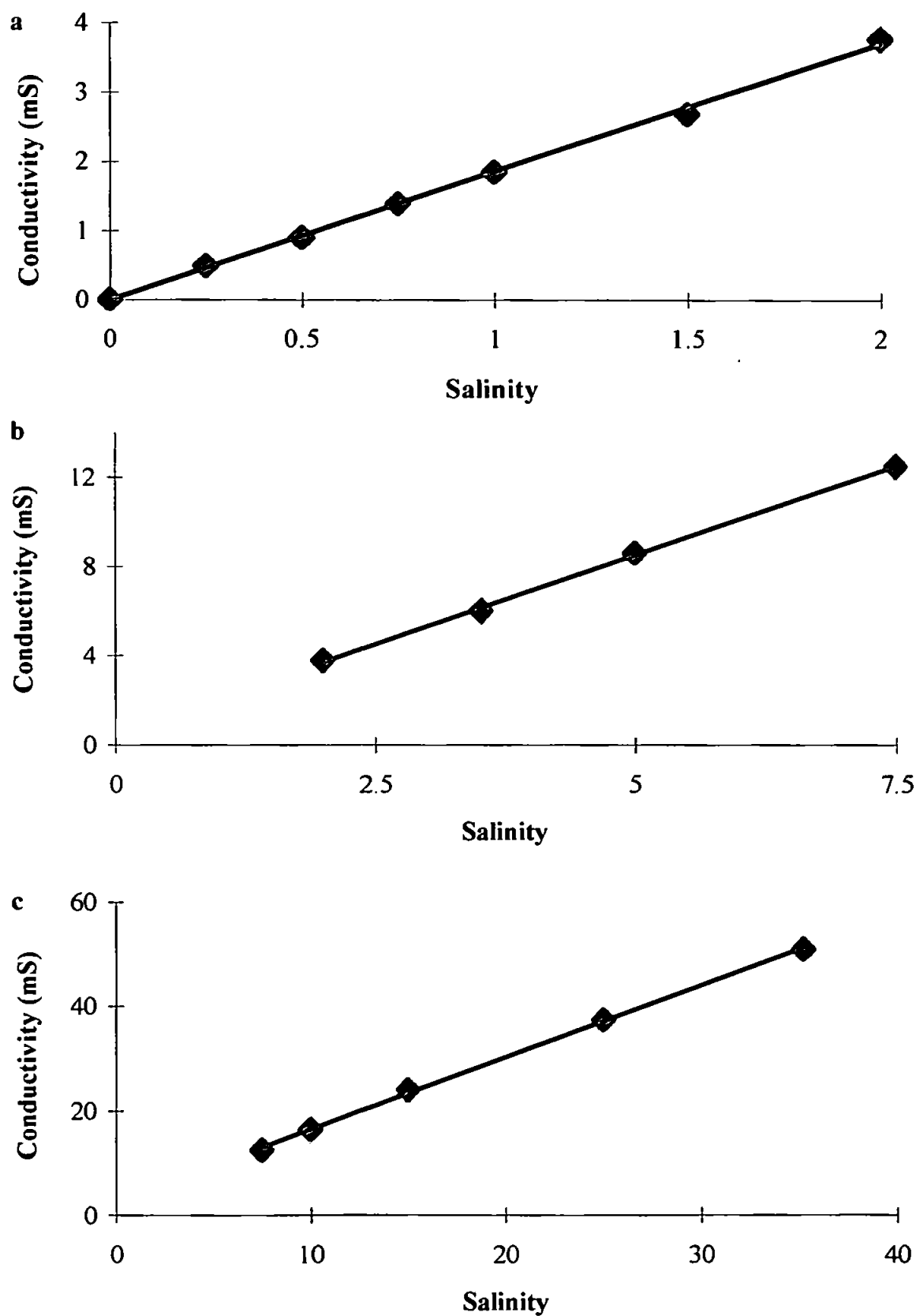
Conductivity measurements were performed in the field using a pHOX 52E conductivity meter. The instrument was calibrated daily against a reference seawater which had previously been analysed using a salinometer ( $S = 35.268$ ). Salinity values were inferred from the graphical relationship between salinity and conductivity (equation 1).

$$x = \frac{(y - c)}{m} \quad (1)$$

Where,  $y$  = conductivity,  $x$  = salinity,  $m$  = slope and  $c$  = intercept.

However, the relationship between conductivity and salinity is not strictly linear; especially at low salinities (0 to  $\sim 2$ ). Therefore, the calibration plot was split into three ranges in order to obtain the minimum error on the inferred salinity values. Figure 2.1 illustrates typical

Figure 2.1 Typical relationship between conductivity (mS) and salinity. (a) salinity = 0 to 2, (b) salinity = 2 to 7.5 and (c) salinity = 7.5 to 35. The slope, intercept and regression characteristics are show in Table 2.b.



conductivity against salinity calibration plots, the figures display salinities ranging between 0 (Milli-Q water) and 35.268 (seawater) with 14 calibration intervals. The calibration plots were grouped at the following salinity intervals: of 0 to 2 ( $n = 7$ ); 2 to 7.5 ( $n = 4$ ), and; 7.5 to 35 ( $n = 5$ ). The intercept ( $c$ ), slope ( $m$ ) and correlation coefficients ( $R^2$ ) for the inferred salinity observations are presented in Table 2.b.

Table 2.b Intercept and slope characteristics of the salinity-conductivity calibration plots (Figure 2.1).  $R^2$  values are valid at the 99% confidence interval.

| Salinity interval | Observations (n) | Intercept in mS (c) | Slope (m) | Regression ( $R^2$ ) |
|-------------------|------------------|---------------------|-----------|----------------------|
| <i>0 to 2</i>     | 7                | 0.008               | 1867      | 0.998                |
| <i>2 to 7.5</i>   | 4                | 0.531               | 1596      | 0.999                |
| <i>7.5 to 35</i>  | 5                | 2.706               | 1379      | 0.999                |

## 2 pH

The pH of sample waters was determined in the field using a Jenway 3010 pH meter with a combination pH electrode, which was calibrated twice daily using pH 4 and pH 7 buffer solutions (NIST). Laboratory pH measurements of analyte and buffer solutions were undertaken using the same pH meter and probe.

### 3 Temperature and dissolved oxygen

Dissolved oxygen concentrations and temperature measurements in waters were undertaken *in situ* using a Yellow Stone Industries meter (model number 5739) connected to a combined temperature and dissolved oxygen probe.

#### 2.2.2 Batch determination of dissolved Ni, Cu, Co and Zn by AdCSV

##### 1 Reagents

Reagents were purchased from Merck, AnalaR grade unless otherwise stated. The concentration of trace metals in the concentrated acid solutions was reduced by sub-boiling quartz distillation. Ammonia was purified through isopiestic distillation (Howard and Statham, 1993). Standard metal solutions were freshly prepared from BDH Spectrosol standard solutions (typically 1000 mg/l) and acidified to pH 2 using HCl (1  $\mu$ l HCl per 1 ml standard solution). When not in use, reagents and metal standards were stored in HDPE bottles at 4 °C.

The voltammetric determination of dissolved Cu was achieved using either Oxine (8-Hydroxyquinoline) or Tropolone (2 Hydroxy-2,4,6-cycloheptatrienone; Aldrich) as the electrochemical Cu complexing ligand, and N-2-hydroxyethylpiperazine-n'-2-ethanesulfonic acid (HEPES) as pH buffer at pH 7.78 (van den Berg, 1986a; Donat and van den Berg, 1992). A stock solution of 0.1 M Oxine was made up by dissolving 0.1452 g of Oxine salt into 10 ml of Milli-Q water. Measurement of total dissolved Cu was undertaken in the presence of 0.2 mM Oxine and 10 mM HEPES (pH = 7.78).

A 0.1 M stock solution of Tropolone was made up by dissolving 0.1221 g of salt into 10 ml of methanol. Labile dissolved Cu determinations were carried out in the presence of 0.4 mM Tropolone and 10 mM HEPES (pH = 7.78). The pH buffer (1 M HEPES) stock solution

was made up by dissolving 59.58 g of HEPES into 250 ml of Milli-Q water, the pH was then adjusted to 7.78 using an appropriate volume of ammonia (typically ~2.5 ml). Contamination of Cu (~0.5 nM) and Zn (~3 nM) were noticed in the 1 M HEPES solution and therefore a 'clean up' procedure was applied to reduce Cu and Zn levels. 250  $\mu$ l of 0.01 M Oxine was added to 250 ml of 1 M HEPES, 10 minutes was allowed for the Oxine to fully complex any trace metal contaminants present. The Oxine metal complexes were subsequently removed from the HEPES solution by passing the stock solution through Sep Pak C-18 (Whatman) cartridges at 1 ml per min using a peristaltic pump (Watson Marlow). Prior to use the C-18 cartridges were activated by passing 10 ml of methanol through the cartridge (1 ml per min). This was followed by a Milli-Q water rinse of the C-18 cartridge at 5 ml per min (for 10 minutes). The first 20 ml of HEPES solution was recycled to ensure that contaminants in the initial solution were removed efficiently. After purifying the HEPES solution, Cu and Zn values were below the limits of detection by AdCSV (i.e. Cu = 0.2 nM and Zn = 0.5 nM).

For the determination of Cu natural ligand concentrations and conditional stability constants, SA (salicylaldoxime) was used for the added Cu complexing ligand with Borate (Boric Acid) as the electrochemical buffer at a final concentration of 25  $\mu$ M and 10 mM respectively. An aqueous stock solution containing 0.01 M SA was prepared in 0.1 M HCl. A 1 M stock solution of Borate was made up to 100 ml in Milli-Q water and the pH adjusted using Ammonia; 100  $\mu$ l of this buffer in 10 ml seawater gave a pH of 8.35 (Campos and van den Berg, 1994).

Dissolved Ni concentrations were determined using dimethylglyoxime (DMG) and HEPES buffer set at pH 7.78 (described above). A stock solution of 0.1 M DMG was made up by dissolving 0.1161 g of DMG salt into 10 ml of methanol. Total dissolved Ni determinations were carried out using final DMG and HEPES concentrations of 0.4 mM and 10 mM

respectively. Labile Ni determinations were carried out at DMG and HEPES concentrations of 0.1 mM and 10 mM respectively (Pihlar *et al.*, 1981).

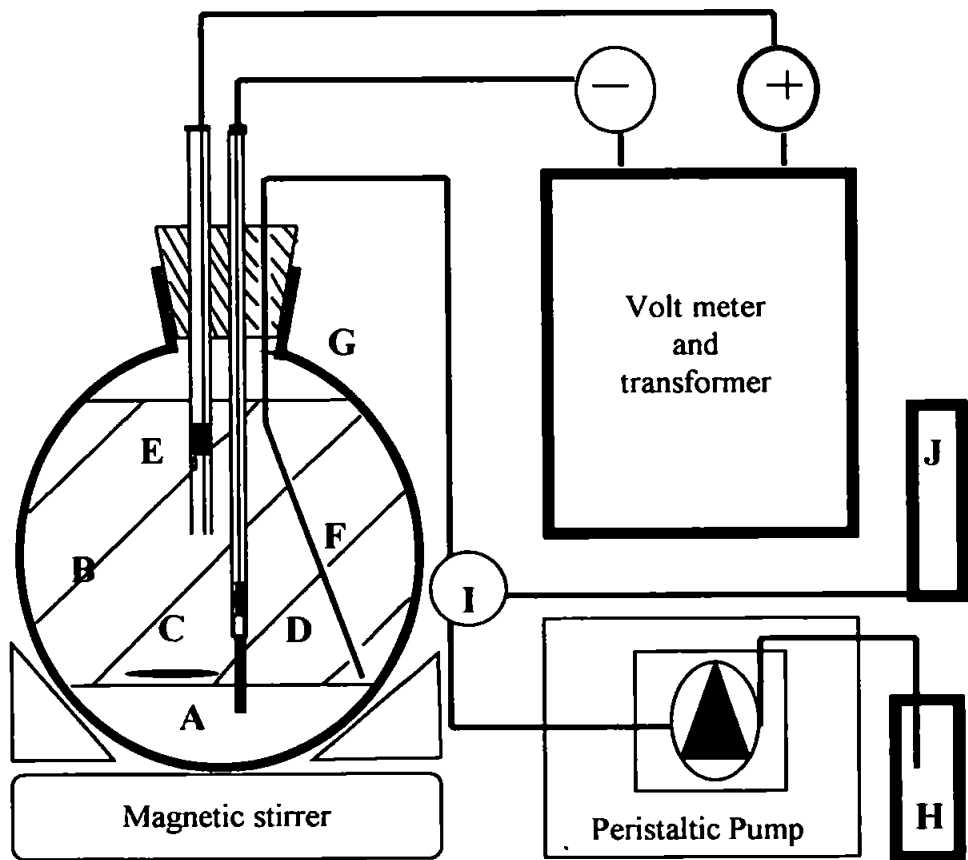
The concentration of dissolved Co was determined by AdCSV in the presence of 0.01 mM Nioxime (1,2-Cyclohexanedione-dioxime), 0.5 M sodium nitrite ( $\text{NaNO}_2$  electrochemical catalyst) and concentrated  $\text{NH}_4\text{Cl}$  (buffer, pH = 9.2) (Vega and van den Berg, 1997). 10 ml of Nioxime was made up by dissolving 0.2383 g of Nioxime salt into 10 ml of Milli-Q water.  $\text{NH}_4\text{Cl}$  was prepared by mixing 10 ml of purified concentrated ammonia with 10 ml concentrated redistilled HCl, the solution was allowed to equilibrate for 10 minutes prior to sealing inside a HDPE bottle. A 5 M stock solution of  $\text{NaNO}_2$  was made up in Milli-Q water by dissolving 172.5 g of salt into 500 ml of Milli-Q water. Elevated concentrations of Co (0.2 nM) were observed in the  $\text{NaNO}_2$  which required the development and construction of an electrolysis cell to reduce the Co concentration to below  $10^{-12}$  M (see below). In addition to the dissolved Co determinations by Nioxime, some Co measurements were undertaken using DMG as the complexing ligand (as described for Ni above; Pihlar *et al.*, 1981).

Dissolved Zn determinations were carried out in the presence of 0.1 mM APDC (Ammonium pyrrolidine dithiocarbamate) and 10 mM TRIS buffer (Hydroxymethyl) methylamine) set at pH 7.4 (van den Berg, 1985). Stock solutions of 0.1 M APDC were made by dissolving 0.1643 g of APDC salt into 10 ml of Milli-Q water and a 1 M stock solution of TRIS was prepared by dissolving 24.23 g TRIS into 200 ml Milli-Q water. The buffer was set at pH 7.4 using an appropriate volume of concentrated redistilled HCl (~3.5 ml).

## 2 Electrolysis method for purifying reagents for trace metal analysis

Trace metals in pristine open ocean waters are present at very low concentration. The analysis of seawater containing low metal levels presents analytical difficulties, which include obtaining 'ultra-clean' analytical reagents. Using static potential electrolysis, trace metal contaminants in reagent solutions can be reduced to below  $10^{-12}$  M (Howard and Statham, 1993). The following section describes the construction of an electrolysis system, which was utilised to reduce the metal concentration in sodium nitrite. Figure 2.2 illustrates the construction of an electrolysis cell. An anode composed of Pt was inserted into the top of the contaminated reagent. Pt was selected as the anode material as it did not oxidise during operation of the system. Mercury forms the cathode and a mercury pool (~560 g) was placed into a 500 ml round bottom flask. The mercury pool increased the surface area of the cathode and thereby reduced the time required for removal of trace metal contaminants. In addition, most transition metals became dissolved in the Hg pool aiding the removal of metals from solution. A carbon rod was inserted into the Hg thereby completing the cell circuit. Carbon was selected as it is relatively un-reactive (most metals form amalgams and would have dissolved into the Hg pool). A transformer power unit was connected to the cell and set at -1.5 V. At -1.5 V metal ions were removed from solution without liberating significant quantities of  $H_{2(g)}$ . A voltmeter was incorporated to monitor the voltage of the cell. To ensure a homogenous solution was maintained the system was stirred using a magnetic stirrer and Teflon bar. To evaluate the efficiency of Co and Ni removal from a contaminated solution using the laboratory built static potential electrolysis system, 500 ml of a Milli-Q water solution containing Ni (10 nM) and Co (10 nM) was transferred into the apparatus. To avoid interference from dissolved oxygen the solution was de-aerated by purging with nitrogen (oxygen free) for 30 minutes, and the cell was set at -1.5 V. 40 ml aliquots were withdrawn from the unit after 24, 48 and 72 hours. The

Figure 2.2 Schematic representation of the static potential electrolysis apparatus, which consisted of; (A) Hg pool, (B) 500 ml of reagent (metal spiked Milli-Q water), (C) a magnetic stirrer, (D) carbon cathode, (E) a platinum wire anode, (F) reagent extraction and nitrogen purge tube, (G) 500 ml round bottom flask, (H) ultra clean HDPE reagent collection vessel, (I) two way junction and (J) nitrogen supply.



solutions were then analysed for dissolved Ni and Co by AdCSV. Table 2.c illustrates the reduction in Ni and Co after three days of electrolysis treatment of the contaminated solution.

The electrolysis system was cheap to construct, robust, simple to use and produced a significant reduction in Ni and Co contamination. It was observed that efficient removal of Co was achieved (Co = ~7 pM after 72 hr). However, less efficient removal of Ni was detected suggesting that longer operating times would be required to further reduce the dissolved Ni concentration. Static potential electrolysis could be applied to the removal of other dissolved trace metal contaminants present in a wide range of reagent solutions.

Table 2.c Efficiency of Ni and Co removal from a Milli-Q water solution using electrolysis

| Cleaning duration<br>(hours) | Total dissolved<br>Ni (nM) | Total dissolved<br>Co (nM) |
|------------------------------|----------------------------|----------------------------|
| 0                            | 10.0                       | 10.0                       |
| 24                           | 6.0                        | 1.13                       |
| 48                           | 2.8                        | 0.062                      |
| 72                           | 2.3                        | 0.007                      |

### 3 AdCSV methodology

AdCSV was utilised for the determination of dissolved trace metals in river, estuarine and seawater samples. The technique was able to distinguish between electrochemically ‘labile’ and total dissolved trace metals. Ligand competition was used for chemical speciation

measurements by AdCSV (e.g. electrochemically 'labile'), whereby the added ligand competes for trace metals with naturally occurring metal-complexing ligands. This method determines inorganic and weakly complexed trace metals (van den Berg, 1984a; van den Berg *et al.*, 1990; Donat and van den Berg, 1992). Labile dissolved trace metal measurements were undertaken after filtration within 4 days of collection and total dissolved measurements of estuarine waters were normally undertaken within 2 weeks of collection.

The AdCSV system adopted utilised a voltammetric analyser  $\mu$ Autolab (Ecochemie) and a 663 VA stand (Metrohm), fitted with a three-electrode cell comprising; a working electrode (hanging mercury drop electrode (HMDE)), reference electrode (Ag/AgCl) and a counter electrode (platinum wire). The  $\mu$ Autolab and stand were controlled by a portable PC (Compaq 386). The AdCSV approach is capable of measuring 27 elements using appropriate voltammetric settings and reagents (van den Berg, 1991a; van den Berg, 1991b; Achterberg and van den Berg 1994b).

The organic ligands in AdCSV contain N and O donor groups (e.g. DMG and oxine), in addition to S donors (e.g. APDC). To be suitable for AdCSV, ligands are required to have two properties: (a) the ability to form a complex with the element of interest and (b) electroactivity (i.e. capability to adsorb onto the surface of the HMDE). Many of the ligands form aromatic ring structures. DMG is an exception, but forms a ring structure on chelation with  $\text{Ni}^{2+}$ . The adsorption of ligands is affected by the deposition potential and it therefore appears that the presence of electrostatic and  $\pi$ -electron interactions are significant for the adsorption process (Achterberg and Braungardt, 1999).

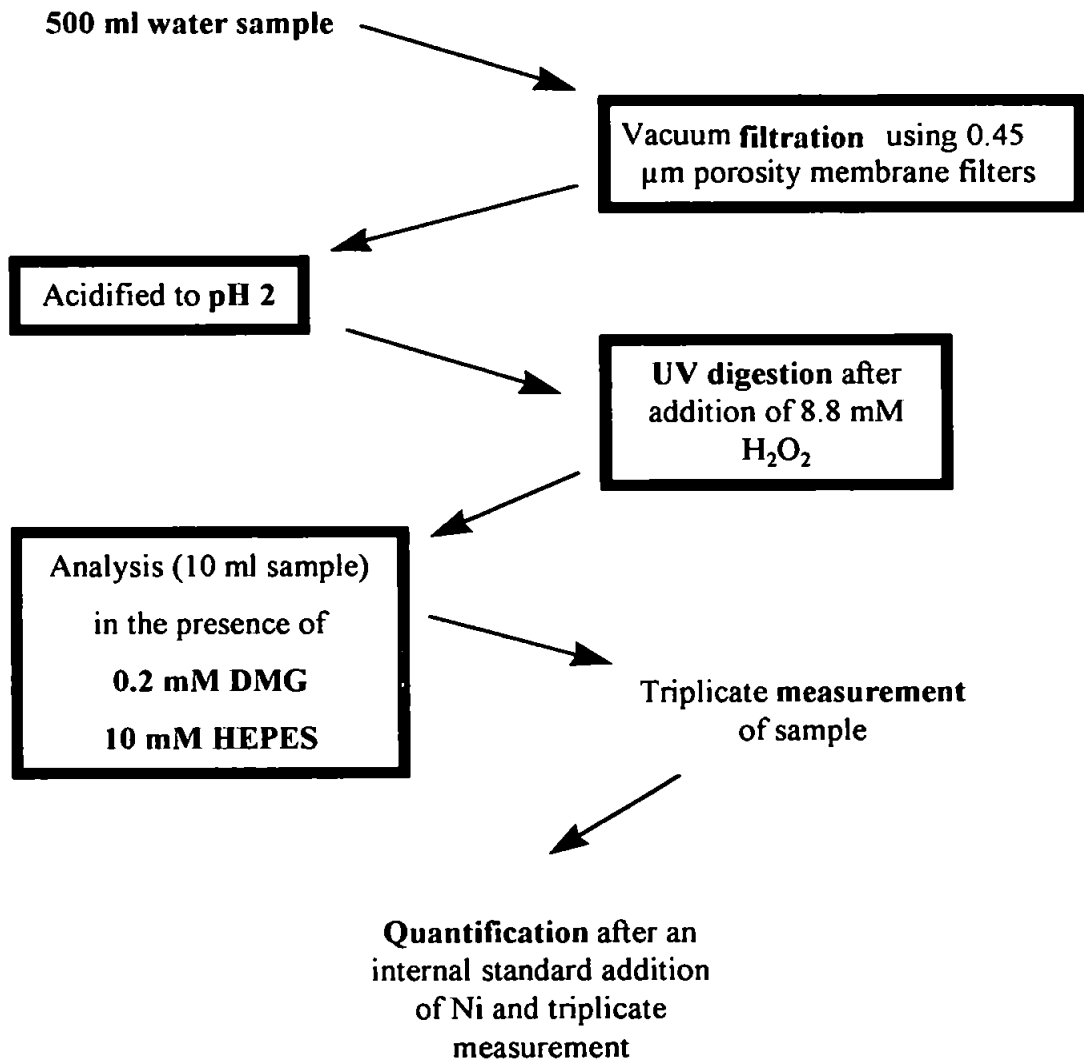
Voltammetric measurements were typically determined by pipetting 10 ml of a water sample into the voltammetric cell that contained an AdCSV metal complexing ligand and a pH buffer. The sample is continuously stirred during degassing, which was achieved by purging

with nitrogen (oxygen free) for 3 minutes. To ensure an uncontaminated working electrode surface was obtained 5 drops of Hg were discarded by the HMDE and a sixth was dislodged. During the deposition stage, the analyte was pre concentrated on the surface of the HMDE. Stirring was continued through the deposition stage, typically set to 30 s and the deposition potential should be set to ca 0.1 V more positive than the reduction potential of the metal-ligand complex. After the deposition period has elapsed the solution is left unstirred for 8 s and then a voltammetric scan was undertaken. The scan type and settings were altered according to the analytical procedure adopted. The scan direction was towards more negative potentials and the resulting current was measured. The current produced is the result of the reduction of the reducible group on the ligand or of the metal itself in the adsorbed complex (equation 2).



Three voltammetric metal measurements were performed and a mean of the peak heights was noted. To quantify the metal concentration, a precise volume of a known metal standard was added to the sample and 3 voltammetric scans performed. The increase in the peak height was used to calculate the original metal concentration. The internal standard addition approach was selected for quantification of trace metal concentrations, as this procedure was not affected by changes in instrument sensitivity, which may occur as the water chemistry of samples varied. Figure 2.3 shows a schematic representation of the batch AdCSV total dissolved trace metal analytical procedure (using Ni as an example). For the measurement of the AdCSV ‘labile’ metal concentration the acidification and UV-digestion steps were omitted. Typically, metal determinations were carried out in duplicate.

Figure 2.3 Analytical protocol for manual batch operation of AdCSV (using Ni as an example)



 = performed in a class 100 laminar flow hood

#### 4 AdCSV reagent, Milli-Q water and procedural blanks

The determination of the level of trace metal contamination in reagents was carried out in Milli-Q water. Since the concentration of metals in reagents could not be undertaken on concentrated solutions of electrochemical reagents due to analytical interference, in practice a blank in Milli-Q water was measured, which comprised the concentration of metals in Milli-Q water combined with the reagent metal concentration. Hence, Milli-Q water and reagent Co, Ni, Zn and Cu blank concentrations were simultaneously determined by AdCSV. Levels of Co, Ni, Cu and Zn in the reagent and Milli-Q water were below the limit of detection (Table 2.d). Milli-Q water and reagent blank values were measured twice daily (e.g. at the start of the day and after mid day). In case blank values for the Milli-Q water and reagent became measureable the analysis was postponed and the source of the contamination was identified. Typically the amount of each reagent was doubled in separate sample aliquots and quantified. This approach allowed the detection of the source of the contamination.

A procedural blank was undertaken by exposing 5 samples of Milli-Q water to the estuarine water collection and sample pre-treatment procedure. Briefly, this was achieved by filling an acid washed 500 ml HDPE bottle with Milli-Q water that was acidified to pH 2 (using HCl; 1  $\mu$ l per 1 ml Milli-Q water), the sample was then left over night (~18 h) at room temperature. The acidified sample was then vacuum filtered through a 0.45  $\mu$ m porosity filter and UV-digested for 3 hours after the addition of H<sub>2</sub>O<sub>2</sub> following the procedure described earlier. The samples were then neutralised using an appropriate volume of ultra clean 25 % v:v ammonia (usually ~2  $\mu$ l 25 % v:v ammonia per 1 ml sample) and after the addition of an appropriate volume of electrochemical reagents (see below) the samples were analysed for their total dissolved Co, Ni, Zn and Cu concentration. The results showed that

Table 2.d Voltammetric measuring and reagent requirements for the determination of dissolved Ni, Co, Zn and Cu.

| Element                                      | Ni             | Co                                                   | Co             | Zn             | Cu               | Cu                                                   | Cu             |
|----------------------------------------------|----------------|------------------------------------------------------|----------------|----------------|------------------|------------------------------------------------------|----------------|
| <i>Ligand</i><br>(mM)                        | 0.2 DMG        | 0.05<br>Nioxime                                      | 0.2<br>DMG     | 0.2<br>APDC    | 0.4<br>Tropolone | 0.025<br>SA                                          | 0.2<br>Oxine   |
| <i>Buffer</i><br>(mM)                        | 10<br>HEPES    | 1:1<br>NH <sub>4</sub> Cl                            | 10<br>HEPES    | 10<br>TRIS     | 10<br>HEPES      | 10<br>Borate                                         | 10<br>HEPES    |
| <i>Scan type (V)</i>                         | Square<br>wave | Diff.<br>Pulse                                       | Square<br>wave | Square<br>wave | Square<br>wave   | Diff.<br>Pulse                                       | Square<br>wave |
| <i>Scan settings</i>                         | 50-200<br>Hz   | Rate = 20<br>mV s <sup>-1</sup><br>Height =<br>25 mV | 50-200<br>Hz   | 50-200<br>Hz   | 50-200<br>Hz     | Rate = 20<br>mV s <sup>-1</sup><br>Height =<br>25 mV | 50-200<br>Hz   |
| <i>Deposition<br/>potential (V)</i>          | - 0.75         | - 0.75                                               | - 0.90         | - 0.95         | - 0.20           | -1.10                                                | - 1.00         |
| <i>Deposition<br/>Time (s)</i>               | 30             | 20                                                   | 30             | 30             | 30               | 30                                                   | 30             |
| <i>Initial scan<br/>potential (V)</i>        | - 0.80         | - 0.95                                               | - 0.95         | - 0.95         | - 0.20           | -0.15                                                | - 0.20         |
| <i>Final scan<br/>potential (V)</i>          | - 1.10         | - 1.20                                               | - 1.20         | - 1.20         | - 0.65           | -0.60                                                | - 0.65         |
| <i>Typical peak<br/>position (V)</i>         | -0.85          | -1.00                                                | -0.95          | -0.40          | -0.35            | -0.25                                                | -0.30          |
| <i>Limit of<br/>detection<br/>(nM) *(pM)</i> | 0.1            | *2.0                                                 | 0.2            | 0.5            | 0.2              | 0.5                                                  | 0.2            |

the concentration of Co, Ni, Zn and Cu in the Milli-Q water samples following this blank procedure were below the limit of detection by AdCSV (Table 2.d).

#### 5 AdCSV analytical settings and limit of detection

The analytical settings typically applied for Zn, Cu, Ni and Co, and limits of detection are presented in Table 2.d. Limits of detection were measured using filtered (through 0.45  $\mu\text{m}$  porosity filters) and acidified (using sub boiled HCl; 1  $\mu\text{l}$  per 1 ml sample) low metal concentration seawater ( $S = 34.52$ ,  $\text{Co} = 0.5 \text{ nM}$ ,  $\text{Ni} = 4.1 \text{ nM}$ ,  $\text{Zn} = 9.2 \text{ nM}$  and  $\text{Cu} = 3.4 \text{ nM}$ ), and were calculated from  $3\sigma$  (of five replicate measurements). The limit of detection is valid throughout the estuarine range of salinities ( $S = 0$  to  $35$ ) as increasing the AdCSV pre concentration (deposition) time can enhance the instrument sensitivity. Furthermore, the sensitivity of AdCSV does not vary greatly (e.g. for the salinity interval  $35$  to  $0$  generally  $\sim 10\%$  signal decrease may occur) throughout the salinity range ( $S = 0$  to  $35$ ) expected in natural waters (van den Berg, 1989; Achterberg *et al.*, 1997; Achterberg and Braungardt, 1999).

#### 6 AdCSV analysis of certified reference materials

NASS-4 (oceanic seawater), CASS-2 (nearshore seawater) and SLEW-2 (estuarine water) supplied by the National Research Council (Canada) were analysed for dissolved Ni, Zn, Cu and Co to verify the accuracy of the adopted AdCSV methods. Five sub aliquots of each reference water were UV-digested in quartz tubes and the metal concentrations were determined using the manual AdCSV procedure with 2 internal standard additions. Table 2.e shows the certified and determined concentrations of dissolved Ni, Co, Cu and Zn. The results of the analysis were in close agreement with the certified values highlighting the acceptable accuracy of the adopted analytical procedure.

Table 2.e Analysis of certified reference waters by AdCSV

| Element        | Analysis  | NASS-4    | CASS-2     | SLEW-2     |
|----------------|-----------|-----------|------------|------------|
| <i>Ni (nM)</i> | Certified | 3.9 ± 0.2 | 5.1 ± 0.6  | 12.7 ± 1.3 |
|                | AdCSV     | 4.1 ± 0.1 | 5.5 ± 0.3  | 13.8 ± 0.7 |
| <i>Cu (nM)</i> | Certified | N/A       | 10.6 ± 0.7 | 27.7 ± 1.5 |
|                | AdCSV     | N/A       | 10.2 ± 0.5 | 27.5 ± 1.2 |
| <i>Co (pM)</i> | Certified | 150 ± 20  | N/A        | 780 ± 120  |
|                | AdCSV     | 160 ± 7   | N/A        | 880 ± 30   |
| <i>Zn (nM)</i> | Certified | 1.8 ± 0.3 | 30.1 ± 2.0 | 13.2 ± 2.6 |
|                | AdCSV     | 2.1 ± 0.1 | 30.2 ± 3.8 | 14.2 ± 0.8 |

### 2.2.3 Validation of an automated AdCSV dissolved nickel monitor for estuarine studies

This Section evaluates the performance of an automated AdCSV system and demonstrates that high quality, high resolution (up to 6 samples per hour), *in-situ*, dissolved Ni measurements can be performed in systems as complex as estuaries. Automated AdCSV instrumentation was deployed on a bank of the Tamar estuary at Halton Quay during tidal cycle surveys undertaken in summer (17-07-1997) and winter (12-01-1998). A tidal cycle survey describes a sampling style whereby samples are collected from a single geographical location on an estuary over the period of a tidal cycle (13 h).

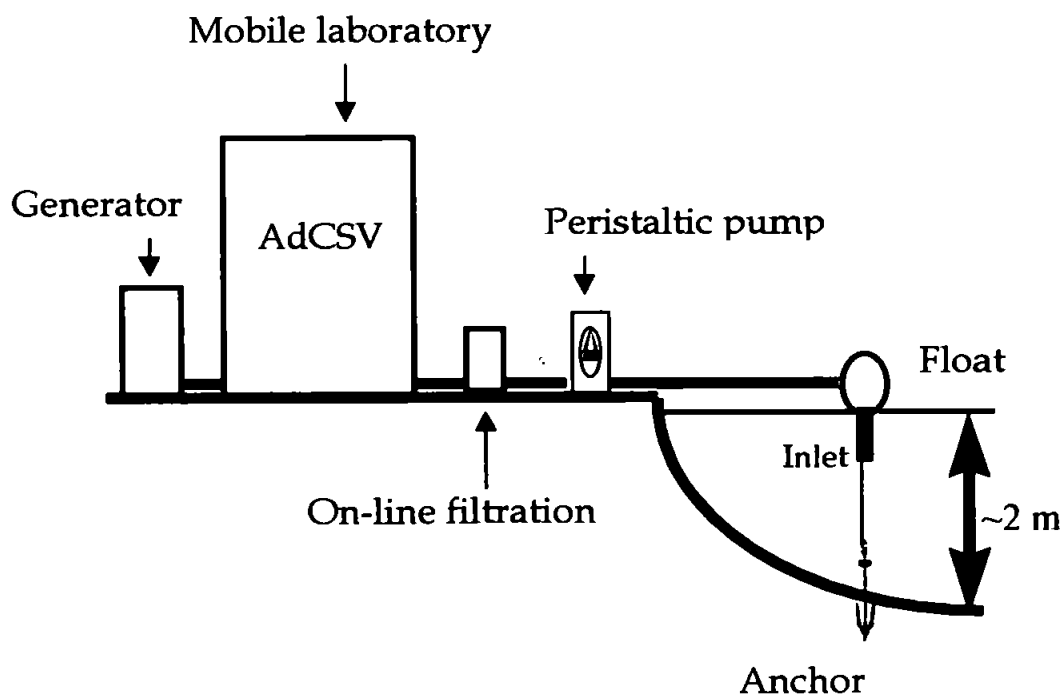
#### 1 On-line sample collection, filtration and UV digestion

Surface estuarine water samples were collected using a float deployed in the river channel (Fig. 2.4). The float was attached to a grab anchor by a 2 m nylon rope. A 30 m length of poly (vinyl chloride) (PVC) tube (9 mm bore diameter) was connected to the float and submerged to a depth of ca 0.5 m. Water was continuously sampled using a peristaltic pump (Cole Parmer) at a rate between 0.5 and 1.5 l min<sup>-1</sup>. On-line tangential filtration was achieved using a modified filter holder (Swinnex, diameter 47 mm, Millipore) (Colombo *et al.*, 1997), fitted with a membrane filter (0.45 µm porosity cellulose nitrate, Whatman). A high water cross flow (>0.5 l min<sup>-1</sup>) at the surface of the filter prevented pore clogging, even at suspended particulate concentrations greater than 500 mg l<sup>-1</sup>. In order to avoid analytical interferences from dissolved organic material and to break down metal complexing organic ligands, the samples were subjected to on-line UV digestion (Achterberg and van den Berg, 1994a). The UV digestion system consisted of a quartz coil and a 400 W medium pressure mercury vapour lamp.

## 2 Mixed AdCSV reagents for use with an automated system

A mixed solution containing 400 mM n-2-hydroxyethylpiperazine-*n*'-2-ethanesulfonic acid (HEPES, pH buffer at pH 7.78) and 16 mM dimethyl glyoxime (DMG, AdCSV ligand for Ni) was prepared daily (van den Berg and Nimmo, 1987). Determination of the reagent blank in Milli-Q water resulted in a value below the limit of detection (0.1 nM, Pihlar *et al.*, 1981). A standard solution of  $1 \times 10^{-5}$  M Ni was prepared from BDH Spectrosol standard solutions (1000 mg/l Ni), and acidified to pH 2.5 using HCl. When not in use, reagents and metal standards were stored in HDPE bottles at 4°C.

Figure 2.4 Monitoring set-up for estuarine surveys consisting of mobile laboratory with power generator, sample collection and treatment system and trace metal monitor.



### 3 Automated AdCSV Ni monitor

Figure 2.5 shows a schematic representation of the sample collection set up and the automated AdCSV instrumentation which were deployed on the bank of the Tamar estuary during the tidal cycle surveys. The automated metal monitor consisted of a voltammetric analyser ( $\mu$ Autolab, Ecochemie) and a hanging mercury drop electrode (663 VA stand, Metrohm). A syringe pump (Cavro) was incorporated to make precise standard additions of Ni, and reagent and sample were propelled using an integrated pump unit (Ecochemie, consisting of 3 Watson Marlow peristaltic pumps, 2 Cole Parmer 3-way inert PTFE solenoid valves and a PTFE sample loop (10.0 ml)). A portable PC (Compaq 386) controlled all devices. Tubing in contact with sample and reagent was composed of PTFE, and Marprene tubing (Watson Marlow) was used in the peristaltic pumps. The instrumentation was stored and operated from a temporary mobile laboratory (Ford Transit), and powered by a 5 kW 240 V portable petrol generator (Briggs and Stratton).

Table 2.f shows the operational sequence of the automated AdCSV system. Each analysis required ca 20 ml of filtered sample, and the first 10 ml was allowed to flow through the sample loop into the waste container in order to flush the loop. After the sample loop was filled with fresh sample, the sample pump was stopped and the valves at either side of the sample loop were switched into a position which allowed the sample to be flushed by nitrogen (oxygen free, at 1 bar of pressure) into the measuring cell. A precise volume of mixed reagent (250  $\mu$ l) was pumped into the cell and the sample was de-aerated for 120 s using nitrogen. De-aeration was necessary to avoid interference from dissolved oxygen on the voltammetric determination of Ni. Table 2.f and 2.g details the AdCSV analysis procedure used for the automated determination of dissolved Ni in estuarine samples. Three successive AdCSV scans were undertaken prior to the addition of a known amount of Ni standard using the syringe pump. Three further measurements were performed by the



Figure 2.5 Schematic representation of the on-line sample filtration and digestion systems and the automated AdCSV metal monitor

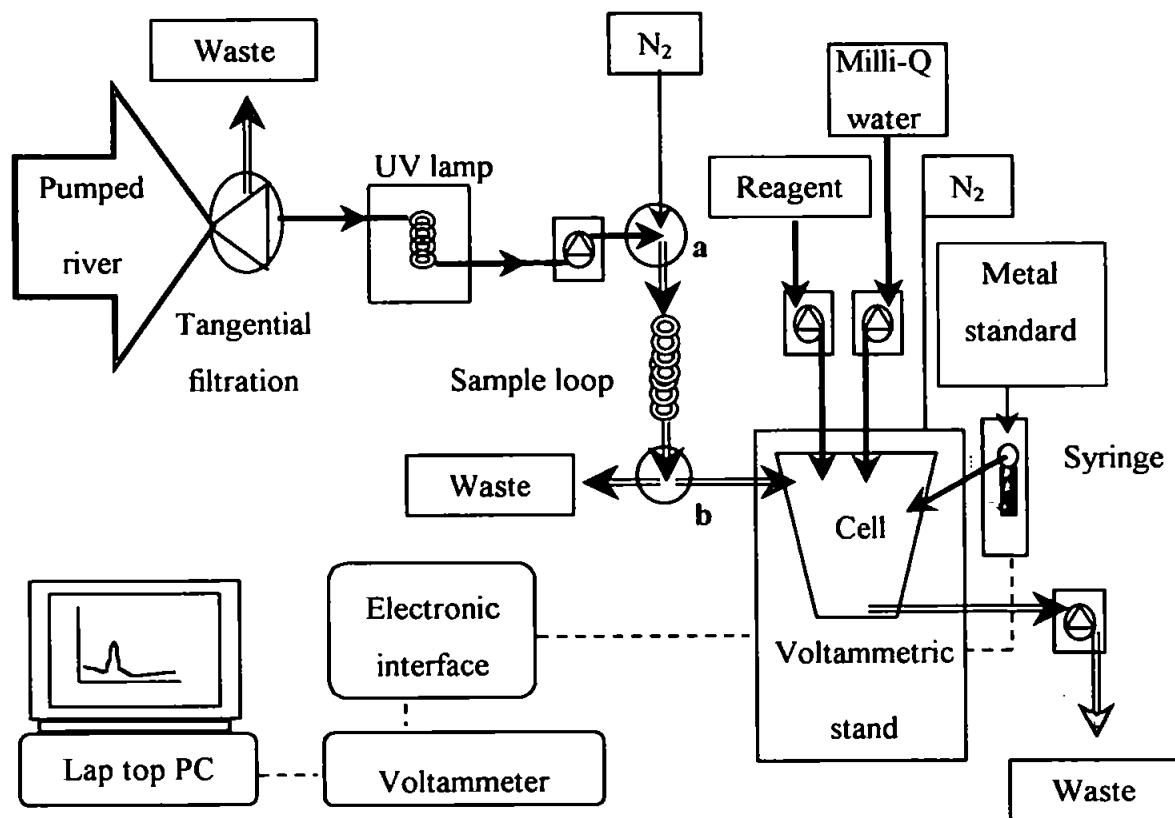


Table 2.f Operational sequence for automated metal measurements by AdCSV; total cycle time ca 10 min

| Stage                   | Valve 1                | Valve 2       | Reagent pump                      | Wash Pump           | Sample pump                     | Voltammeter       | Comments                            |
|-------------------------|------------------------|---------------|-----------------------------------|---------------------|---------------------------------|-------------------|-------------------------------------|
| <i>Sample Capture</i>   | Open to sample         | Open to waste | Off                               | Cell rinsed 3 times | 320 s at 7 ml min <sup>-1</sup> | Idle              | Wash cycle undertaken               |
| <i>Sample transport</i> | Open to N <sub>2</sub> | Open to cell  | 20 s at 0.75 ml min <sup>-1</sup> | Off                 | Off                             | Idle              | Addition of sample and reagents     |
| <i>Sample purge</i>     | Open to sample         | Open to waste | Off                               | Off                 | 320 s at 7 ml min <sup>-1</sup> | Purging for 180 s | Acquisition of new sample           |
| <i>Measurement</i>      | Open to sample         | Open to waste | Off                               | Off                 | Off                             | Measuring         | 10 s purge between measurements     |
| <i>Quantification</i>   | Open to sample         | Open to waste | Off                               | Off                 | Off                             | Measuring         | Measurement after standard addition |
| <i>New cycle</i>        | Open to sample         | Open to waste | Off                               | Cell rinsed 3 times | Off                             | Idle              | Cell wash                           |

Table 2.g Conditions used for determination of dissolved Ni using AdCSV.

| Element | Ligand (mM) | Buffer (mM) | Scan type            | Deposition potential | Initial scan potential | Final scan potential |
|---------|-------------|-------------|----------------------|----------------------|------------------------|----------------------|
| Ni      | 0.20 DMG    | 10.0 HEPES  | Square wave (100 Hz) | -0.75 V              | -0.80 V                | -1.10 V              |

system and, in case the increase in peak height as a result of the Ni addition was insufficient (below 100 % increase), additional Ni standard was added and further 3 scans were performed. The Ni concentration in the sample was calculated from the observed sensitivity. The peak heights of the scans and the time of analysis were stored on the hard disk of the PC. In addition, to allow post-survey verification of the automated peak height determinations by the software, all scans were stored on the hard disk by the PC. The software used for instrument and electrode control, potential scans, data acquisition and event-triggered decision making was an adapted version of EAS 1.0 (Ecochemie) (Achterberg and van den Berg, 1994b). A time lag of 20 min was subtracted from the measurement times to compensate for the time difference between sample collection at the mouth of the PVC tube and the end of the sample measurement procedure.

#### 4 Collection, pre-treatment and analysis of discrete samples

In addition to the automated *in-situ* measurements, discrete surface water samples were collected at hourly intervals during the tidal cycle surveys. For this purpose, 500 ml acid cleaned HDPE bottles were used, and filled with estuarine water after three rinses, stored in polythene bags and kept cool prior to laboratory analysis. The samples were transported to Plymouth University where they were vacuum filtered in a class 100 laminar flow cabinet, using a 500 ml polycarbonate filtration unit (47 mm diameter, Nalgene) fitted with a membrane filter (0.45  $\mu\text{m}$  porosity, cellulose nitrate, Whatman). The filtered samples were acidified to pH 2 using HCl (1  $\mu\text{l}$  per 1 ml).

The acidified samples were UV-digested (400 W medium pressure UV lamp, Photo Reactors) in quartz tubes for 4 h after the addition of  $\text{H}_2\text{O}_2$  (8.8 mM, final concentration). Before analysis by AdCSV, sample aliquots were neutralised using ammonia and manual Ni measurements were carried out under the voltammetric conditions presented in Table

2.g. Dissolved Ni measurements in the discrete samples were performed within 3 days of sample collection.

5 Batch analysis of certified reference materials

CASS-2 (nearshore seawater) and SLEW-2 (estuarine water) supplied by the National Research Council (Canada) were analysed for dissolved Ni to verify the accuracy of the AdCSV method. Five sub-aliquots of each reference water were UV digested in quartz tubes and the Ni concentration was determined using the manual AdCSV procedure with two internal standard additions. Table 2.h shows the certified and determined concentrations of dissolved Ni. The results of the analysis were in close agreement with the certified values.

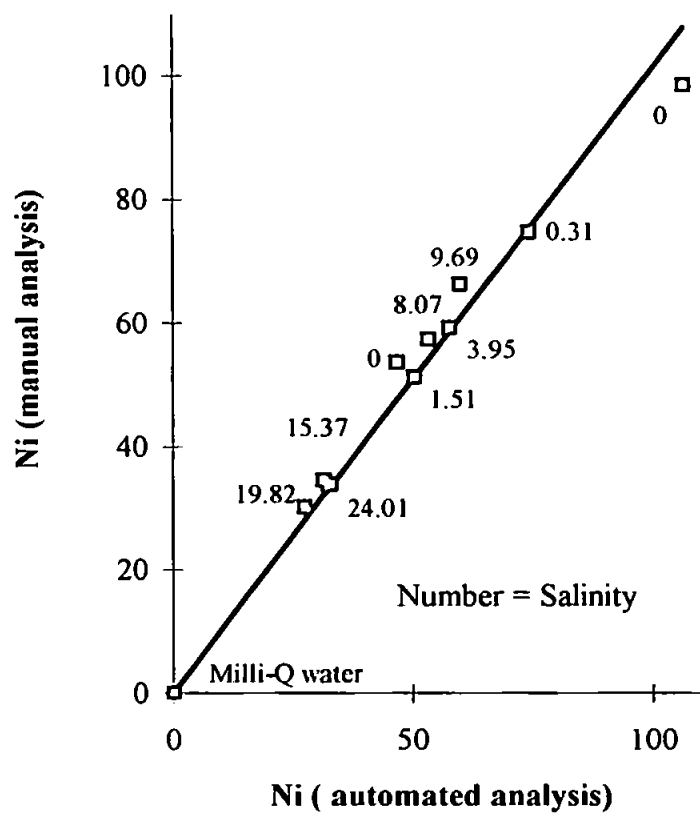
Table 2.h Analysis of certified reference materials.

| Element | Certified (nM) | Uncertainty | <i>AdCSV</i> (nM) | <i>Uncertainty</i> |
|---------|----------------|-------------|-------------------|--------------------|
| CASS-2  | 5.08           | +/- 0.61    | 5.46              | +/- 0.26           |
| SLEW-2  | 12.66          | +/- 1.32    | 13.82             | +/- 0.72           |

6 Validation of automated methodology

In order to asses the accuracy of the automated AdCSV methodology, an intra-laboratory comparison exercise was performed whereby dissolved Ni was determined in the laboratory in discrete samples using manual and fully automated AdCSV methods (Fig. 2.6). The discrete samples were collected during a sampling campaign in the Tamar estuary covering

Figure 2.6 Dissolved Ni concentrations determined in discrete Tamar samples using automated vs manual AdCSV methods. Ni concentrations in an instrumental blank sample (Milli-Q water) are also included. Numbers printed next to the symbols represent salinity of the samples.



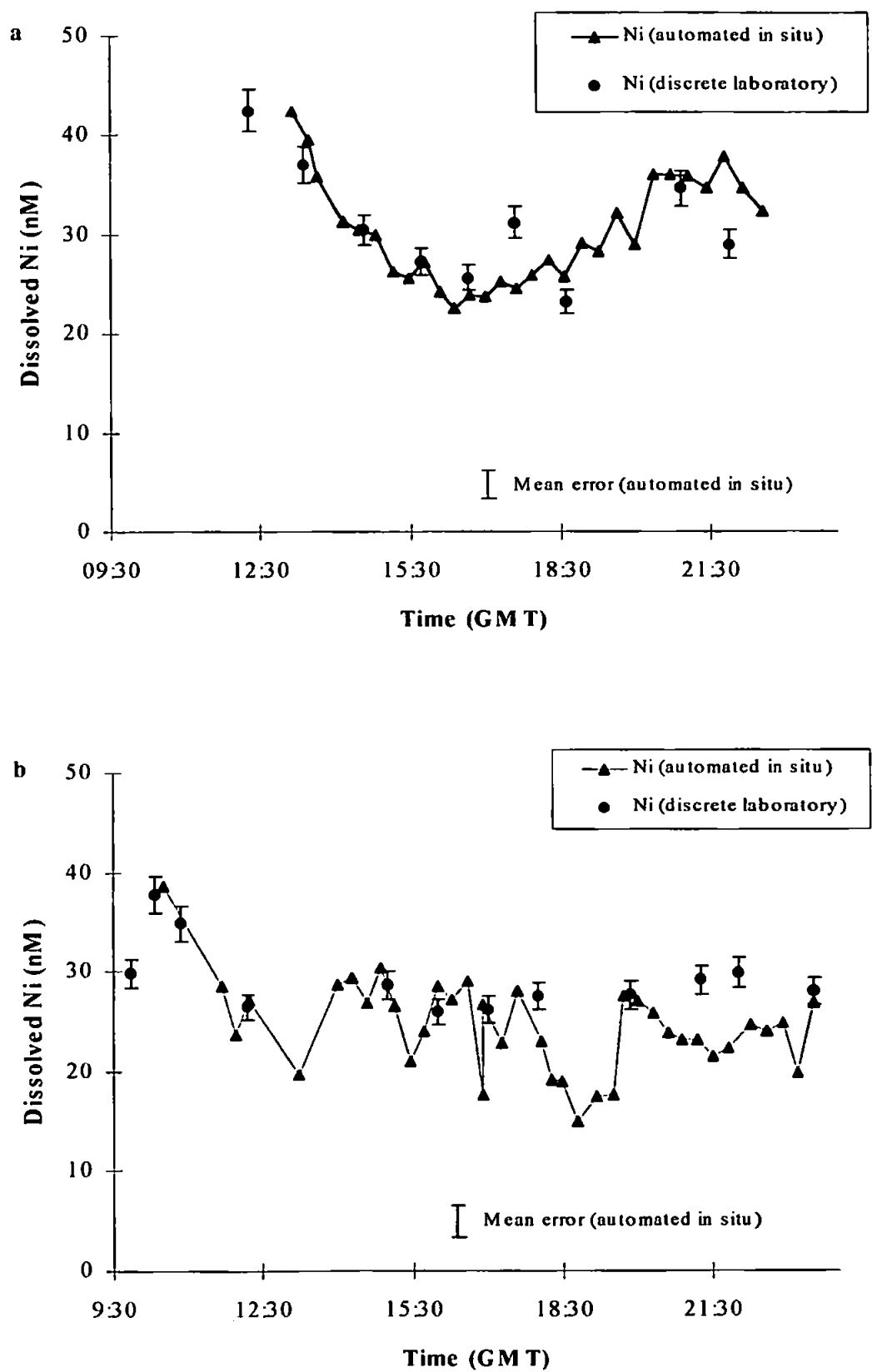
an axial transect (12<sup>th</sup> April 1997). Following the manual AdCSV analysis, the same samples were re-analysed using the automated AdCSV system, which included an auto-sampler (PSA 20.020, Chemlab) for unattended sample changing. Dissolved Ni concentrations in the samples from the Tamar ranged between 24 nM and 106 nM (Fig. 2.6). The data represent a salinity variation of 25 and the highest Ni concentration was observed from the low salinity waters (S = 0; Ni ~100 nM) and lowest concentrations were observed in the high

salinity waters ( $S = 30$ ;  $Ni \sim 30 \text{ nM}$ ). The salinity variation observed in these samples was comparable to those found during the summer 1997 tidal cycle survey in the Tamar estuary. Dissolved Ni concentrations determined using manual and fully automated AdCSV methods were in close agreement. This observation showed that the strong variations in estuarine sample matrix did not negatively affect the performance of the automated AdCSV measurements. A paired t-test for a difference between the two methods of analysis resulted in an observed  $t = 1.45$ , against a critical value of  $t = 2.23$  (at the 95 % confidence interval,  $n = 11$ ). The applied methods, therefore, did not give significantly different dissolved Ni values.

## 7 Field application of automated AdCSV dissolved Ni monitor

Two tidal cycle surveys were performed under contrasting environmental conditions (17<sup>th</sup> July 1997 and 12<sup>th</sup> January 1998), with each survey lasting for 13 h. Automated Ni measurements were performed on a bank of the Tamar. In addition, discrete samples were collected in parallel, at hourly intervals in order to validate the *in-situ* AdCSV analysis. In order to prevent contamination of samples collected for on-line analysis, the discrete samples were collected ca 10 m away from the inlet of the continuous flow sample tubing. Because these samples were not obtained in exactly the same locations, differences in Ni concentration may result from the strong spatial variability in this estuarine system. Figures 2.7.a and 2.7.b show the results from the automated dissolved Ni measurements and the corresponding discrete manual Ni analysis for the tidal cycle surveys performed during the summer and winter period, respectively. The values obtained from the discrete surveys were in close agreement with the data from the automated *in-situ* analysis, with, however, a few differences between the data sets. These differences can most likely be explained by the spatial variation in the estuary affecting dissolved Ni concentrations in the two water

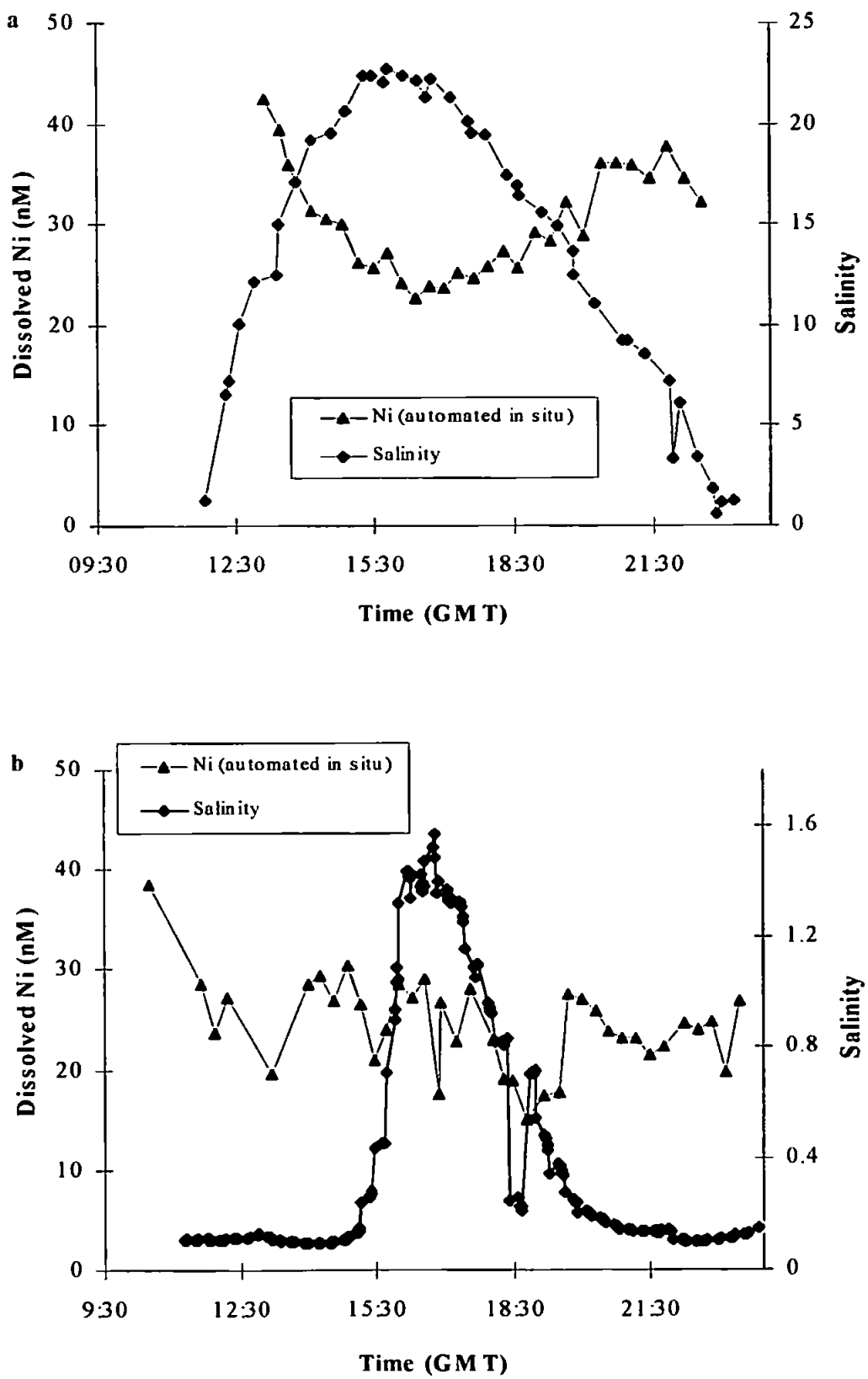
Figure 2.7 Results of discrete laboratory and automated *in-situ* analysis of dissolved Ni versus time for tidal cycle studies in the Tamar estuary a) 17<sup>th</sup> July 1997, and b) 12<sup>th</sup> January 1998.



sampling locations used for discrete and automated sampling. The advantages of the automated metal monitor are evident, with up to 4 dissolved Ni analyses per hour, whereas only 1 discrete Ni sample was obtained per hour.

The Ni concentrations observed during the tidal cycle surveys in the Tamar compared well with previous studies in the Tamar estuary. Van den Berg *et al.*, (1991) collected discrete estuarine samples along the axis of the estuary representing salinity values between 0 and 33. The discrete samples were analysed in the laboratory using manual AdCSV methods and yielded dissolved Ni concentrations between 38 nM and 63 nM, with lowest values at the coastal end of the estuary and highest values at the river end. An important feature of the winter survey was the rapid increase in salinity ( $S = 0.1$  to  $1.5$ ) observed between 15:30 and 16:30 h (Fig. 2.8). This salinity range is reported to be the geochemically most reactive stage of estuarine mixing (Morris, 1986; van den Berg and Nimmo, 1987). During this period only 3 data points were obtained using discrete sampling, whereas 12 values for dissolved Ni were gained from the automated *in-situ* analysis. Geochemical interpretations based on the data set obtained from the limited discrete sampling exercise would have suggested little variation in dissolved Ni throughout the tidal cycle. However, the automated measurements revealed high temporal variability in Ni concentrations (Fig. 2.8). This type of data suggests that trends inferred from discrete sampling exercises would not allow for a full interpretation of the data because of the low sampling frequency and that *in-situ*, high resolution metal monitoring provides an important tool for pollution and geochemical studies. The biogeochemical significance of the total dissolved Ni measurements will be discussed in Chapter 3.

Figure 2.8 Results of automated *in-situ* tidal cycle analysis of dissolved Ni and salinity versus time for tidal studies performed in the Tamar estuary (a) 17th July 1997 and (b) 12th January 1998.



## 8 Conclusions for the use of automated AdCSV

The automated AdCSV metal monitor, presented in this chapter, has been validated for *in-situ* dissolved Ni analysis in estuaries. The metal monitor performed ca 4–6 dissolved Ni measurement per hour when positioned on the bank of the Tamar estuary. The high frequency is important for pollution and geochemical studies in highly variable estuarine systems. The transportable estuarine metal monitor would therefore form an important tool for water quality monitoring organisations.

Each sample was fully calibrated by the automated system used during this study, resulting in high quality dissolved Ni data. This calibration approach is especially important in estuarine conditions with strong and rapid variations in sample matrices. These conditions may result in erroneous metal concentration determinations when external calibration procedures are applied at infrequent intervals.

The automated AdCSV metal monitor can readily be applied to other trace metals by changing the reagents and voltammetric conditions. Preliminary investigation of dissolved Cu has been undertaken and the results suggest that the *in-situ* method can be applied to a suite of trace metals including Zn, Co, U, V, Cr, Cd and Pb. The sensitivity and metal species selectivity of AdCSV make this technique suitable for trace metal speciation analysis. The *in-situ* approach presented in this chapter would ideally suit metal speciation studies because the near immediate analysis upon sampling minimises any shift in chemical equilibrium between the various physico-chemical forms of trace metals present in natural waters (Achterberg and van den Berg, 1994b).

## 2.2.4 Cu natural complexing ligand titration experiments

### 1. Methodology

All sample preparation was performed inside a class 100 laminar flow unit at Plymouth University. To minimise the loss of analyte to the walls of sample containers, polystyrene containers were selected for use in the natural ligand titration experiments (personal communications M. Gledhill). The determination of natural ligand concentrations and their conditional stability constants was performed in samples collected from the Scheldt and Tamar estuaries. The samples had been filtered through 0.45  $\mu\text{m}$  membrane filters and frozen ( $-17\text{ }^{\circ}\text{C}$ ) until their subsequent analysis at Plymouth University (Chapter 2.1.2). For each of the natural ligand titrations 450 ml of sample was required. A filtered 450 ml volume of sample was left overnight (18 hr) at ambient room temperature ( $20\text{ }^{\circ}\text{C}$ ) to allow the waters to gradually defrost. Fifteen sub sample aliquots, each containing 20 ml, were pipetted into 50 ml polystyrene containers. An electrochemical buffer (borate, final concentration = 10 mM, pH = 8.35) and ligand (SA), final concentration = 25  $\mu\text{M}$ ) was subsequently pipetted into the containers. Cu standard solutions were added at increments to the solutions and they were subsequently stirred and covered using individual polystyrene lids. To ensure saturation with Cu of the natural ligands present, which should result in a linear relationship between the observed signal and added Cu, the final addition of Cu was approximately 2 times the total dissolved concentration of Cu present in the original sample (van den Berg 1984b; van den Berg *et al.*, 1990; Campos and van den Berg, 1994). An equilibration period of 24 h was used, which allows chemical equilibrium to be attained and subsequently AdCSV measurements of the 15 sub samples were undertaken (Campos and van den Berg, 1994). The total time required to measure the suite of 15 samples was  $\sim 3$  hr. To monitor potential fluctuation in instrument sensitivity sample 1 was analysed at the start

of the day, midway during the analysis (after sample 7) and at the end of the analysis. The typical variation (RSD) in the measurement of sample 1 was 3.76% ( $n = 6$ ), which indicated that the samples comprising the data set were directly comparable and allowed an accurate estimation of the natural ligand concentrations and their conditional stability constants. The natural Cu complexing ligand concentration and conditional stability constants were computed using the method developed by van den Berg, (1984c); van den Berg *et al.*, (1990); Campos and van den Berg, (1994) which are summarised below.

## 2. Theory

The procedure to evaluate complexing ligand concentrations and conditional stability constants from the titration data series has been described before (van den Berg, 1984b, d, e; van den Berg *et al.*, 1990; Campos and van den Berg, 1994). Briefly, the following relationship is used:

$$[\text{Cu}_{\text{labile}}]/[\text{CuL}] = [\text{Cu}_{\text{labile}}]/C_L + \alpha'/(K'_{\text{CuL}} C_L) \quad (3)$$

where  $[\text{CuL}]$  is the concentration of copper complexed by natural ligands L,  $[\text{Cu}_{\text{labile}}]$  is the labile copper concentration,  $C_L$  is the ligand concentration and  $K'_{\text{CuL}}$  is the conditional stability constant for the formation of CuL in seawater. The labile copper concentration is defined by

$$[\text{Cu}_{\text{labile}}] = \sum [\text{Cu}(\text{SA})_x] + [\text{Cu}'] \quad (4)$$

where  $[\text{Cu}(\text{SA})_x]$  is the concentration of copper complexed by SA and  $[\text{Cu}']$  is the concentration of inorganic copper (all copper not complexed by SA or natural complexing

ligands L).  $\alpha'$  is the overall  $\alpha$ -coefficient of  $\text{Cu}^{2+}$  (excluding complexation by L) (Ringbom and Still, 1972),

$$\alpha' = (\alpha_{\text{Cu}'} + \alpha_{\text{CuSA}}) \quad (5)$$

where  $\alpha_{\text{Cu}'}$  is the  $\alpha$ -coefficient for inorganic complexation of  $\text{Cu}^{2+}$ :

$$\alpha_{\text{Cu}'} = 1 + \sum (\beta'_{\text{CuX}_i} [\text{X}]^i) + \sum (\beta'_{\text{Cu(OH)}_i} / [\text{H}^+]^i) \quad (6)$$

where  $\beta'_{\text{CuX}_i}$  is the stability constant for copper complexes with  $i$  major anions (X) in seawater and  $\beta'_{\text{Cu(OH)}_i}$  the acidity constant for copper valid at the ionic strength for seawater and where  $\alpha_{\text{CuSA}}$  is the  $\alpha$ -coefficient for complexation of copper by SA:

$$\alpha_{\text{CuSA}} = K'_{\text{CuSA}} [\text{SA}'] + \beta'_{\text{Cu(SA)}_2} [\text{SA}']^2 \quad (7)$$

where  $K'_{\text{CuSA}}$  and  $\beta'_{\text{Cu(SA)}_2}$  are the conditional stability constants for the formation of CuSA and  $\text{Cu(SA)}_2$  respectively and  $[\text{SA}']$  is the concentration of SA not complexed by copper (invariably  $[\text{SA}']$  equalled the total SA concentration as this was much greater than the copper concentration).

The  $\alpha$ -coefficient is slightly modified to the one defined by Ringbom and Still, (1972) in that  $[\text{Cu}^{2+}]$  is included only with the inorganic copper concentration (equation 6) to avoid having to make corrections to other equations containing  $\alpha$ -coefficients for complexes of copper (equation 7 and later). For instance, according to Ringbom and Still, (1972)  $\alpha_{\text{CuSA}}$  as defined in equation 7 is  $\alpha_{\text{CuSA}} - 1$ .

Concentrations of CuL were calculated from  $[CuL] = C_{Cu} - [Cu_{labile}]$ , where  $C_{Cu}$  is the total dissolved copper concentration at each point of the titration. A value for  $C_L$  is obtained by least square linear regression from the slope<sup>-1</sup> of a plot of  $[Cu_{labile}]/[CuL]$  as a function of  $[Cu_{labile}]$  (Fig. 2.9), whereas a value for  $K'_{CuL}$  is obtained from  $K'_{CuL} = \alpha' \cdot \text{slope} / Y\text{-axis intercept}$ . Concentrations of  $Cu^{2+}$  were calculated from  $[Cu^{2+}] = [Cu_{labile}]/\alpha'$ .

Though it is possible to determine ligand concentrations without knowing the value for  $\alpha_{CuSA}$ , an accurate value is required to calculate  $K'_{CuL}$  and  $Cu^{2+}$  for seawater conditions. Values for  $\alpha_{CuSA}$  were taken from Campos and van den Berg, (1994) who performed a series of experiments to calibrate values for  $\alpha_{CuSA}$  using competition for Cu between SA and a known chelating agent (EDTA) at several salinities (between 1 and 35) (Table 2.i). The ratio,  $X$ , of the reduction current in the presence of EDTA over that in the absence of

$$\alpha_{CuSA} = [(\alpha_{Cu'} + \alpha_{CuEDTA})X - \alpha_{Cu'}] / (1 - X) \quad (8)$$

Figure 2.9.a shows the results obtained from the titration of seawater collected from Plymouth Sound ( $S = 32.03$ ,  $Cu \text{ (total)} = 16.74 \text{ nM}$ ) during August 1998 and was used to practise the methodology (described above) to estimate Cu natural ligand concentrations and conditional stability constants. From the linear transformation of the data series (Fig. 2.9.b; based on  $[Cu_{labile}]/[CuL]$  as a function of  $[Cu_{labile}]$ ) and using the methodology described above it was possible to determine values for  $C_L$  and  $K'_{CuL}$  ( $C_L = 56.53 \text{ neq Cu l}^{-1}$  and  $K'_{CuL} = 14.01$ ). Van den Berg *et al.*, (1990) reported similar values for  $C_L$  and  $K'_{CuL}$  during investigations of the Tamar estuary and in the English Channel ( $C_L = 6 \text{ to } 83.2 \text{ neq Cu l}^{-1}$  and  $K'_{CuL} = 11.16 \text{ to } 15.10$ ).

Figure 2.9 Example of results from a Cu natural ligand titration experiment showing (a) the raw data obtained by adding increments of Cu and measuring the increase in peak height and (b) the linear transformation of the data series.

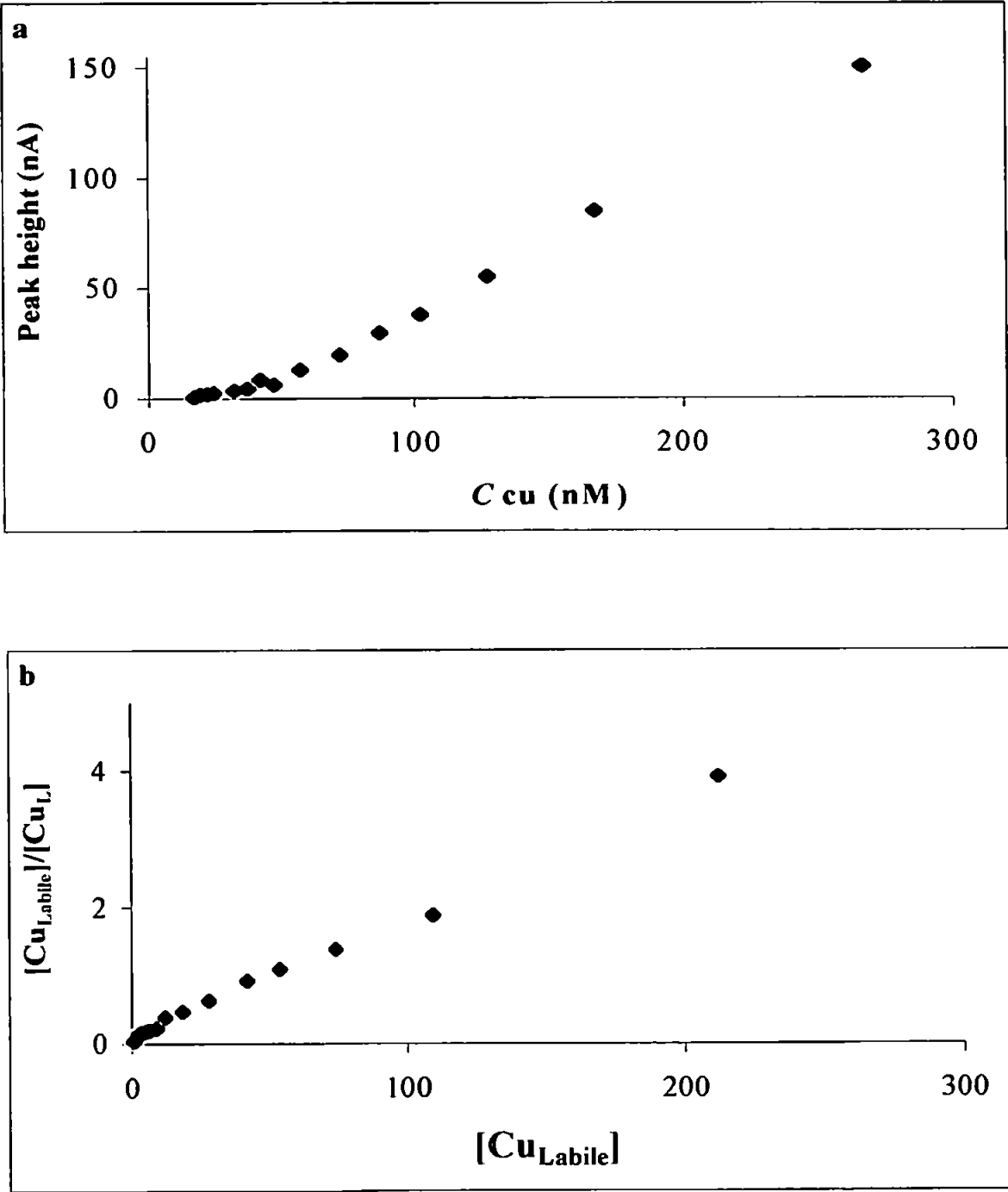


Table 2.i Values for  $\alpha_{\text{CuSA}}$ ,  $K'_{\text{CuSA}}$  and  $\beta'_{\text{Cu(SA)}_2}$  determined by ligand competition with EDTA in seawater at several salinities and at 20°C (taken from Campos and van den Berg, 1994).

| Salinity | [SA] $\mu\text{M}$ | $\log_{10} \alpha_{\text{CuSA}}$ | $\log_{10} K'_{\text{CuSA}}$ | $\log_{10} \beta'_{\text{Cu(SA)}_2}$ |
|----------|--------------------|----------------------------------|------------------------------|--------------------------------------|
| 35       | 1                  | $3.68 \pm 0.08$                  | $9.60 \pm 0.08$              | $14.95 \pm 0.08$                     |
| 35       | 2                  | $3.85 \pm 0.20$                  | $9.41 \pm 0.20$              | $14.70 \pm 0.19$                     |
| 35       | 25                 | $5.83 \pm 0.20$                  | $9.55 \pm 0.20$              | $14.98 \pm 0.20$                     |
| 20       | 25                 | $6.02 \pm 0.05$                  | $9.67 \pm 0.05$              | $15.18 \pm 0.05$                     |
| 10       | 25                 | $6.11 \pm 0.13$                  | $9.75 \pm 0.13$              | $15.26 \pm 0.13$                     |
| 1        | 25                 | $6.60 \pm 0.07$                  | $10.10 \pm 0.07$             | $15.77 \pm 0.07$                     |

## 2.3 Analysis of SPM samples

### 2.3.1 Development of a SPM trace metal extraction procedure

This section will discuss the development of a well defined ligand competition procedure for the investigation of non-lattice bound trace metals associated with SPM. The methodology uses EDTA (ethylenediaminetetraacetic acid) as the added competing ligand. The use of EDTA for soil and sediment extraction procedures has been reported by other workers (McGrath, 1996; Ure *et al.*, 1993). However, little or no work appears to have been carried out using EDTA extraction for SPM associated metals. The developed procedure for

analysis of SPM associated trace metals could complement ligand competition techniques that determine trace metal complexation by dissolved organic ligands in natural waters (Achterberg and van den Berg, 1997; Achterberg *et al.*, 1997).

The extraction scheme allows the application of a well defined metal binding strength and provides an indication of the biogeochemical availability of SPM associated metals. The approach is simple, requires little sample handling, and has a low requirement of SPM (minimum 15 mg). A total digestion using HF complements the ligand competition extraction scheme and allows the assessment of the contribution of biogeochemically available trace metals to the total particulate metal concentration in SPM.

## 1 EDTA solutions

To ensure chemical consistency of the EDTA extraction solutions, a single 2.5 l stock solution of 0.5 M EDTA was freshly prepared and used for all the extraction studies. The pH of the EDTA stock solution was set at pH 7.6 using an appropriate volume of concentrated  $\text{NH}_3$  (ca 6.5 ml).

## 2 Collection and treatment of experimental sample

In order to obtain a large quantity of material for optimising a particulate metal extraction protocol using EDTA, approximately 300 g of freshly deposited particulate material was collected from the sediment-water interface at Halton Quay on the Tamar Estuary (United Kingdom). It was postulated that a surface sediment sample from this locality would closely reflect characteristics of estuarine SPM (Grabemann *et al.*, 1997). The sample was collected from the sediment-water interface (~2 cm depth) at a water depth of ca 30 cm and transferred into a re-sealable polythene bag using a HDPE scrapper. Air was expelled and the bag was resealed and then stored at 4 °C for transport to the laboratory. In the

laboratory, the particulate material was immediately air dried at 45 °C for 48 h. In order to achieve a homogenous fine grained material, the dried sample was crushed into a fine powder (below ~200 µm) using an acid washed agate mortar and pestle, subsequently placed in a polythene bag and left for 24 h on a motorised end-to-end shaker (Baird and Tatlock, United Kingdom) operating at 40 rpm. The organic carbon content (OC) in the Halton Quay particulate material was determined following the loss on ignition method (Mook and Hoskin, 1982). For this purpose acid was added to the material (10 ml of 1 M HCl to 1 g particulate matter) to remove inorganic carbon (mainly calcium carbonate), and subsequently the material was dried at 105 °C until constant weight was achieved after cooling in a dessicator (weight A). Subsequently, the material was ashed in a muffle furnace at 600 °C for 8 h, cooled in a dessicator and weighed (weight B). The organic carbon content was calculated as the percentage of dry weight

$$\text{Percentage OC} = 100 \frac{A - B}{A} \quad (9)$$

The determination of the OC content was performed in triplicate.

### 3 Use of EDTA as an extractant of particulate trace metals

The interaction between an added chelating ligand and metals complexed by naturally occurring ligands in the aquatic environment may be slow. Experiments involving competition for dissolved Cu in seawater between an added metal chelating ligand (SA), and naturally occurring dissolved organic ligands have indicated that the establishment of an equilibrium may take more than 8 h (Campos and van den Berg, 1994). In order to investigate the rate of interaction between EDTA and particle bound trace metals,

incubation experiments were performed. The aim of these studies was to establish the minimum time required for the EDTA-particulate metal extraction procedure.

The incubation experiments were performed using 2 different ratios of extraction solution to particulate matter (200:1 and 2000:1 (v:w)), in order to investigate the influence of particulate matter concentration on the extraction efficiency. Furthermore, 2 different EDTA concentrations (0.005 M and 0.05 M) were investigated. Table 2.j includes the different experiments that were undertaken. The pH of the EDTA solution was set at a pH value of 7.6, which is close to the natural pH observed in large parts of estuarine systems. The pH of the EDTA extraction solutions was determined after the experiments to ensure that dissolution of material from the particles did not modify the pH of the experiments. No change in pH was observed at the end of the EDTA extraction experiments.

Figure 2.10 gives a schematic representation of the particle extraction procedures applied during all extraction experiments. Samples were agitated during the incubation period using an end-to-end shaker set at 40 rpm. A centrifuge (Sanyo, Centaur 2, 3000 rpm for 10 min) was utilised to separate the extraction solution from the particulate material. The supernatant was acidified to pH ~2 using concentrated  $\text{HNO}_3$  (1  $\mu\text{l}$  per 1 ml solution) to avoid loss of metals onto the wall of the bottles, and then stored at 4 °C prior to metal analysis by ICP-MS. All experiments were carried out in triplicate using separate fractions of freshly deposited particulate material collected from Halton Quay or SPM from the Scheldt.

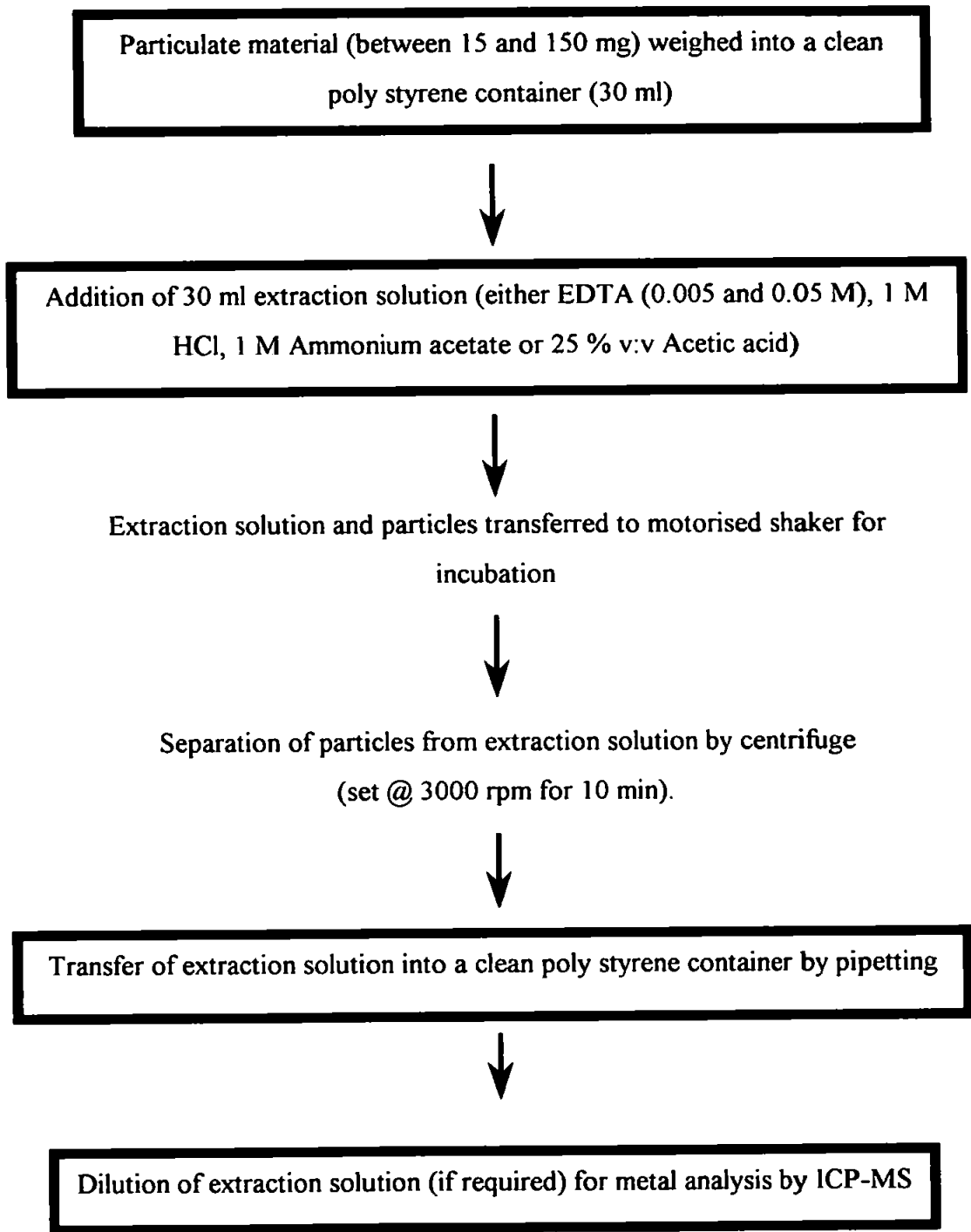
#### 4 Other SPM particulate trace metal extraction protocols

Commonly employed single extraction protocols for marine SPM and sediment particles were utilised to allow comparison with the efficiency of the EDTA protocol. The protocols applied included the extraction of metals from particulate material using 1 M HCl for 6 h

Table 2.j Procedures used for particle extraction experiments using particulate material from Halton Quay with EDTA, HCl, ammonium acetate and acetic acid as extractants.

| Experiment | Reagent                    | Ratio<br>extractant<br>: particle<br>(v:w) | Dilution for<br>metal analysis<br>by ICP-MS | Incubation<br>time (h)    | Elements<br>analysed                     |
|------------|----------------------------|--------------------------------------------|---------------------------------------------|---------------------------|------------------------------------------|
| 1          | 0.05 M<br>EDTA             | 200 : 1                                    | 10                                          | 1, 4.5, 10,<br>24, 48     | Cu, Co, Ni,<br>Zn, Fe, Mg                |
| 2          | 0.005 M<br>EDTA            | 200 : 1                                    | 0                                           | 1, 4.5, 10,<br>24, 48     | Cu, Co, Ni,<br>Zn, Fe, Mg                |
| 3          | 0.05 M<br>EDTA             | 200 : 1                                    | 10                                          | 18, 24, 36,<br>48, 60, 72 | Cu, Co, Ni,<br>Zn, Fe, Al,<br>Pb, Mn, Mg |
| 4          | 0.05 M<br>EDTA             | 2000 : 1                                   | 10                                          | 18, 24, 36,<br>48, 60, 72 | Cu, Co, Ni,<br>Zn, Fe, Al,<br>Pb, Mn, Mg |
| 5          | 1 M HCl                    | 200 : 1                                    | 10                                          | 6                         | Cu, Co, Ni,<br>Zn, Fe, Al,<br>Pb, Mn, Mg |
| 6          | 25 % v:v<br>acetic acid    | 200 : 1                                    | 10                                          | 16                        | Cu, Co, Ni,<br>Zn, Fe, Al,<br>Pb, Mn, Mg |
| 7          | 1 M<br>ammonium<br>acetate | 200 : 1                                    | 10                                          | 6                         | Cu, Co, Ni,<br>Zn, Fe, Al,<br>Pb, Mn, Mg |

Figure 2.10 Schematic representation of the procedure adopted for particulate metal extraction experiments.



 Denotes part of procedure performed in class 100 laminar flow cabinet

(Bryan and Langston, 1992; Burton *et al.*, 1993; Millward and Glegg, 1987), 25 % acetic acid at pH 4.5 for 16 h (Morris, 1986), 1 M ammonium acetate at pH 7 for 6 h (Ure *et al.*, 1993) and 0.05 M EDTA at pH 7.6 for 72 h. The extraction procedures are summarised in Table 2.j and Fig. 2.10 and were applied to certified reference material (CRM). BCR 320 (riverine sediment) and BCR 277 (estuarine sediment) supplied by the Commission of the European Communities, Community Bureau of Reference. Furthermore, a total digestion of the CRMs was performed using HNO<sub>3</sub> and HF following a method adapted from Rantala and Loring, (1985) to verify the accuracy of the extraction and analytical procedures (below). For the total digestion, 150 mg of certified reference material was placed into a 30 ml PTFE decomposition vessel, 10 ml of concentrated HNO<sub>3</sub> was added and the vessel was put on a hotplate (120 °C), for a reflux period of 24 h. Subsequently, 2 ml of concentrated HF was added and the reflux was continued for a further 48 h at 120 °C. The vessel was then uncovered and 4 ml of HNO<sub>3</sub> added and the contents of the vessel was evaporated to dryness on the hotplate (120 °C). 10 ml of concentrated HNO<sub>3</sub> was added and the contents of the vessel evaporated to dryness at 70 °C; this step was repeated twice. Then 10 ml of 0.1 M HNO<sub>3</sub> (Aristar) was added to the vessel and the solution was transferred into a 25 ml HDPE volumetric flask containing 0.93 g of H<sub>3</sub>BO<sub>3</sub>. The volumetric flasks were made up to volume using 0.1 M HNO<sub>3</sub> and stored in the refrigerator at 4 °C for subsequent metal analysis by ICP-MS. The total digestion of the CRMs was performed in triplicate. Procedural blanks were processed and used for correction of particulate metal data.

#### 5 CRM's: Particulate Cu, Ni, Co, Zn, Fe, Mn, Si, Al, Mg and Pb analysis by ICP-MS

Particulate trace metal determinations undertaken on SPM extraction solutions were carried out by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) using a VG elemental, PQ2 turbo (Winsford, Cheshire) instrument. The ICP-MS was fitted with an 'Ebdon' high

solids 'V' grove nebuliser (Argon gas flow set at  $0.9 \text{ l min}^{-1}$ ), connected to a 'Scott' double pass spray chamber (Argon coolant,  $15 \text{ l min}^{-1}$ ). The plasma gas flow was fixed at  $1 \text{ l min}^{-1}$ . Samples were fed into the manifold at  $1 \text{ ml min}^{-1}$ . Analyte was ionised at 1350 W and the detection dwell time was 10.24 ms. Fe measurements were determined from the  $^{57}\text{Fe}$  concentration, as  $^{56}\text{Fe}$  could not be directly determined due to interference from ArO. Furthermore, analyte Fe concentrations below  $50 \text{ }\mu\text{g/l}$  could not be determined due to the interference from ArO causing non linearity in Fe calibrations at low concentrations ( $<50 \text{ }\mu\text{g/l}$ ). Calibration was undertaken prior to analysis using BDH Spectrosol standard solutions ( $1000 \text{ mg l}^{-1}$ ), the metal standards were matrix matched to the analyte solutions. For example, if the sample  $\text{HNO}_3$  concentration was 20 % v:v, then the standard solutions would have been prepared in 20% v:v  $\text{HNO}_3$ . Furthermore, the samples and standards were spiked with  $^{115}\text{In}$  ( $100 \text{ }\mu\text{g l}^{-1}$ ) in order to correct for analytical drift, which can occur during the operation of the ICP-MS.

To ensure analytical precision of the extraction procedure and the trace metal measurements certified reference materials representative of estuarine particulate material were analysed. Certified reference materials BCR 320 (riverine sediment) and BCR 277 (estuarine sediment) were analysed for total particulate Pb, Zn, Fe, Cu, Co, Ni, Al, Mg and Mn, after digestion using HF and  $\text{HNO}_3$ . The results of the analysis are presented in Table 2.k. The data show that analysed and certified values were in close agreement.

## 6 EDTA extraction studies

Experiments 1 and 2 (see Table 2.j) were designed to compare the effect of the EDTA concentration and the incubation time on the extraction efficiency for 0.005 M and 0.05 M EDTA at a ratio of extraction solution to particulate material ratio of 200:1 (v:w; 30 ml EDTA solution with 150 mg of particulate material). Figure 2.11 shows the concentrations

Table 2.k Analysis of total particulate metal concentration in certified reference materials BCR 277 and BCR 320.

|                       | BCR 277                    |                           | BCR 320                    |                           |
|-----------------------|----------------------------|---------------------------|----------------------------|---------------------------|
| Compound              | Certified<br>Concentration | Observed<br>Concentration | Certified<br>Concentration | Observed<br>Concentration |
| Mn mg g <sup>-1</sup> | 1.5 <sup>a</sup>           | 1.5 ± 0.01                | 0.8 <sup>a</sup>           | 0.67 ± 0.02               |
| Mg mg g <sup>-1</sup> | 11 <sup>a</sup>            | 11 ± 0.03                 | 21 <sup>a</sup>            | 19 ± 0.5                  |
| Al mg g <sup>-1</sup> | 51 <sup>a</sup>            | 49 ± 0.8                  | 87 <sup>a</sup>            | 80 ± 0.8                  |
| Fe mg g <sup>-1</sup> | 46 <sup>a</sup>            | 41 ± 0.4                  | 49 <sup>a</sup>            | 37 ± 0.7                  |
| Co µg g <sup>-1</sup> | 16 ± 0.8                   | 14 ± 0.5                  | 19 ± 0.9                   | 16 ± 1.9                  |
| Ni µg g <sup>-1</sup> | 41 ± 4.4                   | 43 ± 1.6                  | 75 ± 1.4                   | N/A                       |
| Zn µg g <sup>-1</sup> | 547 ± 12                   | 536 ± 31                  | 142 ± 3.0                  | 123 ± 10                  |
| Cu µg g <sup>-1</sup> | 102 ± 1.6                  | 100 ± 9.0                 | 44 ± 1.0                   | 36 ± 2.9                  |
| Pb µg g <sup>-1</sup> | 146 ± 3.0                  | 152 ± 6.6                 | 42 ± 1.6                   | 60 ± 2.7                  |

<sup>a</sup>value for uncertainty not certified      N/A = analysis not undertaken

of Fe, Cu, Zn, Co, Ni, and Mg extracted using EDTA and normalised with respect to the particulate matter concentration, plotted against time for these experiments. The maximum incubation periods used for the 0.005 M and 0.05 M EDTA extractions were 48 h and 72 h, respectively. The results suggest that after 48 h the extracted concentrations of Fe, Mg and Cu were lower in the 0.005 M EDTA extraction solution compared with in the 0.05 M solution. The difference was small and within the experimental error for Zn, Co and Ni. Furthermore, metals were extracted more rapidly and a plateau in metal concentration was reached earlier using the 0.05 M EDTA solution compared with the 0.005 M EDTA. Therefore, an equilibrium between metals complexed by EDTA, and those associated with particulate matter, was reached more rapidly using the 0.05 M EDTA solution. The use of a lower EDTA concentration (0.005 M) will therefore extract a lower amount of Fe, Mg and Cu from particulate material, but will also require a longer incubation time to attain equilibrium, compared to a higher EDTA concentration (0.05 M EDTA).

The influence of the concentration of particulate material on the metal extraction efficiency was investigated by employing 2 different ratios of extraction solution (0.05 M EDTA) to particulate material: 200:1 and 2000:1 (v:w; 30 ml EDTA solution with 150 mg and 15 mg of particulate material, respectively). In addition to the metals analysed during the previous experiment, Mn, Pb and Al were also analysed. The incubation period was 72 h in order to allow more time for the attainment of equilibrium (experiments 3 and 4, Table 2.j). The results of this experiment are shown in Figs. 2.11 and 2.12, and indicate that increasing the extractant to particle ratio from 200:1 to 2000:1 (v:w) had no effect on the particulate matter normalised metal complexed by EDTA (MeEDTA) concentrations, with the differences between MeEDTA concentrations within analytical errors (with the exception of Al; Fig. 2.12.c). This observation may be explained by the use of an excess concentration of EDTA during the experiments, of which a large fraction was not complexed to metal ions.

The different behaviour observed for Al may be attributed to the fact that an equilibrium for Al between EDTA and sorption sites on the particles is attained only very slowly (see below).

## 7 Modelling of EDTA kinetic incubation experiments

Experiments 1-4 indicated that the competition between EDTA and particle bound metals was not instantaneous (Fig. 2.11 and 2.12). The data from experiments 1 and 3 (0.05 M EDTA extraction solution to particle ratio of 200:1 (v:w)) were therefore used to model the interaction between EDTA and metals.

The competition between the EDTA solution and the surface sites of the particles (S) for the trace metals (Me) can be described using a first order reversible reaction model, equation (10). The concentration of metal associated with particles is denoted by [MeS] and the EDTA complexed metal concentration by [MeEDTA]. The first order reversible reaction model was chosen since not all of [MeS] was complexed by [MeEDTA] during the extraction procedure hence, an equilibrium was achieved. The reaction can be characterised by two rate constants:  $k_1$  for the forward and  $k_2$  for the backward reaction (Morel, 1983). The time dependent linear differential equation for reaction (10) is expressed by equation (11), assuming that the EDTA concentration used is in excess of the metal concentrations, and therefore is constant. Furthermore, it is assumed that the concentration of S is much greater than the concentration of MeS, and that an increase in concentration of S with time is negligible.



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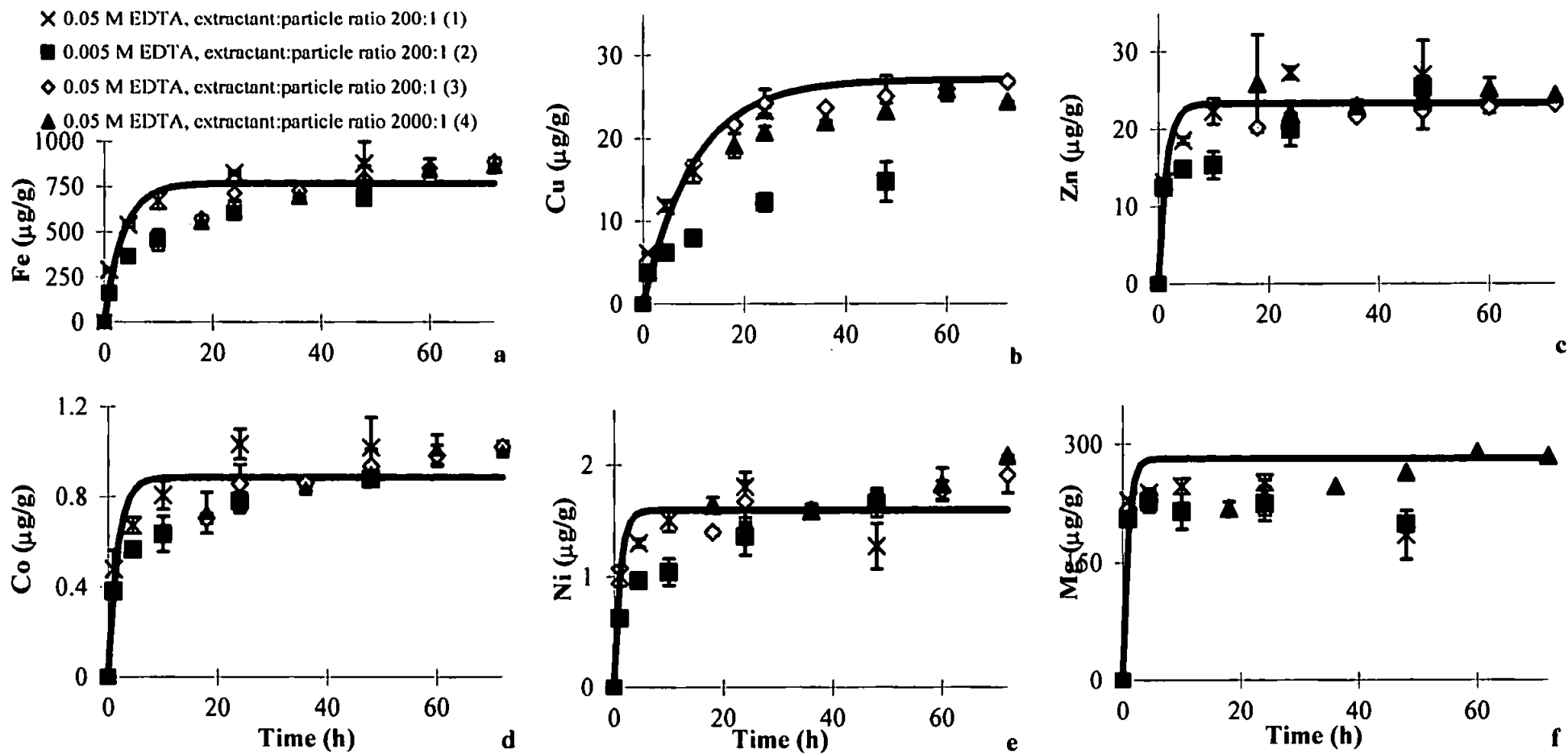


Figure 2.11 Concentration of particulate metal (Fe (a), Cu (b), Zn (c), Co (d), Ni (e), Mg) extracted using 0.05 M EDTA with an extraction solution to particulate matter ratio of 200:1 and 2000:1 (v:w), and 0.005 M EDTA with a ratio of 200:1, plotted against time. Legend key presented on Fig. 2.11.a and number between brackets refers to experiment (Table 2.j).

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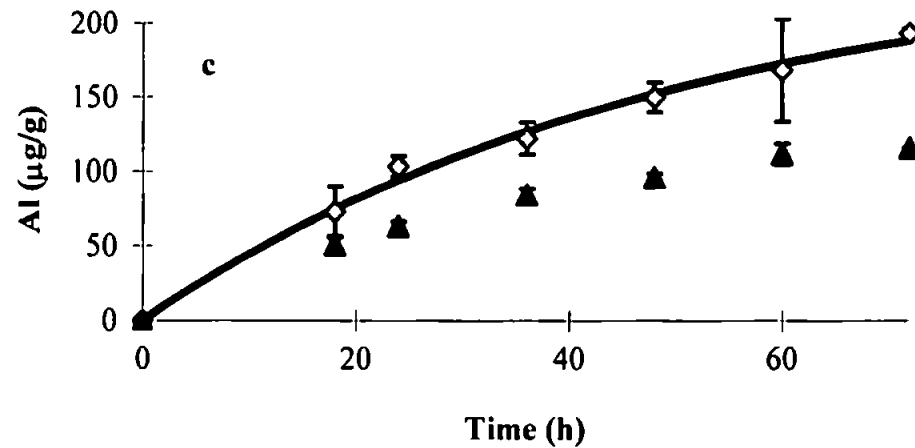
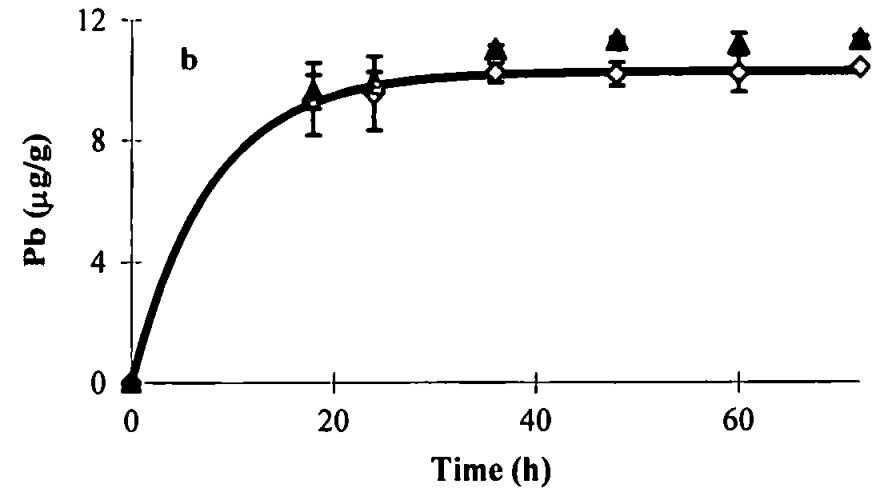
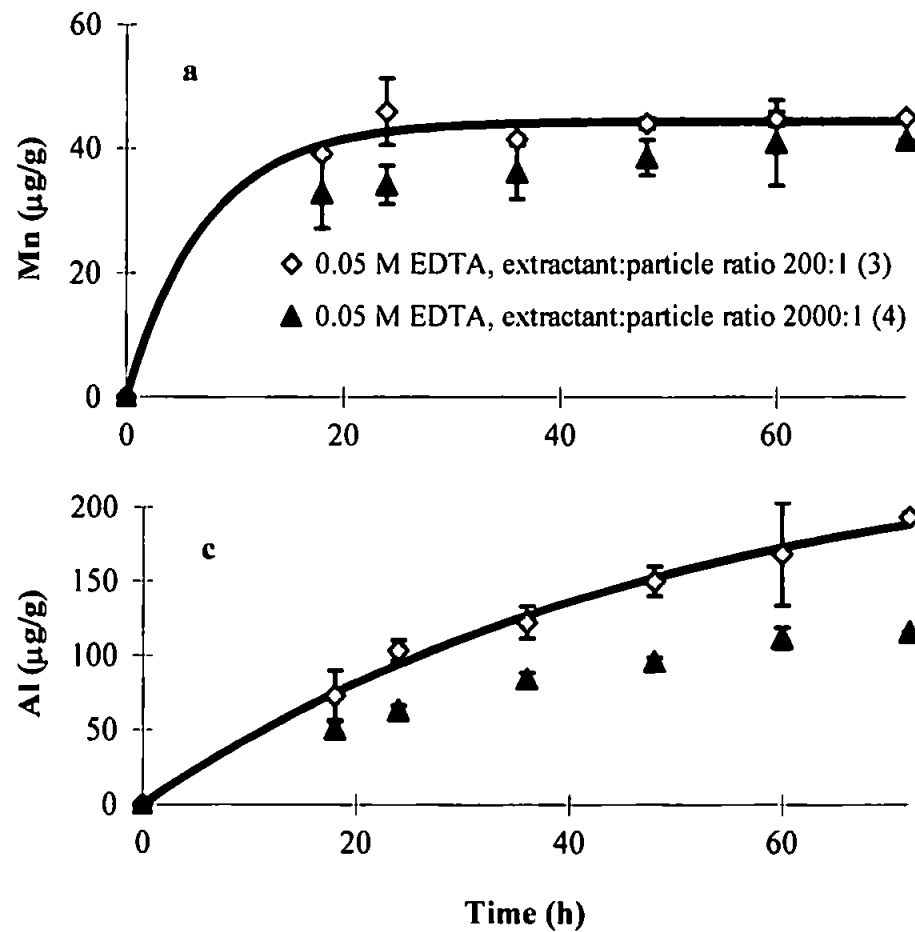


Figure 2.12 Concentration of particulate metal (Mn (b), Pb (b) and Al (c)) extracted using 0.05 M EDTA with an extraction solution to particulate matter ratio of 200:1 and 2000:1 (v:w). Legend key presented on Fig. 2.12.a, and number between brackets refers to experiment (Table 2.j).

$$\frac{d[\text{MeEDTA}]}{dt} = k_1[\text{MeS}] - k_2[\text{MeEDTA}] \quad (11)$$

Using the assumption that at  $t = 0$  the amount of the metal complexed with EDTA is zero, the solution to equation (11) is

$$[\text{MeEDTA}] = \frac{k_1}{k_1 + k_2} [\text{MeS}]^{t=0} - \frac{k_1}{k_1 + k_2} e^{-(k_1 + k_2)t} [\text{MeS}]^{t=0} \quad (12)$$

With the use of curve fitting software (CurveFitExpert 1.3) and an exponential function of the form  $y = a(1 - e^{-bx})$ , the concentration of  $[\text{SMe}]^{t=0}$  was estimated as being the concentration of  $[\text{MeEDTA}]$  at equilibrium. The curves obtained from the model calculations are presented in Figs. 2.11 and 2.12 Table 2.1 shows results of calculations of the minimum time required for the different elements to attain equilibrium with the extraction solution. The minimum times required to achieve 95 % ( $t_{95\%}$ ) and 100 % ( $t_{100\%}$ ) of the equilibrium concentration were calculated. Furthermore, the estimated equilibrium concentrations of  $[\text{MeEDTA}]$  for  $t_{100\%}$  determined using this approach are presented in Table 2.1. The time required to obtain 95 % ( $t_{95\%}$ ) of the equilibrium concentration was 30 h or less for all metals, except Al. The slow release of Al from the lattices of clay particles is most likely responsible for its  $t_{95\%}$  value of 149 h. The calculated  $t_{100\%}$  for Al was greater than 3000 h, and for Cu and Mn greater than 400 h. Extractions over this period of time are practically impossible, and would most likely result in analytical artefacts including re-adsorption of metals on particles and walls of the sample container and perhaps bacterial alteration of the metal speciation. An extraction time of 72 h for the experiments involving EDTA was therefore chosen as the optimum condition, because most of the metal extractions reached a state of at least 95 % of their equilibrium within this time period.

Table 2.1 Threshold times and equilibrium concentrations calculated using the kinetic model.

| Element   | T <sub>95%</sub> (h) | t <sub>100%</sub> (h) | eq. conc. (µg g <sup>-1</sup> ) |
|-----------|----------------------|-----------------------|---------------------------------|
| <i>Fe</i> | 10                   | 210                   | 768                             |
| <i>Mg</i> | 2.5                  | 50                    | 317                             |
| <i>Mn</i> | 22                   | 442                   | 44                              |
| <i>Cu</i> | 30                   | 608                   | 27                              |
| <i>Zn</i> | 4.3                  | 87                    | 23                              |
| <i>Pb</i> | 25                   | 503                   | 10                              |
| <i>Ni</i> | 3.3                  | 66                    | 1.6                             |
| <i>Co</i> | 5.2                  | 105                   | 0.9                             |
| <i>Al</i> | 149                  | 3020                  | 245                             |

## 8 Comparison of extraction efficiencies of EDTA and other single extractants

Further experiments were performed using the BCR 320 and BCR 277 sediments in order to compare the concentration of exchangeable metals extracted from these sediments using 0.05 M EDTA with other commonly used single extraction procedures (1 M HCl, 25 % v:v acetic acid and 1 M ammonium acetate; experiments 5-8, Table 2.j). Figures 2.13 and 2.14 show the results of these experiments with the extracted metal concentration presented as a fraction of the total metal concentration obtained after total digestion of the sample.

Figure 2.13 shows that for most metals (with the exception of Al and Zn), 1 M HCl extracted a higher fraction of particulate metal in BCR 320 compared with the other extractants (e.g. Co = 44 %, Ni = 50 % and Fe = 36 %). This observation indicates that metals were not easily removed from the estuarine sediment using mild extraction procedures at pH values between 4.5 and 7.6. The low pH of the HCl extraction solution, may have resulted in the dissolution of carbonate phases in the sediment particles, and hence released matrix bound particulate metals. The fraction of particulate metals extracted from the BCR 320 sediment using the 0.05 M EDTA (pH 7.6) and the 25 % v:v acetic acid solution. The fractions of metal extracted using 1 M HCl were generally similar for BCR 277 compared with BCR 320 (Fig. 2.14). However, the other extractants showed higher yields for BCR 277. The particulate metals in the BCR 277 estuarine sediment therefore appeared to be present in a more available form compared with BCR 320. As was the case for BCR 320, the ammonium acetate extractions with BCR 277 resulted in the lowest yield. Furthermore, the 0.05 M EDTA and 25 % v:v acetic acid extractions resulted again in comparable yields.

Figure 2.13 Fraction of particulate metals Mg, Mn, Fe, Co, Ni and Cu (a) and Al, Zn and Pb (b) extracted from BCR 320 using 1 M HCl, 25 % v:v acetic acid, 0.05 M EDTA and 1 M ammonium acetate. The digestion using HF and HNO<sub>3</sub> represents total particulate metal concentration (100 %). Legend presented in Fig. 2.13.b.

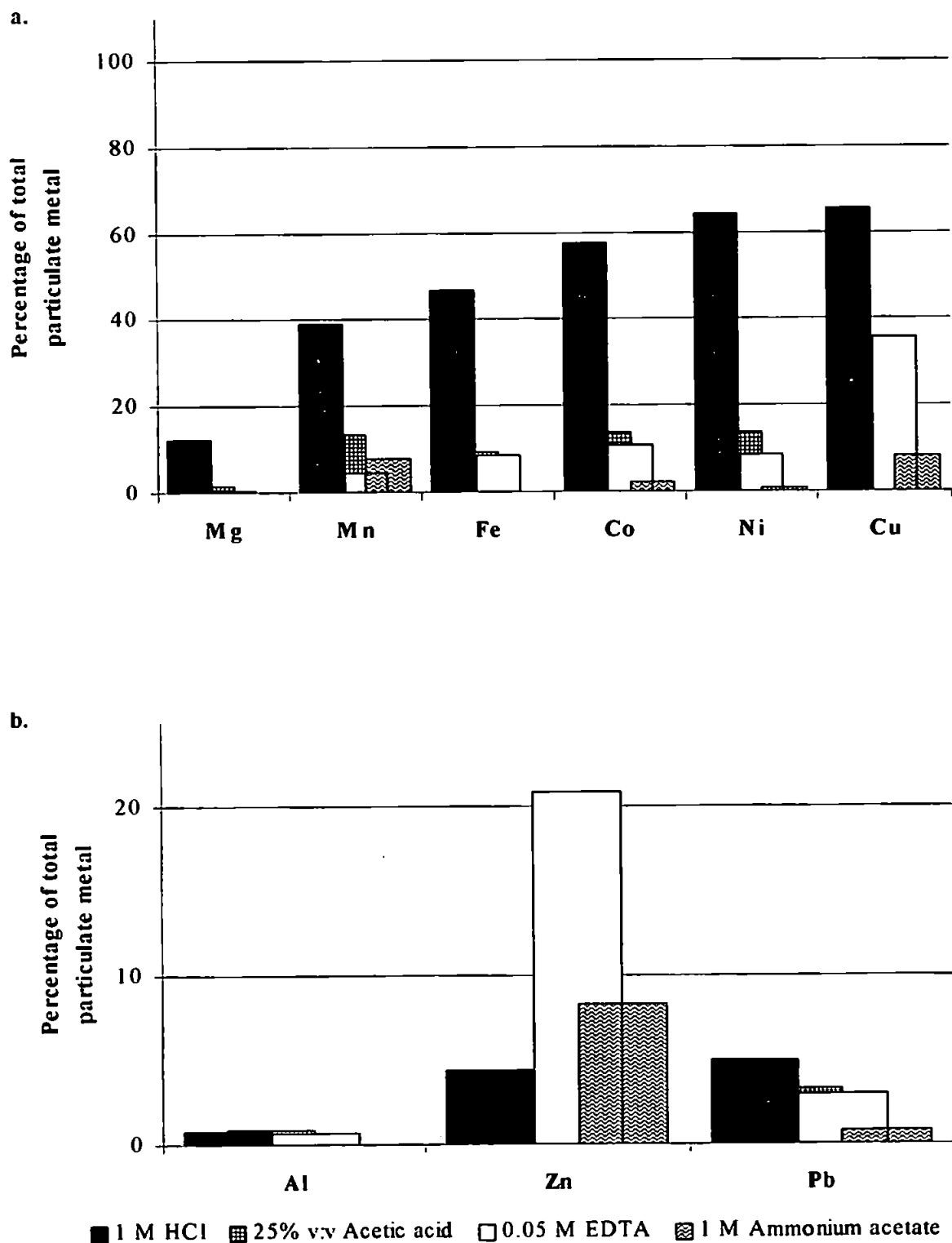
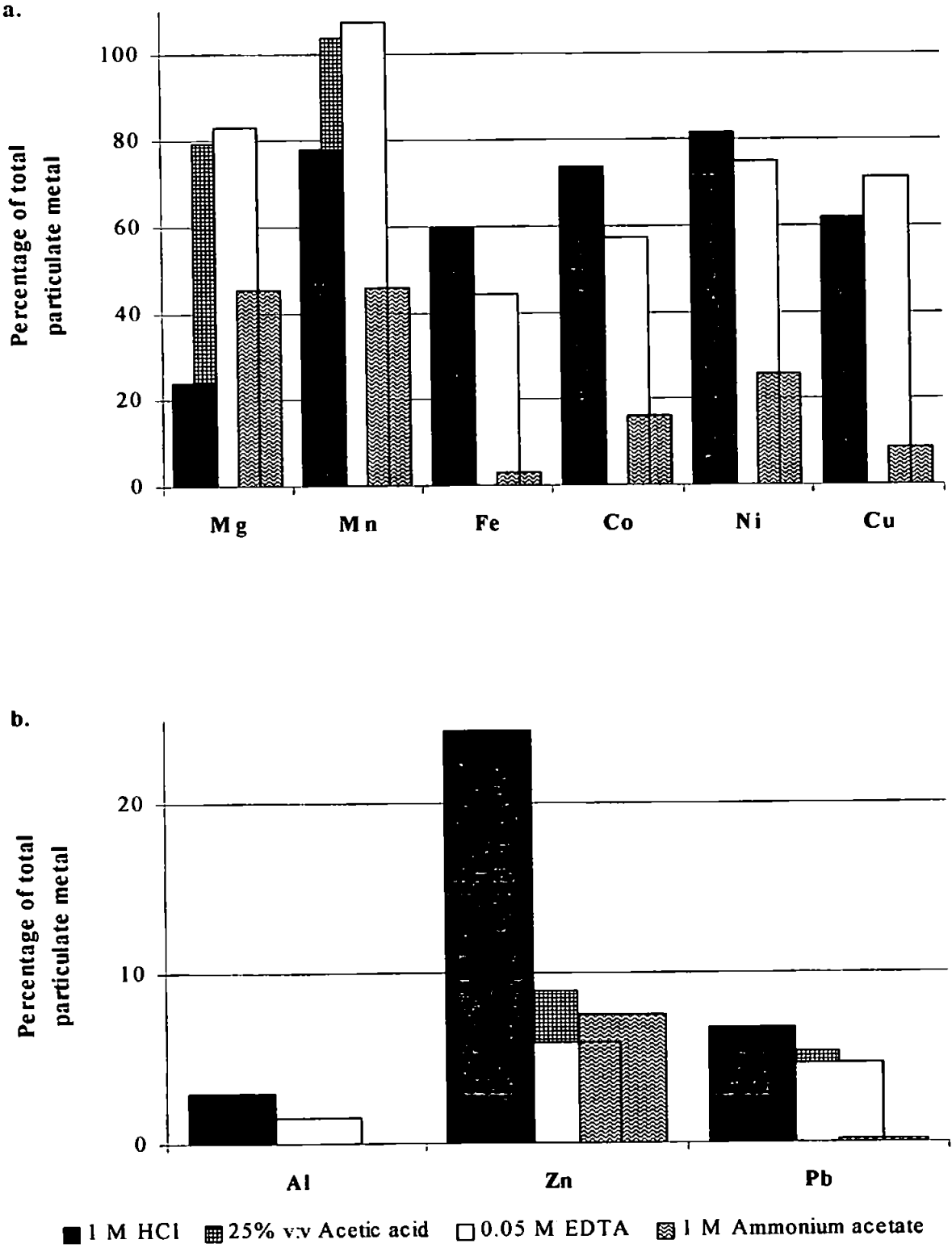


Figure 2.14 Fraction of particulate metals Mg, Mn, Fe, Co, Ni and Cu (a) and Al, Zn and Pb (b) extracted from BCR 277 using 1 M HCl, 25 % v:v acetic acid, 0.05 M EDTA and 1 M ammonium acetate. The digestion using HF and HNO<sub>3</sub> represents total particulate metal concentration (100 %). Legend presented in Fig. 4.14.b.



## 9 Conclusions for the use of EDTA as an extraction solution for particulate trace metals

EDTA was utilised to investigate non-lattice bound trace metals associated with SPM.

Optimum extraction conditions are presented below:

- 0.05 M EDTA solution set to pH 7.6,
- Extractant : particulate matter ratio of 200 : 1 (v:w),
- Incubation period of 72 h.

This approach is along similar lines as the ligand competition techniques used for determination of trace metal complexation by dissolved organic ligands in natural waters (Achterberg *et al.*, 1997; Achterberg and van den Berg 1997). Assessment of the contribution of biogeochemically available trace metals to the total particulate metal concentration in SPM can be performed when the extraction scheme is complemented by a total digestion using HF and HNO<sub>3</sub>. The extraction scheme has a low requirement of SPM (Minimum SPM = 15 mg), is simple and requires a minimal amount of reagents and sample handling and hence has an inherent low risk of sample contamination. The occurrence of re-adsorption of metals during extraction has been reported, where metal initially released by the reagent then re-precipitates or partitions back onto the solid phase (Tipping *et al.*, 1985). Rendell *et al.*, (1980), reported that extractions using EDTA are not affected by this problem. The experiments also indicated that none of the trace metals investigated showed post extraction re-adsorption effects during the incubation period. The 0.05 M EDTA SPM extraction methodology was applied to the analysis of particulate Mn, Ni, Zn and Cu in the Scheldt estuary (Chapter 4).

### 3 The behaviour and chemical speciation of dissolved Co, Ni, Zn and Cu in the Tamar Estuary

#### 3.1 Introduction

The Tamar estuary is situated on the South coast of Britain and forms a natural boundary between Devon and Cornwall (Fig. 3.1 and Fig. 3.2). Its length between weir head and Plymouth Sound is ~31 km. The water depth in the main channel varies between 2 and 8 m below mean high water springs in the upper estuary, and between 8 and 40 m in the lower estuary. Current velocities in the main channel vary between ~1 and ~0.5 m<sup>3</sup>/s in the upper estuary, and between ~0.5 and 0.3 m<sup>3</sup>/s in the lower estuary. Gunnislake weir, situated ~31 km from the mouth of the estuary, prevents the encroachment of seawater further upstream except during storm events and during times of freak high tides. The Tamar has a relatively short water residence time in the order of a 7 to 14 days (Millward and Turner, 1995) and is characterised as a partially mixed coastal plain estuary with a tidal range between 2.2 m (mean neap tide) and 4.7 m (mean spring tide) at the mouth and with semi-diurnal and asymmetric tides (Uncles *et al.*, 1994; Uncles *et al.*, 1985; Grabemann *et al.*, 1997; Environmental Agency, 1999).

The Tamar valley was once a focus for the extraction of industrial materials including As, Cu and W ores and even today china clay mining operations remain important to the local economy. Hence, the estuary has a legacy of trace metal pollution, which can be noticed in the river waters where elevated concentrations of i.e. Cu (up to 300 nM), and Zn (up to 600 nM) have been observed (Ackroyd *et al.*, 1986; van den Berg, 1991c; Morris, 1986). The mouth of the estuary comprises a heavily populated region (e.g. Plymouth, ~250,000 people), hence pollutants associated with municipal wastewater treatment and maritime

Figure 3.1 Location map of the Tamar estuary, Southwest United Kingdom. A scale and orientation is included.

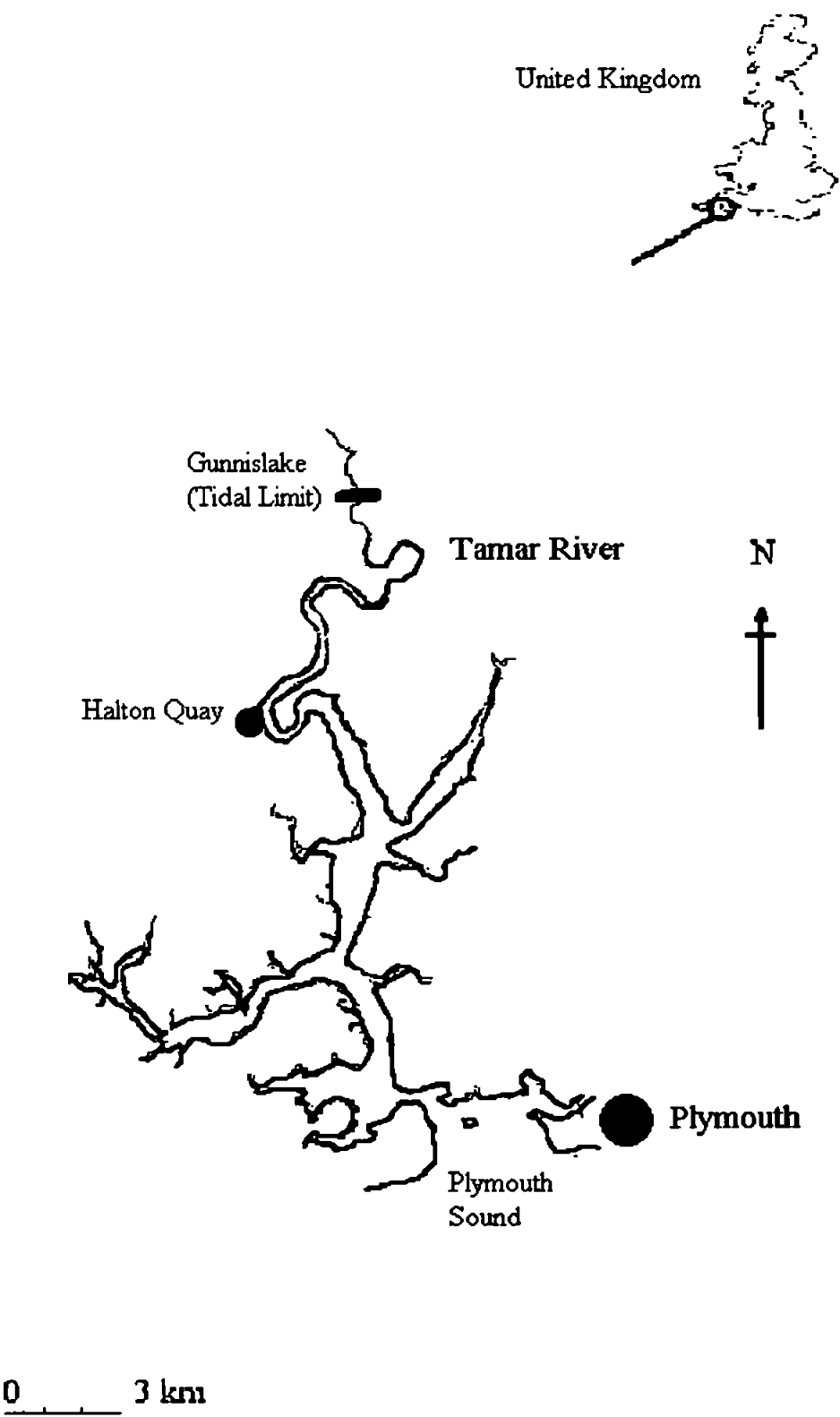


Figure 3.2 Physical overview of the Tamar River and catchment characteristics

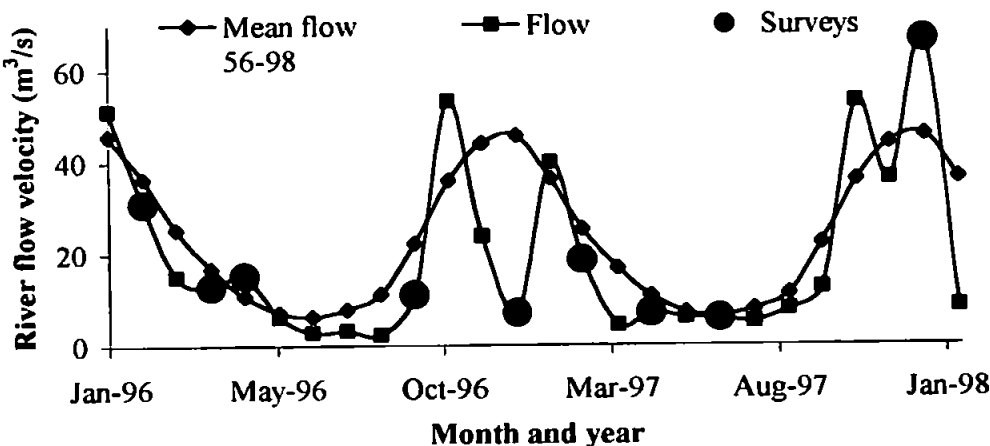
Geology and land use

Rural catchment of moderate relief, draining very disturbed lower Carboniferous slates, shales, grits and volcanics. Significant alluvial flats in middle reaches and Devonian slates low down. A range of agriculture, grazing and forestry as land use.

River gauging station

|                      |                                                    |
|----------------------|----------------------------------------------------|
| Tamar river          | Gunnislake                                         |
| Grid reference       | 20 (SX) 426 725                                    |
| Site information     | IH Station Number 47001 Station type Velocity-area |
| Catchment Area       | 916.9 km <sup>2</sup>                              |
| Rainfall (1961-1990) | 1216 mm per annum                                  |

Tamar River flow statistics



\* Tamar river flow statistics measurements were conducted by the Environment Agency, UK at Gunnislake Weir. Mean flow represents average monthly river flow based on measurements conducted between 1956 and 1998, Flow indicates monthly river flow during the study period and survey represent sampling exercises.

operations e.g. anti-foulant use, which contain high concentrations of materials that are toxic to marine organisms (including Cu and Zn).

A limited number of trace metal speciation studies have been reported for estuaries (van den Berg, 1986b; Gerringa *et al.*, 1996; Turner *et al.*, 1998; van den Berg *et al.*, 1987). This chapter will report on the dissolved speciation of Co, Ni, Zn and Cu in the Tamar estuary. The aims of the current investigation include:

- 1 Investigation of the behaviour of Co, Ni, Zn and Cu in the Tamar estuary,
- 2 Assessment of the effect of seasonal variability on the behaviour of Co, Ni, Zn and Cu,
- 3 Investigation of the chemical speciation of Co, Ni, Zn and Cu in the Tamar.

The results of dissolved chemical speciation studies of Cu, Ni, Co and Zn undertaken by AdCSV will be presented in this Chapter. To allow a seasonal comparison of dissolved trace metals (Co, Ni, Zn and Cu) values in the Tamar estuary the sampling campaigns will be grouped into respective seasons (winter, spring, summer and autumn). Each element will be discussed separately. An overview contrasting the behaviour of Co, Ni, Zn and Cu in the Tamar estuary and other estuarine systems will be discussed at the end of the Chapter.

An intensive sampling campaign was conducted in the Tamar estuary to systematically investigate dissolved chemical speciation of trace metals (Zn, Cu, Ni and Co). The Tamar estuary was selected as the focus of the investigation as there had been previous studies of total dissolved Cu, Ni and Zn (Ackroyd *et al.*, 1986; van den Berg *et al.*, 1990; van den Berg *et al.*, 1991; Newton and van den Berg, 1987; Morris, 1986; Morris *et al.*, 1986), which allow comparison with this investigation. Furthermore, the close geographical proximity between the field study area and the laboratory made the trace metal speciation study easier to conduct as the short transport time between collection of water samples and

their subsequent analysis (between 8 and 36 hours) ensured minimal perturbation in dissolved trace metal speciation.

## **3.2 Methodologies**

### *3.2.1 Collection of water and suspended particulate material*

Water and SPM samples were collected during ten surveys of the Tamar estuary between 13-02-1996 and 12-01-1998 using a combination of axial transect and tidal cycle sampling methodologies. An axial transect sampling survey involved the collection of samples along the axis of the Tamar estuary between Plymouth Sound and fresh river water at Gunnislake (Fig. 3.1). The advantages of adopting axial transect surveys in the Tamar included, rapid collection of samples (within ~4 hr) and the ability to collect a set of estuarine samples covering the whole range of salinities ( $S = \sim 0$  to  $\sim 35$ ). During tidal cycle surveys, samples were collected from a single geographical location (Halton Quay) at hourly intervals. The change in physicochemical conditions observed over the tidal cycle (13 hours) were generated by water mixing driven by tidal processes. This type of study was adopted at Halton Quay in the Tamar estuary as the tidal limit was relatively short (~25 km with a tidal range of between ~1 and ~4 m); consequently, large salinity gradients could be observed ( $S$  (variation) =  $\sim 0$  to  $\sim 28$ ). Further advantages of adopting tidal cycle sampling techniques at Halton Quay included good accessibility by road, low cost of the studies compared with ship board sampling and the possibility to undertake in situ dissolved Ni measurements. A summary of the types of sampling and trace metal analysis undertaken on samples collected from the Tamar estuary is presented in Table 3.a. To minimise differences in tidal state between surveys, all axial transect samples were all collected within an hour of high tide.

| <b>Survey</b>      | <b>Sampling methodology</b> | <b>Number of samples</b> | <b>Co analysis</b>         | <b>Ni analysis</b>          | <b>Zn analysis</b>          | <b>Cu analysis</b>                                                             | <b>Tidal state (high tide; low tide [m]) and time (GMT)</b> |
|--------------------|-----------------------------|--------------------------|----------------------------|-----------------------------|-----------------------------|--------------------------------------------------------------------------------|-------------------------------------------------------------|
| Winter<br>13-02-96 | Axial transect              | 13                       | Total dissolved            | Total dissolved             | Total dissolved             | Total dissolved                                                                | <b>4.59 at 12:00</b><br>1.87 at 05:00                       |
| Spring<br>14-04-96 | Axial transect              | 12                       | Total dissolved            | Total and labile dissolved. | Total dissolved             | Total and labile dissolved; dissolved natural Cu complexing ligand titrations. | <b>4.66 at 15:11</b><br>1.46 at 08:45                       |
| Spring<br>22-05-96 | Axial transect              | 12                       | Total dissolved            | Total and labile dissolved. | Total dissolved             | Total and labile dissolved.                                                    | <b>4.78 at 08:15</b><br>1.37 at 14:33                       |
| Autumn<br>02-10-96 | Axial transect              | 20                       | Total dissolved            | Total and labile dissolved. | Total dissolved             | Total and labile dissolved; dissolved natural Cu complexing ligand titrations. | <b>5.33 at 08:36</b><br>1.31 at 14:58                       |
| Winter<br>27-01-97 | Tidal cycle                 | 10                       | Total dissolved            | Total dissolved             | Total and labile dissolved. | Total and labile dissolved.                                                    | <b>5.27 at 07:41</b><br>1.16 at 13:58                       |
| Spring<br>18-3-97  | Tidal cycle                 | 10                       | Total and labile dissolved | Total and labile dissolved. |                             |                                                                                | <b>4.08 at 13:23</b><br>2.26 at 07:15                       |
| Spring<br>06-5-97  | Tidal cycle                 | 12                       | Total and labile dissolved | Total and labile dissolved. | Total and labile dissolved. | Total and labile dissolved.                                                    | <b>5.46 at 17:25</b><br>0.49 at 11:13                       |
| Summer<br>17-7-97  | Tidal cycle                 | 18                       | Total dissolved            | Total and labile dissolved. | Total and labile dissolved. | Total and labile dissolved.                                                    | <b>4.75 at 15:14</b><br>1.79 at 09:12                       |
| Summer<br>17-7-97  | Axial transect              | 12                       | Total dissolved            | Total and labile dissolved. | Total and labile dissolved. | Total and labile dissolved.                                                    | <b>4.75 at 15:14</b><br>1.79 at 09:12                       |
| Winter<br>12-01-98 | Tidal cycle                 | 15                       | Total dissolved            | Total dissolved             | Total dissolved             | Total and labile dissolved.                                                    | <b>5.12 at 17:35</b><br>1.10 at 11:22                       |

Table 3.a Overview of the analysis undertaken on the Tamar estuary between 12-02-96 and 12-01-98.

The methodology adopted for the collection of discrete water and SPM samples has been discussed in Chapter 2. Measurement of estuarine master variables (salinity, pH, dissolved oxygen and temperature) was carried out in situ using hand held meters and probes, which allowed an interactive approach during sampling (Chapter 2).

### *3.2.2 Analysis of total and labile dissolved Co, Ni, Zn and Cu*

Filtered (using 0.45  $\mu\text{m}$  porosity filters) total and labile dissolved Co, Ni, Zn and Cu measurements were undertaken in discrete samples at Plymouth University laboratories using AdCSV. Prior to analysis discrete waters samples were stored at 4°C. AdCSV dissolved labile measurements were conducted on filtered waters within ~36 hours of collection. The methodologies and analytical characterisation (e.g. LOD's, reagent and procedural blanks) for analysis of labile and total dissolved Co, Ni, Zn and Cu by AdCSV have been described in Chapter 2. In addition, the protocol for determination of Cu natural ligand concentrations and conditional stability constants was previously described in Chapter 2.

Stringent efforts were undertaken to prevent contamination and cross contamination of water and SPM samples, which included analysis of metal blank concentrations. Results of analysis of AdCSV reagent, Milli-Q and procedural blanks showed that Co, Ni, Zn and Cu were below the LOD by AdCSV (Co = 0.2 nM, Ni = 0.1 nM, Zn = 0.5 nM and Cu 0.2 = nM; Chapter 2). Despite the strong salinity gradients ( $S = 0$  to 35) observed in estuarine environments, the sensitivity of AdCSV techniques remained high (LOD; Co = 0.2 nM, Ni = 0.1 nM, Zn = 0.5 nM and Cu 0.2 = nM) throughout the range of estuarine waters (Chapter 2).

### 3.3 Results

#### 3.3.1 Analysis of dissolved Co, Ni, Zn and Cu in certified reference materials

Triplicate analysis of certified reference waters CASS-3 (coastal seawater) and SLEW-2 (estuarine water) was undertaken to verify the accuracy of total dissolved Co, Ni, Zn and Cu measurements undertaken by AdCSV. The reference waters were supplied acidified to pH ~1.65 using nitric acid and the certified values for Ni, Co, Zn and Cu are presented in Table 3.b. The determination of total dissolved Co, Ni, Zn and Cu concentrations in SLEW-2 and CASS-3 was undertaken using separate sub aliquots of each reference solution after the waters had been subjected to UV digestion (Chapter 2). The results of the total dissolved Co, Ni, Zn and Cu determinations by AdCSV compared well with the certified concentrations of SLEW-2 and CASS-3 (Table 3.b).

Table 3.b Analysis of total dissolved Co, Ni, Zn and Cu concentrations in certified reference materials CASS-3 and SLEW-2.

| Reference material | Ligand    | Buffer | CASS-3 Certified | CASS-3 Observed | SLEW-2 Certified | SLEW-2 Observed |
|--------------------|-----------|--------|------------------|-----------------|------------------|-----------------|
| Zn (nM)            | APDC      | Tris   | 19.0 ± 3.8       | 20.2 ± 0.6      | 13.6 ± 2.6       | 12.7 ± 0.6      |
| Zn (nM)            | Oxine     | HEPES  | 19.0 ± 3.8       | 22.3 ± 1.0      | 13.6 ± 2.6       | 13.4 ± 1.4      |
| Cu (nM)            | SA        | Borate | 8.14 ± 1.0       | 8.3 ± 0.4       | 27.7 ± 1.5       | 28.2 ± 0.5      |
| Cu (nM)            | Tropolone | HEPES  | 8.1 ± 1.0        | 8.6 ± 0.3       | 27.7 ± 1.5       | 28.5 ± 0.3      |
| Cu (nM)            | Oxine     | HEPES  | 8.1 ± 1.0        | 8.5 ± 0.4       | 27.7 ± 1.5       | 28.7 ± 0.3      |
| Ni (nM)            | DMG       | HEPES  | 6.6 ± 1.1        | 6.7 ± 0.5       | 12.7 ± 1.3       | 12.1 ± 0.4      |
| Co (nM)            | DMG       | HEPES  | 0.7 ± 0.2        | 0.9 ± 0.1       | 0.8 ± 0.1        | 0.9 ± 0.1       |

### 3.3.2 Tamar estuary: river flow, temperature pH and SPM observations

River flow rates, temperature, pH and SPM variability can have a dramatic influence on the trace metal distribution, chemical speciation of trace metals and biological activity. Southwest Britain is a temporal region that experiences strong seasonality, which can strongly influence trace metal behaviour and distribution owing to changes in river flow and productivity rates. The distribution of mean water temperature measurements undertaken during each of the surveys is presented in Table 3.c. These data show that the Tamar experiences strong seasonality and water temperatures vary by ~13 °C between summer and winter. Furthermore, there was only a small variation between the water temperature in the upper and lower estuaries. Seasonally averaged river flow velocities are presented in Table 3.c. These data show that river flow rates in winter were strongly enhanced compared with summer flow rates. The re-suspension of benthic sediments and the associated injection of metal enriched interstitial waters have been invoked to explain elevated trace metal concentrations in many estuaries (Ackroyd *et al.*, 1986; Morris, 1986; Zwolsman *et al.*, 1997). In periods of enhanced river flow rates sediments can become deeply reworked, which can have profound affect on the SPM load and consequently modify the behaviour of dissolved metal concentration and speciation. Therefore, in the case of the Tamar, where flow rates increase in the winter months by almost an order of magnitude, one may expect temporal variability in dissolved trace metal speciation and distribution. Furthermore, variability in river flow velocities can be responsible for the seasonal migration of sediments throughout the estuary (Uncles *et al.*, 1985; Grabemann *et al.*, 1997), which can cause seasonally driven contrasting dissolved sorption properties of SPM (Millward and Turner, 1995).

Table 3.c Seasonal variation in river flow rates and temperature in the Tamar estuary.

| Season                              | Winter<br>(Dec to Feb) | Spring<br>(Mar to May) | Summer<br>(Jun to Aug) | Autumn<br>(Sep to Nov) |
|-------------------------------------|------------------------|------------------------|------------------------|------------------------|
| * River flow<br>(m <sup>3</sup> /s) | 34.9                   | 13.4                   | 5.9                    | 11.1                   |
| * Temperature<br>(°C)               | 6.0 ± 0.9              | 11.7 ± 1.6             | 18.5 ± 0.8             | 14.0 ± 0.6             |

\* Mean of the monthly averaged values for the period 13-02-1996 to 12-01-1998

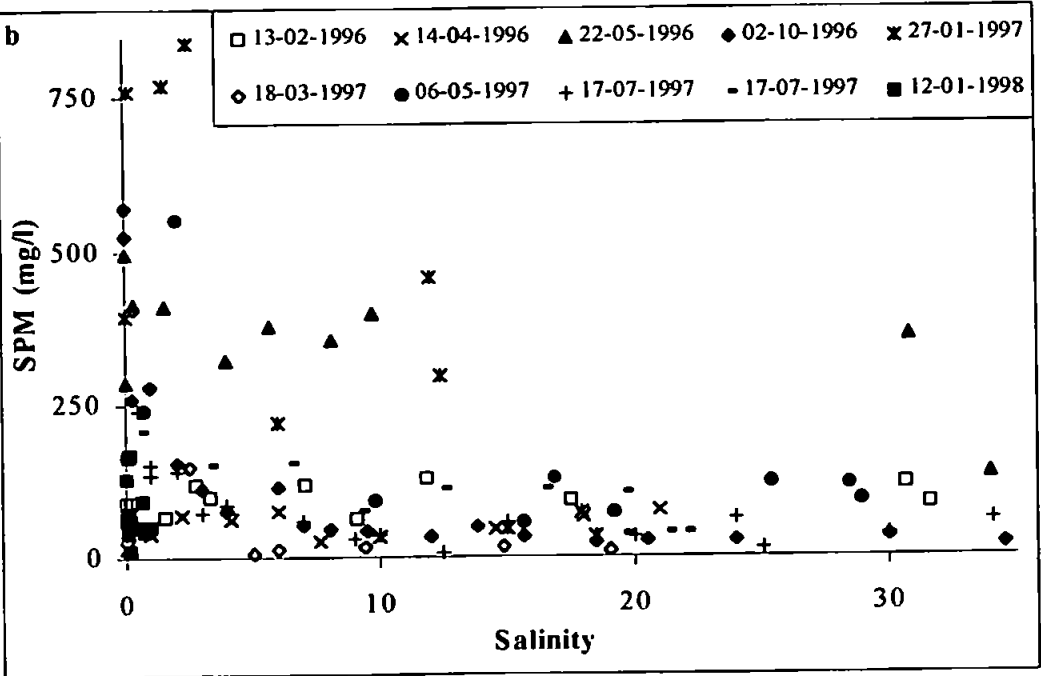
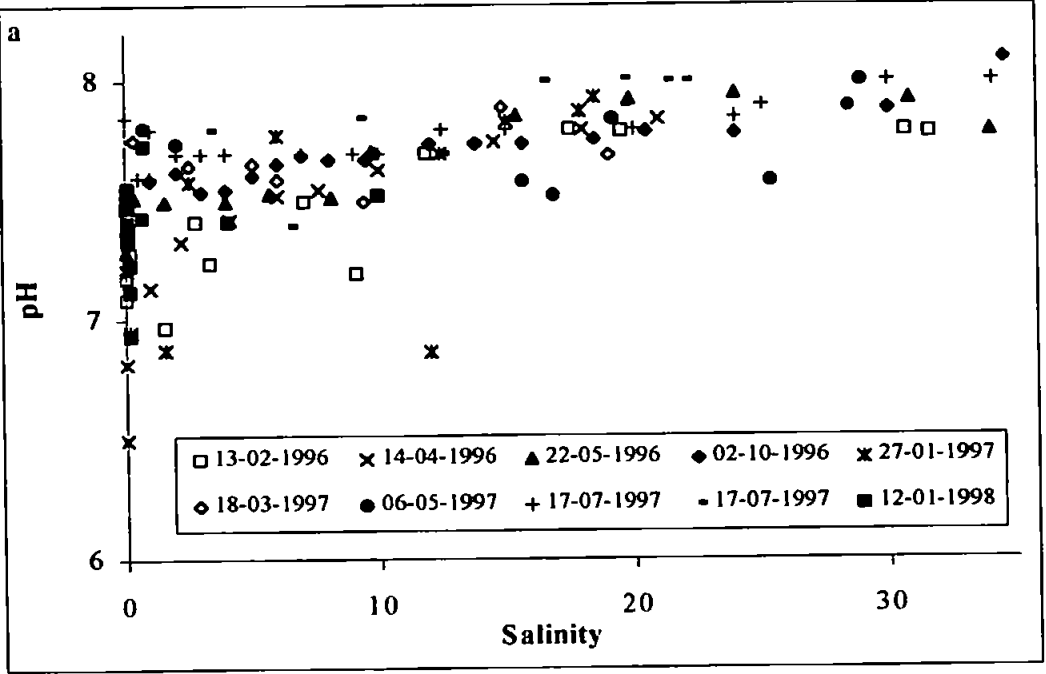
Figure 3.3 shows pH values and SPM concentrations observed between 13-02-1996 and 12-01-1998 in the Tamar estuary. Values for pH were between 8.09 and 6.50 with values generally increasing towards the lower estuary. The pH in the upper estuary is characterised by high seasonal variability. In contrast, the lower estuary exhibits low variability in pH. Similarly, SPM concentrations were enhanced and exhibited higher variability in the upper estuary when compared to the lower estuary. Furthermore, SPM concentrations were enhanced during autumn and winter as a result of higher river flows.

### 3.3.3 Assessment of dissolved speciation and temporal variability of Co

#### Winter

An overall estuarine concentration of Co<sub>tot</sub> based on the three winter surveys was  $7.0 \pm 3.4$  nM,  $n = 36$  (Fig. 3.4). Co<sub>tot</sub> exhibited highest concentrations and variability during 12-01-1998 ( $8.6 \pm 4.1$  nM). Similar distributions and concentrations of Co<sub>tot</sub> were observed during 13-02-1996 and 27-01-1997 ( $6.1 \pm 2.4$  nM and  $3.6 \pm 2.0$  respectively) despite the contrasting sampling styles adopted for the collection of samples. The most notable difference between the three surveys was the enhanced river flow rates encountered during

Figure 3.3 Water (a) pH values and (b) SPM concentrations in the Tamar estuary between 13-02-1996 and 12-01-1998.



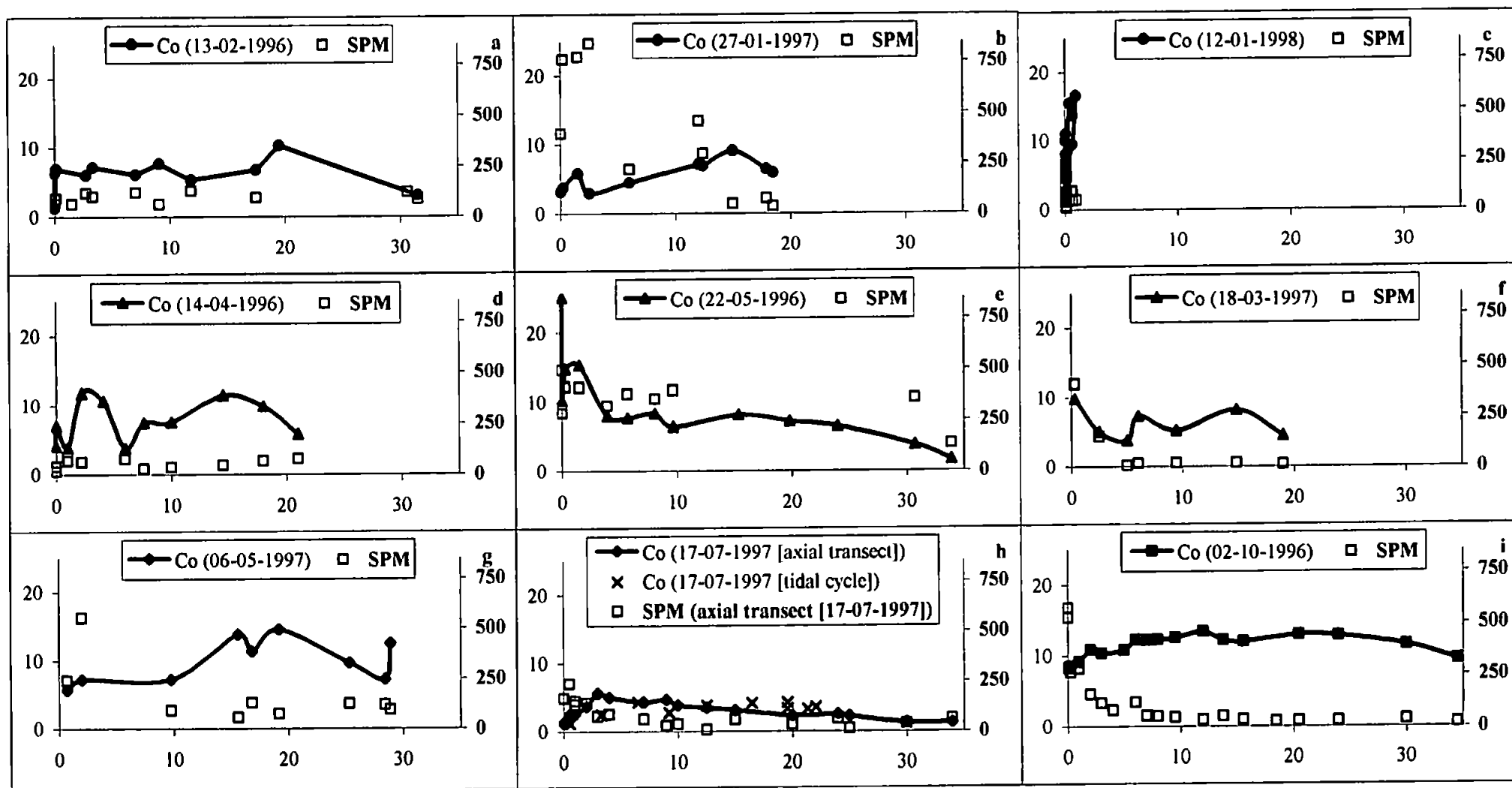


Figure 3.4 Distribution of total dissolved Co (nM) and SPM (mg/l) during (a, b and c) winter, (d, e, f and g) spring, (h) summer and (i) autumn surveys of the Tamar estuary between 13-02-1996 and 12-01-1998.

12-01-1998 of  $66.6 \text{ m}^3/\text{s}$ , compared with  $31.0 \text{ m}^3/\text{s}$  and  $7.0 \text{ m}^3/\text{s}$  for 13-02-1996 and 27-01-1997 respectively. Hence, the short salinity gradient observed during 12-01-1998 ( $S = 0$  to  $\sim 1.5$ ) throughout the survey (13 hr), was low compared with a salinity gradient of  $\sim 20$  observed during 27-01-1997 at the same sampling locality.  $\text{Co}_{\text{tot}}$  exhibited a low variability during 13-02-1996 and 27-01-1997 throughout the estuary (variation in  $\text{Co}_{\text{tot}} = 38.7 \%$  and  $35.4 \%$  for 13-02-1996 and 27-01-1997 respectively). The very high river flow velocities experienced during 12-01-1998 can possibly explain the high  $\text{Co}_{\text{tot}}$  concentrations and high variability (variation in  $\text{Co}_{\text{tot}} = 47.3 \%$ ) owing to reworking of sediments and associated injection of Co enriched interstitial waters.

### Spring

A mean spring concentration for  $\text{Co}_{\text{tot}}$  in the Tamar was  $8.3 \pm 4.3 \text{ nM}$  with high variability of between  $25.0$  and  $1.6 \text{ nM}$ ,  $n = 40$  (Fig. 3.4). The variation in  $\text{Co}_{\text{tot}}$  concentrations during the spring surveys was relatively high ( $43.0 \%$ ) although generally concentrations fluctuated around the mean estuarine value ( $8.3 \pm 4.3 \text{ nM}$ ) throughout the estuary.

During the 22-05-1996 survey  $\text{Co}_{\text{tot}}$  exhibited higher concentrations and spatial variability in the upper estuary ( $\text{Co}_{\text{tot}} = 25.0$  to  $7.9 \text{ nM}$ ;  $S = 0$  to  $\sim 4$ ) compared with the lower estuary ( $\text{Co}_{\text{tot}} = 6.4$  to  $1.7 \text{ nM}$ ;  $S \sim 25$  to  $\sim 34$ ), which could be explained by the removal of  $\text{Co}_{\text{tot}}$  in the low salinity ( $S = 0$  to  $5$ ) high turbidity ( $\sim 400 \text{ mg/l}$ ) zone. Co depletion in the upper estuary could, therefore, have been caused by adsorption of Co on to the surface SPM or by co-precipitation with Mn oxy-hydroxides. Ackroyd *et al.*, (1986) and Morris *et al.*, (1982) have previously observed the precipitation of Mn in the low salinity high turbidity of the Tamar estuary and Knauer *et al.*, (1982) observed a tendency for Co to co-precipitate with Mn in the San Francisco Bay estuary. Furthermore, mid estuarine (between  $S = 5$  to  $20$ ) Co maxima can be observed in all of the spring surveys. Ackroyd *et al.*, (1986) ascribed infusion of Mn enriched anoxic interstitial waters to explain the persistent feature of a mid estuarine Mn maxima, which could similarly explain the high concentrations of

Co observed in the mid estuary. Indeed, interstitial water could have profound effect on the estuarine system following deposition of organic material after spring phytoplankton bloom events (Achterberg *et al.*, 1997).

### Summer

Axial transect and tidal cycle surveys were carried out on the same day (17-07-1997) to assess the distribution and behaviour of  $\text{Co}_{\text{tot}}$  throughout the estuary and secondly to compare the results obtained using the contrasting sampling methodologies (Fig. 3.4 and Table 3.d). The data show that despite the contrasting sampling styles the results of the surveys yielded similar results.

A mean concentration of  $\text{Co}_{\text{tot}}$  for the summer was  $3.2 \pm 1.2$  nM. These data showed that  $\text{Co}_{\text{tot}}$  exhibited low variability throughout large parts of the estuary ( $S = \sim 4$  to  $\sim 34$ ) and can be characterised by  $R^2 = 0.68$ ,  $n = 19$ , intercept = 5.1 nM, slope = -0.11 at the 99 % confidence interval, which indicates relatively conservative mixing between Co enriched upper estuarine water and Co depleted seawater. However, in the low salinity ( $S = 0$  to 5) zone a high variability in  $\text{Co}_{\text{tot}}$  concentrations was encountered ( $\text{Co}_{\text{tot}}$  variability = 55.9 % compared with 31.9 %;  $S = 0$  to  $\sim 3.5$  and 4 to  $\sim 34$  respectively). The estimated  $\text{Co}_{\text{tot}}$  concentration at  $S = 0$  ( $\text{Co}_{\text{tot}} = 5.1$  nM) from the linear relationship between  $\text{Co}_{\text{tot}}$  and salinity ( $S = \sim 4$  to  $\sim 34$ ) compares with an observed value  $\text{Co}_{\text{tot}} = 1.2$  nM; at  $S = 0$ , which could indicate input of  $\text{Co}_{\text{tot}}$  in the low salinity zone ( $S = 0$  to 5). The enrichment of Co in the upper estuary could have been accounted for by the infusion of Co enriched interstitial waters into the overlying waters from anoxic sediments following deposition of organic material after seasonally enhanced phytoplankton activity (Achterberg *et al.*, 1997).

### Autumn

Figure 3.4 shows the results of  $\text{Co}_{\text{tot}}$  analysis from samples collected in the autumn of 1996 during an axial transect survey.  $\text{Co}_{\text{tot}}$  exhibited a low spatial variability throughout the estuary ( $\text{Co}_{\text{tot}} = 11.1 \pm 1.7$  nM). The distribution of  $\text{Co}_{\text{tot}}$  can be described as relatively

Table 3.d Comparison of results obtained from an axial transect and tidal cycle undertaken on the same day.

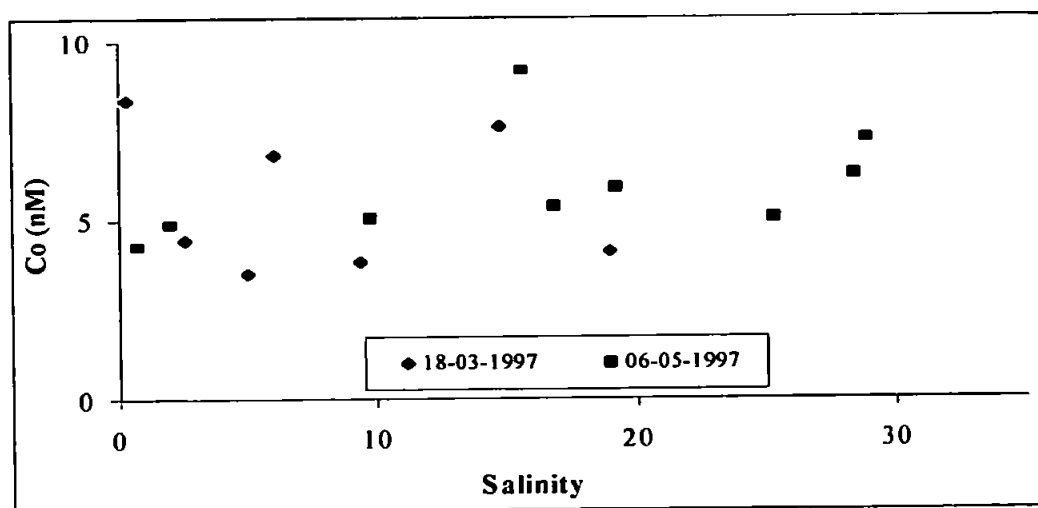
|     | Salinity   | SPM (mg/l)  | Temperature<br>(°C) | PH        | Co <sub>tot</sub> (nM) | Survey                       |
|-----|------------|-------------|---------------------|-----------|------------------------|------------------------------|
|     | 13.1 ± 7.8 | 103 ± 56.9  | 18.7 ± 1.1          | 7.8 ± 0.1 | 3.3 ± 1.0              | Axial<br>transect<br>17-7-97 |
| Min | 0.6        | 36.0        | 16.3                | 7.4       | 1.2                    |                              |
| Max | 22.1       | 208         | 20.0                | 8.0       | 4.3                    |                              |
|     | 8.4 ± 7.8  | 90.6 ± 65.4 | 18.4 ± 0.4          | 7.7 ± 0.8 | 3.3 ± 1.2              | Tidal<br>cycle<br>17-7-97    |
| Min | 0          | 28.2        | 17.7                | 7.6       | 1.2                    |                              |
| Max | 24         | 238         | 18.7                | 7.9       | 5.6                    |                              |

consistent throughout the estuary (Co<sub>tot</sub> = 8.3 and 9.5 nM; S = 0 and ~35 respectively). The concentration of Co<sub>tot</sub> was high throughout the estuary during 02-10-1996 compared with winter, spring, and summer surveys. This could possibly be explained by disturbance of anoxic sediments. Seasonally enhanced primary productivity and low river flow rates during the preceding months (river flow (mean value 07-1996; 08-1996; 09-1996) = 2.73 ± 0.50 m<sup>3</sup>/s) may have resulted in the deposition of organic rich anoxic sediment throughout the estuary (Uncles *et al.*, 1985). Autumn high river flow (10-1996 = 11.09 m<sup>3</sup>/s) coupled with a strong tide (~4 m) could have lead to deep reworking of anoxic sediments and injection of large quantities of Co enriched water, which would explain the seasonally enhanced Co concentrations throughout the estuary. The suggestion is supported by the enhanced SPM concentrations (SPM = (mean) 130 mg/l; between 569 mg/l and 20 mg/l) observed during 02-10-1996.

## Dissolved chemical speciation of Co

As a result of analytical interferences (possibly the presence of surfactants) during the measurement of filtered labile dissolved Co ( $\text{Co}_{\text{lab}}$ ) it was only possible to undertake these measurements on the samples collected during 18-03-1997 and 06-05-1997. The  $\text{Co}_{\text{lab}}$  fraction of  $\text{Co}_{\text{tot}}$  has been plotted against salinity and presented in Figure 3.5. Co was predominantly present as  $\text{Co}_{\text{lab}}$  during 18-03-1997 ( $\text{Co}_{\text{lab}}$  (% of  $\text{Co}_{\text{tot}}$ ) ~70 % to ~90 %). During 06-05-1997 an important fraction of  $\text{Co}_{\text{tot}}$  was in a non-labile form in the lower estuary ( $\text{Co}_{\text{lab}}$  (% of  $\text{Co}_{\text{tot}}$ ) ~30% to 50 %). This may well have been the result of organic complexation of Co during seasonally enhanced primary production rates and algal spring

Figure 3.5 Distribution of labile dissolved Co ( $\text{Co}_{\text{lab}}$ ) during spring in the Tamar estuary.



bloom events. The analytical technique adopted utilised DMG for the measurement of the electrochemical labile Co fraction. DMG forms a strong complex with Co ( $\text{Log}_{10} K_{\text{Co}_{\text{DMG}}} = 10^{18}$ ), hence only very strongly bound complexes with Co would have remained undetected. Nonetheless, a significant fraction of organically complexed Co was observed

during the two studies, which indicates the presence of relatively stable Co complexing ligands in the estuary.

### Overview of Co distribution in the Tamar Estuary

Based on the measurements from the entire data series mean estuarine  $\text{Co}_{\text{tot}} = 7.1 \pm 4.0$  nM,  $n = 120$ , with a range of between 1.2 nM and 25.0 nM ( $S = 0$  to 35). The concentration of  $\text{Co}_{\text{tot}}$  in the low salinity region of the upper estuary was  $7.5 \pm 5.0$  nM ( $S = 0$  to 1,  $n = 35$ ), which compares with  $\text{Co}_{\text{tot}} = 4.58 \pm 4.23$  nM in the lower estuary ( $S = 30$  to 35,  $n = 7$ ). There were no previously reported values for  $\text{Co}_{\text{tot}}$  concentrations in the Tamar estuary to compare with this study. However, minimum values of  $\text{Co}_{\text{tot}} = 1.21$  nM in Plymouth sound ( $S = 34$ ) were comparable with previously reported values of between  $\text{Co}_{\text{tot}} = 0.03$  to 0.93 nM ( $S = 35$ ) for the Western English Channel (Tappin *et al.*, 1993; Achterberg *et al.*, 1999). The authors concluded that significantly enhanced concentrations of Co noticed close to coastal zones were associated with Co enriched alluvial inputs, which would explain the high concentration of Co in the lower estuary ( $\text{Co}_{\text{tot}} = 4.6 \pm 4.2$  nM;  $S = 30$  to 35) (Tappin *et al.*, 1993; Achterberg *et al.*, 1999; Paucot and Wollast, 1997; Zhang and Wollast, 1990; Zhang *et al.*, 1989). Few measurements of dissolved Co have been reported for estuarine environments. However, reported values for  $\text{Co}_{\text{tot}}$  concentrations in the Scheldt estuary were comparable with Co values for the Tamar estuary (values for the Scheldt estuary;  $\text{Co}_{\text{tot}} = [5.1 \pm 4.7 \text{ nM}]$  Chapter 4;  $[\text{Co}_{\text{tot}} \sim 4 \text{ nM}]$  Zhang and Wollast, 1990). The Scheldt estuary is regarded as a perturbed system (Zwolsman *et al.*, 1997; Paucot and Wollast, 1997; Regnier and Wollast, 1993), which suggests that the enhanced Co concentrations in the Tamar are also related to human impact on this estuary.

The overall data series (Fig. 3.4) shows that  $\text{Co}_{\text{tot}}$  exhibited strong spatial and temporal variability (mean  $\text{Co}_{\text{tot}} = 7.1 \pm 4.0$ ,  $n = 120$ ). Despite the high inter seasonal variability observed for Co its behaviour can be described by the following features and in Table 3.e;

- 1 Depletion of Co in the low salinity ( $S = 0$  to  $\sim 3$ ) high turbidity zone ( $SPM = 100$  to  $847$  mg/l), which could be explained by adsorption of Co onto the surface of SPM and co-precipitation with Mn oxy-hydroxides.
- 2 Mid estuarine ( $S = \sim 3$  to  $\sim 25$ ) enrichment of  $Co_{tot}$  concentrations, which were probably associated with infusion of anoxic Co enriched interstitial waters owing sediment disturbance by enhanced river flow and/or tidal action.
- 3 Lower estuarine dilution of Co enriched waters with relatively depleted seawater ( $S = \sim 25$  to  $\sim 35$ ).

Table 3.e Simplified overview of seasonal variability in Co behaviour and distributions in the Tamar estuary

| Season | Salinity range<br>( $S = \sim 0$ to $\sim 3$ )                    | Salinity range<br>( $S = \sim 3$ to $25$ )                           | Salinity range<br>( $S = \sim 25$ to $\sim 35$ ) | Mean<br>Co (nM) |
|--------|-------------------------------------------------------------------|----------------------------------------------------------------------|--------------------------------------------------|-----------------|
| Winter | High variability removal at high SPM values.                      | Enrichment with mid estuarine maxima.                                | Dilution with Co depleted seawater.              | $7.0 \pm 3.4$   |
| Spring | High variability with input and removal in the low salinity zone. | Enrichment with mid estuarine maxima and depletion at high salinity. | Dilution with Co depleted seawater.              | $8.3 \pm 4.3$   |
| Summer | Low variability, removal at high SPM values.                      | Dilution with Co depleted seawater.                                  | Dilution with Co depleted seawater.              | $3.1 \pm 1.2$   |
| Autumn | Removal at high SPM values.                                       | Enrichment with mid estuarine maxima.                                | Dilution with Co depleted seawater.              | $11.1 \pm 1.7$  |

Ackroyd *et al.*, (1986) observed similar behaviour for dissolved Mn in the Tamar estuary, which could imply that the geochemical pathways for Mn and Co are linked in the Tamar. Elevated Co concentrations were observed during 02-10-1996, which followed a period of low river flow and high productivity, hence it was suggested that autumn disturbances of anoxic sediments deposited during the summer months were responsible for the high Co concentrations observed throughout the estuary during 02-10-1996.

The highest fraction non-labile Co fraction was observed in the lower estuary during 06-05-1997 and can possibly be explained by complexation of Co by algal exudates and breakdown products.

#### *3.3.4 Assessment of dissolved speciation and temporal variability of Ni*

##### Winter

Total dissolved Ni measurements have been plotted against salinity and presented in Figure 3.6. These data indicate a mean estuarine winter value of total dissolved Ni ( $Ni_{tot}$ ) =  $39.1 \pm 21.6$  nM,  $n = 37$ . Morris *et al.*, (1986) observed removal of Ni in the low salinity high turbidity zone of the Tamar estuary. Similarly, depletion of  $Ni_{tot}$  in the low salinity ( $S = 0$  to 3) high turbidity zone (SPM = 100 to 850mg/l) was noticed in this study during 13-02-1996 and 27-01-1997, which would indicate adsorption of Ni onto the surface of SPM. Figure 3.7 shows the results of on line automated  $Ni_{tot}$  measurements undertaken from a tidal cycle during 12-01-1998. Due to high river flow rates ( $66.59 \text{ m}^3/\text{s}$ ) a short salinity gradient ( $S = \sim 0$  to  $\sim 1.5$ ) was observed throughout the 13 hours of continuous monitoring, which compared with a larger salinity gradient ( $S = \sim 0$  to  $\sim 19$ ) and lower river flow velocities ( $7.03 \text{ m}^3/\text{s}$ ) observed during the 27-01-1997 tidal cycle. Values for  $Ni_{tot}$  observed during 12-01-1998 suggested low variability of  $Ni_{tot}$  concentrations in the very low salinity ( $S = 0$  to 1.5) region of the estuary ( $Ni_{tot}$  (mean) =  $30.6 \pm 4.7$  nM;  $n = 38$ ), which corresponded with low concentrations of SPM (SPM (mean) =  $72 \pm 46$  mg/l). The low

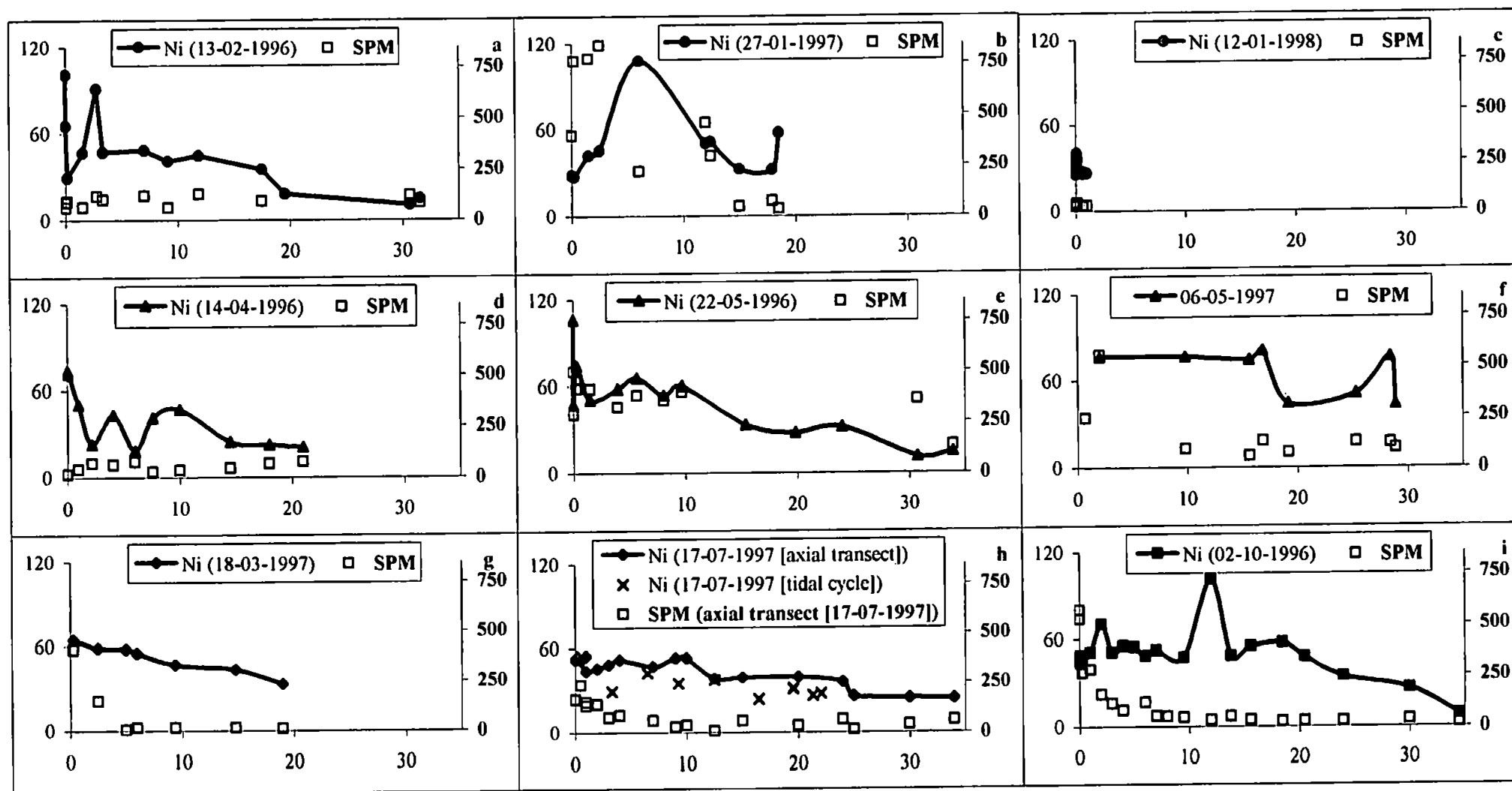
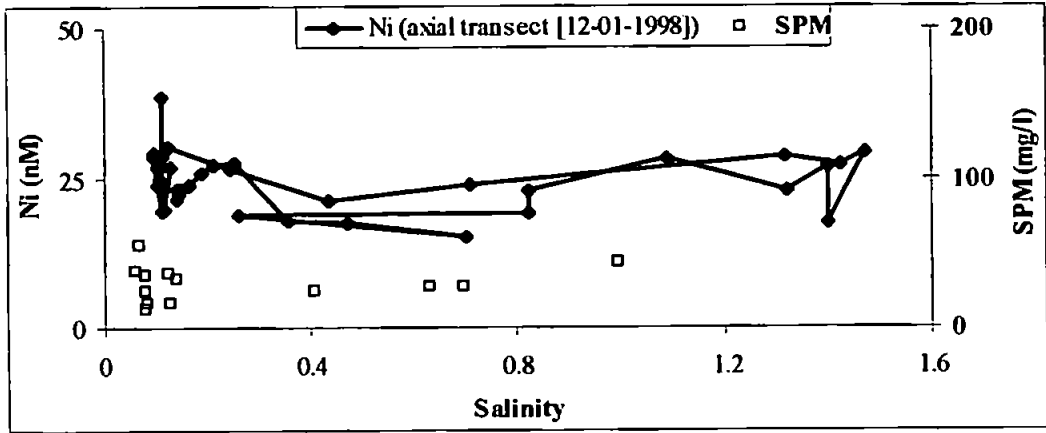


Figure 3.6 Distribution of total dissolved Ni (nM) and SPM (mg/l) during (a, b and c) winter, (d, e, f and g) spring, (h) summer and (i) autumn surveys of the Tamar estuary between 13-02-1996 and 12-01-1998.

Figure 3.7 Distribution of  $Ni_{tot}$  and SPM against salinity during an axial transect of the Tamar estuary 125-01-1998.  $Ni_{tot}$  measurements were undertaken by automated AdCSV operated over a 13 period and SPM samples were collected at 1 h resolution.



variability in  $Ni_{tot}$  concentrations could indicate that  $Ni_{tot}$  concentrations were not strongly influenced by salinity changes of between 0 and 1.5 during 12-01-1998 and indicates that variability in SPM concentrations could be the major influence in  $Ni_{tot}$  concentrations in the very low salinity zone.

A negative relationship existed between  $Ni_{tot}$  and salinity ( $S = \sim 3$  to  $\sim 35$ ), which was characterised by  $R^2 = 0.64$ ,  $n = 14$  (for surveys 13-02-1996 and 27-01-1997), slope = -1.46, intercept = 60.0 nM at the 99 % confidence interval. The negative relationship between  $Ni_{tot}$  and salinity suggests that, between the salinity interval  $\sim 3$  to  $\sim 35$ ,  $Ni_{tot}$  exhibited a relatively conservative behaviour during mixing between Ni enriched upper estuarine water ( $Ni_{tot} = 47.0$  nM,  $S = 3.30$ ) with relatively Ni depleted seawater ( $Ni_{tot} \sim 14.2$  nM,  $S = 31.58$ ). The relatively high intra-seasonal  $Ni_{tot}$  variability in the low salinity zone observed during winter could be explained by seasonal variability in e.g. river flow velocity, rain fall

and tidal amplitude. Despite the negative relationship observed between  $Ni_{tot}$  and salinity ( $S = \sim 3$  to  $\sim 35$ ),  $Ni_{tot}$  behaviour is described as non conservative owing to mid estuarine ( $S = \sim 3$  to  $\sim 20$ ) enrichment ( $Ni_{tot} = \sim 100$  nM at  $S = \sim 3$  and  $\sim 7$  for 13-02-1997 and 27-01-1997 respectively). Mid estuarine input of  $Ni_{tot}$  could possibly be explained by infusion of anoxic, Ni enriched, interstitial waters as a result of sediment disturbances.

The measurement of the labile dissolved Ni concentrations in the winter survey samples was attempted, however, owing to analytical interference from unknown species present in the waters (possibly surfactants), it was not possible to undertake measurements of non UV digested water samples.

### Spring

The mean spring concentration of  $Ni_{tot}$  based on the four spring surveys was  $50.1 \pm 21.4$  nM with high intra-seasonal variability (Fig. 3.6). With the exception of the 06-05-1997 survey,  $Ni_{tot}$  exhibited a negative relationship with salinity that was characterised by  $R^2 = 0.69$ ,  $n = 30$ , slope = -1.81, intercept = 69.9 nM at the 99 % confidence interval, which indicates that  $Ni_{tot}$  distributions were influenced by mixing between relatively  $Ni_{tot}$  enriched upper estuarine water with seawater. During 06-05-1997,  $Ni_{tot}$  exhibited a low variability throughout the salinity range ( $Ni_{tot} = 64.4 \pm 15.4$  nM;  $S = 0.71$  to 28.91) and this suggests that  $Ni_{tot}$  was well mixed in the estuary during 06-05-1997.

Removal of  $Ni_{tot}$  was observed in the high turbidity (SPM =  $\sim 100$  to  $\sim 500$  mg/l) low salinity ( $S = 0$  to  $\sim 5$ ) zone during 14-04-1996 and 22-05-1996, which suggests adsorption of  $Ni_{tot}$  onto surface sites of SPM. Input of  $Ni_{tot}$  was generally observed in the mid salinity range ( $S = \sim 5$  to  $\sim 15$ ) of the mid estuary, which has previously been accounted for by infusion of anoxic metal enriched interstitial waters upon tidal disturbance of sediments (Morris *et al.*, 1986; Ackroyd *et al.*, 1986). At mid to high salinities ( $S = 15$  to 35)  $Ni_{tot}$  can be characterised by mixing between Ni enriched estuarine waters and relatively Ni depleted seawater.

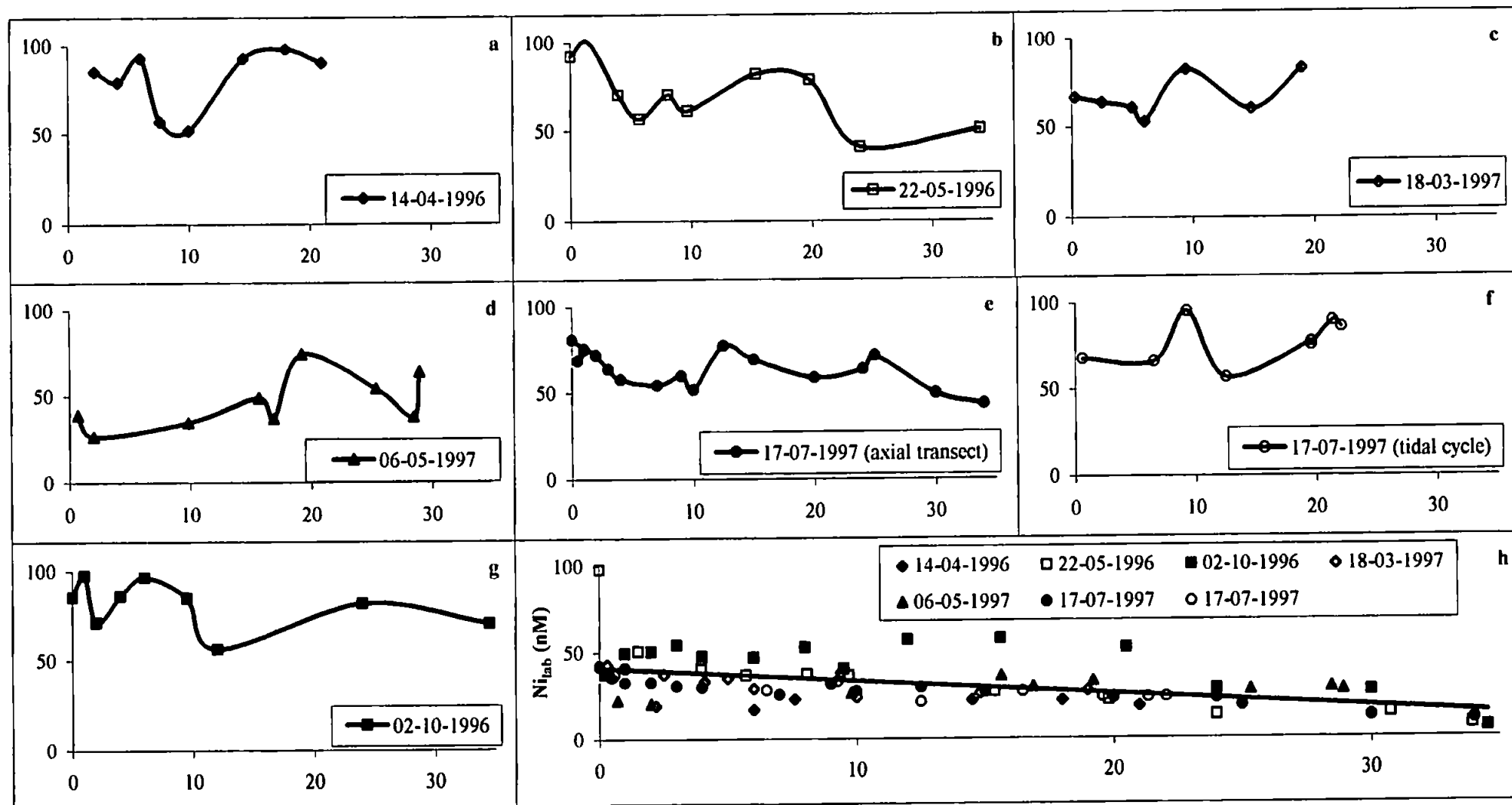


Figure 3.8 Distribution of the labile dissolved Ni ( $Ni_{lab}$ ) as a fraction (%) of total dissolved Ni ( $Ni_{tot}$ ) against salinity during (a, b, c and d) spring, (e and f) summer, (g) autumn, and (h)  $Ni_{lab}$  (nM) against salinity for all surveys of the Tamar estuary between 13-02-1996 and 12-01-1998 a regression line has been plotted that can be characterised by  $R^2 = 0.3$ , intercept = 41.3 (nM), slope = -0.78,  $n = 75$ , which is valid at the 99 % confidence level.

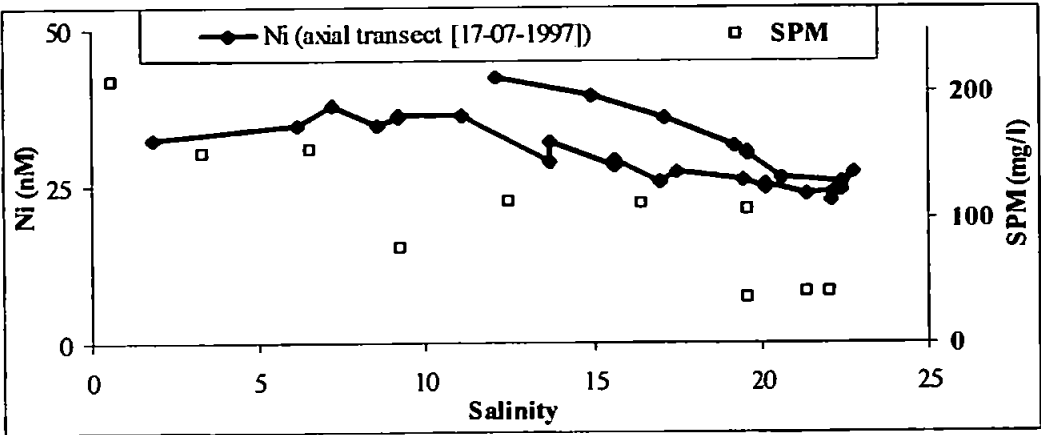
Determinations of labile Ni ( $Ni_{lab}$ ) were carried out in samples collected from each of the spring surveys. These data have been plotted against salinity and presented in Figure 3.8. With the exception of the 22-05-1996 axial transect, the  $Ni_{lab}$  fraction of  $Ni_{tot}$  exhibited a low variability within each survey (mean variation  $Ni_{lab}$  (% of  $Ni_{tot}$ ) = 15.7 %) but important differences existed between each survey ( $Ni_{lab}$  (% of  $Ni_{tot}$ ) = 46.2 % to 82.0 %). In order to assess the relevance of the  $Ni_{lab}$  measurements the binding strength of the added ligand must be considered. DMG was used as the AdCSV ligand to conduct  $Ni_{lab}$  measurements. Ni forms a strong complex with DMG, hence only strong organic complexes comprising Ni would have remained undetected ( $\text{Log}_{10} K_{Ni_{DMG}} = 10^{17}$ ) (Pihlar *et al.*, 1981). Highest fractions of organically complexed Ni ( $Ni_{org}$ ) were observed in the lower estuary (Plymouth sound (22-05-1996);  $S = 33.93$ ,  $Ni_{org}$  (% of  $Ni_{tot}$ ) = 49.4 %), which indicates that in Plymouth Sound sources of the organic material are present which are capable of forming strong complexes with dissolved Ni. Indeed, there are sewage outfalls that discharge large quantities of treated and untreated organic effluent into the lower Tamar estuary and Plymouth Sound (Environmental Agency, 1999). With the implementation of more effective sewage treatment facilities, this problem should be reduced. The transport of organic material from Plymouth Sound to the middle and upper estuary could account for the high fraction of organically complexed Ni observed. Furthermore, strong complexation of Ni by algal material (e.g. algal exudates, break down products) may be invoked to explain the high variability and fraction of non-labile Ni throughout the estuary. Similar observations of Ni complexation were made in Lake Esthwaite water (Achterberg *et al.*, 1997).

## Summer

Analysis of dissolved Ni was undertaken on samples collected from an axial transect and tidal cycle surveys performed on 17-07-1997 (Fig. 3.6). In addition, to the discrete samples collected and analysed for  $Ni_{tot}$ ,  $Ni_{lab}$  measurements were undertaken using on line

sampling and in situ automated analysis by AdCSV (Fig. 3.9 and Chapter 2). The contrasting sampling protocols resulted in similar  $Ni_{tot}$  distributions and concentrations (mean  $Ni_{tot}$  =  $33.5 \pm 9.3$  nM,  $42.7 \pm 10.6$  nM and  $30.3 \pm 5.4$  nM for the axial transect, tidal cycle and tidal cycle with in situ  $Ni_{tot}$  analysis respectively). The three data series exhibited a negative relationship with salinity ( $S = 0$  to  $35$ ), which can be characterised by  $R^2 = 0.81$ , slope =  $-0.85$ , intercept =  $52.6$  nM,  $n = 17$ , at the 99 % confidence interval;  $R^2 = 0.52$ , slope =  $-0.86$ , intercept =  $44.8$  nM,  $n = 9$ , at the 90 % confidence interval;  $R^2 = 0.52$ , slope =  $-0.68$ , intercept =  $41.1$  nM,  $n = 30$ , at the 99 % confidence interval (for the axial transect, tidal cycle and tidal cycle with in situ  $Ni_{tot}$  analysis respectively). The negative relationship between  $Ni_{tot}$  and salinity suggested that mixing of Ni enriched upper estuarine waters with relatively Ni depleted seawater was an important feature of  $Ni_{tot}$  behaviour during the summer.

Figure 3.9 AdCSV automated, on line, in situ measurements of  $Ni_{tot}$  and SPM plotted against salinity for tidal cycle undertaken on 17-07-1997.



However, low variability of  $Ni_{tot}$  ( $Ni_{tot} = 43.7 \pm 8.6$  nM;  $n = 20$ ) was observed throughout the low salinity zone ( $S = \sim 0$  to  $\sim 10$ ) during the tidal cycles and axial transect surveys, despite dilution with lower estuarine waters (Fig. 3.8). This could indicate input of  $Ni_{tot}$  into low salinity waters by either infusion of sediment interstitial waters and/or the release of  $Ni_{tot}$  from surface sorption sites of SPM owing to cation competition (Morris, 1986; Turner *et al.*, 1998).

The absence of a pronounced Ni maxima at mid salinities and in the mid estuary during the summer surveys (17-07-1997; axial transect and tidal cycles [online and discrete]) compared with the winter and spring surveys could be due to the very low summer river flow velocity ( $5.9$  m<sup>3</sup>/s), which would have caused minimal disturbances to the sediments. The behaviour of  $Ni_{tot}$  in at mid and high salinity ( $S = 15$  to  $\sim 35$ ) for all surveys undertaken on 17-07-1997 can be characterised by  $R^2 = 0.37$ , slope =  $-0.71$ , intercept =  $43.2$  nM,  $n = 36$ , at the 95 % confidence interval, which suggests conservative mixing behaviour for  $Ni_{tot}$  at higher salinities.

Analysis of the  $Ni_{lab}$  fraction in samples collected during the axial transect and tidal cycle surveys showed that between  $\sim 45\%$  to  $\sim 95\%$  of Ni was complexed by strong ligands (Fig. 3.6). Samples collected during the axial transect exhibited maxima in  $Ni_{lab}$  fractions in the upper ( $S = 0$  to  $4$ ) and mid estuary ( $S = 10$  to  $25$ ). Minimum  $Ni_{lab}$  fractions were observed during the axial transect in the salinity ranges  $\sim 4$  to  $\sim 10$  and  $\sim 25$  to  $\sim 35$ , which could indicate an influx of Ni complexing ligands, perhaps due to enhanced levels of primary productivity.

## Autumn

An axial transect survey was undertaken during 02-10-1996 and the samples were analysed for  $Ni_{tot}$  and  $Ni_{lab}$ , the results have been plotted against salinity and presented in Figure 3.6 and 3.8. A mean estuarine concentration of  $Ni_{tot} = 48.4 \pm 13.4$  nM with values decreasing to low levels in towards the lower estuary ( $Ni_{tot} = 70.6$  nM and  $8.0$  nM;  $S = 2.00$  and  $34.52$

respectively).  $Ni_{tot}$  shared a negative relationship with salinity, which was characterised by  $R^2 = 0.46$ ,  $n = 19$ , slope = -0.88, intercept = 57.5 nM, at the 95 % confidence interval and suggests that dilution of upper estuarine waters with  $Ni_{tot}$  depleted seawater influenced the distribution of  $Ni_{tot}$ . In the upper estuary  $Ni_{tot}$  values exhibited low spatial variability ( $Ni_{tot} = 52.3 \pm 6.8$  nM;  $S = 0$  to  $\sim 10$ ), which suggests that  $Ni_{tot}$  was buffered during the early mixing between upper and lower estuarine waters. The buffering could be accounted for by a redistribution of Ni between the particulate and dissolved phases owing to enhanced SPM concentrations in the upper estuary (mean SPM = 203.10 mg/l;  $S = 0$  to  $\sim 10$ ) and infusion of Ni enriched interstitial waters owing to sediment disturbances.

Mean estuarine  $Ni_{lab}$  (% of  $Ni_{tot}$ ) was  $88.5 \pm 10.6$  % and exhibited low spatial variability in the estuary. Observed labile Ni fractions were relatively high in the Tamar estuary during the autumn survey compared with spring and summer surveys. This can possibly be explained by lower primary productivity during autumn, with lower amounts of Ni complexing organic compounds produced.

#### Overview of Ni distributions in the Tamar estuary

Values for  $Ni_{tot}$  were in agreement with previous determinations of Ni carried out during studies in the Tamar estuary ( $Ni_{tot} = \sim 10$  nM to  $\sim 100$  nM; Morris *et al.*, 1986; Newton and van den Berg, 1987; van den Berg *et al.*, 1991). Table 3.f gives a broad overview of the distribution and behaviour of  $Ni_{tot}$  in the Tamar estuary. Based on the complete data series ( $n = 123$ ) a mean estuarine  $Ni_{tot}$  concentration was calculated and showed low inter-seasonal variability (mean estuarine  $Ni_{tot} = 44.4 \pm 18.2$  nM; inter-seasonal variability = 14.0 %). Outside the low salinity zone a negative relationship between  $Ni_{tot}$  and salinity was observed ( $S = \sim 3$  to  $\sim 35$ ), which was characterised by  $R^2 = 0.25$ ,  $n = 77$ , slope = -0.91, intercept = 50.2 nM at the 95 % confidence interval and indicates that Ni exhibited relatively conservative behaviour through much of the estuary as a result of the mixing of Ni enriched upper estuarine water with seawater. Previous authors have observed similar

$Ni_{tot}$  distributions in the Tamar estuary ( $[Ni_{tot}] \sim 10 \text{ nM}$  to  $\sim 45 \text{ nM}$ ] Morris *et al.*, 1986;  $[Ni_{lab}] \sim 5 \text{ nM}$  to  $40 \text{ nM}$ ] Newton and van den Berg 1987;  $[Ni_{tot}] \sim 30 \text{ nM}$  to  $\sim 70 \text{ nM}$ ] van den Berg *et al.*, 1991). Morris, (1986) also observed high variability of Ni in the low salinity zone and relatively conservative behaviour in the mid to lower Tamar estuary (Morris *et al.*, 1986).

$Ni_{tot}$  exhibited low inter seasonal variability and its behaviour was relatively similar despite (Table 3.f). The high variability of  $Ni_{tot}$  in waters collected in the mid and low salinity zone

Table 3.f Simplified overview of seasonal variability in Ni behaviour and distributions in the Tamar estuary

| Season | Salinity range<br>(S = ~0 to ~3)                  | Salinity range<br>(S = ~3 to ~15)  | Salinity range<br>(S = ~15 to ~35) | Mean Ni<br>(nM) |
|--------|---------------------------------------------------|------------------------------------|------------------------------------|-----------------|
| Winter | Removal at elevated concentrations of SPM.        | Mid estuarine maxima.              | Relatively conservative behaviour. | $39.1 \pm 21.6$ |
| Spring | High variability characterised by removal events. | Mid estuarine maxima.              | Relatively conservative behaviour. | $50.1 \pm 21.4$ |
| Summer | Low variability characterised by input events.    | Relatively conservative behaviour. | Relatively conservative behaviour. | $39.3 \pm 10.9$ |
| Autumn | Low variability characterised by input events.    | Mid estuarine maxima.              | Relatively conservative behaviour. | $49.9 \pm 18.0$ |

( $S = 0$  to  $\sim 15$ ) suggests that the behaviour of Ni was non-conservative in the upper estuary. Non conservative behaviour of Ni could be due to reworking of sediment, which can lead to the injection of metal enriched sediment interstitial waters ( $S = \sim 5$  to  $\sim 15$ ), the mobilisation of particulate Ni into the dissolved phase as a result of cation competition ( $S = \sim 3$  to  $\sim 10$ ) and adsorption of dissolved Ni onto SPM surfaces in the high turbidity (SPM = 100 to 850 mg/l) low salinity ( $S = 0$  to  $\sim 3$ ) zone (Morris, 1986; Morris *et al.*, 1986; Turner *et al.*, 1998). In the lower estuary and at high salinities ( $S = \sim 15$  to  $\sim 35$ )  $Ni_{tot}$  exhibited relatively conservative mixing behaviour with  $Ni_{tot}$  becoming diluted with increasing salinity

$Ni_{lab}$  exhibited a negative relationship with salinity throughout the estuary, which can be characterised by  $R^2 = 0.31$ ,  $n = 75$ , slope = -0.91, intercept = 41.3 nM at the 99 % confidence interval. The source of the dissolved organic material in the lower estuary remains unknown, but sources may include the large number of treated and untreated sewage outfalls that discharge organic waste into Plymouth Sound and phytoplankton related material.

### 3.3.5 The distribution of dissolved Zn in the Tamar Estuary

#### Winter

The mean estuarine winter concentration of  $Zn_{tot}$  was  $117 \pm 76.8$  nM ( $n = 38$ ), based on the complete winter data series (Fig. 3.10). Despite the high spatial variability of  $Zn_{tot}$  in the estuary,  $Zn_{tot}$  exhibited a low intra-seasonal variability (mean  $Zn_{tot} = 153$  nM, 109 nM and 90.9 nM, for 1996, 1997 and 1998 respectively). Lowest concentrations of  $Zn_{tot}$  were observed at high salinities in the lower estuary ( $Zn_{tot} = 40.3$  nM,  $S = 31.58$ ).  $Zn_{tot}$  exhibited removal in the low salinity ( $S = 0$  to  $\sim 2$ ) high turbidity (SPM =  $\sim 100$  to  $\sim 850$  mg/l) region of the estuary during 13-02-1996 and 27-01-1997. Ackroyd *et al.* (1986) previously observed Zn depletion in the low salinity high turbidity region of the Tamar estuary and

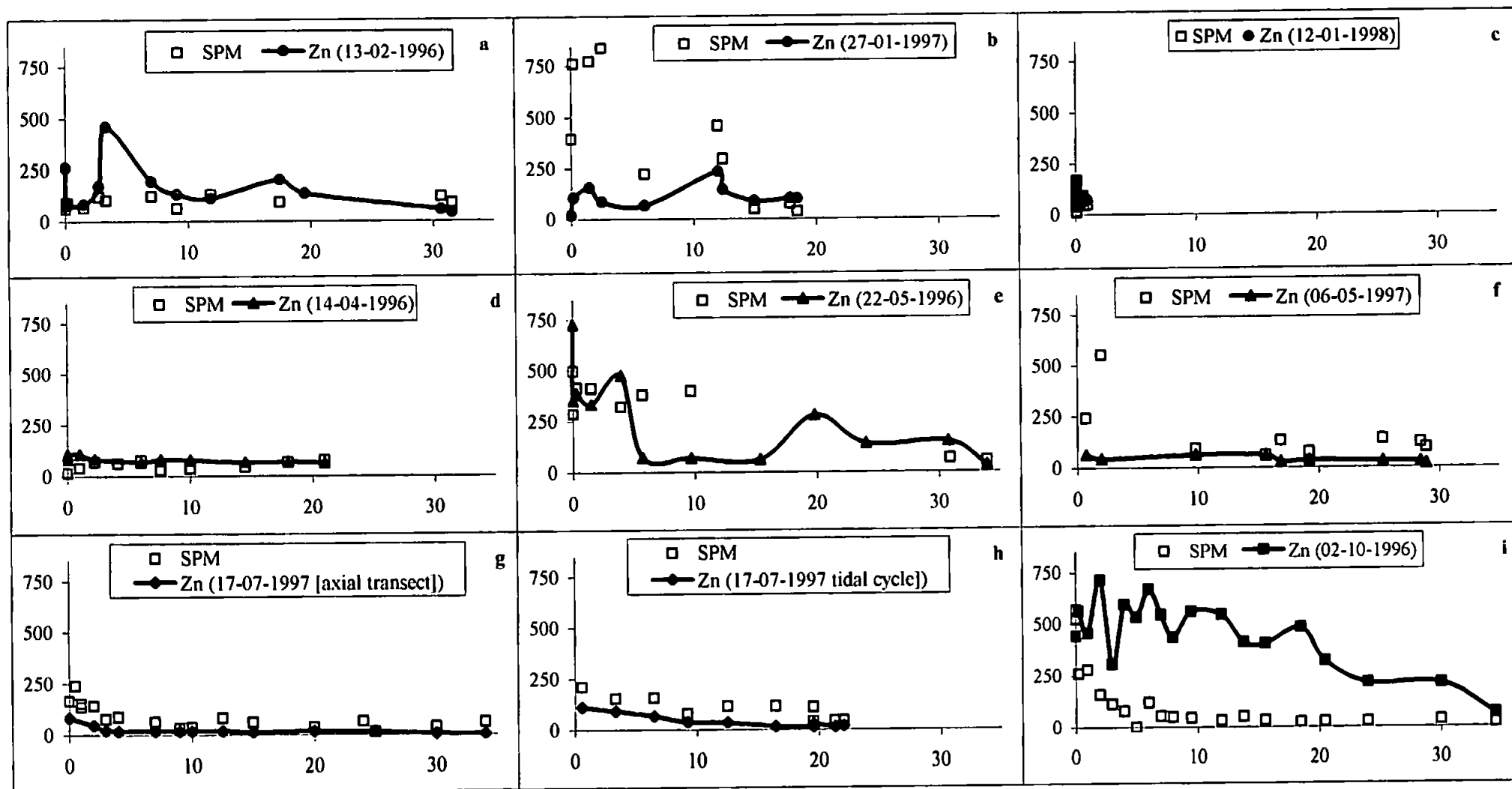


Figure 3.10 Distribution of total dissolved Zn (nM) and SPM (mg/l) against salinity during (a, b and c) winter, (d, e and f) spring, (g and h) summer and (i) autumn surveys of the Tamar estuary between 13-02-1996 and 12-01-1998.

suggested adsorption onto the surface of SPM as a possible mechanism for  $Zn_{tot}$  removal. Measurements of  $Zn_{tot}$  undertaken on samples collected from a tidal cycle during 12-01-1998 showed low variability of  $Zn_{tot}$  ( $Zn_{tot} = 90.9 \pm 26.3$  nM) and SPM ( $71.5 \pm 46.2$  mg/l) values in low salinity waters ( $S = 0$  to  $\sim 1.5$ ), which could indicate the importance of large SPM gradients for the  $Zn_{tot}$  distribution of the low salinity region.

$Zn_{tot}$  concentrations exhibited a mid estuarine maxima of  $138 \pm 52.5$  nM ( $S \sim 10$  to  $\sim 20$ ) compared with  $Zn_{tot} = 115 \pm 82.9$  nM observed for the low salinity region ( $S = 0$  to  $10$ ). Mobilisation of  $Zn_{tot}$  from particulate phases into the dissolved phase as a result of cation competition (e.g.  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^{+}$ ) for surface adsorption sites and the complexation of particulate Zn by e.g. chloride could account for  $Zn_{tot}$  enrichment in the mid estuary (Zwolsman *et al.*, 1997; Morris, 1986; van den Berg, 1991c). In addition, Ackroyd *et al.*, (1986) and van den Berg, (1991c) suggested that mid estuarine inputs of  $Zn_{tot}$  in the Tamar estuary could have been related to diffusion of anoxic Zn enriched interstitial waters into the over-lying water column. The  $Zn_{tot}$  data series obtained from both the axial transect (13-02-1997) and tidal cycle (27-01-1997) generated a similar distribution and concentration pattern when compared with salinity, which suggests that the differing sampling procedure produced complimentary data sets.

Due to analytical interferences from dissolved compounds in the sample waters the measurement of electrochemically labile Zn ( $Zn_{lab}$ ) was only possible on samples collected during 27-01-1997, these data have been plotted against salinity and presented in Figure 3.11. Since oxine was used for the determination of electrochemically labile Zn, only relatively strong complexes with Zn would remain undetectable and therefore, the majority of the non detectable Zn fraction was likely to comprise dissolved organic complexes (van den Berg, 1986a). The lowest  $Zn_{lab}$  proportion of  $Zn_{tot}$  ( $Zn_{lab}$  (% of  $Zn_{tot}$ ) = 12.6 %,  $S = 0.2$ ) was observed in the upper estuary and the fraction of  $Zn_{lab}$  increased to reach a plateau at low to mid salinities ( $Zn_{lab}$  plateau =  $91.9 \pm 11.3$  % of  $Zn_{tot}$ ;  $S = 12$  to  $18.5$ ). The relationship between  $Zn_{lab}$  and salinity suggests that the electrochemically undetectable Zn

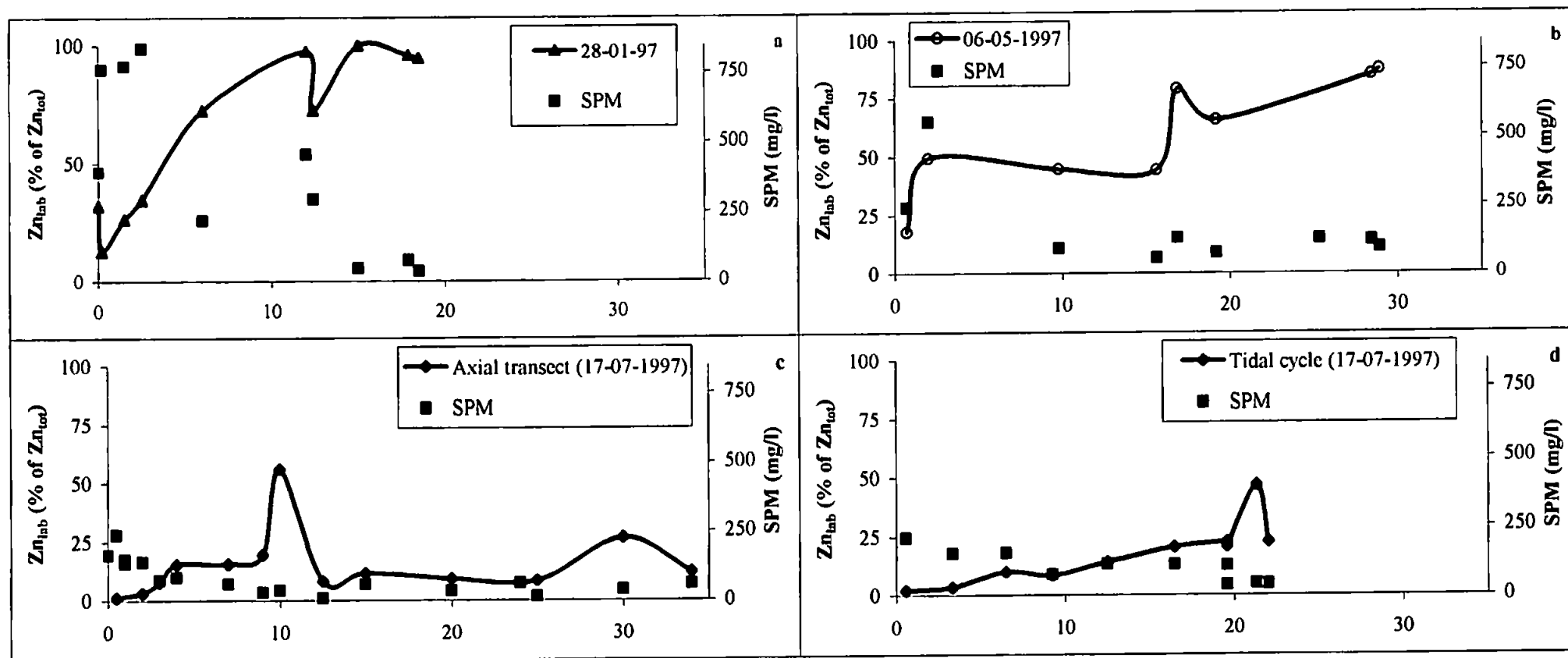


Figure 3.11 Distribution of labile dissolved Zn ( $Zn_{lab}$ ) and SPM against salinity during (a) winter, (b) spring, (c) summer axial transect and (d) summer tidal cycle surveys undertaken on the Tamar estuary between February 1996 and January 1998.

complexes, which comprise organically complexed Zn compounds ( $Zn_{org}$ ), were preferentially removed from solution as the salinities increased. This observation and the low fraction of  $Zn_{lab}$ , observed in the low salinity region, suggests that humic material and fulvic acids may have been involved in the complexation of Zn in the Tamar. Humic and fulvic acids can flocculate from solution with increasing salinities, which could add to the depletion of Zn in the low salinity high turbidity zone (Davis, 1984; Paulson *et al.*, 1994a, b; Petterson *et al.*, 1997).

### Spring

The results of  $Zn_{tot}$  analysis from waters collected during spring have been plotted against salinity and are presented in Figure 3.10.  $Zn_{tot}$  exhibited high intra-seasonal variability (mean  $Zn_{tot}$  =  $79.7 \pm 15.5$  nM,  $255 \pm 210$  nM and  $39.9 \pm 17.4$  nM for 14-04-1996, 22-05-1996 and 06-05-1997 respectively). Broadly,  $Zn_{tot}$  exhibited a similar distribution during 14-04-1996 and 06-05-1996 and this can be described by a negative relationship with salinity with  $R^2 = 0.61$ , slope = -1.58, intercept = 92.4 nM, at the 95 % confidence interval and  $R^2 = 0.59$ , slope = -1.27, intercept = 60.7 nM,  $n = 9$ , at the 95 % confidence interval respectively. The negative relationship between  $Zn_{tot}$  and salinity observed during the 14-04-1996 and 06-05-1997 indicated that dilution of  $Zn_{tot}$  enriched low salinity estuarine water with relatively  $Zn_{tot}$  depleted high salinity waters was an important feature of  $Zn_{tot}$  distributions in the estuary.

During the 22-05-1996 survey  $Zn_{tot}$  exhibited very high spatial variability with elevated concentrations observed in the upper estuary.  $Zn_{tot}$  exhibited removal in the low salinity ( $S = 0$  to  $\sim 3$ ) high turbidity zone ( $SPM = \sim 400$  mg/l;  $S = 0$  to  $\sim 3$ ), which was possibly associated with adsorption of Zn onto the surface of SPM and possibly the flocculation of dissolved organically complexed Zn. Removal of  $Zn_{tot}$  was observed in the salinity range  $\sim 8$  to  $\sim 15$  during 22-05-1996 and could indicate uptake of Zn by phytoplankton during the spring period of enhanced productivity. Mid estuarine enrichment ( $S = \sim 20$ ) of Zn was

encountered (22-05-1996), which may have been caused by disturbance of anoxic sediments and subsequent infusion of Zn enriched interstitial waters.

The  $Zn_{lab}$  fraction of  $Zn_{tot}$  has been plotted against salinity and presented in Figure 3.11. These data were obtained from samples collected during an axial transect undertaken during 06-05-1997. A positive relationship was observed between  $Zn_{lab}$  (% of  $Zn_{tot}$ ) and salinity, which can be characterised by  $R^2 = 0.76$ , slope = 1.99, intercept = 28.8 nM,  $n = 8$ , at the 98 % confidence interval. The positive relationship between  $Zn_{lab}$  (% of  $Zn_{tot}$ ) and salinity indicates that  $Zn_{org}$  complexes were preferentially removed from solution as the salinity increased. However, a small fraction of non-labile Zn remained at high salinities, which suggests that relatively stable dissolved Zn complexes existed throughout the estuary (minimum  $Zn_{org}$  (% of  $Zn_{tot}$ ) = 13.1 %).

#### Summer

$Zn_{tot}$  and  $Zn_{lab}$  were measured in samples collected during a tidal cycle and an axial transect survey in the Tamar estuary, these data have been plotted against salinity and presented in Figures 3.10 and 3.11.  $Zn_{tot}$  distributions and concentrations observed in samples collected from contrasting surveying styles resulted in comparable results with values decreasing to lower levels at high salinity ( $Zn_{tot}$  (mean) =  $24.2 \pm 21.5$  nM, salinity = 0 to 20 and  $Zn_{tot}$  (mean) =  $34.5 \pm 26.9$  nM, salinity = 0.60 to 22.05 for the axial transect and tidal cycle respectively). The mean concentration of  $Zn_{tot}$  in the estuary during 17-07-1997 ( $Zn_{tot} = 30.7 \pm 28.7$  nM) was lower than those observed during the winter ( $Zn_{tot} = 117 \pm 76.8$  nM), spring ( $Zn_{tot} = 136 \pm 161$  nM) and autumn ( $Zn_{tot} = 445 \pm 165$  nM) surveys. It is suggested that seasonally low river flow rates (17-07-1997 river flow velocity = 5.9 m<sup>3</sup>/s) may have resulted in minimal disturbances of benthic sediments and hence, Zn enriched interstitial waters would have contributed little to the  $Zn_{tot}$  concentration in the estuary. Furthermore, seasonally enhanced primary productivity could have lead to elevated rates of  $Zn_{tot}$  uptake by phytoplankton.

Samples collected from the axial transect show removal of  $Zn_{tot}$  in the low salinity ( $S = 0$  to  $\sim 3$ ) high turbidity ( $SPM = 200 \text{ mg/l}$ ), which was probably due to adsorption of Zn by surface sorption sites on SPM. Previous investigators have observed a mid estuarine  $Zn_{tot}$  maxima, which was accounted for by infusion of sediment interstitial waters (Ackroyd *et al.*, 1986; Morris *et al.*, 1986). However, a mid estuarine  $Zn_{tot}$  maxima was not observed during 17-07-1997, which could indicate that seasonally low summer river flow regimes could result in minimal sediment disturbance. Consequently, low volume of Zn enriched interstitial water entered the estuary during summer and could result in lower concentration of Zn in estuarine waters during the summer months. Furthermore, Zn could become further depleted during summer months owing to enhanced phytoplankton production and removal of dissolved Zn due to uptake of Zn and/or absorption onto algal surfaces.

The  $Zn_{lab}$  (% of  $Zn_{tot}$ ) was relatively low throughout the estuary during both the tidal cycle and axial transect survey and suggests that stable organic complexes of Zn were persistent throughout the estuary (mean  $Zn_{lab}$  (% of  $Zn_{tot}$ ) =  $17.1 \pm 13.0 \%$  and  $15.0 \pm 14.0 \%$  for the tidal cycle and axial transect respectively). The organic complexation of Zn can therefore, probably be explained by dissolved algal breakdown products and algal exudates. Interestingly, the  $Zn_{lab}$  (% of  $Zn_{tot}$ ) distribution with salinity differed in samples collected from axial transect compared with the tidal cycle. The results of  $Zn_{lab}$  (as % of  $Zn_{tot}$ ; Fig. 3.11) measurements conducted on samples collected from the tidal cycle exhibited a positive relationship with salinity ( $R^2 = 0.71$ , slope =  $-1.12$ , intercept =  $1.4 \%$ ,  $n = 9$  at the 98 % confidence interval), which indicates the removal of  $Zn_{org}$  with increasing salinity possibly due to flocculation of organic complexes comprising Zn (Pettersen *et al.*, 1997). In contrast samples collected during the axial transect indicate a high fraction of  $Zn_{org}$  ( $Zn_{org}$  (% of  $Zn_{tot}$ ) =  $85.0 \pm 14 \%$ ) throughout the estuary. The discrepancy between the tidal cycle and the axial transect distribution of  $Zn_{lab}$  could be due to the contrasting environmental conditions (e.g. variability in channel characteristics and variability in types of land use) encountered during axial transect survey.

## Autumn

Figure 3.10 shows the results of  $Zn_{tot}$  analysis of samples collected during an axial transect undertaken on 02-10-1996. The mean estuarine of  $Zn_{tot}$  for 02-10-1996 was  $445 \pm 165$  nM with high variability of between 715 nM at the low salinity ( $S = 2$ ) to 65.6 nM at high salinity ( $S = 34.5$ ). The mean estuarine value observed during 02-10-1996 ( $Zn_{tot} = 445 \pm 165$  nM) was more than twice that of the mean values for the winter ( $Zn_{tot} = 117 \pm 76.8$  nM), spring ( $Zn_{tot} = 136 \pm 161$  nM) and summer ( $Zn_{tot} = 30.7 \pm 165$  nM) surveys. The high values for  $Zn_{tot}$  observed during the 02-10-1996 survey could be due to seasonally enhanced river flow (River flow (October mean) =  $11.09 \text{ m}^3/\text{s}$ ) leading to deep reworking of anoxic sediment. The months preceding 02-10-1996 were characterised by a prolonged period of low river flow (River flow (July, August and September mean) =  $2.73 \text{ m}^3/\text{s}$ ), which could have lead to the deposition of large quantities of organic material following enhanced productivity. Mobilisation of anoxic sediments and interstitial waters during 02-10-1996 could have caused the dramatically enhanced  $Zn_{tot}$  values compared with winter, spring and summer.

The measurement of  $Zn_{lab}$  was not undertaken during the 02-10-1996 due to analytical interferences from dissolved organic material (possibly surfactants) in the samples.

## Overview of Zn distributions in the Tamar estuary

A mean estuarine concentration of  $Zn_{tot}$  based on the complete data series (mean  $Zn_{tot} = 161 \pm 179$  nM,  $n = 111$ ) was in agreement with previously reported values of  $Zn_{tot}$  in the Tamar estuary ( $[Zn_{tot} \sim 15 \text{ nM to } \sim 300 \text{ nM}]$  Ackroyd *et al.*, 1986;  $[Zn_{tot} \sim 45 \text{ nM to } \sim 180 \text{ nM}]$  van den Berg, 1991c;  $[Zn_{tot} \sim 40 \text{ to } \sim 170 \text{ nM}]$  Morris, 1986). An overview of the behaviour of  $Zn_{tot}$  is presented in Table 3.g. The overall data series shows that  $Zn_{tot}$  exhibits high inter-seasonal variability, however, the mechanisms responsible for the behaviour of  $Zn_{tot}$  in the Tamar estuary were in broad agreement with those identified by Ackroyd *et al.*, (1986), which are summarised below:

- 1 Zn depletion was observed in the low salinity ( $S = 0$  to  $\sim 3$ ) high turbidity region ( $SPM = 100$  to  $850$  mg/l). Adsorption of Zn onto the surface of SPM was probably responsible for removal of Zn. In addition, the removal of  $Zn_{org}$  complexes was observed with increasing salinity ( $S = 0$  to  $\sim 10$ ) and could have contributed to depletion of  $Zn_{tot}$  at low salinities possibly due to flocculation of dissolved organic material (Ackroyd *et al.*, 1986; Morris *et al.*, 1986; Davis, 1984).
- 2 Enrichment of  $Zn_{tot}$  was observed in the mid estuary ( $S = \sim 3$  to  $25$ ), which was accounted for by infusion of anoxic sediment interstitial waters, cation competition for surface adsorption sites on SPM and the complexation of Zn by chloride ( $S = \sim 5$  to  $\sim 15$ ) (Ackroyd *et al.*, 1986; Morris *et al.*, 1986; van den Berg, 1991c).
- 3 At high salinities ( $S = \sim 25$  to  $\sim 35$ ) and in the lower estuary Zn was characterised by relatively conservative mixing between enriched upper estuarine water with relatively Zn depleted seawater.

$Zn_{tot}$  exhibited lowest mean estuarine concentrations during the summer months and this suggests that low rates of rainfall, low river flow rates, minimal water column turbulence and also the removal of dissolved Zn as a result of enhanced algal productivity influenced the seasonal depletion of  $Zn_{tot}$ . In contrast, seasonal disturbances of anoxic sediments, following summer deposition of organic rich sediments may have lead to significantly enhanced Zn concentrations throughout the estuary during 02-10-1996.

The measurement of  $Zn_{lab}$  was not possible in the majority of the water samples collected as a result of interferences from dissolved organic material. Where it was possible to undertake  $Zn_{lab}$  measurements during 27-01-1997, 06-05-1997 and 17-07-1997 a positive relationship was observed between  $Zn_{lab}$  (% of  $Zn_{tot}$ ) and salinity, which suggests that the removal of organic complexes comprising Zn occurred in the low salinity zone. Previous researchers have shown that dissolved organic material, some capable of complexing dissolved metals, can flocculate from solution with increasing salinity (Pettersson *et al.*,

1997; Davis, 1984; Paulson *et al.*, 1994a, b), which could be an additional mechanism for Zn removal in the low salinity zone.

Table 3.g Simplified overview of seasonal variability in Zn behaviour and distributions in the Tamar estuary

| Season | Salinity interval<br>(S = 0 to ~3)        | Salinity interval<br>(S = ~3 to ~25)                                                               | Salinity interval<br>(S = 25 to 35)                                       | Mean<br>Zn<br>(nM) |
|--------|-------------------------------------------|----------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------|--------------------|
| Winter | Removal with elevated SPM concentrations. | Input owing to: infusion of interstitial waters; cation competition; and complexation by chloride. | Mixing of enriched low salinity waters with relatively depleted seawater. | 117 ± 76.8         |
| Spring | Removal with elevated SPM concentrations. | Input owing to: infusion of interstitial waters; cation competition; and complexation by chloride. | Mixing of enriched low salinity waters with relatively depleted seawater. | 136 ± 161          |
| Summer | Removal with elevated SPM concentrations. | Mixing of enriched low salinity waters with relatively depleted seawater.                          | Mixing of enriched low salinity waters with relatively depleted seawater. | 30.7 ± 28.7        |
| Autumn | Removal with elevated SPM concentrations. | Input owing to: infusion of interstitial waters; cation competition; and complexation by chloride. | Mixing of enriched low salinity waters with relatively depleted seawater. | 445 ± 165          |

### 3.3.6 Assessment of dissolved speciation and temporal variability of Cu

#### Winter

Total dissolved Cu ( $Cu_{tot}$ ) exhibited non conservative behaviour in the estuary with values generally decreasing from high values in the upper estuary to low concentrations (~70 nM

and  $\sim 20$  nM;  $S = \sim 0$  and  $\sim 35$ , respectively) in the lower estuary Figure 3.12. These data show that in winter,  $Cu_{tot}$  exhibited a low intra-seasonal variability (mean winter  $Cu_{tot} = 63.1 \pm 23.7$  nM).  $Cu_{tot}$  exhibited a negative relationship with salinity, which can be characterised by  $R^2 = 0.51$ , slope =  $-1.93$ , intercept =  $74.5$  nM,  $n = 38$ , at the 99 % confidence interval. The negative relationship indicates a relatively conservative mixing between  $Cu_{tot}$  enriched low salinity water with relatively depleted seawater. The intercept at  $S = 0$  based on the linear transformation of the winter data series was in agreement with the observed  $Cu_{tot}$  concentration at  $S = 0$  to  $1$  ( $Cu_{tot}$  estimated intercept ( $S = 0$ ) =  $74.5$  nM,  $Cu_{tot}$  observed ( $S = 0$  to  $1$ ) =  $75.5 \pm 18.3$  nM). Hence, the linear transformation of the data series gives a reasonable characterisation of the distribution of  $Cu_{tot}$  during winter in the freshwater end member. However, examination of the individual surveys suggest that  $Cu_{tot}$  exhibited removal in the low salinity ( $S = 0$  to  $\sim 5$ ) high turbidity zone (SPM =  $100$  to  $850$  mg/l) and enrichment in the mid estuary. Ackroyd *et al.*, (1986) observed a similar behaviour for  $Cu_{tot}$  in the Tamar estuary and suggested removal of Cu in the low salinity high turbidity zone was due to adsorption onto SPM surfaces and mid estuarine Cu maxima was caused by infusion of sediment interstitial waters.

During the 12-01-1998 tidal cycle, seasonally enhanced river flow velocities (river flow =  $66.6$  m<sup>3</sup>/s) resulted in a limited salinity gradient ( $S = 0$  to  $\sim 1.5$ ).  $Cu_{tot}$  values during 12-01-1998 exhibited high variability ( $74.3 \pm 20.2$  nM) despite the small salinity gradient, which suggests that  $Cu_{tot}$  concentrations were strongly influenced in the low salinity region.

Dissolved labile Cu ( $Cu_{lab}$ ) measurements were undertaken on samples collected during 27-01-1997 and 12-01-1998. These data have been plotted against salinity and presented in Figure 3.13. Tropolone was used for the determination of labile Cu ( $Cu_{lab}$ ), which is a relatively weak Cu complexing ligand ( $\log_{10} K_{Cu-Tropolone} \sim 12$ ; van den Berg and Nimmo, 1987; Donat and van den Berg, 1992). A low proportion of non-labile Cu ( $Cu_{org}$ ) was observed throughout the estuary (mean  $Cu_{org}$  (% of  $Cu_{tot}$ ) =  $10.0 \pm 8.2$  %). Cu forms

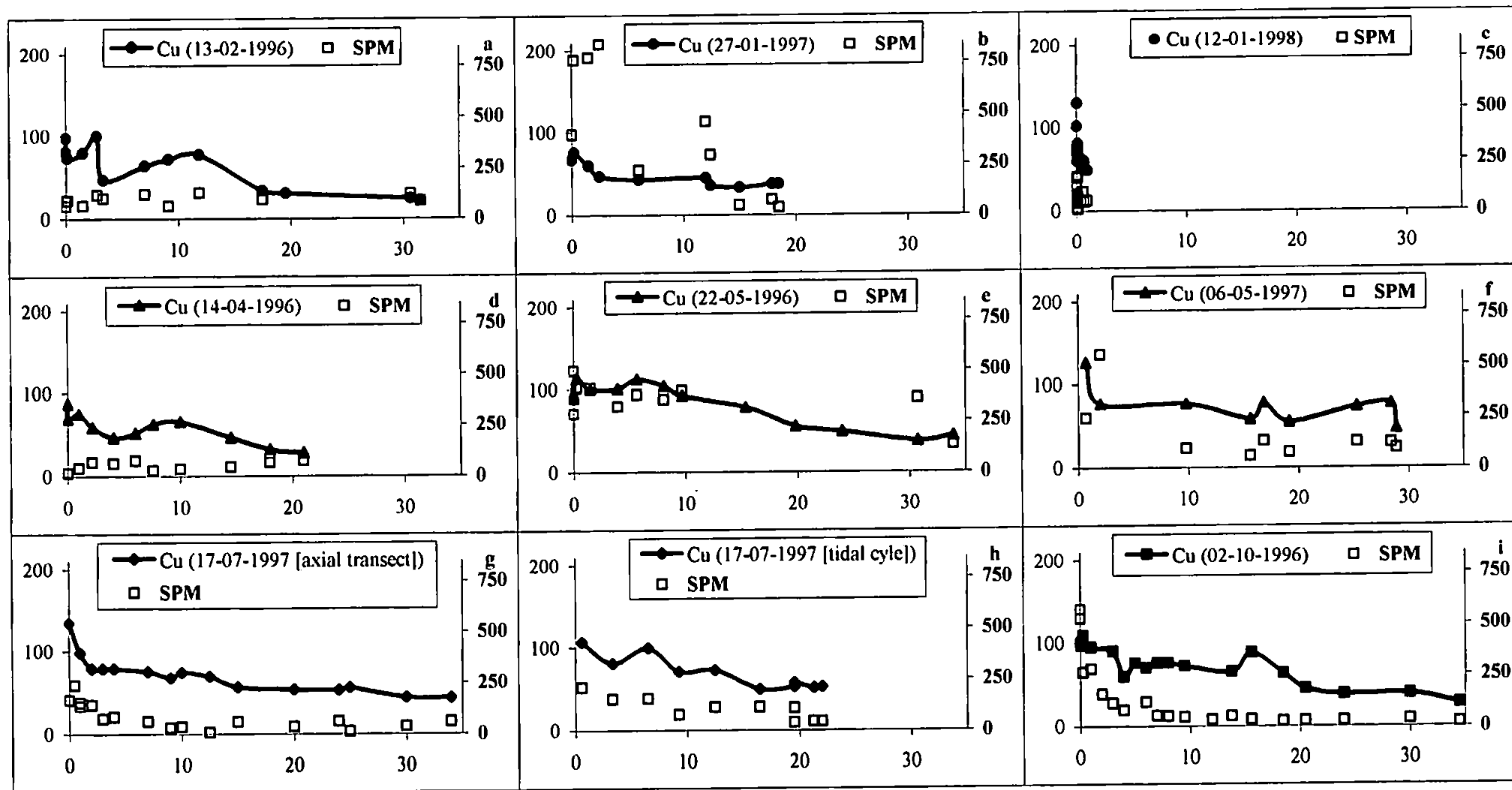


Figure 3.12 Distribution of total dissolved Cu (nM) and SPM (mg/l) against salinity during (a, b and c) winter, (d, e and f) spring, (g and h) summer and (i) autumn surveys of the Tamar estuary between 13-02-1996 and 27-01-1998.

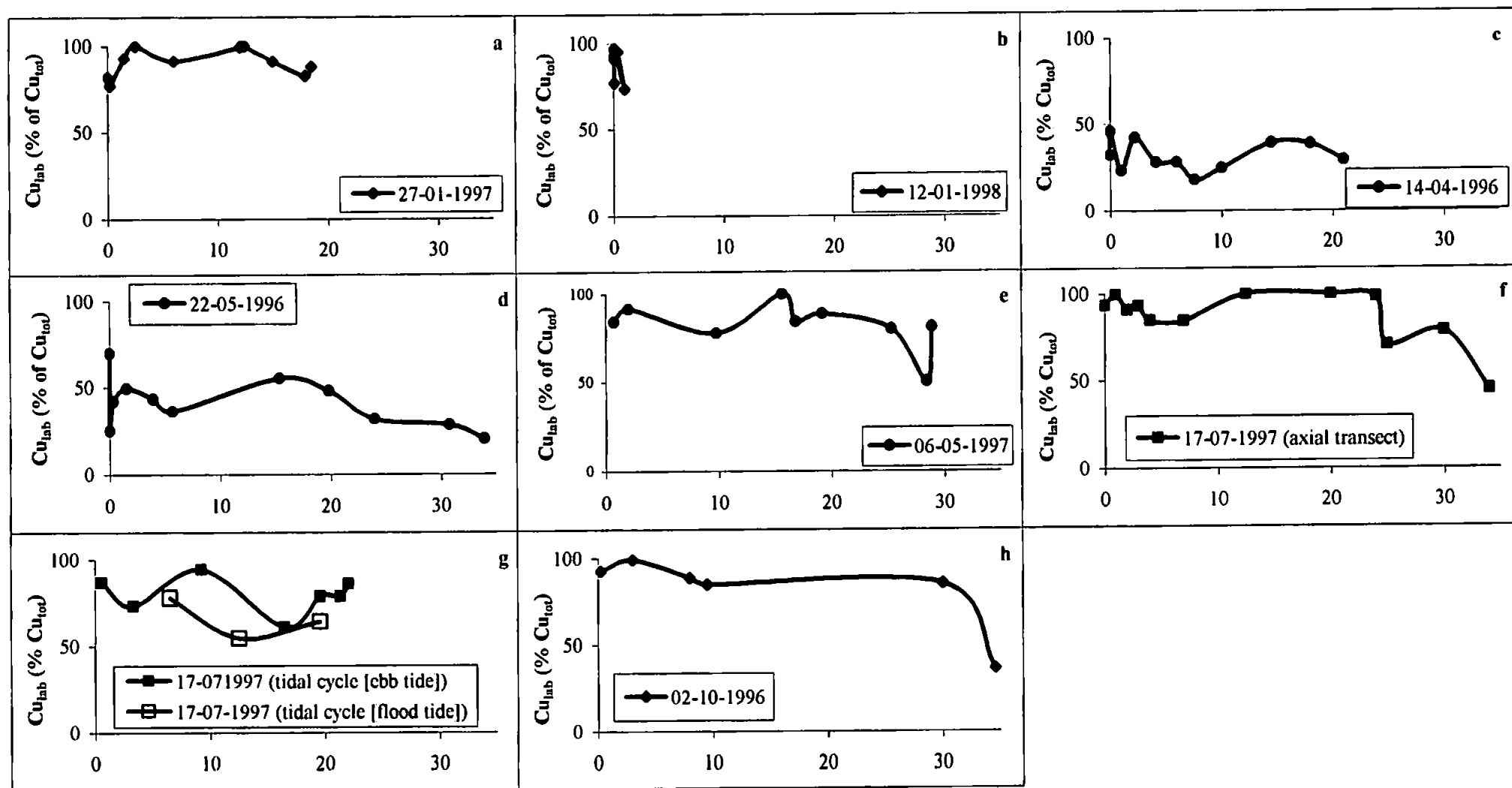


Figure 3.13 Distribution of labile dissolved Cu ( $Cu_{lab}$ ) during (a and b) winter, (c, d and e) spring, (f and g) summer, (h) autumn surveys of the Tamar estuary between February 1996 and January 1998.

relatively weak complexes with dissolved inorganic species, hence only organic complexes comprising Cu have would remained undetectable using the method adopted to determine  $Cu_{lab}$  and this indicates that a low proportion of relatively stable  $Cu_{org}$  complexes were observed throughout the estuary.

### Spring

$Cu_{tot}$  exhibited a low intra-seasonal variability ( $71.4 \pm 25.2$  nM) between the two axial transects (14-04-1996; 22-05-1996) and one tidal cycle survey (06-05-1997) undertaken during spring 1996 and 1997 (Fig. 3.12). Enhanced  $Cu_{tot}$  concentrations were observed in the upper estuary with values decreasing to lower levels in the lower estuary ( $Cu_{tot} = 90.0$  nM and 43.0 nM;  $S = 0$  and 33.93 respectively). Generally,  $Cu_{tot}$  exhibited a negative relationship with salinity during the three spring surveys, which can be characterised by  $R^2 = 0.37$ , slope = -1.47, intercept = 88.6 nM,  $n = 33$ , at the 95 % confidence interval. The negative relationship between  $Cu_{tot}$  and salinity for the spring surveys suggests that the dilution of  $Cu_{tot}$  enriched low salinity water with relatively Cu depleted seawater is an important feature of Cu distributions. However, the behaviour of  $Cu_{tot}$  can be described as non conservative owing to input and removal events observed in the upper and mid estuary. Removal of Cu was observed in the low salinity ( $S = \sim 0$  to  $\sim 5$ ) high turbidity (SPM =  $\sim 100$  to 500 mg/l) region, which could be explained by the adsorption of Cu onto surface sites of SPM. Indeed, for the 14-04-1996 survey a negative relationship was observed between  $Cu_{tot}$  and SPM that can be characterised by  $R^2 = 0.63$ , slope = -0.63, intercept = 86.1 nM,  $n = 10$ , at the 95 % confidence interval and indicates  $Cu_{tot}$  adsorption onto SPM. A statistically relevant correlation between  $Cu_{tot}$  and SPM was not observed during the other spring surveys, which could indicate that sorption properties of SPM exhibit seasonal variability (Morris *et al.*, 1986; Morris, 1986; Millward and Turner, 1995). Green colouration of the waters in the upper estuary and of the filtrate (visual observations) suggested the presence of a spring bloom during the 14-04-1996 survey, which may have

altered adsorption properties of SPM, thereby, increasing particle uptake of  $Cu_{tot}$ . Mid estuarine  $Cu_{tot}$  maximas at  $S = 10$  and  $S = 7$  were observed for 14-04-1996 and 22-05-1996 surveys respectively. Ackroyd *et al.*, (1986) suggested that mid estuarine maxima of Cu were caused by sediment disturbances leading to infusion of anoxic Cu enriched interstitial waters (Morris *et al.*, 1986; van den Berg, 1991c).

$Cu_{lab}$  exhibited high intra-seasonal variability with contrasting distributions and concentrations observed in each of the three surveys (Fig. 3.10). The  $Cu_{lab}$  (% of  $Cu_{tot}$ ) was high during 06-05-1997 compared with 14-04-1996 and 22-05-1996, which indicates that seasonally enhanced concentrations of dissolved organic Cu complexing ligands during spring 1996. Paulson *et al.*, (1994a, b) suggested a relationship between organic complexation of Cu and the release of organic exudes from biota. During the 14-04-1996 survey a green colouration was visually observed in waters collected from the upper estuary, which indicates enhanced levels of phytoplankton production and could account for the high fraction of  $Cu_{org}$ . Highest fractions of  $Cu_{org}$  were encountered at high salinity, which is consistent with previous studies of high salinity waters where up to 99 % of  $Cu_{tot}$  was found to be organically complexed (van den Berg *et al.*, 1990).

## Summer

The concentrations of  $Cu_{tot}$  were determined in samples collected during a tidal cycle and an axial transect on the same day (17-07-1997). These data showed that both sampling protocols revealed similar  $Cu_{tot}$  distributions.  $Cu_{tot}$  distributions for the combined 17-07-1997 data series (axial transect and tidal cycle) can be characterised by a negative relationship with salinity ( $R^2 = 0.72$ , slope = -1.91, intercept = 95.4 nM,  $n = 25$ , at the 99 % confidence interval), which indicates the dilution of Cu enriched upper estuarine water with seawater ( $Cu_{tot} = 135$  nM and 43.5 nM;  $S = 0$  and 34). Removal of  $Cu_{tot}$  was observed in the low salinity ( $S = \sim 3$ ) high turbidity (SPM =  $\sim 200$  mg/l) region, which was probably due to adsorption of Cu onto SPM. Cu enrichment ( $Cu_{tot} = 99.46$  nM) was observed in the

mid salinity region of the tidal cycle profile at  $S = 6.51$ . The relatively low river flow velocities and short tidal amplitude probably resulted in a minimal input of  $Cu_{tot}$  from sediment interstitial waters. Hence, enrichment of  $Cu_{tot}$  at  $S = 6.51$  was probably due to cation exchange of Cu at surface sites of SPM and perhaps the complexation of Cu by e.g. chloride and dissolved organic species (Zwolsman *et al.*, 1997; Paucot and Wollast, 1997; Ackroyd *et al.*, 1986).

The  $Cu_{lab}$  fraction of  $Cu_{tot}$  has been plotted against salinity in Figure 3.13. The tidal cycle data series has been split into two categories; the first represents the samples collected during the ebb tide and these data are compared with the axial transect data series, which was undertaken during the same state of the tide. The second axial transect data series represents samples collected during the flood tide. Samples from the axial transect were collected during the ebb tide and correspond with samples obtained during the tidal cycle (ebb tide data set) and  $Cu_{lab}$  concentrations compared well (mean  $Cu_{lab}$  (% of  $Cu_{tot}$ ) (ebb tide) = 80.0 %). However, the fraction of  $Cu_{lab}$  was significantly lower in samples collected during the flood tide (mean  $Cu_{lab}$  (% of  $Cu_{tot}$ ) (flood tide) = 65.6 %). The  $Cu_{lab}$  fraction of  $Cu_{tot}$  was lowest in samples collected from the lower estuary ( $Cu_{lab}$  (% of  $Cu_{tot}$ ) = 44.8 %;  $S = 34$ ), which indicates that a source of natural Cu complexing ligands could be the lower estuarine waters. Therefore, during the flood tide, when water is transported upstream due to tidal action, organic complexing ligands could have been transported into the mid estuary.

### Autumn

The distribution of  $Cu_{tot}$  has been plotted against salinity and presented in Figure 3.12. Highest concentrations of  $Cu_{tot}$  were observed in the upper estuary with values decreasing in the lower estuary ( $Cu_{tot} = 100$  nM and 27.7 nM;  $S = 0$  and 34.52 respectively). A negative relationship was observed between  $Cu_{tot}$  and salinity, which can be characterised by  $R^2 = 0.77$ , slope = -1.92, intercept = 92.9 nM,  $n = 18$ , at the 99 % confidence interval.

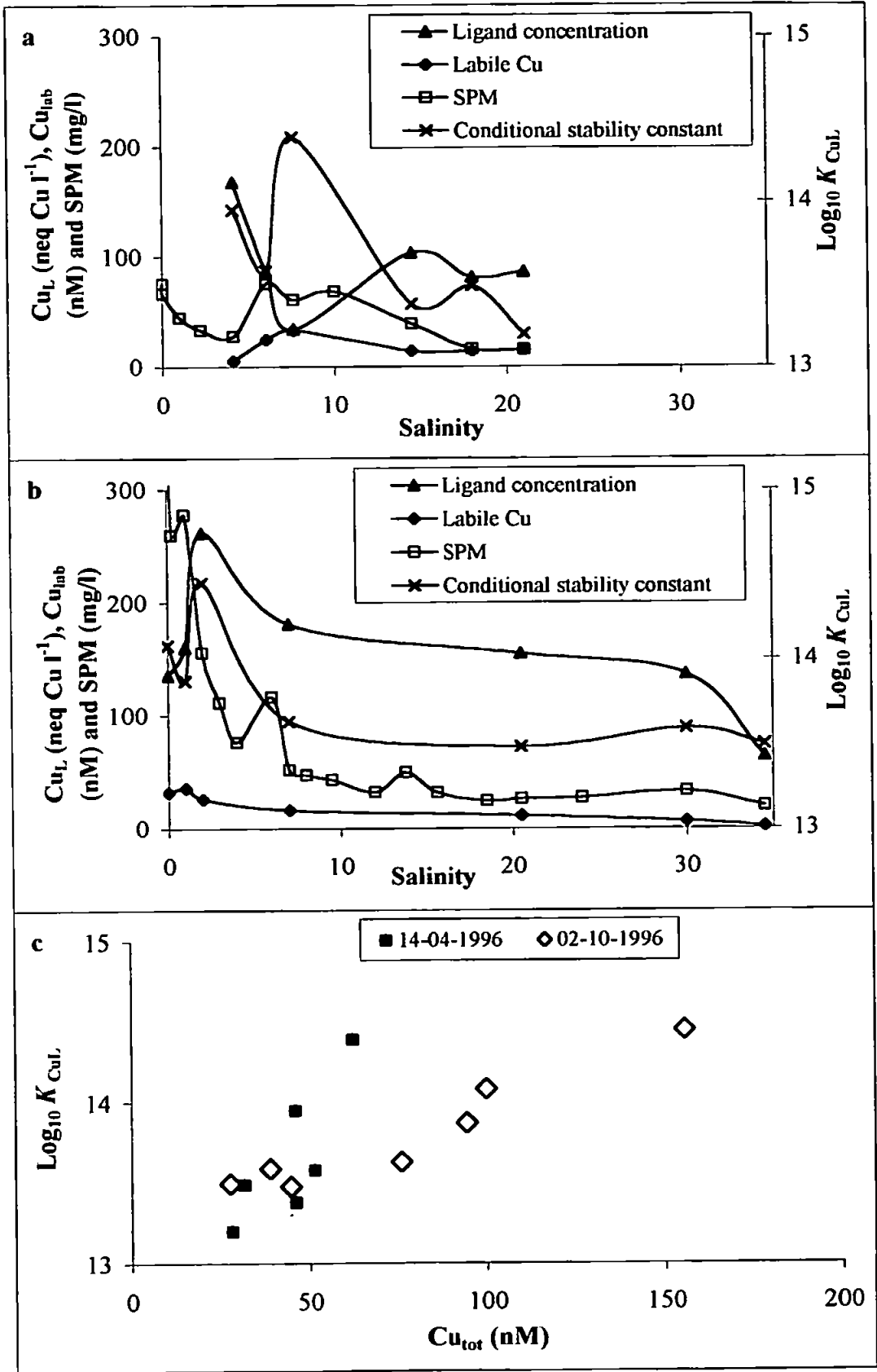
The linear relationship between  $Cu_{tot}$  and salinity indicates mixing behaviour between  $Cu_{tot}$  enrich upper estuarine water with relatively  $Cu_{tot}$  depleted seawater. The linear transformation of the  $Cu_{tot}$  over salinity data series was in good agreement with the observed data set at  $S = 0$  (intercept at  $S = 0$  (calculated) = 92.9 nM,  $Cu_{tot} = 100$  nM at  $S = 0$ ). However removal of  $Cu_{tot}$  can be observed in the low salinity ( $S = 0$  to  $\sim 5$ ) high turbidity zone ( $SPM = \sim 100$  to  $600$  mg/l), which indicates adsorption of Cu onto surface sites of SPM. In the mid estuary ( $S = 15.60$ ) Cu exhibited enrichment, which was probably related to infusion of Cu enriched sediment interstitial waters (Ackroyd *et al.*, 1986; Morris *et al.*, 1986).

Figure 3.13 shows the distribution of  $Cu_{lab}$  (% of  $Cu_{tot}$ ) plotted against salinity. These data show that the fraction of  $Cu_{lab}$  was high in the low salinity zone with lowest values observed at high salinity ( $Cu_{lab}$  (% of  $Cu_{tot}$ ) = 92.6 % and 36.2 %;  $S = 0.25$  and  $34.52$  respectively). In contrast the fraction of  $Cu_{lab}$  was high in the upper estuary, which suggests that low salinity waters contain a low concentration of organic complexing ligands capable of forming complexes with Cu during autumn.

#### Cu complexing natural ligands in the Tamar estuary

The concentration of Cu complexing natural ligands ( $Cu_L$ ) and their conditional stability constants ( $\log_{10} K_{Cu_L}$ ) have been plotted against salinity for 14-04-1996 and 02-10-1996 (Fig. 3.14).  $Cu_L$  concentrations in waters collected during 14-04-1996 exhibited high spatial and temporal variability (mean estuarine (14-04-1996)  $Cu_L = 93.2 \pm 43.2$  neq  $Cu\ l^{-1}$  and  $\log_{10} K_{Cu_L} = 13.67 \pm 0.40$ ). Across the region of enhanced SPM concentrations ( $S = \sim 8$ ), the  $Cu_L$  concentration fell to minimum values, which could indicate that organic complexes were removed from solution in the region of the turbidity maximum. In contrast, the concentration of  $Cu_{lab}$  (measured using SA) and  $\log_{10} K_{Cu_L}$  values were enhanced across the region of enhanced SPM concentrations. The 14-04-1996 survey was

Figure 3.14 Cu ligand ( $Cu_L$ ) concentrations, conditional stability constants ( $\text{Log}_{10} K_{CuL}$ ) and labile dissolved Cu ( $Cu_{lab}$ ) for the Tamar Estuary in samples collected during (a) 14-04-1996 and (b) 02-10-1996 and (c) the relationship between  $Cu_L$  ( $\text{Log}_{10} K$ ) and total dissolved Cu ( $Cu_{tot}$ ) concentrations.



undertaken during a period of enhanced phytoplankton activity (visual observations; green colouration of upper estuarine waters). The enhanced  $\text{Cu}_L$  concentration in the upper estuary may, therefore, have been due to the presence of Cu complexing exudates and algal breakdown products (Paulson *et al.*, 1994a, b; Achterberg *et al.*, 1997).

$\text{Cu}_L$  concentrations and  $\text{Log}_{10} K_{\text{Cu}_L}$  values exhibited non conservative behaviour during 02-10-1996 when high values were observed in the upper estuary ( $\text{Cu}_L = 135 \text{ neq Cu l}^{-1}$  and  $\text{Log}_{10} K_{\text{Cu}_L} = 14.08$ ;  $S = 0$ ).  $\text{Cu}_L$  concentrations and  $\text{Log}_{10} K_{\text{Cu}_L}$  values generally decreased to low levels in the lower estuary ( $\text{Cu}_L = 63.9 \text{ neq Cu l}^{-1}$  and  $\text{Log}_{10} K_{\text{Cu}_L} = 13.49$ ;  $S = 35.52$ ). Following a pronounced turbidity maximum ( $\text{SPM} = 569.64 \text{ mg/l}$ ;  $S \sim 1$ ) both  $\text{Cu}_L$  concentration and  $\text{Log}_{10} K_{\text{Cu}_L}$  exhibited elevated values, which could have been associated with desorption processes leading to the redistribution of  $\text{Cu}_L$  between the particulate and dissolved phase. In the mid and lower estuary  $\text{Cu}_L$  concentrations and  $\text{Log}_{10} K_{\text{Cu}_L}$  values were relatively constant with lowest values observed in the lower estuary. Interestingly, the highest concentrations of  $\text{Cu}_{\text{lab}}$  (determined using SA) were encountered in the upper estuary, which coincided with the high  $\text{Cu}_L$  concentrations and binding strengths. The mid and lower estuary comprised a group of relatively weak  $\text{Cu}_L$  at low concentrations that were stable throughout the estuary. In contrast, the upper estuary comprised a group of strong  $\text{Cu}_L$  at elevated concentrations that were environmentally unstable and were removed from the dissolved phase in the low salinity zone ( $S = 0$  to  $10$ ). A positive relationship between  $\text{Log}_{10} K_{\text{Cu}_L}$  and  $\text{Cu}_{\text{tot}}$  was observed, which can be characterised by an  $R^2 = 0.92$ , slope =  $0.01$ , intercept =  $13.21$ ,  $n = 7$ , at the 99% confidence interval (02-10-1996) and  $R^2 = 0.65$ , slope =  $0.03$ , intercept =  $12.44$ ,  $n = 6$ , at the 90 % confidence interval (14-04-1996). The positive relationship between  $\text{Log}_{10} K_{\text{Cu}_L}$  and  $\text{Cu}_{\text{tot}}$  could indicate that high concentrations of  $\text{Cu}_{\text{tot}}$  could have been sustained in the dissolved phase as a result of Cu complexation with strong dissolved ligands (Gerringa *et al.*, 1996; van den Berg *et al.*, 1987; Paulson *et al.*, 1994a, b; Chapter 2).

## Overview of Cu distributions in the Tamar estuary

A mean estuarine value for  $Cu_{tot}$  was  $68.4 \pm 23.7$  nM,  $n = 116$  with a concentration range of between  $\sim 20$  nM and 135 nM was in agreement of previously reported values of  $Cu_{tot}$  for the Tamar estuary ( $[Cu_{tot} = \sim 30$  nM to  $\sim 180$  nM] Ackroyd *et al.*, 1986;  $[Cu_{tot} = \sim 20$  nM to  $\sim 300$  nM] van den Berg *et al.*, 1990;  $[Cu_{lab} = \sim 10$  nM to  $\sim 60$  nM] van den Berg, 1991c;  $[Cu_{tot} = \sim 30$  nM to  $\sim 190$  nM] Morris *et al.*, 1986). Maximum values were observed in the low salinity region ( $Cu_{tot}$  mean =  $97.8 \pm 14.6$  nM;  $S = 0$  to 10;  $n = 32$ ) and compare well with previously reported concentrations of up to  $\sim 180$  nM at  $S = 0$  (Ackroyd *et al.*, 1986; van den Berg *et al.*, 1990; Morris *et al.*, 1986). These values are in excess of the Environmental Quality Standard (78.7 nM) for saline water quoted by the Environmental Agency, which indicates  $Cu_{tot}$  concentrations in the upper Tamar estuary are of environmental concern. Cu concentrations in the region of Plymouth Sound ( $Cu_{tot} = 34.0 \pm 10.4$  nM;  $S = 30$  to  $\sim 35$ ;  $n = 6$ ) were similar to those observed by Achterberg *et al.*, (1999) and Tappin *et al.*, (1993) in English coastal and estuarine zones ( $Cu_{tot} = \sim 25$  nM).

A simplified overview of the behaviour of Cu is presented in Table 3.h. A negative relationship was observed between  $Cu_{tot}$  and salinity, which was characterised by an  $R^2 = 0.42$ , slope = -1.52, intercept = 83.6 nM,  $n = 114$ , at the 99 % confidence interval (based on all measurements). Mixing of Cu enriched low salinity waters with Cu depleted high salinity water was an important factor for the distribution of Cu throughout the estuary. However, the behaviour of Cu in the Tamar estuary was characterised by non conservative mixing. Similar findings were reported by Ackroyd *et al.*, (1986), van den Berg, (1991c) and Morris *et al.*, (1986). Despite seasonal variability encountered during this investigation, three main features generally describe the behaviour of Cu in the Tamar estuary:

- 1 Removal of  $\text{Cu}_{\text{tot}}$  was observed in the low salinity ( $S = 0$  to  $\sim 5$ ) high turbidity region, which was accounted for by adsorption of Cu onto the surface of SPM particles.
- 2 In the mid estuary ( $S = \sim 5$  to  $\sim 15$ ) enrichment of  $\text{Cu}_{\text{tot}}$  was observed, which was probably due to disturbance of anoxic interstitial waters, cation competition for surface adsorption sites on SPM and complexation of Cu by chloride.
- 3 In the salinity interval  $\sim 15$  to  $\sim 35$ ,  $\text{Cu}_{\text{tot}}$  exhibited a relatively conservative mixing behaviour between Cu enriched upper estuarine water and relatively Cu depleted seawater.

The  $\text{Cu}_{\text{lab}}$  fraction of  $\text{Cu}_{\text{tot}}$  was rather constant throughout the surveys with the notable exception of 14-04-1996 and 22-05-1996, when elevated concentrations of  $\text{Cu}_{\text{org}}$  were encountered. The increased fraction of  $\text{Cu}_{\text{org}}$  was accounted for by an increase in the activity of phytoplankton. Other workers have also reported that dissolved algal organic exudates are responsible for the complexation of dissolved Cu (Patterson *et al.*, 1997). A negative relationship was observed between  $\text{Cu}_{\text{lab}}$  and salinity, which was characterised by  $R^2 = 0.26$ , slope =  $-1.50$ , intercept =  $70.0 \text{ nM}$ ,  $n = 88$ , at the 98 % confidence interval. The negative relationship between  $\text{Cu}_{\text{lab}}$  and salinity could be explained by the mixing of Cu enriched low salinity water with depleted seawater, which compares well to previous observations of Cu in coastal waters that indicated that Cu was predominantly organically complexed (van den Berg, 1984c; Campos *et al.*, 1994).

The determination of  $\text{Cu}_L$  concentration and  $\text{Log}_{10} K_{\text{Cu}_L}$  values in waters collected during 14-04-1996 and 02-10-1996 indicated that low salinity waters contained different groups of ligands compared with high salinity waters. It was suggested that whilst  $\text{Cu}_L$  concentrations and  $\text{Log}_{10} K_{\text{Cu}_L}$  were lower in high salinity waters, the groups of  $\text{Cu}_L$  in seawaters were more stable than those in low salinity waters ( $S = 0$  to  $10$ ). Furthermore, positive relationships were observed between  $\text{Log}_{10} K_{\text{Cu}_L}$  and  $\text{Cu}_{\text{tot}}$ , which could indicate

that high concentrations of Cu<sub>tot</sub> might have been related to complexation by dissolved organic ligands.

Table 3.h Simplified overview of seasonal variability in Cu behaviour and distributions in the Tamar estuary

| Season | Salinity interval<br>(S = 0 to ~5)             | Salinity interval<br>(S = ~5 to ~15)                                                   | Salinity interval<br>(S = ~15 to ~35)     | Mean<br>Cu (nM) |
|--------|------------------------------------------------|----------------------------------------------------------------------------------------|-------------------------------------------|-----------------|
| Winter | Characterised by adsorption onto SPM surfaces. | Input largely owing to increase in major ion concentrations and sediment disturbances. | Relatively conservative mixing behaviour. | 63.1 ± 23.7     |
| Spring | Characterised by adsorption onto SPM surfaces. | Input largely owing to increase in major ion concentrations and sediment disturbances. | Relatively conservative mixing behaviour. | 71.4 ± 25.2     |
| Summer | Characterised by adsorption onto SPM surfaces. | Input largely owing to increase in major ion concentrations and sediment disturbances. | Relatively conservative mixing behaviour. | 70.3 ± 22.0     |
| Autumn | Characterised by adsorption onto SPM surfaces. | Input largely owing to increase in major ion concentrations and sediment disturbances. | Relatively conservative mixing behaviour. | 71.5 ± 23.3     |

3.3.7 Trace metal behaviour and variability between four estuarine systems

An overview of dissolved trace metal behaviour and concentration ranges in four estuaries has been presented in Table 3.i. Cu exhibited comparable concentrations for the Tamar

estuary, Scheldt estuary (Paucot and Wollast, 1997; Zwolsman *et al.*, 1997) and San Francisco Bay (Sanudo-Wilhelmy *et al.*, 1996). Low seasonal variability and non conservative behaviour was observed for Cu in the Tamar estuary (This study; Ackroyd *et al.*, 1986; van den Berg, 1991c). In contrast, due to seasonal factors causing anoxia in the Scheldt estuary, Cu exhibited high seasonal variability in this system (Zwolsman and Van Eck, 1993; Zwolsman *et al.*, 1997).

The range in Ni concentrations was similar for each of the estuaries presented in Table 3.i. However, the behaviour of Ni contrasted between estuarine systems. In the Tamar and Scheldt estuaries, low inter-seasonal variability and relatively conservative behaviour was observed in between the mid to lower estuary ( $S = \sim 20$  to  $\sim 35$ ). In contrast, high seasonal variability was encountered in the Forth estuary with Ni exhibiting relatively conservative behaviour during winter months and mid estuarine enrichment during summer (Laslett and Balls, 1995).

Co concentrations were comparable between the Scheldt and Tamar estuaries (Table 3.h). In the Scheldt estuary (Paucot and Wollast, 1997), Co exhibited relatively conservative behaviour, which compares with high inter-seasonal variability and low intra seasonal variation in concentrations for the Tamar estuary.

The concentration of Zn was similar in each of the estuarine systems reported in Table 3.i. High inter-seasonal variability was observed for Zn in the Tamar, Scheldt and Forth estuaries (Zwolsman *et al.*, 1997; Laslett and Balls, 1995). Non conservative behaviour was observed for Zn the upper and mid estuarine zones ( $S = 0$  to  $\sim 25$ ) and Zn was characterised by high spatial and temporal variability. Mechanisms invoked to explain the non conservative behaviour for Zn were the redistribution of this element between particulate and dissolved phase, Zn influxes from sediment pore waters and desorption of particulate Zn as a result of the increasing concentration of major ions in the mid estuary (Morris *et al.*, 1986; Ackroyd *et al.*, 1986; van den Berg, 1991c; Zwolsman *et al.*, 1997). In contrast, relatively conservative Zn behaviour was observed at mid and high salinities ( $S =$

Table 3.i Comparisons of trace metal concentrations and behaviour in four estuaries.

| Element | Tamar <sup>a,b,c</sup>                                                                                                                                        | Scheldt <sup>d,e,f</sup>                                                               | Forth <sup>e</sup>                                                                                   | San Francisco Bay <sup>h</sup>              |
|---------|---------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|---------------------------------------------|
| Cu (nM) | 20 to 300; Low seasonal variability. Removal in low salinity high turbidity zone and mid estuarine maxima.                                                    | 10 to 150; High seasonal variability with mid estuarine input.                         |                                                                                                      | 5 to 40; Relatively conservative behaviour. |
| Ni (nM) | 8 to 110; Low seasonal variability. High variability in low salinity zone. Relatively conservative behaviour in mid to lower estuary.                         | 10 to 100; Relatively conservative behaviour. Low seasonal variability.                | 5 to 30; High seasonal variability. Conservative in winter mid estuarine enrichment during summer.   | 7 to 40; Mid estuarine enrichment.          |
| Co (nM) | 1 to 20; High seasonal variability and strong spatial variability in upper estuary.                                                                           | 1 to 20; Relatively conservative behaviour. High spatial variability in upper estuary. |                                                                                                      |                                             |
| Zn (nM) | 3 to 700; High seasonal variability and strong spatial variability in the upper estuary. Removal in low salinity high turbidity zone and mid estuarine input. | 50 to 250; High seasonal variability with mid estuarine input.                         | 10 to 100; High seasonal variability. Conservative in winter mid estuarine enrichment during summer. | 8 to 20; Relatively conservative behaviour. |

<sup>a</sup>This study, <sup>b</sup>Morris *et al.*, 1986, <sup>c</sup>Ackroyd *et al.*, 1986, <sup>d</sup>This study (Chapter 6), <sup>e</sup>Paucot and Wollast, 1997, <sup>f</sup>Zwolsman *et al.*, 1997, <sup>g</sup>Laslett and Balls, 1995 and <sup>h</sup>Sanudo-Wilhelmy *et al.*, 1996

~10 to ~35) in San Francisco Bay (Sanudo-Wilhelmy *et al.*, 1996). Furthermore, summer anoxic events have lead to mid estuarine enrichment of Zn as a result of circulation of anoxic waters and the infusion of sediment interstitial waters in the Scheldt and Forth estuaries (Zwolsman *et al.*, 1997; Laslett and Balls, 1995).

### 3.4 Conclusions

Mean estuarine values for Ni ( $\text{Ni}_{\text{tot}} = 44.6 \pm 19.4 \text{ nM}$ ;  $n = 124$ ), Zn ( $\text{Zn}_{\text{tot}} = 161 \pm 179 \text{ nM}$ ;  $n = 111$ ) and Cu ( $\text{Cu}_{\text{tot}} = 68.4 \pm 23.7 \text{ nM}$ ;  $n = 114$ ) were in agreement with previously reported concentrations for the Tamar estuary (Ackroyd *et al.*, 1986; Morris *et al.*, 1986; Morris, 1986; van den Berg *et al.*, 1991c; Newton and van den Berg, 1987; van den Berg *et al.*, 1990). Levels of  $\text{Co}_{\text{tot}}$  ( $\text{Co}_{\text{tot}}$  (mean estuarine value) =  $7.3 \pm 4.1 \text{ nM}$ ;  $n = 120$ ) have not been previously reported for the Tamar estuary. However, minimum values ( $\text{Co}_{\text{tot}} = \sim 1 \text{ nM}$ ) observed in the lower estuary were comparable to previously reported values in estuarine plume waters around the English coast (Acherberg *et al.*, 1999; Tappin *et al.*, 1995).

Cu and Ni exhibited low inter seasonal variability (RSD = 6 % and 14 % respectively) compared with  $\text{Co}_{\text{tot}}$  and  $\text{Zn}_{\text{tot}}$  (RSD = 45 % and 105 % respectively) (Table 3.j). Co and Zn depletion was observed during summer (17-07-1997), that could indicate uptake of Zn and Co, by phytoplankton during seasonally enhanced rates of primary production.

Despite differences in Co, Ni, Zn and Cu concentrations and temporal variability their behaviour was similar and can be characterised by three persistent features that are summarised below and in Table 3.k.

1. The removal of Co, Ni, Cu and Zn was observed in the low salinity ( $S = 0$  to  $5$ ), high turbidity region ( $\text{SPM} = 100$  to  $850 \text{ mg/l}$ ), which was due to adsorption of metals onto the surface of particulate material. In addition, removal of organically

Table 3.j Comparison of seasonal variability in dissolved Co, Ni, Zn and Cu concentrations in the Tamar estuary (13-02-1996 to 12-01-1998).

|                                          | Co (nM)              | Ni (nM)               | Zn (nM)               | Cu (nM)                |
|------------------------------------------|----------------------|-----------------------|-----------------------|------------------------|
| Winter <sup>a</sup>                      | 7.0 ± 3.4<br>n = 36  | 39.1 ± 21.6<br>n = 37 | 116 ± 76.8<br>n = 38  | 63.1 ± 23.7<br>n = 38  |
| Spring <sup>b</sup>                      | 8.3 ± 4.3<br>n = 40  | 50.1 ± 21.4<br>n = 40 | 109 ± 161<br>n = 31   | 71.4 ± 25.2<br>n = 33  |
| Summer <sup>c</sup>                      | 3.1 ± 1.2<br>n = 26  | 39.3 ± 11.0<br>n = 27 | 30.7 ± 28.7<br>n = 23 | 70.29 ± 22.0<br>n = 25 |
| Autumn <sup>d</sup>                      | 11.1 ± 1.7<br>n = 18 | 50.0 ± 18.0<br>n = 19 | 445 ± 165<br>n = 19   | 71.5 ± 23.3<br>n = 18  |
| <b>RSD (%)</b><br><b>(a, b, c and d)</b> | <b>44.7</b>          | <b>14</b>             | <b>105</b>            | <b>6</b>               |

Table 3.k Overview of the general behaviour of dissolved Co, Ni, Zn and Cu in the Tamar estuary.

| Behaviour      | Removal                                                      | Input                                                                | Relatively conservative                                                  |
|----------------|--------------------------------------------------------------|----------------------------------------------------------------------|--------------------------------------------------------------------------|
| Mechanism      | Adsorption onto the surface of SPM                           | Infusion of interstitial waters and desorption                       | Dilution with depleted seawater                                          |
| Salinity range | Co = 0 to ~5<br>Ni = 0 to ~7<br>Zn = 0 to ~3<br>Cu = 0 to ~5 | Co = ~3 to ~25<br>Ni = ~3 to ~15<br>Zn = ~3 to ~25<br>Cu = ~5 to ~15 | Co = ~25 to ~35<br>Ni = ~15 to ~35<br>Zn = ~25 to ~35<br>Cu = ~15 to ~35 |

complexed metals (especially Zn) was observed at low salinities ( $S = 0$  to  $\sim 10$ ), which indicates that the flocculation of organic material could be a secondary mechanism causing metal depletion at low salinity.

- 2 Enrichment of Co, Ni, Cu and Zn was observed in the mid estuary ( $S = 5$  to  $25$ ) and was accounted for by infusion of interstitial waters and desorption of metals as a result of a re-distribution of metals between the particulate and dissolved phases caused by increases in major ion concentrations.
- 3 Co, Ni, Zn and Cu exhibited relatively conservative mixing behaviour in the lower estuary ( $S = \sim 25$  to  $\sim 35$ ) with metal concentrations falling to low concentrations near typical for coastal seawaters (Tappin *et al.*, 1993; Achterberg *et al.*, 1999).

Similarly, Ackroyd *et al.*, (1986) observed depletion of Zn and Cu in the low salinity high turbidity zone, followed by a mid estuarine maxima enrichment of Cu and Zn during surveys carried out in the Tamar estuary between 1976 and 1985.

The chemical speciation measurements of Co was possible in samples collected from two surveys, and indicated that Co was predominantly present in the labile form. Labile measurements indicated that waters collected in Plymouth Sound generally contained the highest fractions of organically complexed Co, Ni and Cu. In contrast, in the upper estuary organically complexed Zn was removed from solution with increasing salinity and a small fraction of relatively stable organic Zn complexes were persistent throughout the estuary. Davis, (1984) and Paulson *et al.*, (1994a, b) reported that dissolved organic compounds (e.g. humic substances and fulvic acids), which can form complexes with dissolved metals, can flocculate in the low salinity zone as a result of an increasing ionic strength. Hence, it is suggested that an additional mechanism for the depletion of Zn in the low salinity zone could be the flocculation of organically complexed Zn.

Measurements of Cu natural ligand conditional stability constants and natural ligand concentrations were undertaken in waters collected during two surveys. These data

indicated that high concentrations of Cu complexing ligands and high Cu ligand conditional stability constants were observed in low salinity waters ( $S = 0$  to  $5$ ). Furthermore, the strong Cu complexing ligands were removed from solution in the low salinity zone. Previous investigations of Cu ligands in estuarine waters indicated organically complexed Cu complexes were removed from solution in the low salinity zone as a result of flocculation of dissolved organic compounds (Pettersson *et al.*, 1997; Gerringa *et al.*, 1996; Paulson *et al.*, 1994a, b). A positive relationship was observed between the strength of Cu complexing ligands ( $\text{Log}_{10} K_{\text{Cu}_L}$ ) and total dissolved Cu concentration, which could indicate that strong complexing ligands could help to buffer Cu concentrations in the dissolved phase. By comparing trace metal concentrations and distributions in other estuaries it was evident that trace metal behaviour is often specific to individual estuarine systems.

### 3.5 Future work

Plymouth University has recently become a centre of excellence for marine chemists that encompasses a wide range of expertise, which includes trace metal, trace nutrient, trace organic speciation and physical oceanographic studies. Ideally, future work could include multidisciplinary collaborative studies that would generate more through investigations of estuarine studies, which have only recently been possible. Future investigations could include further studies of Cu natural ligand titrations studies in order to elucidate the long term distribution and behaviour of Cu in the Tamar estuary. The continuation of regular monitoring of Zn, Cu, Ni and Co concentrations in the Tamar would help create a data base for these elements and would aid in the development of reliable trace metal distribution models.

## **4. Behaviour and chemical speciation of Ni, Co, Cu and Zn in the Scheldt Estuary (Belgium)**

### **4.1 Introduction**

Total dissolved trace metal and trace metal speciation measurements were undertaken for Co, Ni, Zn and Cu in water samples collected during an axial transect of the Scheldt Estuary (Belgium). In contrast to the partly mixed nature of the Tamar (Chapter 3), the Scheldt is characterised by well mixed waters draining a heavily industrialised region of Western Europe (Fig. 4.1) (Zwolsman and Van Eck, 1993; Wollast and Peters, 1978). As a result of anthropogenic inputs of organic matter and nutrients from untreated sewage outfalls, the Scheldt exhibits seasonally anoxic conditions, which can have a profound effect on dissolved and particulate trace metal partitioning (Wollast, 1988). For example, the activity of sulphate reducing bacteria in the anoxic part of the Scheldt, can cause enhanced sulphide concentrations in anoxic waters. Removal of dissolved Zn and Cu in the form of insoluble metal sulphides can result in the depletion of these elements in the water column of the upper estuary. Re-oxygenation of the estuarine waters may then result in dissolution of Cu and Zn sulphides leading to enhanced concentrations of dissolved Cu and Zn in mid and lower estuarine waters during these events (Zwolsman *et al.*, 1997; Paucot and Wollast 1997; Regnier *et al.*, 1996; Baeyens *et al.*, 1998). Furthermore, the dissolved/particulate partitioning of Ni and Co has been linked to the behaviour of Mn owing to co-precipitation of Ni and Co with flocculation of Mn oxy/hydroxides (Laslet and Balls, 1995; Knauer *et al.*, 1982). Mn is a redox sensitive element, which is present as the aqueous Mn(II) form in anoxic waters and can precipitate in oxic waters becoming oxidised to Mn(IV), in the form of particulate Mn(IV) oxy-hydroxides. Hence, where



anoxic waters are present in the Upper Scheldt Estuary particulate Mn can become depleted as a result of the reduction of particulate Mn(IV) to aqueous Mn(II). Conversely, Mn(II) can become oxidised to particulate Mn(IV) to form a particulate Mn maxima in the mid estuary as a result of the mixing of anoxic low salinity water with oxygen enriched seawater (Kersten and Fostner, 1986; Leinemann *et al.*, 1997).

#### 4.1.1 Study area

The Scheldt river is located in the North of France, west of Belgium and Southwest of the Netherlands (Fig. 4.1). Its hydrographic basin represents a surface of 20,331 km<sup>2</sup> covering one of the most populated and industrialised areas of Europe. This river is highly polluted (Paucot and Wollast, 1997; Baeyens, 1998) often receiving untreated industrial and domestic waste waters with high concentrations of organic and inorganic compounds.

The Scheldt estuary is characterised by a mean river discharge of 116 m<sup>3</sup>/s (based on a mean value for the years 1991 to 1994) but with important seasonal fluctuations (e.g. from 28 to 700 m<sup>3</sup>/s in 1993). The estuary is subject to a large tidal influence, with a maximum amplitude of 4.5 m at its mouth (Wollast and Peters, 1978). The salinity intrusion extends more than 110 km upstream and the variations in tide level can still be observed at Gent, 150 km from the mouth. As shown by Regnier *et al.*, (1996) the residual movements of water are, however, small and this explains the relatively long residence time of the freshwater in the estuary, which is of the order of one to three months under normal river discharge conditions (~120 m<sup>3</sup>/s). Freshwater and seawater are well mixed in the lower estuary and partially mixed more upstream. The vertical salinity gradient is small but sufficient to affect the circulation of water and particles owing to the development of a pycnocline (Wollast, 1982; Wollast, 1988).

The majority of particulate matter, organic or inorganic, transported by rivers (globally) is negatively charged and the increase of the ionic strength during mixing of freshwater and

seawater neutralises the surface charges by adsorption of cations (i.e.  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) (Stumm and Morgan, 1981; Stumm and Morgan, 1996). The consequence is that the particles, often colloidal, flocculate in the low salinity region ( $S = 1$  to  $5$ ) and thus are allowed to settle (Wollast and Peters, 1980). Furthermore, a region of zero net current near the bottom is found at 60 to 80 km from the mouth, in Antwerp harbour (Wollast and Peters, 1978). These two phenomena combine to generate a maximum of suspended matter deposition in the upper part of the estuary where intensive shoaling occurs.

Moreover, anthropogenic activities have altered the particulate load transported by the Scheldt. It has been estimated that at least two thirds of the suspended load is directly related to human activities (Wollast, 1988). Indeed, deposited suspended material can be easily identified by their high organic carbon content (due to domestic and agricultural discharges) and their exceptionally high concentrations of trace elements (consequence of the industrial discharges) (Paucot and Wollast, 1997).

This chapter will report on the results of analysis of dissolved Co, Ni, Zn and Cu obtained from a single survey in the Scheldt estuary. As a result of the profound influence of the oxygen gradient on the dissolved/particulate partitioning of Co, Ni, Zn and Cu, as reported previously for the Scheldt (Paucot and Wollast, 1997; Regnier and Wollast, 1993; Zwolsman *et al.*, 1996; Zwolsman *et al.*, 1997), the analysis of particulate Ni, Cu, Zn and Mn was undertaken on SPM collected during the axial transect survey. A particulate trace metal extraction procedure utilising 0.05 M EDTA and  $\text{HF}/\text{HNO}_3$  (Chapter 1 and 2) was used to assess the easily exchangeable and total particulate concentration of Mn, Ni, Cu and Zn. The advantages of the use of EDTA as a SPM particulate trace metal extraction protocol and analytical methodology and characterisation have been previously discussed in Chapter 2 (Whitworth *et al.*, 1999). The aims of the axial transect survey undertaken on the Scheldt estuary were:

1. Investigate the distribution of dissolved Co, Ni, Zn and Cu in the Scheldt during December 1996,
2. Assess the partitioning of Ni, Zn and Cu between the dissolved and particulate phases,
3. Investigate the dissolved complexation of Cu by naturally organic ligands in the Scheldt Estuary.

## 4.2 Methodologies

### 4.2.1 Collection and storage of water and SPM samples

Sub surface (~3 m) water and SPM samples were collected from 15 locations during a longitudinal transect of the Scheldt Estuary (Belgium) between 9-12-1996 and 14-12-1996 from the research vessel, *Belgica*. Samples were collected using a 10 l Niskin sampling bottle fitted with a PTFE liner. To prevent sample contamination the Niskin bottle was soaked in 5 M HCl (1 week) and 2 M HNO<sub>3</sub> (1 week) then thoroughly rinsed with Milli-Q water prior to sampling. Sub sample aliquots were collected from the Niskin bottle after three rinses with the sample, in thoroughly acid washed HDPE bottles (3 x 500 ml, 1 x 250 ml, Chapter 2). The bottles were completely filled then sealed and placed inside re-sealable polythene bags. One bottle containing 250 ml of sample was placed directly into the ship's freezer (-20 °C) and three 500 ml sample bottles were transferred into a class 100 laminar flow unit in the on board laboratory. Two 500 ml water samples were then vacuum filtered through 0.45 µm, acid washed, cellulose nitrate membrane filters (Chapter 2). Subsequently, one was acidified to pH ~2 (using 1 µl sub boiled HCl per 1 ml of sample) and was later (within 1 month at Plymouth University) analysed for total dissolved Co, Ni, Cu, Zn and the other was frozen (-20 °C) for later (~1.5 year at Plymouth University) Cu natural complexing ligand experiments. The samples were later (at Plymouth University) analysed for dissolved Cu complexing natural ligands, dissolved AdCSV labile

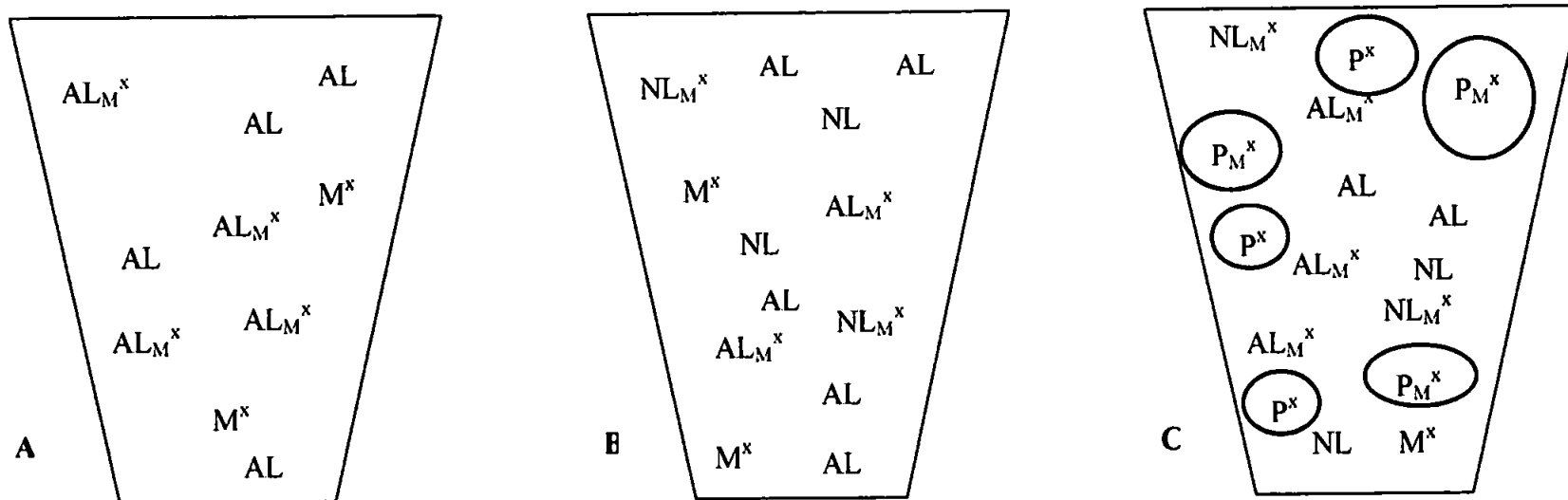
(filtered and unfiltered) and total Cu, Zn, Co and Ni. The remaining 500 ml of sample was analysed on board ship for dissolved non filtered labile Zn, Cu, Ni and Co. Once analysis had been completed the remaining ~250 ml of sample was then filtered and the filtrate was subsequently analysed for dissolved labile Zn, Cu, Ni and Co. Between analysis the samples were stored at 4 °C.

Water samples were collected using 10 l Niskin samplers deployed at ~3 m depth. After 3 rinses with Scheldt water, a sample of 2.5 l was collected in an acid washed HDPE container. In the ship's laboratory, the water samples were filtered using a polysulfone vacuum filtration unit (Nalgene) fitted with acid washed (1 % v:v HCl), pre-weighed membrane filters (47 mm diameter, 0.45 µm porosity, cellulose nitrate, Whatman). Seawater salts were rinsed from the filters containing SPM by washing with 50 ml of Milli-Q water. The filters were then dried at 45 °C for 24 h and frozen at -17 °C for transport to the laboratory in Plymouth. In the laboratory, the filters were kept for a further 24 h at 45 °C and subsequently re-weighed on a precision balance (Sartorius). The weight of SPM on the filters was calculated as the difference between the weight of the filter containing SPM and the original filter (Chapter 2).

#### *4.2.2 Analysis of dissolved and particulate Zn, Cu, Ni, Co and Mn*

Three categories of Zn, Cu, Ni and Co measurements were undertaken on each of the water samples and the nature of the metal measurements requires consideration (Fig. 4.2). (1) The total dissolved metal measurements refer to the analysis of filtered and acidified (pH 2 using 1 µl sub-boiled distilled HCl per 1 ml sample) water that had been exposed to UV light for 4 hours after the addition H<sub>2</sub>O<sub>2</sub> (2 µl H<sub>2</sub>O<sub>2</sub> per 1 ml sample) in order to destroy any dissolved organic compounds (Chapter 2). Sample filtration and acidification was undertaken in situ (within 6 hours of sample collection) in a class 100 laminar flow cabinet

Figure 4.2 Schematic representation of the species present in typical water samples during AdCSV analysis of (A) total dissolved, (B) filtered labile, and (C) non filtered labile metals.  $AL_M^x$  indicates the AdCSV detectable fraction.



(A)  $[TM^x] = \Sigma[AL_M^x] + [M^x]$

(B)  $[TM^x] = \Sigma[AL_M^x] + [M^x] + [NL_M^x]$

(C)  $[TM^x] = \Sigma[AL_M^x] + [M^x] + [NL_M^x] + [P_M^x]$

Where,  $M^x$  = Free metal ions,  $AL$  = Free AdCSV added ligand,  $NL$  = Free naturally occurring ligand,  $TM^x$  = Total potentially detectable metals,  $NL_M^x$  = Metals complexed by naturally occurring ligands,  $P^x$  = empty sorption sites on SPM and  $P_M^x$  = Exchangeable particulate metals

on board the research vessel the *Belgica*. The measurements of electrochemical labile metal concentrations were undertaken on (2) filtered and (3) unfiltered water. The term ‘electrochemically labile’ has already been discussed in Chapter 2. However, the determination of unfiltered labile metals has important implications for the fraction of metals detected. Firstly, filtered labile measurements reflect the concentration of dissolved metals detectable in the presence of an added AdCSV complexing ligand. The added ligand competes for the metals and forms complexes with free metal ions and liberates metals bound to naturally occurring ligands, which comprise (usually) organic species with  $\alpha$ -coefficient equal to and below that of the added ligand metal complex (Chapter 2). The analysis of unfiltered waters measured an additional potential pool of electrochemically detectable trace metals, which are the “rapidly exchangeable” metals bound to ligands at the surface of particulate material. These measurements may help assess the potential concentration of rapidly exchangeable trace metals present at surface binding sites of SPM. The methodology adopted for the AdCSV detection of Zn, Cu, Co and Ni is described in Chapter 2.

Marine chemists have applied a variety of extraction solutions to assess the “easily exchangeable” particulate Zn, Cu, Co, Ni and Mn concentrations of SPM in estuarine and coastal systems. For this study it was decided to apply a ligand competition extraction methodology utilising a 0.05 M solution of EDTA. Definition and optimisation of the method for the determination of 0.05 M EDTA exchangeable and total residual particulate Zn, Cu, Ni Co and Mn is described in Chapter 2 (Whitworth *et al.*, 1999).

#### *4.2.3 Determination of Cu complexing natural ligand concentrations and their conditional stability constants*

The methodology and theory utilised to determine water Cu natural complexing ligand concentrations and conditional stability constants have been described in Chapter 2. Table

4.a summarises the sample characteristics and the Cu titration intervals. Values for peak height (Table 4.a) refer to the peak height measured from sample one, which was analysed at the start, during and after the experiment in order to ensure no significant changes in instrument sensitivity occurred that may have affected estimates of Cu complexing ligand concentrations and conditional stability constants.

Table 4.a Sample characterisation and experimental overview of the procedure to characterise Cu complexes natural ligand concentrations and their conditional stability constants. The significance of peak height ( $n = 9$ ) measurements is explained in the text.

| Sample | Salinity | Cu <sub>tot</sub><br>(nM) | Cu <sub>lab</sub><br>(nM) | Cu titration intervals (nM)                                         | Peak<br>height (nA) |
|--------|----------|---------------------------|---------------------------|---------------------------------------------------------------------|---------------------|
| 8      | 0.44     | 126.74                    | 18.56                     | 0, 2.5, 5, 7.5, 15, 20, 25, 30, 40,<br>55, 70, 85, 110, 150 and 250 | $0.56 \pm 0.02$     |
| 10     | 5.3      | 132.77                    | 10.76                     | “ ”                                                                 | $1.06 \pm 0.08$     |
| 6      | 6.87     | 43.21                     | 13.75                     | “ ”                                                                 | $6.35 \pm 0.33$     |
| 4      | 13.63    | 30.94                     | 25.11                     | “ ”                                                                 | $1.92 \pm 0.08$     |
| 2      | 17.42    | 35.96                     | 19.26                     | “ ”                                                                 | $2.35 \pm 0.05$     |
| 11     | 22.55    | 21.63                     | 9.41                      | “ ”                                                                 | $5.51 \pm 0.04$     |
| 14     | 30.18    | 25.93                     | 12.79                     | “ ”                                                                 | $1.35 \pm 0.04$     |

#### 4.2.4 Organic and inorganic carbon

The particulate concentration of organic (POC) and inorganic carbon species has important implications for the speciation and concentrations of dissolved and particulate trace metals

(Davis, 1984; Turner *et al.*, 1998). The data sets for organic and inorganic C were supplied courtesy of Prof. R. Wollast (University of Brussels). Organic carbon was analysed using a high temperature catalytic oxidation method (Shimadzu TOC 5000). These data are intended for comparison with the data set presented in this chapter.

## **4.3 Results and discussion**

### *4.3.1 Analysis of certified reference materials SLEW-2 and CASS-2*

To verify the accuracy of AdCSV Cu, Zn, Ni and Co measurements of SLEW-2 (standard estuarine water) and CASS-2 (nearshore seawater) supplied by the National Research Council (Canada) were performed. Five sub-aliquots of reference water were UV digested prior to the determination of total Zn, Cu, Ni and Co using AdCSV (Chapter 2.). Total dissolved Zn, Cu, Ni and Co were measured in separate 10 ml sub-samples and the analyte concentration was calculated from the increase in signal measured after two internal standard additions (Chapter 2). The results of the analysis are presented along with the certified concentrations in Table 4.b. It is apparent that the obtained data were in close agreement with the certified values.

### *4.3.2 Effect of sample freezing on Zn, Cu, Ni and Co speciation and concentrations*

Since the water samples intended for analysis of dissolved labile trace metals and natural Cu complexing ligands (filtered and non filtered) were frozen and defrosted prior to analysis it was prudent to assess whether the storage procedure significantly modified measured concentrations of labile Co, Ni, Zn and Cu. This was undertaken by analysing selected samples prior to freezing then re-analysing the same samples after defrosting (1.5 yr). As estuaries comprise large chemical gradients, dissolved trace metal speciation could

Table 4.b Analysis of total dissolved Zn, Cu, Ni and Co concentrations in certified reference materials CASS-2 and SLEW-2.

| Reference material | Ligand    | Buffer | CASS-2 Certified | CASS-2 Observed | SLEW-2 Certified | SLEW-2 Observed |
|--------------------|-----------|--------|------------------|-----------------|------------------|-----------------|
| <i>Zn (nM)</i>     | APDC      | Tris   | 30.1 ± 1.8       | 30.2 ± 3.8      | 13.6 ± 2.6       | 14.2 ± 0.84     |
| <i>Zn (nM)</i>     | Oxine     | HEPES  | 30.1 ± 1.8       | 33.9 ± 1.3      | 13.6 ± 2.6       | 15.3 ± 0.8      |
| <i>Cu (nM)</i>     | SA        | Borate | 10.6 ± 0.6       | 10.4 ± 0.7      | 27.7 ± 1.5       | 28.5 ± 1.4      |
| <i>Cu (nM)</i>     | Tropolone | HEPES  | 10.6 ± 0.6       | 10.4 ± 0.3      | 27.7 ± 1.5       | 28.7 ± 0.8      |
| <i>Cu (nM)</i>     | Oxine     | HEPES  | 10.6 ± 0.6       | 10.2 ± 0.5      | 27.7 ± 1.5       | 27.5 ± 1.2      |
| <i>Ni (nM)</i>     | DMG       | HEPES  | 5.1 ± 0.6        | 5.5 ± 0.3       | 12.7 ± 1.3       | 13.8 ± 0.7      |
| <i>Co (pM)</i>     | DMG       | HEPES  | 420 ± 100        | 636 ± 150       | 780 ± 120        | 880 ± 30        |

exhibit contrasting responses to freezing for estuarine water samples of different salinities (i.e.  $S = 0$  to 35). For this reason water samples were chosen from 5 locations on the estuary, each exhibiting contrasting chemistries ( $S = 0.44, 6.87, 13.63, 20.6$  and  $32.8$ ). The concentrations of labile (filtered and unfiltered) Co, Ni, Zn and Cu were determined in situ (within 24 hr) and the corresponding frozen and defrosted measurements are presented in Table 4.c. The results suggested that freezing of filtered waters had little affect on the measured concentration of labile Co, Ni, Zn and Cu (mean variation of the measurement of defrosted sample was  $-0.6\%$ ,  $-1.9\%$ ,  $1.5\%$  and  $-3.5\%$  respectively). The trend of the measurements of Zn, Cu, Ni and Co suggest that values obtained from filtered, frozen and defrosted waters was generally lower but within analytical uncertainty ( $\sim 5\%$ ) of the measurements performed on-board ship within 24 hr of collection. These data suggest that freezer storage of filtered water samples for up to 1.5 year did not significantly alter the dissolved labile Cu, Ni, Zn and Cu determinations.

However, the results of the experiment involving freezing of unfiltered waters showed that the measurement of unfiltered labile Co, Ni, Zn and Cu generally resulted in a significantly enhanced estimation of labile metal concentrations (mean variation of the measurement of defrosted sample was  $95\%$ ,  $58\%$ ,  $47\%$  and  $59\%$  respectively). Visual observation of the unfiltered waters when held up to the light showed that after defrosting the sample waters the particulate material had formed large (up to 1 mm) flocs which were not observed prior to freezing. It is suggested that freezing of unfiltered sample waters altered the nature of the particulate material, which influenced the AdCSV lability of determined trace metals. Hence, it was deemed possible to undertake further analysis using unfiltered frozen water samples (e.g. natural Cu complexing ligand titrations of unfiltered water samples).

Table 4.c The effect of freezing on the dissolved speciation and concentration of Zn, Co, Ni and Cu. Labile measurements were undertaken on corresponding water samples before (1 and a) and after freezing (2 and b).

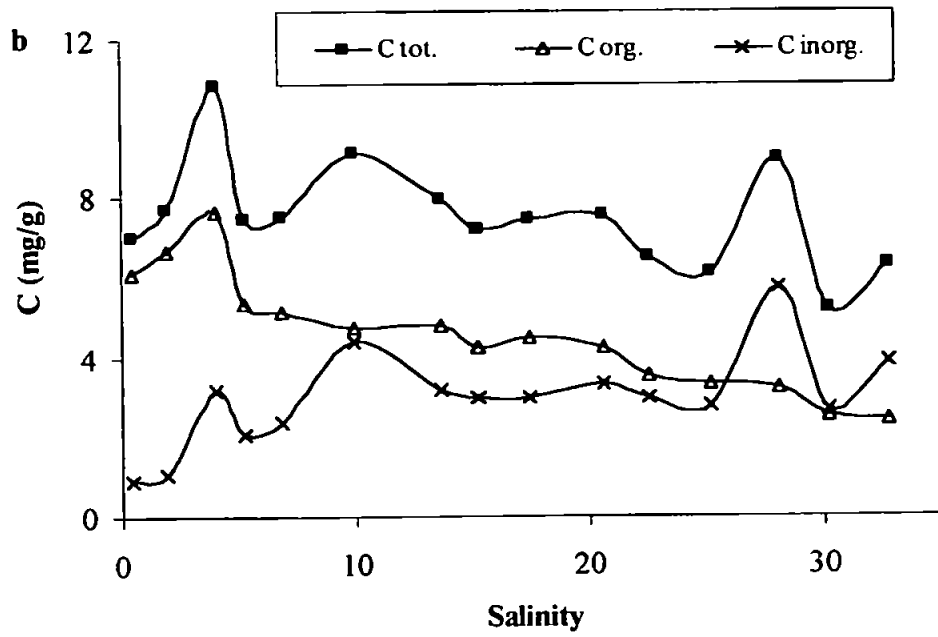
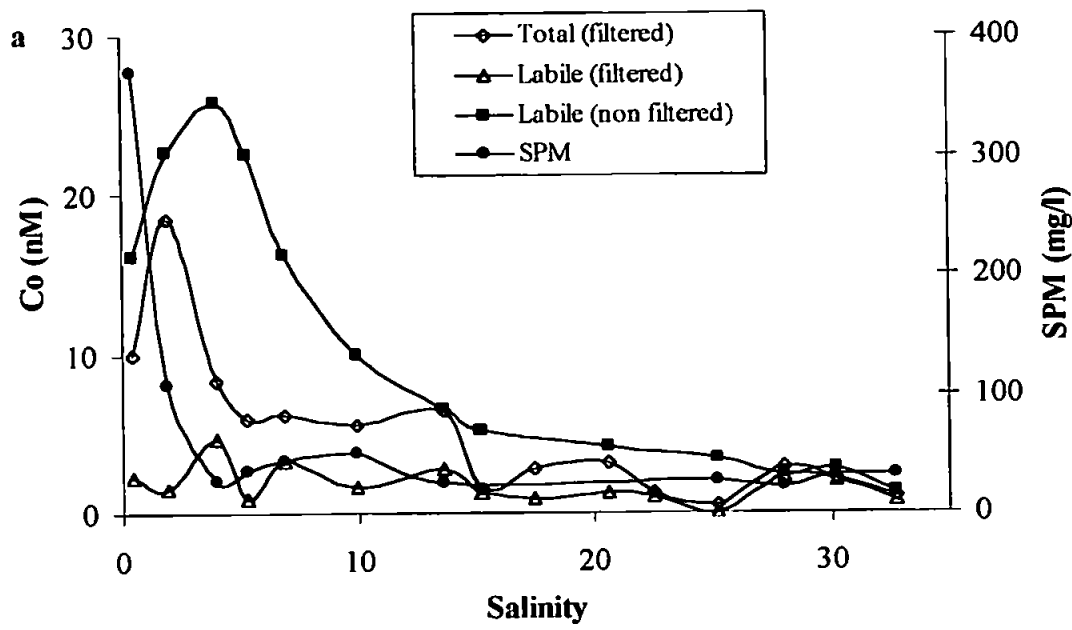
|                |          |        | Shipboard analysis<br>(within 24 hr) |                        |                                                              | Laboratory analysis      |                        |
|----------------|----------|--------|--------------------------------------|------------------------|--------------------------------------------------------------|--------------------------|------------------------|
| Element        | Salinity | Sample | Unfiltered<br>Labile (1)             | Filtered<br>Labile (a) |                                                              | Unfiltered<br>Labile (2) | Filtered<br>Labile (b) |
|                |          |        |                                      |                        |                                                              |                          |                        |
| <i>Zn (nM)</i> | 0.44     | 8      | 398                                  | 70.9                   | S<br>T<br>O<br>R<br>E<br>D<br><br>F<br>R<br>O<br>Z<br>E<br>N | 1082                     | 68.2                   |
|                | 6.87     | 6      | 426                                  | 34.1                   |                                                              | 682                      | 33.8                   |
|                | 13.63    | 4      | 209                                  | 82.5                   |                                                              | 453                      | 76.3                   |
|                | 20.56    | 1      | 228                                  | 48.8                   |                                                              | 587                      | 44.1                   |
|                | 32.75    | 15     | *                                    | 38.8                   |                                                              | *                        | 40.1                   |
| <i>Cu (nM)</i> | 0.44     | 8      | 18.5                                 | 18.6                   |                                                              | 98.7                     | 18.2                   |
|                | 6.87     | 6      | 58.0                                 | 13.8                   |                                                              | 102                      | 13.2                   |
|                | 13.63    | 4      | 64.4                                 | 25.1                   |                                                              | 95.6                     | 23.6                   |
|                | 20.56    | 1      | 40.6                                 | 17.7                   |                                                              | 123                      | 16.8                   |
|                | 32.75    | 15     | 10.2                                 | 8.94                   |                                                              | 28.6                     | 12.1                   |
| <i>Ni (nM)</i> | 0.44     | 8      | 121                                  | 51.6                   |                                                              | 603                      | 53.9                   |
|                | 6.87     | 6      | 152                                  | 36.3                   |                                                              | 374                      | 34.7                   |
|                | 13.63    | 4      | 115                                  | 48.8                   |                                                              | 276                      | 46.3                   |
|                | 20.56    | 1      | 88.8                                 | *                      |                                                              | 240                      | *                      |
|                | 32.75    | 15     | 27.5                                 | *                      |                                                              | 42.3                     | *                      |
| <i>Co (nM)</i> | 0.44     | 8      | 16.2                                 | 2.2                    |                                                              | 22.3                     | 2.1                    |
|                | 6.87     | 6      | 16.3                                 | 3.3                    |                                                              | 22.0                     | 3.0                    |
|                | 13.63    | 4      | 6.6                                  | 2.8                    |                                                              | 12.6                     | 2.7                    |
|                | 20.56    | 1      | 4.2                                  | 1.3                    |                                                              | 7.2                      | 1.3                    |
|                | 32.75    | 15     | 1.3                                  | 0.7                    |                                                              | 1.3                      | 0.8                    |

\* Indicates that analysis could not be undertaken due to analytical interferences

### 6.3.3 Behaviour of dissolved Co in the Scheldt Estuary

The total dissolved ( $Co_{tot}$ ), electrochemically labile filtered ( $Co_{flab}$ ) and unfiltered ( $Co_{lab}$ ) concentration of Co was determined in waters collected from an axial transect of the Scheldt estuary at salinities of between  $\sim 0$  and  $\sim 34$  during 12-1996 (Fig. 4.3).  $Co_{tot}$  exhibited high spatial variability with values decreasing towards the lower estuary. Highest  $Co_{tot}$  concentrations were observed in the upper estuary ( $Co_{tot} = 10$  nM and  $Co_{tot} = 18.53$  nM;  $S = 0.44$  and  $1.91$  respectively) and lower values were encountered in the lower estuary ( $Co_{tot} = 0.96$  nM,  $S = 32.75$ ). The concentrations of  $Co_{tot}$  observed were in agreement with previously reported values for  $Co_{tot}$  in the Scheldt estuary ( $\sim 5$  nM and  $\sim 1.2$  nM;  $S = \sim 0$  and  $\sim 34$  respectively, Zhang *et al.*, 1989; Zhang *et al.*, 1990). The behaviour of  $Co_{tot}$  could not be explained by conservative mixing between the  $Co_{tot}$  enriched waters of the upper estuary with the  $Co_{tot}$  depleted waters of the lower estuary, which suggests that additional factors influenced the behaviour of  $Co_{tot}$  in the estuary. An initial increase in  $Co_{tot}$  was encountered at the onset of seawater mixing and immediately following the turbidity maximum ( $Co_{tot} = 10$  nM, SPM = 369 mg/l and  $Co_{tot} = 19$  nM, SPM = 100 mg/l;  $S = 0.44$  and  $1.91$  respectively). The enhanced concentrations of SPM could indicate disturbance of benthic sediments, which could indicate the injection of Co enriched anoxic interstitial waters to the overlying water. Furthermore, desorption of Co from surface sorption sites on particulate material owing to the competition from major cations (e.g.  $Ca^{2+}$ ,  $Na^{+}$ ,  $Mg^{2+}$ ) could have contributed to the enhanced  $Co_{tot}$  concentrations where elevated SPM concentrations were encountered (Morris, 1986). Following the enhanced concentrations of  $Co_{tot}$  observed in the upper estuarine low salinity zone ( $S = 1.91$ ), removal of  $Co_{tot}$  can be observed ( $Co_{tot} = 8.35$  nM at  $S = 4.03$ ). Previous workers have suggested that removal of trace metals (including Co, Ni, Zn and Cu) is a feature common in the low salinity region of estuaries (Knauer *et al.*, 1982; Morris, 1986; Valenta *et al.*, 1986). Regnier *et al.*, (1990) and Knauer *et al.*, (1982) have suggested that the geochemical

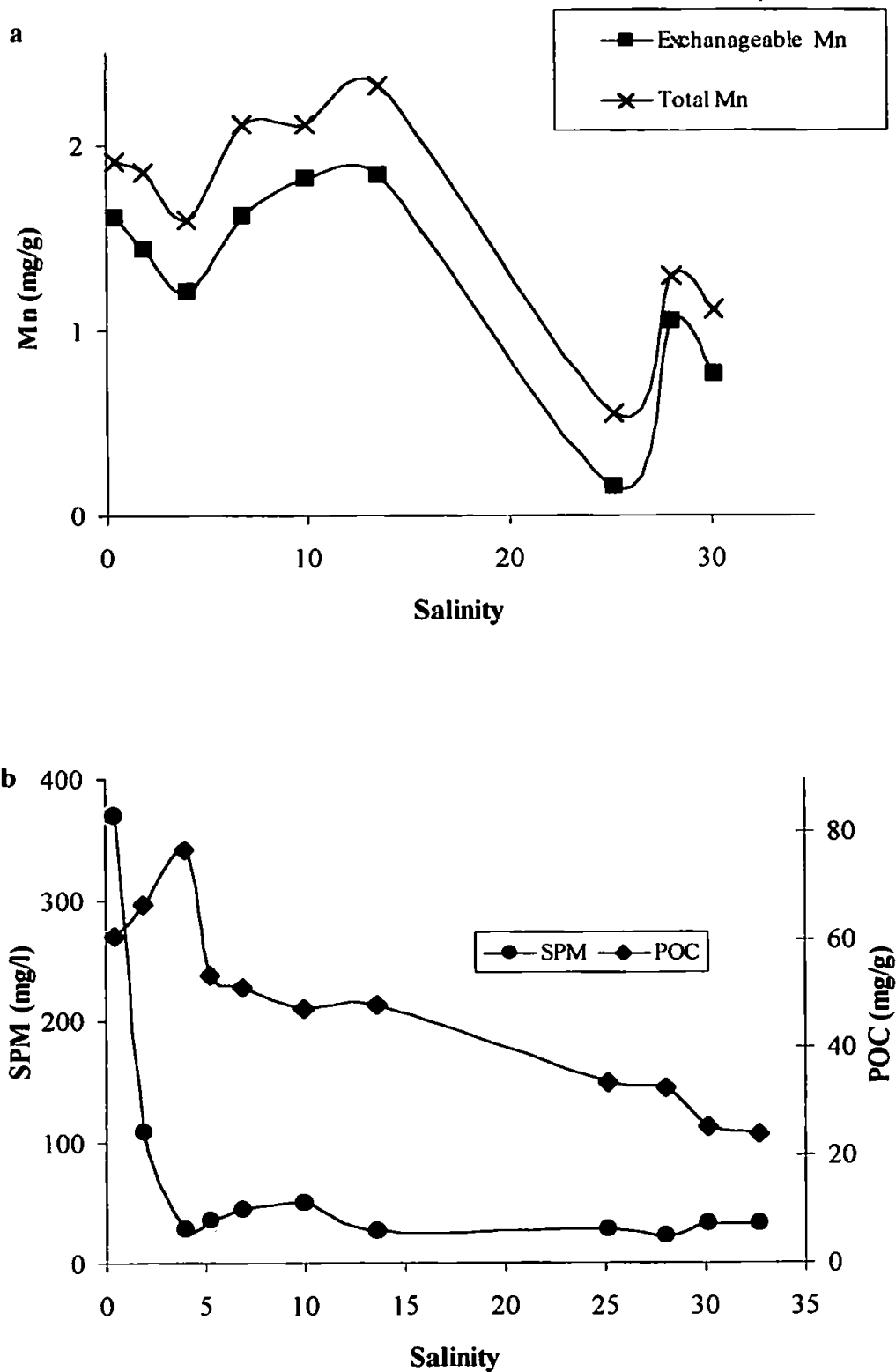
Figure 4.3 Distribution of dissolved Co species (a) and, C (b) in the Scheldt Estuary, December 1996.



cycling of  $\text{Co}_{\text{tot}}$  in estuarine and coastal systems is linked with the formation and dissolution of Mn oxy-hydroxides. Co can be removed from the dissolved phase owing to co-precipitation with Mn oxy-hydroxides (Lienemann *et al.*, 1997). Conversely, under reducing conditions (anoxic), the dissolution of Mn oxy-hydroxides could lead to release of dissolved Co from the sediment. The Scheldt is characterised by an unusually high organic and nutrient load owing to the large number of inhabitants in the drainage basin, the development of agricultural and industrial activities and the poor wastewater treatment facilities. A consequence of the high organic load is the existence of permanent anoxic conditions in the water column in the upper estuary over a distance of approximately 30 km, which may exceed 70 km during the summer. The presence of these anaerobic waters plays an important role in the transfer of various dissolved or particulate elements through the estuary (Wollast, 1988). Turner *et al.*, (1991), reported a particulate Mn maxima ( $\sim 1.5$  mg/g) for the Scheldt in the salinity range 15 to 25. The mid estuarine particulate Mn maximum was ascribed to the oxidation of Mn(II) downstream of an anoxic zone in response to an increase of pH and dissolved oxygen concentrations resulting in less soluble Mn species of higher oxidation states ( $\text{MnOOH}$  and  $\text{MnO}_2$ ). Furthermore, preliminary experiments carried out with  $^{60}\text{Co}$  (Zhang and Wollast, unpublished work) on water samples collected in the Scheldt estuary indicated that Co was co-precipitated with Mn. Hence the removal of  $\text{Co}_{\text{tot}}$  observed in the mid estuary ( $S = \sim 10$  to  $\sim 25$ ) may have been related to the observed increase in the particulate Mn concentration that was noticed in the mid estuary (particulate Mn maxima = 2.32 mg/g;  $S = 13.63$ ) owing to co-precipitation (Fig. 4.4).

The concentration of  $\text{Co}_{\text{lab}}$  showed enrichment ( $\text{Co}_{\text{lab}}$  comprises a fraction of Co that was associated with SPM) in the low salinity region of the estuary ( $S = 0.44$  to  $\sim 5$ ) suggesting an increase in the easily exchangeable concentration of Co at surface sites of SPM. However, the highest values of  $\text{Co}_{\text{lab}}$  were observed after the SPM maximum at a salinity of  $\sim 4$ , which suggests adsorption of Co was an important feature of partitioning between

Figure 4.4 Distribution of (a) particulate Mn and (b) SPM and POC against salinity in the Scheldt Estuary, December 1996



the dissolved and particulate phase in the upper estuary. As the association between Co and Mn oxy-hydroxides was likely to be important, the maximum of  $Co_{lab}$  could be observed downstream of the maximum of  $Co_{tot}$ . The overall concentration of  $Co_{tot}$  in the upper and mid estuary (mean  $Co_{tot} = 6.3$  nM;  $S = 0.44$  to  $22.55$ ) was high compared with values in the lower estuary (mean  $Co_{tot} = 1.61$  nM;  $S = 25.19$  to  $32.75$ ), which was probably associated with anthropogenic inputs (Paucot and Wollast, 1997). The reduction in the concentration of  $Co_{tot}$  in the lower estuary can be accounted for by dilution of Co enriched estuarine water with relatively Co depleted waters originating from the outer estuary and removal of Co by co-precipitation with Mn oxy-hydroxides.

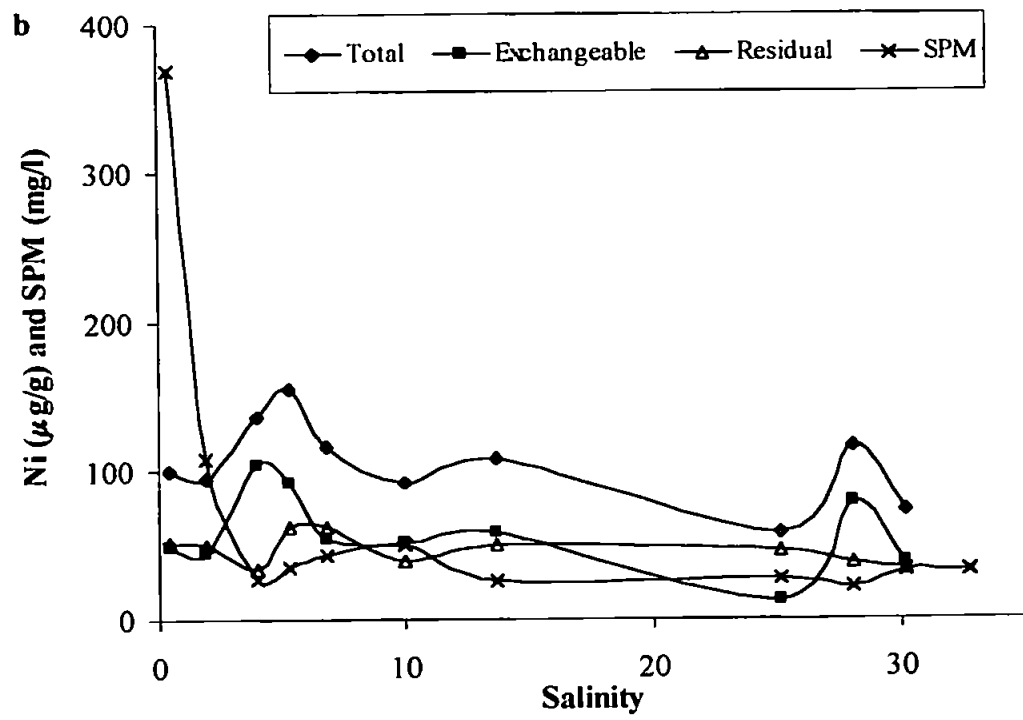
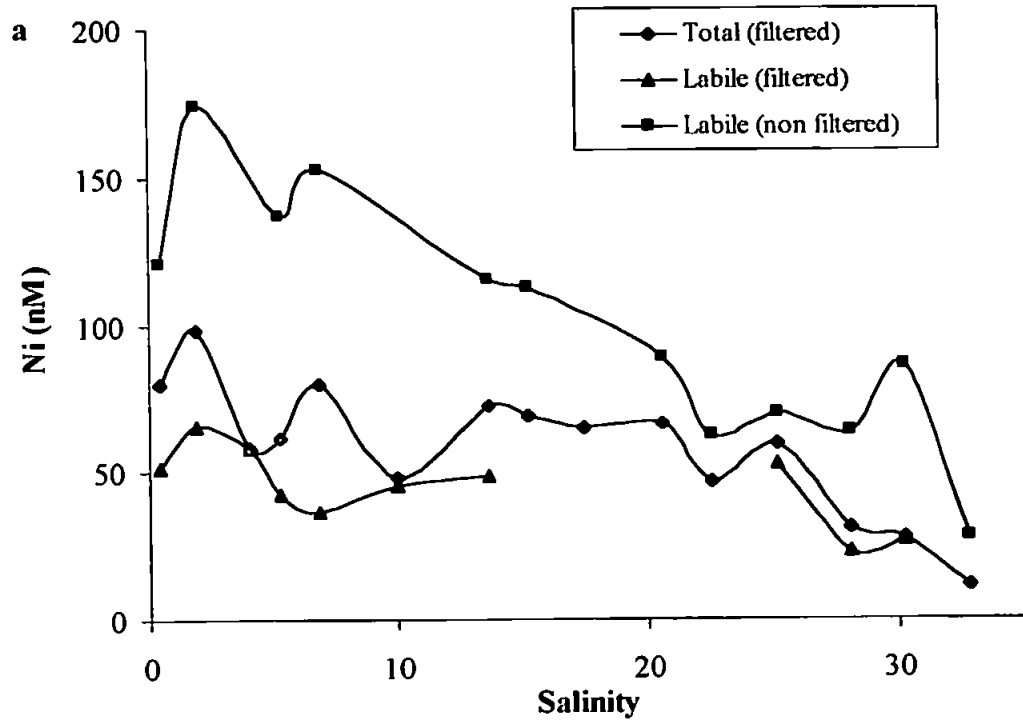
In contrast the  $Co_{lab}$  concentrations fluctuated around a mean value of  $1.9 \pm 1.1$  nM throughout the estuary ( $Co_{lab} = 2.2$  and  $0.7$  nM;  $S = 0.44$  and  $32.75$  respectively). By comparing  $Co_{lab}$  with  $Co_{tot}$  it was possible to show that a higher proportion of organically bound Co ( $Co_{org}$ ) ( $Co_{org} = Co_{tot} - Co_{lab}$ ) was present in the upper estuary ( $Co_{org} = 7.8$  and  $0.2$  nM;  $S = 0.44$  and  $32.75$  respectively). Furthermore, since the distribution of  $Co_{lab}$  was relatively constant throughout the estuary, it is suggested that in the upper and mid estuary, the greater influence on the dissolved distribution of Co the fate of  $Co_{org}$ . The nature of the electrochemical ligand used for the measurement of labile Co suggests that only strong Co complexes would remain undetected and hence contribute to  $Co_{org}$  ( $\log_{10} K_{Co_{DMG}} > 18$ , Zhang *et al.*, 1990). Strong naturally occurring ligands were present in the upper estuary which were not observed in the lower estuary. Interestingly,  $Co_{org}$  exhibited a positive relationship with POC ( $R^2 = 0.47$ , intercept =  $-6.0$  nM, slope =  $2.04$ ,  $n = 14$ , at the 90 % confidence interval), where high values were detected in the upper estuary and concentrations generally fell in the lower estuary. Previous workers have also suggested a positive relationship between organic compounds, some capable of complexing trace metals, and POC (Zwolsman and Van Eck, 1993; Gerringa *et al.*, 1996; Regnier and Wollast, 1993). Consequently, lower concentrations of organic ligands capable of binding Co may be expected at the seaward end of the estuary.

#### 4.3.4 Behaviour of dissolved and particulate Ni in the Scheldt Estuary

Total dissolved ( $Ni_{tot}$ ) and labile (filtered ( $Ni_{lab}$ ) and unfiltered ( $Ni_{lab}$ )) Ni concentrations have been plotted against salinity and are presented in Figure 4.5.a. Figure 4.5.b shows the results obtained from a study of the 0.05 M EDTA exchangeable ( $Ni_{ip}$ ) and total ( $Ni_{ip}$ ) concentration of particulate Ni from equivalent SPM samples. The data for total dissolved and total particulate Ni were in agreement with previous studies in the Scheldt estuary ( $Ni_{tot} = 11.44$  to  $98.24$  nM,  $Ni_{ip} = 57.93$  to  $154.27$   $\mu\text{g/g}$ , compared with Paucot and Wollast 1997,  $Ni_{tot} = \sim 15$  and  $\sim 170$  nM,  $Ni_{ip} = \sim 30$  and  $\sim 100$   $\mu\text{g/g}$ ).

$Ni_{tot}$  exhibited a negative relationship with salinity ( $S = 0.44$  to  $32.75$ ), which can be characterised by  $R^2 = 0.63$ , intercept =  $84.5$  nM, slope =  $-1.67$ ,  $n = 15$ , at the 99 % confidence interval. Paucot and Wollast, (1997) encountered conservative behaviour of  $Ni_{tot}$  in the Scheldt estuary where a reduction in  $Ni_{tot}$  was observed with increasing salinity ( $R^2 = 0.95$ ) and suggested that Ni distribution was controlled by the dilution of freshwater with seawater low in dissolved Ni. However, in this study there appeared to be a high spatial variability in  $Ni_{tot}$  particularly in the upper estuary where the relationship between  $Ni_{tot}$  and salinity was not statistically significant ( $S = 0.44$  to  $9.97$ ,  $R^2 = 0.45$ ,  $n = 6$ ), which compared to  $R^2 = 0.86$ ,  $n = 9$ , at the 95 % confidence interval for the salinity interval  $13.63$  to  $32.75$ . Previous studies have also shown that highest variation of dissolved trace metal concentrations were observed in the upper Scheldt estuary (Zwolsman and Van Eck, 1993; Regnier and Wollast, 1993; Zwolsman *et al.*, 1997). The processes invoked for the non-conservative behaviour of trace metals in the upper estuary included adsorption and desorption of metals from the surfaces of SPM, sediment re-suspension, injection of anoxic metal enriched interstitial waters and point source anthropogenic trace metal inputs. Injection of metal enriched sediment interstitial waters is commonly associated with sediment disturbance and re-suspension and can be identified by enhanced SPM

Figure 4.5 Distribution of dissolved (a), particulate (b) Ni species in the Scheldt Estuary, December 1996.



concentrations, a feature associated with the upper estuary (mean SPM = 105.4 and 27.88 mg/l;  $S = 0.44$  to 9.97 and 13.63 to 32.75 respectively).

The concentration of  $Ni_{lab}$  was high in the upper estuary and lower estuary ( $Ni_{lab} = 51.6$  nM and 27.0 nM;  $S = 0.44$  and 30.18 respectively). It was not possible to undertake labile measurements throughout the estuary owing to analytical interferences possibly from the presence of dissolved organic surfactants. A higher fraction of non labile Ni ( $Ni_{org}$ ) complexes were present in the upper estuary ( $Ni_{org}$  (% of  $Ni_{tot}$ ) = 35.3 and 2.7 %;  $S = 0.44$  and 30.18 respectively), which suggests a more important role of organic complexation of Ni in the upper estuary. Ni forms a strong complex with DMG, hence only very strong Ni complexes would remain undetectable ( $\text{Log}_{10} K_{Ni_{DMG}} = 10^{17}$ ) (van den Berg and Nimmo, 1987).

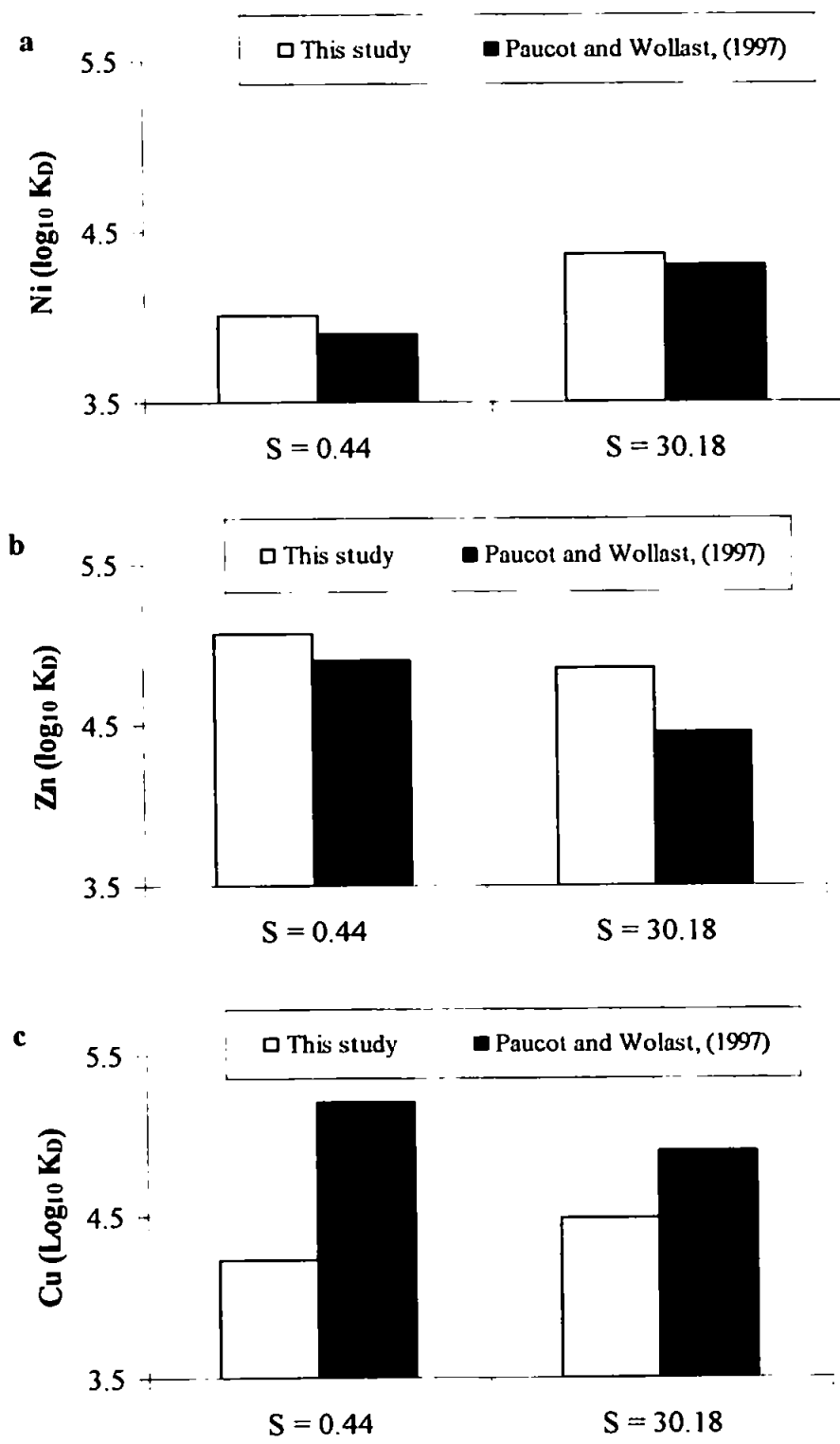
$Ni_{lab}$  exhibited a similar distribution to  $Ni_{tot}$  where a negative relationship with salinity was observed ( $R^2 = 0.80$ , slope = -3.34, intercept = 157 nM,  $n = 12$ , at the 99 % confidence interval). The concentration of  $Ni_{lab}$  was approximately double that of the  $Ni_{lab}$  and suggests that the measurements included a large fraction of rapidly exchangeable particulate Ni. Metals originating from anthropogenic sources can become associated with the surfaces of the particulate material and are, therefore, more loosely bound than residual metals held in the lattices of particles (Zwolsman *et al.*, 1997).  $Ni_{lab}$  exhibited a maximum at low salinity following the turbidity maximum and thus is likely to be related to the SPM concentration. The  $Ni_{lab}$  maximum existed after the turbidity maximum, which suggests that adsorption of Ni onto SPM surfaces is invoked in the low salinity region. Considering that high concentrations of  $Ni_{lab}$  were noticed in the upper estuary, particles may play an important role in the removal of Ni in the upper estuary. The overall decrease in the concentration of  $Ni_{lab}$  towards the seawater dominated end of the estuary was probably related to the seaward reduction in the SPM concentration. In addition, particulate material from the seawater end of the estuary originated from the Southern North Sea. Studies by Regnier and Wollast, (1993) have shown that SPM from the lower estuary contained a

relatively low concentration of particulate Ni, hence the reduction in  $Ni_{lab}$  concentration in samples collected from the lower estuary may have been a reflection of the changing SPM population. Furthermore, the difference between the  $Ni_{tot}$  and  $Ni_{lab}$  concentrations was smallest at the seawater end of the estuary, which may suggest that particles at the seawater end of the estuary contain a lower concentration of readily exchangeable Ni (Nimmo *et al.*, 1989). A positive relationship between  $Ni_{lab}$  and dissolved organic C was observed, which can be characterised by  $R^2 = 0.79$ , slope = 27.7, intercept = -18.0 nM,  $n = 15$ , at the 99 % confidence interval and suggests that organic complexes at the surface of SPM could actively remove Ni from the dissolved phase. Interestingly, the  $Ni_{lp}$  (labile particulate Ni) maximum ( $Ni_{lp} = 103.66 \mu\text{g/g}$ ) coincided with the POC maxima (7.68 mg/g), which supports the suggestion that organic coatings on SPM can act as complexation sites for dissolved Ni species, particularly in the upper estuary where POC concentrations were highest.

The  $Ni_{mp}$  (residual particulate Ni) exhibited a relatively low variation throughout the estuary with a mean estuarine value of  $46.4 \pm 10.6 \mu\text{g/g}$ , which indicates that the lithogenic composition of the particles could be similar throughout the estuary. In contrast, the  $Ni_{lp}$  distribution exhibited high spatial variability and suggests that the fate of dissolved Ni was strongly influenced by the surface characteristics of SPM. The lowest concentrations of  $Ni_{lp}$  were observed in the lower estuary, which suggested that the lower estuary contained a relatively high component of marine particles depleted in Ni.

The distribution coefficient ( $K_D$ ), is defined as the concentration of the trace element in the particulate phase ( $\mu\text{g/kg}$ ) divided by that in the dissolved phase ( $\mu\text{g/l}$ ). This coefficient indicates the affinity of the element for the solid phase and its tendency to be transported as a particulate material. Figure 4.6 shows values of the Ni  $\log_{10} K_D$  at low and high salinities ( $\log_{10} K_D = 4.01$  and  $4.37$ ;  $S = 0.44$  and  $30.18$  respectively), which suggests that Ni has a higher affinity for the particulate phase in the lower estuary. This observation suggests that the organic rich SPM in the upper estuary has a higher number of weaker binding sites for

Figure 4.6 Comparison of  $\text{Log}_{10} K_D$  values for (a) Ni, (b) Zn and (c) Cu in the Scheldt estuary at low and high salinities. Values obtained during this study are compared with values obtained by Paucot and Wollst, (1997) study of the Scheldt estuary.

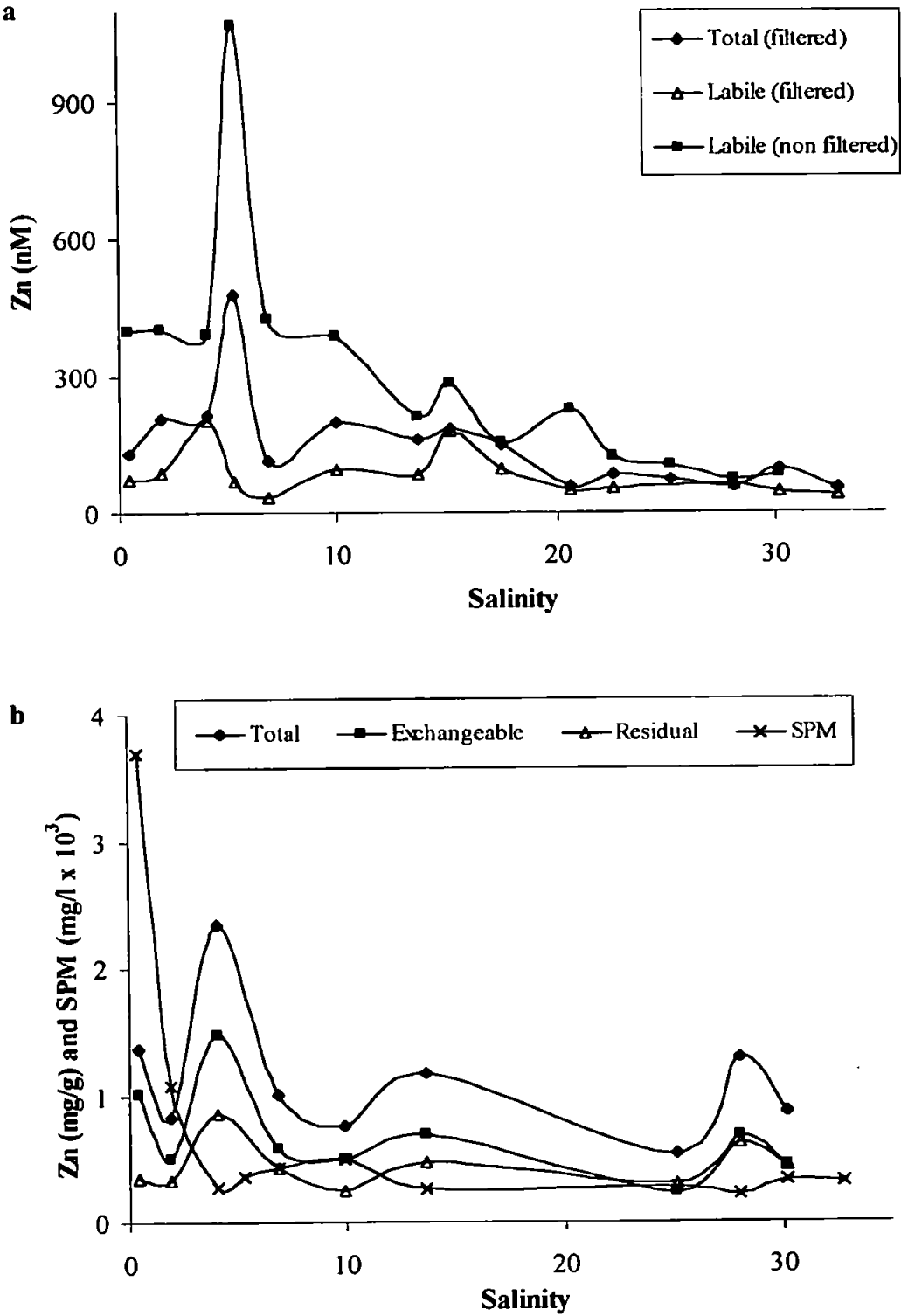


Ni and the SPM in the lower estuary has a lower number of stronger binding sites. Paucot and Wollast, (1997) reported similar findings following their studies of dissolved and particulate Ni in the Scheldt ( $\text{Log}_{10} K_D \sim 3.9$  and  $\sim 4.3$ ;  $S = \sim 0$  and  $\sim 30$  respectively).

#### 4.3.5 Behaviour of dissolved and particulate Zn in the Scheldt Estuary

The distribution and speciation of dissolved and particulate Zn is presented in Figure 4.7. Total dissolved ( $Zn_{tot}$ ) and total particulate ( $Zn_{tp}$ ) Zn concentrations were in agreement with previously reported measurements in the Scheldt estuary (mean estuarine  $Zn_{tot} = 105.8 \pm 107.1$  and  $Zn_{tp} = 1.13 \pm 0.53$  mg/l) (Zwolsman *et al.*, 1997; Zwolsman and Van Eck, 1993; Paucot and Wollast 1997; Baeyens, 1998; Baeyens *et al.*, 1987). Highest concentrations of  $Zn_{tot}$  were observed in the upper estuary and the overall concentrations decreased towards the seawater dominated lower estuary ( $Zn_{tot} = 132$  nM and  $54.0$  nM;  $S = 0.44$  and  $32.75$  respectively).  $Zn_{tot}$  exhibited high spatial variability, particularly in the upper estuary where highest concentrations were observed ( $Zn = 258 \pm 152$  nM;  $S = 0.44$  to  $5.3$  and  $112 \pm 53$  nM;  $S = 6.87$  to  $32.75$ ). Relatively high concentrations of  $Zn_{tot}$  persisted well into the mid-estuary despite mixing of the riverine input with relatively Zn depleted seawater ( $Zn_{tot} = 147.9$ ;  $S = 17.42$ ). Similarly, previous investigations of  $Zn_{tot}$  distributions in the Scheldt have shown enhanced concentrations throughout the estuary (Paucot and Wollast, 1997; Zwolsman *et al.*, 1997; Zwolsman and Van Eck, 1993; Zwolsman *et al.*, 1996). This could be due to anthropogenic wastewater discharges, sediment re-suspension events and injection of anoxic Zn enriched sediment interstitial waters. Owing to discharges from public wastewater treatment outfalls, a large quantity of metals, nutrients and organic material enters the Scheldt estuary. The activity of microorganisms metabolising organic material can cause the depletion of oxygen in sediments and in the water column. Under anoxic/sub oxic conditions sulphide can become stable in interstitial water and the water column, which can lead to the formation of

Figure 4.7 Distribution of dissolved (a), particulate (b) Zn species in the Scheldt Estuary, December 1996.



sulphide minerals. Zn sulphides have been observed in the Scheldt sediments and dissolved sulphide has been measured in the water column (Zwolsman and Van Eck, 1993). Anoxic/suboxic conditions are prevalent in the water column during summer months, and where water circulation is restricted, can persist throughout the year. The metabolic rate of bacteria is reduced during the winter months (survey season) consequently, oxic conditions return to large parts of the estuary. However, circulation of sub oxic waters and disturbance of sulphidic sediments can have a profound effect on the dissolved trace metal concentrations during winter months. Zn sulphides become rapidly oxidised in oxygen rich waters and can increase the concentration of dissolved Zn in the water column. Therefore, it is probable that the enhanced concentrations of  $Zn_{tot}$ , which persisted throughout the estuary, were a result of a combination of direct anthropogenic discharges in addition to the oxidation of Zn sulphide minerals upon disturbance of bottom water and sediment. Zwolsman and Van Eck, (1993) suggested that the oxidation of metal sulphides could enhance the dissolved concentration of  $Zn_{tot}$  in the upper estuary during winter months at times of high river discharge rates, where benthic sediments can be intensively reworked. Furthermore, the re-adsorption of  $Zn_{tot}$  onto surface adsorption sites on SPM is inhibited in the mid estuary owing to the inorganic complexation of the released metals with e.g. chloride and possibly dissolved organic ligands. In this way elevated concentrations of  $Zn_{tot}$  could persist into the mid and lower estuary. Further seaward, a decrease in  $Zn_{tot}$  occurred owing to dilution with coastal seawater.

The  $Zn_{flab}$  concentration exhibited high spatial variability, particularly in the upper estuary (mean estuarine  $Zn_{flab} = 83.4 \pm 50.0$  nM). The majority of  $Zn_{tot}$  consisted of  $Zn_{flab}$  (mean estuarine  $Zn_{flab}$  (% of  $Zn_{tot}$ ) = 58.1 %). The dissolved inorganic complexation of Zn in seawater by chloride has been widely reported (Zwolsman *et al.*, 1997; Paucot and Wollast, 1997; Regnier and Wollast, 1993). Zn forms a strong complex with the electrochemical ligand used for the determination of  $Zn_{flab}$  and  $Zn_{lab}$  (van den Berg *et al.*, 1987) and, therefore, the  $Zn_{lab}$  and  $Zn_{flab}$  measurements would comprise the fraction of

dissolved Zn complexed by chloride. This consideration and the weak organic complexes formed by Zn could explain the low proportion of non labile Zn ( $Zn_{org}$ ) observed in the lower and mid estuary.

Interestingly, the  $Zn_{tot}$  and  $Zn_{lab}$  maximas broadly coincided with the maximum concentration of  $Zn_{tp}$ ,  $Zn_{lp}$  and POC ( $Zn_{tot} = 479$  nM,  $Zn_{lab} = 1070$  nM,  $Zn_{tp} = 2.38$  mg/l,  $Zn_{lp} = 1.48$  mg/l and POC = 7.68 mg/g). This suggests that the increase in dissolved  $Zn_{org}$  ( $Zn_{org}$  (% of  $Zn_{tot}$ ) = 85.2 %;  $S = 5.30$ , mean estuarine value = 37.8 %) was associated with a significant input of particulate Zn ( $Zn_{tp} = 2.34$  mg/l;  $S = 4.03$ , mean estuarine value = 1.13 mg/l). The point source input of particulate and dissolved Zn in the upper estuary ( $S \sim 5$ ) could have been achieved by a combination of the following: (1) a point source discharge of particulate and dissolved Zn from an industrial facility, or (2) disturbance of benthic sediments, which could have provoked infusion of metal enriched sediment pore waters and SPM. The former seems more likely, as sediment disturbances are commonly associated with enhanced SPM concentrations, a feature absent from this point in the estuary (SPM = 36 mg/l;  $S = 5.3$ ). The particulate distribution of Zn was broadly similar to the dissolved concentration of Zn throughout the estuary. Higher concentrations were observed in the upper estuary and the levels decreased to lower levels in the lower estuary ( $Zn_{tp} = 1.36$  mg/l,  $Zn_{lp} = 1.01$  mg/l and  $Zn_{tp} = 0.87$  mg/l,  $Zn_{lp} = 0.44$  mg/l;  $S = 0.44$  and 30.18 respectively). Dilution between riverine SPM with seawater SPM was an important feature of the estuarine water and SPM mixing. However, the particulate Zn distribution exhibited a strong variation that could not be accounted for by mixing between two end members (mean estuarine  $Zn_{tp} = 1.12 \pm 0.52$  mg/l and  $Zn_{lp} = 0.68 \pm 0.37$  mg/l). Owing to the formation of chloride complexes in seawater, desorption processes could contribute to a reduction in of the particulate Zn concentration and in particular the easily exchangeable particulate Zn, which can be observed in both the  $Zn_{lp}$  and  $Zn_{lab}$  measurements.

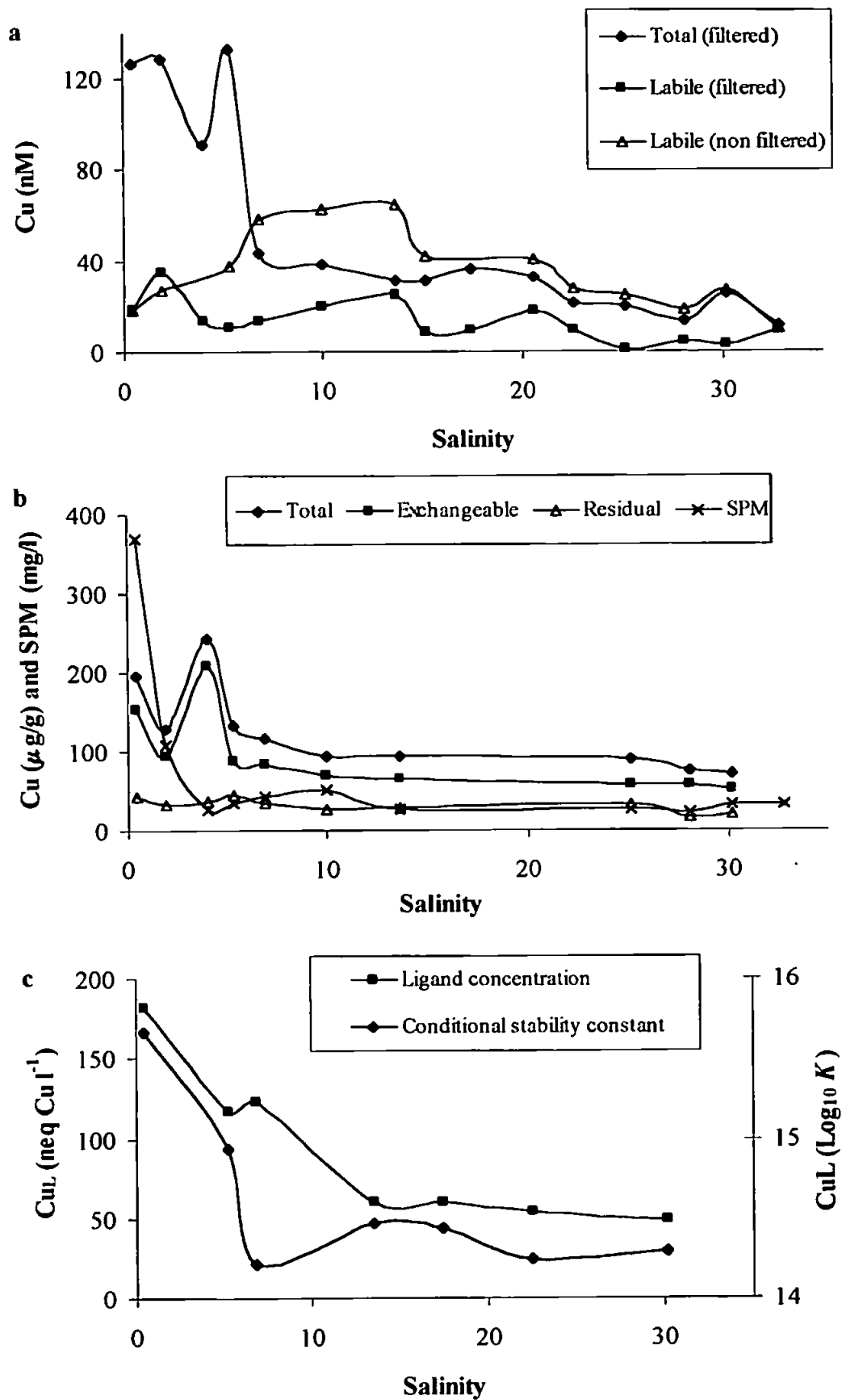
As mentioned previously, it is often useful to consider a distribution coefficient that can give an indication of the affinity of an element to the particulate phase (Fig. 4.6). These

data indicate that higher values of  $K_D$  were observed in low salinity waters compared to high salinity waters ( $\text{Log}_{10} K_D = 5.07$  and  $4.85$ ;  $S = 0.44$  and  $30.18$  respectively). Paucot and Wollast, (1997) observed similar distributions. The somewhat reduced  $K_D$  values observed in the lower estuary suggest that Zn has a higher affinity for the dissolved phase in high salinity waters, which can possibly be explained by the dissolved complexation of Zn by e.g. chloride in the seaward end of the estuary (Zwolsman and Van Eck, 1993; Moran *et al.*, 1996; Regnier and Wollast, 1993).

#### 4.3.6 Behaviour of dissolved and particulate Cu in the Scheldt Estuary

The distribution of total dissolved ( $\text{Cu}_{\text{tot}}$ ) and labile filtered ( $\text{Cu}_{\text{lab}}$ ) and unfiltered ( $\text{Cu}_{\text{lab}}$ ) Cu concentrations has been plotted against salinity and presented in Figure 4.8. Values obtained from the analysis of  $\text{Cu}_{\text{tot}}$  compare well with previous studies of the Scheldt estuary (mean estuarine value  $\text{Cu}_{\text{tot}} = 52.2 \pm 84.2$  nM, Baeyens *et al.*, 1998; Gerringa *et al.*, 1996; Zwolsman *et al.*, 1996; Regnier and Wollast, 1993; Paucot and Wollast, 1997). Highest concentration and variability of  $\text{Cu}_{\text{tot}}$  was observed in the upper estuary (mean  $\text{Cu}_{\text{tot}} = 119.8 \pm 19.5$  nM;  $S = 0.44$  to  $5.30$ ). Above a salinity of  $\sim 6$   $\text{Cu}_{\text{tot}}$  concentrations decreased to a minimum value of  $11.3$  nM at salinity of  $32.75$  (mean  $\text{Cu} = 27.7 \pm 10.2$  nM;  $S = 6.87$  to  $32.75$ ). Furthermore,  $\text{Cu}_{\text{tot}}$  shared a negative relationship with salinity (where  $S = 6.87$  to  $32.75$ ) and can be characterised by  $R^2 = 0.79$ , slope =  $-1.08$ , intercept =  $49.4$  nM,  $n = 11$ , at the 99 % confidence interval. The negative relationship between  $\text{Cu}_{\text{tot}}$  and salinity suggests that dilution between  $\text{Cu}_{\text{tot}}$  enriched waters of the upper estuary with relatively depleted  $\text{Cu}_{\text{tot}}$  lower estuarine waters was an important feature of the behaviour of  $\text{Cu}_{\text{tot}}$  in the Scheldt estuary. However, the high concentration and spatial variability in the behaviour of  $\text{Cu}_{\text{tot}}$  in the upper estuary ( $S = 0$  to  $5$ ) suggests that  $\text{Cu}_{\text{tot}}$  is strongly affected by input and removal processes in the upper estuary. The initial decrease in the  $\text{Cu}_{\text{tot}}$  concentration was followed by an input event ( $\text{Cu}_{\text{tot}} = 128.8, 90.8$  and  $132.8$  nM;  $S =$

Figure 4.8 The distribution of dissolved Cu (a), particulate Cu (b) and natural ligand ( $\text{Cu}_L$ ) concentrations ( $\text{Cu neq l}^{-1}$ ) and conditional stability constants ( $\text{Log}_{10} K$ ) (c) in the Scheldt estuary, December 1996.



1.91, 4.03 and 5.30 respectively). The removal of  $Cu_{tot}$  observed in the upper estuary ( $S = 4.03$ ) coincided with a maxima in the easily exchangeable concentration of particulate Cu ( $Cu_{lp}$ ) and may be explained by the adsorption of Cu onto the surface of SPM. Interestingly, the increase in  $Cu_{tot}$  concentration coincided with an increase in the  $Zn_{tot}$ . Similarly, a geographically restricted source input of  $Cu_{tot}$  is suggested to explain the increase in  $Cu_{tot}$  as there was little evidence to suggest sediment re-suspension and injection of Cu enriched interstitial waters ( $SPM = 27.14$  mg/l). Previous studies of Cu distribution in the Scheldt estuary have noticed that Cu can become incorporated into sulphide minerals in anoxic regions of the estuary (Zwolsman and Van Eck, 1993; Zwolsman *et al.*, 1997). As previously mentioned, anoxic conditions are prevalent in the sediments and the water column in the upper Scheldt estuary. Owing to the large tidal range ( $\sim 5$  m) and the high river discharges encountered during the winter months, oxygenation of the upper estuarine anoxic sediments was likely. The oxidation of Cu sulphides could account for the high variability and  $Cu_{tot}$  enrichment in the upper estuary.

An interesting feature of the  $Cu_{lab}$  and  $Cu_{flab}$  distribution was that their concentrations were approximately equal in the upper estuary, as previously noted,  $Cu_{lab}$  measurements comprise a fraction of particulate Cu ( $Cu_{lab}$  and  $Cu_{flab} \sim 18$  nM,  $SPM = 369$  mg/l;  $S = 0.44$ ). It was not possible to discern the difference between  $Cu_{lab}$  and  $Cu_{flab}$ , which suggests that rapidly exchangeable particulate Cu concentrations were very low in the upper estuary even where enhanced SPM concentrations were observed. A low fraction of  $Cu_{flab}$  was encountered throughout the estuary and this suggests that Cu was strongly complexed by strong dissolved organic ligands (mean estuarine  $Cu_{org}$  (% of  $Cu_{tot}$ ) =  $66.3 \pm 24.0$  %). The upper estuary has a relatively high concentration of POC, which suggests that strong organic Cu complexes could have been present. Elevated concentrations of  $Cu_{lab}$  were noticed in the mid estuary and suggested an increase the rapidly exchangeable particulate Cu concentration. The increase in  $Cu_{lab}$  coincided with a decrease in the  $Cu_{tot}$  concentration ( $S = 6.87$  to  $15.18$ ) and could be explained by the redistribution of Cu between the

dissolved and particulate phase. Zwolsman *et al.*, (1997) suggested that the co-precipitation of Cu with e.g.  $\text{Mn}^{2+}$  could be responsible for the reduction in  $\text{Cu}_{\text{tot}}$  in the mid estuary. The seaward reduction in particulate Cu and  $\text{Cu}_{\text{lab}}$  measurements could be explained by the mixing of Cu enriched upper estuarine particles with cleaner marine particles.

Figure 4.8 shows the results from Cu natural ligand ( $\text{Cu}_L$ ) titration experiments that were carried on samples from seven locations along the estuary and show the concentration of Cu complexing natural ligands ( $\text{Cu}_L = 54.2 \text{ neq Cu l}^{-1}$ ;  $S = 22.55$ ) and their conditional stability constants ( $\text{Log}_{10} K_{\text{Cu}_L} = 14.24$ ;  $S = 22.55$ ). These data compare well with previous studies where the determination of Cu conditional stability constants and complexing ligand concentrations were undertaken in the mid and lower estuary ( $\text{Cu}_L = 70 \text{ neq Cu l}^{-1}$ ,  $\text{Log}_{10} K_{\text{Cu}_L} = \sim 14$ ;  $S \sim 15$  Gerringa *et al.*, 1996; van den Berg *et al.*, 1987; van den Berg 1984b, d). The highest concentrations of  $\text{Cu}_L$  were encountered in the upper estuary, which coincided with the highest fraction of dissolved  $\text{Cu}_{\text{org}}$ . Furthermore, the strongest Cu binding complexes were encountered in the upper estuary, which would account for the low fraction of  $\text{Cu}_{\text{flab}}$  and  $\text{Cu}_{\text{lab}}$  encountered. The concentration of  $\text{Cu}_L$  and their  $\text{log}_{10} K_{\text{Cu}_L}$  values was higher in the upper estuary than in the mid and lower estuary, where values remained relatively constant. It is suggested that the compounds present at high abundance in the upper estuary comprise a strong ligand group. The group of strong Cu ligands ( $\text{Log}_{10} K_{\text{Cu}_L} = 15.5$ ,  $\text{Cu}_L = 160 \text{ neq Cu l}^{-1}$ ;  $S = 0.44$  to  $5.30$ ) were removed from solution as the salinity increased. Furthermore, at low salinities, stability constants can increase owing to reduced competition by major cations (e.g.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ) compared with seawater. A weaker group of Cu complexing ligands were present at mid and high salinities, which were not strongly influenced by variation of salinity ( $\text{Log}_{10} K_{\text{Cu}_L} = 14.3 \pm 0.12$ ,  $\text{Cu}_L = 69.3 \pm 30.6 \text{ neq Cu l}^{-1}$ ;  $S = 6.87$  to  $30.18$ ). The high concentrations of  $\text{Cu}_L$  observed in the upper estuary could have been derived from run-off of humic substances, direct anthropogenic inputs of organic material, or from injection of sediment  $\text{Cu}_L$  enriched

interstitial waters owing to disturbances of benthic sediments (Gerringa *et al.*, 1996). Very little is known about the behaviour of organic metal complexes. Complexed metal ions have been shown to adsorb on metal oxide surfaces (Bourg and Schindler, 1978; Elliot and Haung, 1979; Davis, 1984). Particles in natural waters are known to be coated with organic molecules (Hunter and Liss, 1982) and it can, therefore, be expected that some metal-organic complexes will also adsorb onto such particles (van den Berg *et al.*, 1987; Gerringa *et al.*, 1996; Apte *et al.*, 1990).

The results obtained from exposure of SPM to a 0.05 M EDTA extraction procedure ( $Cu_{lp}$ ) and total digestion of the residual fraction ( $Cu_{mp}$ ) are presented in Figure 4.8. A high fraction of  $Cu_{lp}$  was encountered in the upper estuary ( $S = 0.44$  to  $5.3$ ). This observation was also noticed in the  $Zn_{lp}$  distribution and it was proposed that elevated particulate Zn could have been encountered owing to the re-suspension of sulphidic benthic sediments. As previously mentioned, Cu can be readily complexed by sulphide upon early diagenesis in the sediments and in the water column. Since the assessment of  $Cu_{lp}$  was undertaken in an oxic environment, it was likely that Cu sulphides would have been oxidised and thus become measurable in the 0.05 M EDTA extraction experiments. The overall downstream reduction in  $Cu_{lp}$  concentration was probably due to the increase in the fraction of relatively Cu depleted particulate material entering the lower estuary. Furthermore, the  $Cu_{lp}$  maximum ( $207.47 \mu\text{g/g}$ ) coincided with the POC maximum ( $7.68 \text{ mg/g}$ ) and suggests that high concentrations of POC could influence the partitioning of Cu between the particulate and dissolved phases. The residual particulate concentration of  $Cu_{mp}$  exhibited low spatial variability throughout the estuary ( $Cu_{mp} = 31.75 \pm 8.82 \mu\text{g/g}$ ) and indicates that processes responsible for the behaviour of particulate Cu ( $Cu_{lp} = 92.62 \pm 49.84 \mu\text{g/g}$ ) were confined to the surface of SPM (Zwolsman *et al.*, 1997).

The partitioning of Cu ( $K_D$ ) between the dissolved ( $Cu_{tot}$ ) and particulate phase ( $Cu_{lp}$ ) at the high and low end of the Scheldt estuary has been presented in Figure 4.6. In contrast to previous studies (Paucot and Wollast, 1997), Cu exhibited a greater affinity for the

dissolved phase at the high salinity end of the estuary ( $\text{Cu Log}_{10} K_D = 4.23$  and  $4.49$ ;  $S = 0.44$  and  $30.18$  respectively). The high concentration of  $\text{Cu}_L$  and hence the dissolved complexation of Cu by strong organic ligands possibly explains the increased tendency for Cu to reside in the dissolved phase in the estuary. Furthermore, the discrepancy between the data sets (this study and Paucot and Wollast, 1997) could be due to differences in analytical procedures and/or different solid phases in the particulate material. Paucot and Wollast, (1997) based their  $K_D$  studies on a extraction procedure based on the analysis of total particulate Cu. However, this study allowed  $K_D$  to be computed using the  $\text{Cu}_{lp}$  concentration which comprised a smaller proportion of particulate Cu.

#### 4.4 Conclusions

Cu and Zn exhibited a similar behaviour and distribution in the Scheldt estuary, where concentrations were enhanced in the upper estuary probably due to oxygenation of sulphidic sediments and mixing of the water column. Dissolved and particulate Cu and Zn concentrations exhibited downstream dilution with relatively metal depleted seawater. However, the mixing of Zn and Cu enriched upper estuarine water with depleted seawater was non conservative which was explained by the organic complexation of Zn and particularly Cu, and the formation of dissolved complexes e.g. chloride.

Maximum concentration of 0.05 M EDTA exchangeable particulate Cu, Zn and Ni broadly coincided with the POC maxima, hence organic coating on SPM were implicated in their adsorption from the dissolved phase. The reduction in values for Cu natural complexing ligands and conditional stability constants indicates that Cu could become removed in the low salinity region ( $S = 0$  to  $\sim 10$ ) owing to the flocculation of dissolved organic Cu complexing ligands. Ni and Co were not as strongly implicated with organic complexation by dissolved ligands as Zn and Cu and this indicates that their distribution was controlled by sources of anthropogenic inputs situated in the upper estuary.

The measurement of unfiltered labile metals gave an indication of the redistribution of metals between the dissolved and particulate phases. For example, in the upper estuary the  $Cu_{lab}$  concentration was equal to the  $Cu_{flab}$  concentration, which indicates that the concentration of rapidly exchangeable particulate Cu was not measurable in the upper estuary. In contrast,  $Cu_{lab}$  values were up to double the concentration of  $Cu_{flab}$  in the mid estuary and this indicates the possible adsorption of rapidly exchangeable Cu onto SPM in the mid estuary. The measurement of Co, Ni, Zn and Cu in unfiltered waters were undertaken on-board ship, which suggest that unfiltered labile measurements of metals could be more widely undertaken in estuarine studies yielding novel measurements of metal partitioning between the dissolved and particulate phase.

#### **4.5 Future work**

Owing to the opportunistic nature of the survey it was only possible to undertake one survey of the Scheldt Estuary. It would be interesting to undertake a seasonal evaluation of trace metal speciation of Zn, Cu, Co and Ni, which would require at least 4 further cruises. Of particular interest would be an evaluation of Cu and Zn natural ligand titration experiments during periods of enhanced primary production (e.g. Spring and Autumn), which could elucidate the influence of organic exudes on the dissolved Zn and Cu speciation. Owing to the difficulty in measuring low dissolved Co concentrations in estuaries there remains a limited database and understanding of the distribution of Co in the Scheldt estuary. Hence, it would be advantageous to undertake further Co distribution studies in the estuary to better define its biogeochemical behaviour.

## 5 Distribution of dissolved Co and Ni in North and South Atlantic surface waters

### 5.1 Introduction

In contrast to the estuarine environment, Co and Ni are present at very low concentrations in open oceanic waters of the North and South Atlantic (Ni ca 2.5 nM and Co ca 0.04 nM). Due to the logistical and technical challenges associated with acquiring databases for open ocean Ni and Co concentrations, there remains a poor understanding of their biogeochemical fate and affect on marine biota (Landing *et al.*, 1995). Systematic measurements of Ni and Co concentrations in surface waters of the North and South Atlantic will enhance our understanding of their behaviour and distribution. Previous trace metal studies of the Atlantic have been restricted to distinct oceanic provinces, which have provided useful insights into the behaviour of these dissolved trace metals but have been geographically limited (Hydes *et al.*, 1986; Landing *et al.*, 1995; Westerlund and Ohman, 1991; Yeats, 1993). Furthermore, an assessment of trace metal fluxes from anthropogenic sources can only be assessed after baseline Ni and Co concentrations have been established. The work presented in this chapter will aid our understanding of background Co and Ni distributions and abundances.

Co and Ni are among the essential micro nutrients involved in the growth of marine organisms. Indeed, previous research has indicated that Co and Ni have a shallow remineralisation cycle like phosphate and nitrate, as well as an apparently deeper cycle which would be responsible for the correlation with silicate in old deep waters of the Pacific and Indian Oceans (Sclater *et al.*, 1976; Bruland, 1980; Danielsson, 1980; Saager *et al.*, 1992). Co is an important element in many essential biological compounds, notably the central atom of vitamin B12. The low concentrations of this element in the marine environment may have as a consequence that it is a limiting nutrient in some oceanic

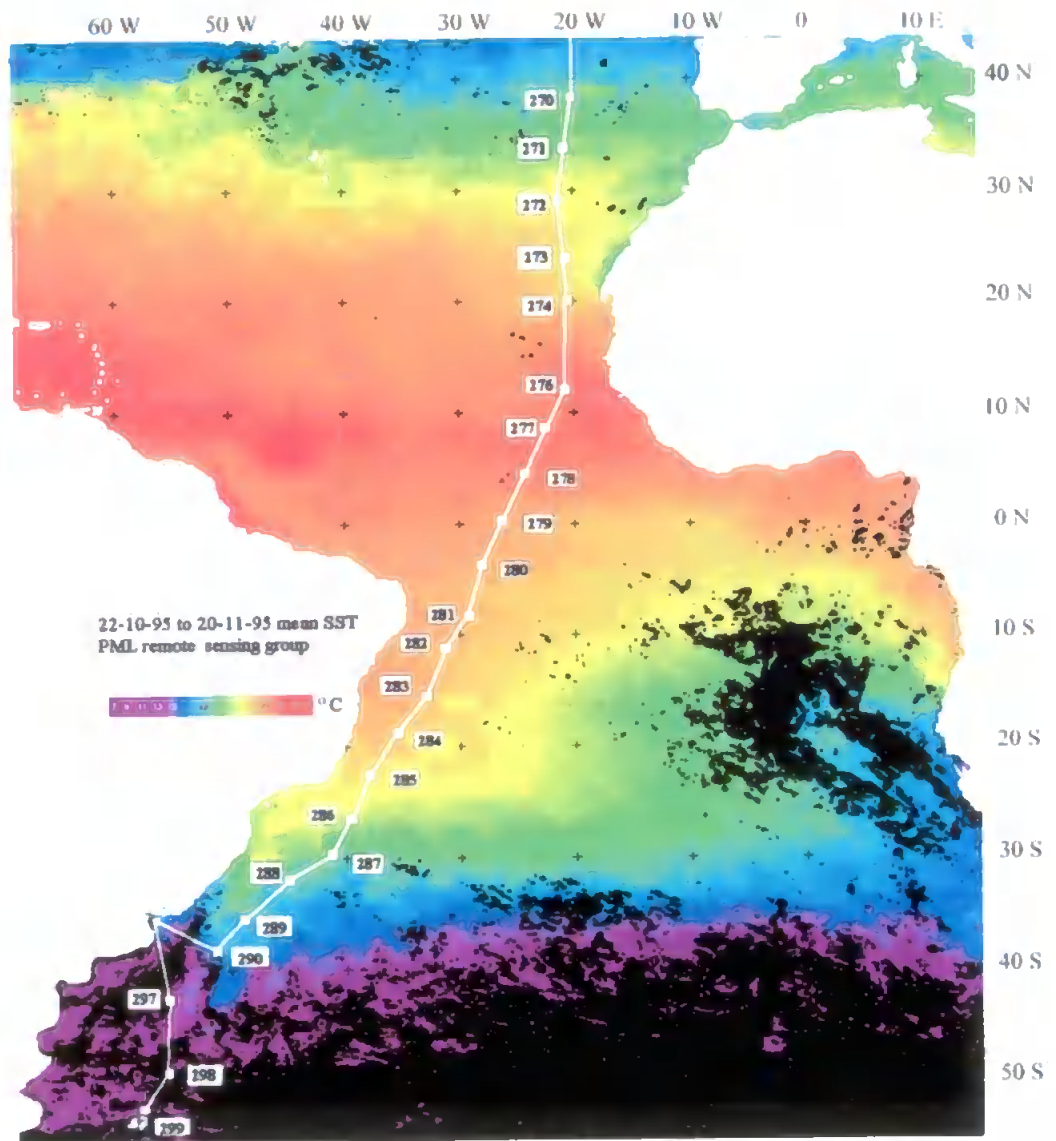
conditions (Knauer *et al.*, 1982). Co and Ni can be present in the form of highly stable complexes with dissolved organic compounds and possibly associated with humic acids in coastal waters; early diagenesis can cause mobilisation of Co and Ni into pore water even for oxic environments (Hamilton, 1994; Huynh-Ngoc *et al.*, 1989).

The aims of the research presented in this chapter were:

1. Generate a unique high quality data set for Ni and Co from samples collected in the open oceanic environment.
2. Investigate the behaviour and distribution of Ni and Co in the mixed layer.
3. Evaluate the input and removal mechanisms affecting Co and Ni in the Atlantic Ocean.

Adsorptive cathodic stripping voltammetry (AdCSV) was utilised for the determination of dissolved Ni and Co in the Atlantic waters (Pihlar *et al.*, 1981; van den Berg, 1989; Vega and van den Berg, 1997). Advantages of using AdCSV for the detection of dissolved Co and Ni include direct measurement of the analyte without prior pre-concentration and high instrument sensitivity. Discrete seawater samples were collected during an Atlantic Meridional Transect (AMT), which was located between the Southampton (UK) and the Falkland Islands (UK) (Fig. 5.1). The data series obtained from this study of dissolved Co and Ni can be compared with future investigations of trace metal distributions in Atlantic surface waters. These types of data could become useful for an estimation of background Co and Ni concentrations especially if mineral (hydrocarbon) exploration close to the Falkland Islands will commence.

Figure 5.1 Atlantic Ocean monthly averaged satellite Sea Surface Temperature (SST) observations. A temperature scale is provided showing warm waters in red and cooler waters in blue. The Atlantic Meridional Transect (AMT) route has been included and numbers represent sampling locations.



## 5.2 Methodologies

### 5.2.1 Sample collection and treatment

Unfiltered surface water samples (~7 m) were collected at approximately 5° (latitude) intervals during a north to south meridional transect of the Atlantic Ocean. The cruise was part of a Natural Environment Research Council sponsored program (AMT-3), which followed a route between Southampton, United Kingdom (42 54.0° N 05 41.4° W, 22-09-96) and the Falkland Islands, United Kingdom (51 55.9° S 57 53.6° W, 24-10-96). Figure 5.1 shows the AMT-3 transect and the satellite sea surface temperature (SST) for the period 22-10-95 to 20-11-95. The SST observations indicate that warmest waters were encountered in equatorial regions, with coolest waters at higher latitudes. In addition to surface water collection, 41 samples were obtained from 5 stations at depths varying between 0 m and 200 m.

Samples were collected from a Conductivity Temperature Depth (CTD) rosette that held 10 PTFE lined, Niskin bottles (10 l). The CTD unit was fitted with conductivity, temperature and depth probes capable of real time measurements. The Niskin bottles were electronically activated at depths of between 5 m and 200 m (Morley *et al.*, 1988). Furthermore, a Coulter Particle Counter (CPC) was fitted to the CTD, which gave an indication of the relative abundance of suspended particulate material (SPM). The CPC measurements were based on an arbitrary scale of light scatter that was relative to SPM abundance.

Sub sample aliquots were taken by Mr Bowie, from the Niskin bottles in thoroughly acid cleaned 250 ml HDPE bottles. After 3 rinses with sample the bottles were filled to the brim, closed and sealed inside re-sealable polythene bags (Chapter 2). Within ca. 30 minutes of collection the samples were opened in the ship's laboratory in a class 100 laminar flow unit and acidified to pH 2 using quartz distilled HCl (9 M; 1 µl per 1 ml). The

samples were subsequently re-sealed and placed in the dark for transport to Plymouth University (United Kingdom) laboratories. No sample filtration was undertaken during the AMT cruises in order to reduce risk of sample contamination. Low SPM concentrations were expected in the samples and therefore the omission of a filtration step was deemed to have a negligible effect on the trace metal concentrations. The validity of this strategy was supported by a similar study in the Weddell Sea, Antarctica (Westerlund and Ohman, 1991). A comparison of total dissolved Co, Ni, Cu, Pb and Zn concentrations obtained by these workers in filtered and unfiltered water samples showed no significant differences. Hence, the metal analysis of unfiltered water was considered as the dissolved concentration.

#### *5.2.2 Total dissolvable Ni and Co analysis of discrete seawater samples*

On arrival at Plymouth University (after ca. 6 months), the samples were transferred to a class 1000 clean room facility in preparation for dissolved trace metal analysis. The risk of sample contamination was further minimised by undertaking sample handling inside a class 100 laminar flow unit. Measurements of total dissolved Ni and Co was undertaken on discrete samples using AdCSV (Pihlar *et al.*, 1981; Vega and van den Berg, 1997). The types of AdCSV ligands, buffers and instrument settings used to determine dissolved Co and Ni concentrations have been discussed in Chapter 2. To avoid interferences from dissolved organic compounds sub aliquots of acidified sample were exposed to UV irradiation prior to Ni and Co analysis (Chapter 2). The system was operated in manual batch mode as described in Chapter 2. Due to the low volume of sample available (total allocation 60 ml), each metal determination was undertaken using 7 ml of UV digested sample. To ensure good analytical reproducibility analysis was performed in duplicate on separate sub aliquots of sample and if the difference between the values for a given analysis was greater than 5 %, the samples were re-analysed. Furthermore, to monitor

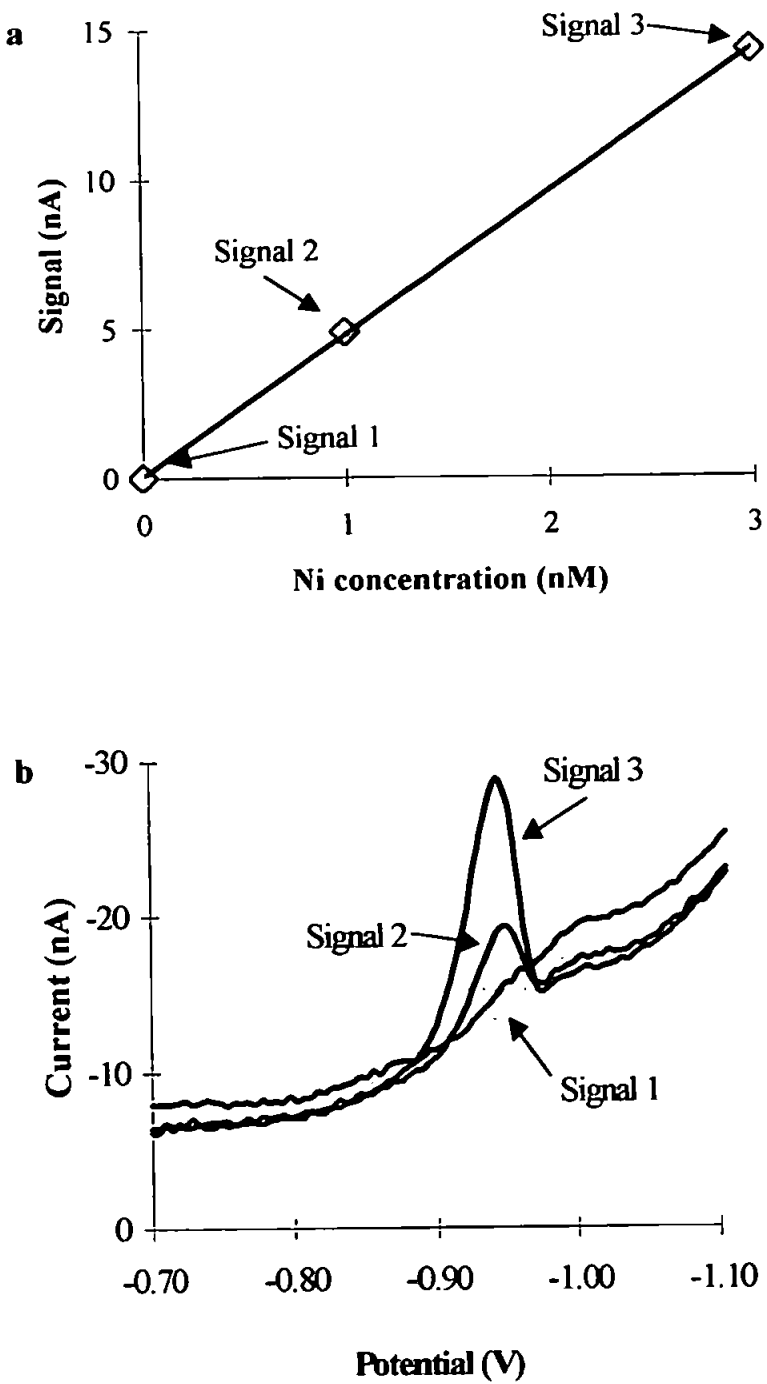
instrument and reagent cross contamination, analyses of Milli-Q water and reagent blanks were undertaken after every fifth sample (described in Chapter 2). Procedural blank determinations of Ni and Co were undertaken and the results showed that blank concentrations were below the limit of detection by AdCSV (Chapter 2). In case that the Ni and Co concentrations were above Ni = 0.2 nM and Co = 5 pM, the analysis was postponed until the contamination source was eradicated. AdCSV analytical procedures are summarised in Chapter 2. The limits of detection for Ni (determined using the Pihlar *et al.*, 1981 methodology) and Co (determined using the Vega and van den Berg, 1997 methodology), sensitivity and reproducibility are summarised in Table 5.a.

Table 5.a Analytical characterisation of Ni and Co determinations by AdCSV (LOD, sensitivity and reproducibility). This characterisation was undertaken using filtered, acidified (pH 2), UV digested aged seawater collected in the Southern North Sea (14-12-96).

| Element | Concentration | LOD  | RSD (%) | Observations | Sensitivity<br>(nA/nM) |
|---------|---------------|------|---------|--------------|------------------------|
| Co (pM) | 452           | 15   | 0.74    | 10           | 152                    |
| Ni (nM) | 4.1           | 0.19 | 1.5     | 10           | 9.41                   |

Figure 5.2 shows the results of a typical determination of Ni in Milli-Q water. Analysis generally comprised of 12 voltammetric measurements and the voltammetric peak heights

Figure 5.2 Results of the determination of Ni in Milli-Q water using 0.4 mM DMG and 10 mM HEPES (Chapter 2). (a) observed signal (0 nM Ni added = signal 1), and signal increase in the presence of 1 nM (signal 2) and 3 nM (signal 3) internal standard additions of Ni, (b) voltammogrammes in the presence of 0 nM, 1 nM and 3 nM Ni.

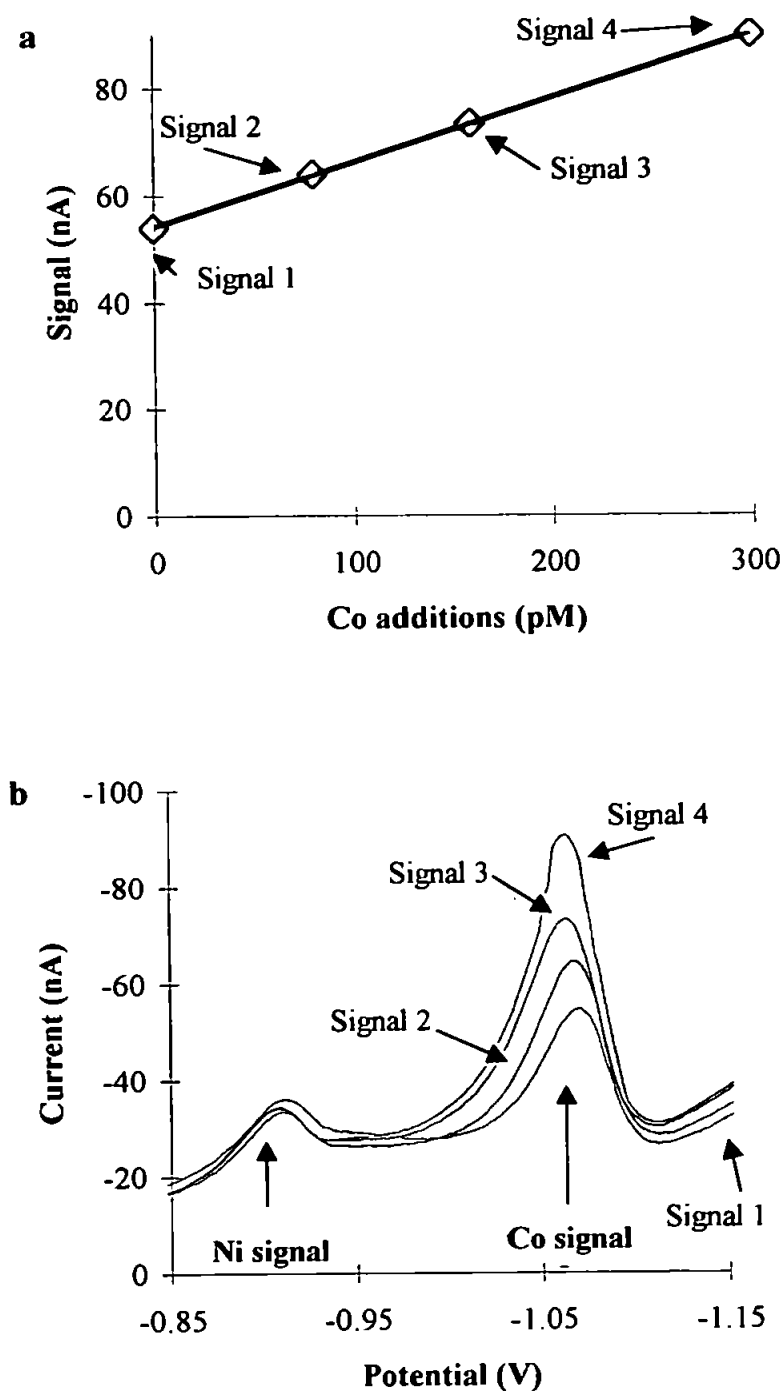


were used to compute analyte concentrations: (a) Three scans of the sample (Milli-Q water). The concentration of Ni was so low that a signal was not visible (Signal 1); (b) Following the addition of Ni metal standard solution (which increased the Ni concentration by 1 nM) a further three voltammetric measurements were performed (Signal 2); and, (c) After a further addition of Ni (which increased the Ni concentration by a further 2 nM) the mean of 3 additional measurements of peak height was calculated. The 3 mean signal peak height values were plotted against the concentration of Ni added (Fig. 5.2). Figure 5.2.b shows the increase in signal generated by a 1 nM addition of Ni (5 nA/nM, voltammetric conditions are summarised in Chapter 2), thus measurements of Ni at low nM concentration can be performed reliably with a low degree of uncertainty on the measurement. Figure 5.3, shows the results of the determination of Co in sea water collected from the Southern North Sea (Belgium) which was used for the initial analytical optimisation experiments. Co concentrations were calculated from peak height as described for Ni above. Figure 5.3.b, shows an additional peak (ca -0.9 V) that was identified as Ni by making a standard addition. Early optimisation experiments suggested that it was possible to simultaneously measure Ni and Co. However, at very low Ni concentrations (ca <3 nM), the quantification of the Co (where Co < 0.5 nM) signal interfered with the Ni signal and consequently it was not possible to fully quantify Ni. Therefore, simultaneous measurements of Ni and Co may be possible in polluted or coastal waters, but not in oceanic waters containing very low metal concentrations.

### *5.2.3. Supporting environmental data series*

The work discussed in this chapter was part of a collaborative research programme which was designed to analyse Atlantic surface water for a number of environmental variables in order to gain a better understanding of the processes responsible for the biogeochemical fate of trace metals. This chapter will discuss the fate of Co and Ni within Atlantic surface

Figure 5.3 Determination of Co in seawater after 3 internal standard additions of Co standard solutions (added Co; signal 1 = 0 pM, signal 2 = 80 pM, signal 3 = 160 pM and signal 4 = 300 pM). (b) voltammogrammes show the signal increase after Co standard additions.



waters. It will also give an overview of other trace metal and nutrient data that was collected by other participants within the AMT-3 program in order to assist in the interpretation of the Ni and Co distributions. Mr Bowie, undertook the analysis for total dissolvable Al and Fe at the University of Plymouth (Bowie *et al.*, 1998; Hydes and Liss, 1976). Nutrient data (Phosphate, Nitrite, Silicate and Chlorophyll-a) was analysed and supplied courtesy of Mr Malcolm Woodward, from the Plymouth Marine Laboratories.

### 5.3. Results

#### 5.3.1. Analysis of certified reference materials NASS-4 and CASS-2

Certified reference seawaters NASS-4 (open oceanic seawater) and CASS-3 (nearshore seawater) supplied by the National Research Council (Canada) were analysed to verify the accuracy of the Co and Ni measurements. 10 sub-aliquots of reference water were UV digested prior to the determination of Ni and Co using AdCSV (Chapter 2). Total dissolved Ni and Co were measured in separate 7 ml sub-samples and the analyte concentration was calculated from the increase in signal measured after two internal standard additions (Chapter 2). The results of the analysis are presented along with the certified concentrations in Table 5.b. The data were in close agreement with the certified values.

#### 5.3.2. Co distribution in Atlantic sub surface waters

The nature of metal measurements in these samples requires considerations since the samples were not filtered prior to acidification and storage (pH 2 for 1 year). Previous trace metal analysis of open ocean waters has been conducted on filtered and non-filtered waters. In case the SPM concentrations were very low (ca 200 µg/l), the authors concluded that filtration was not necessary (Powell *et al.*, 1995; Yeats *et al.*, 1995; Westerlund and

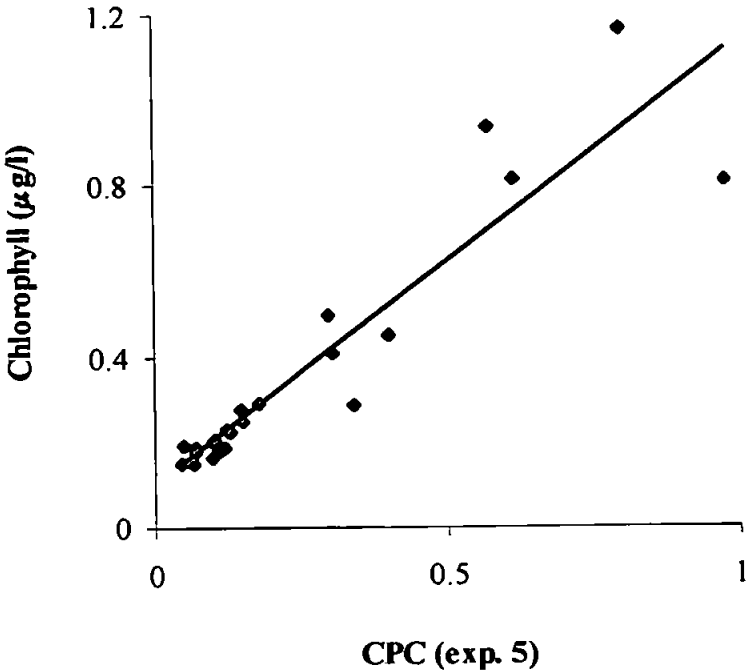
Table 5.b Analysis of total dissolved Ni and Co concentrations in certified reference materials NASS-4 and CASS-2.

| Reference material | Ni (nM)<br>Certified | Ni (nM)<br>Observed | Co (pM)<br>Certified | Co (pM)<br>Observed |
|--------------------|----------------------|---------------------|----------------------|---------------------|
| NASS-4             | 3.9 ± 1.5            | 4.1 ± 0.2           | 150 ± 17             | 158 ± 7.2           |
| CASS-3             | 6.6 ± 1.1            | 7.1 ± 0.3           | 696 ± 150            | 817 ± 25            |

Ohman, 1991). To avoid sample contamination, the samples collected during the AMT surveys were not filtered. However, high levels of atmospheric particulate deposition were encountered during the AMT surveys and may have resulted in dissolution of particulate trace metals in the samples, which could have affected the dissolved trace metal concentration. Indeed, under the conditions of storage (pH 2 for 1 year) the exchangeable fraction of the particulate metals could have been released into the dissolved phase. Thus metal determinations undertaken on AMT samples, describe the dissolved concentration of metals plus any particulate trace metals liberated in 0.01 M HCl. Therefore, metal measurements for the current study will be described as the total dissolvable (TD) concentration (e.g. TD-Co and TD-Ni). In some oceanic environments, atmospheric inputs contribute to the SPM load (Hamilton, 1994; Chester and Johnson, 1971). The total dissolvable trace metal determinations could, therefore, include dissolved and easily exchangeable trace metals from atmospheric particles.

It has been suggested that in most open ocean environments the majority of particles constitute fragments of marine organisms (Gorden *et al.*, 1998; Yeats *et al.*, 1995). Figure 5.4 shows the relationship between SPM (inferred from CPC measurements) and chlorophyll-a, which gives an indication of the abundance of primary producers (e.g.

Figure 5.4 Relationship between chlorophyll-a and suspended particulate material (inferred from CPC counts) in Atlantic surface waters (42° N and 52° S).



phytoplankton). The data are characterised by a positive linear relationship ( $R^2 = 0.86$ , slope = 1.04, intercept = 0.1,  $n = 24$ , at the 99 % confidence interval) the statistical relationship supports the suggestion that in ocean open waters of the North and South Atlantic, SPM is predominantly of biological origin. Therefore, the TD-metal measurements in these open ocean environments represent the dissolved fraction plus easily exchangeable particulate metals predominantly of biogenic origin. However, the degree of scatter increases for the relationship between CPC and chlorophyll-a at high values (chlorophyll-a  $\sim 0.5 \mu\text{g/l}$ ; CPC  $\sim 0.5 \times 10^5$ ). This could have been due to changes in the fraction (increase) of terrigenous material owing to enhanced aeolian deposition, since the high values of chlorophyll-a and CPC were generally localities close to South America and North West Africa.

The surface water concentrations (at 7 m depth) of TD-Co are shown in Figure 5.5, together with the mean ocean TD-Co concentration and the upper and lower standard deviation (SD) boundaries (mean = 40 pM, SD = 13,  $n = 28$  Table 5.c). The mean ocean TD-Co concentration and SD were calculated without the values from station 274 as this was a region of very high TD-Co concentrations attributed to high inputs of atmospherically derived particulate material (see below). In order to establish a broad characterisation of TD-Co distribution in the Atlantic ocean, values significantly above the nominal SD were considered regions of metal enrichment and Co concentration below the mean SD were considered Co depleted zones. The surface water concentrations of TD-Co exhibited an inhomogeneous distribution, TD-Co values ranged between 110 pM ( $20.05^\circ \text{S}$   $20.37^\circ \text{W}$ ) and 20 pM ( $12.45^\circ \text{S}$   $32.08^\circ \text{W}$ ). The majority of the measurements ( $n = 30$ ) fell close to the mean value ( $42 \pm 14 \text{ pM}$ ).

It is clear from Figure 5.5 that four distinct features may be observed in the TD-Co profile:

- (1) TD-Co depleted surface waters in the Northeast Atlantic (mean TD-Co = 32 pM between  $42^\circ \text{N}$  and  $24^\circ \text{N}$ );
- (2) Enrichment occurs in surface waters off the North West African coast ( $20^\circ \text{N}$  to  $5^\circ \text{N}$ , mean TD-Co = 69 pM);
- (3) Homogeneous TD-Co

Figure 5.5 Total dissolvable Co distribution in Atlantic surface waters (7 m depth). The mean oceanic Co concentration (pM) has been plotted in addition to the standard deviation.

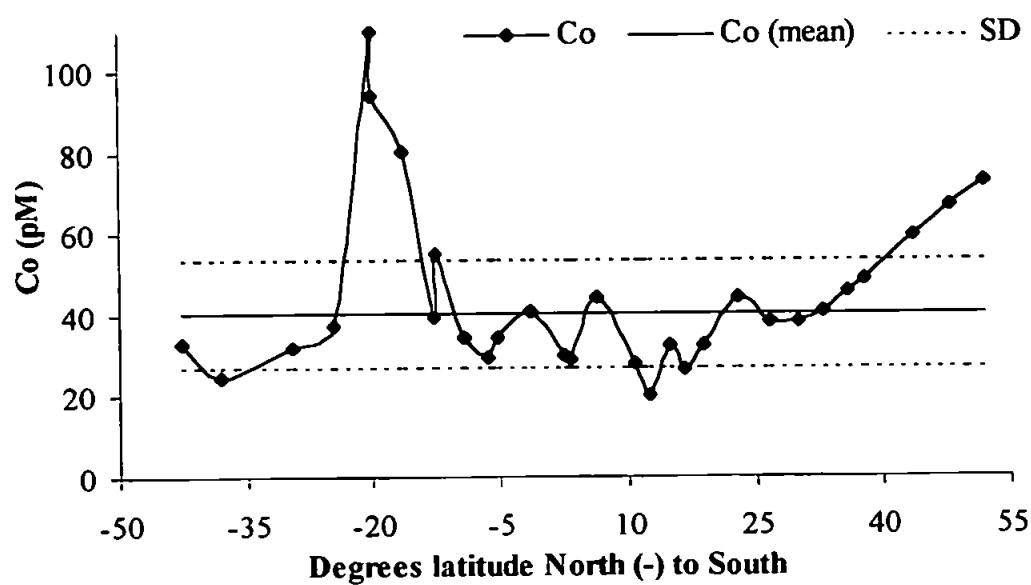


Table 5.c Summary of TD-Co, TD-Ni, TD-Al and TD-Fe concentrations in the Atlantic surface waters (at 7 m depth).

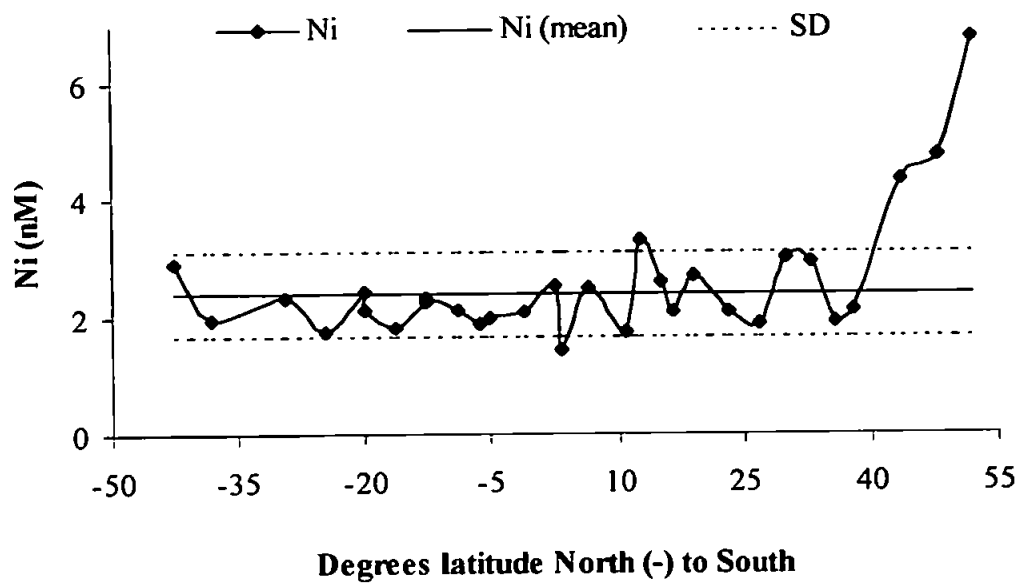
| Element           | Mean | Standard<br>Deviation | RSD<br>(%) | Max. | Min. | Observations |
|-------------------|------|-----------------------|------------|------|------|--------------|
| <i>TD-Co (pM)</i> | 42   | 14                    | 34         | 93   | 20   | 34           |
| <i>TD-Ni (nM)</i> | 2.4  | 0.7                   | 29         | 6.8  | 1.4  | 34           |
| <i>TD-Al (nM)</i> | 24.2 | 9.0                   | 37         | 50   | 11   | 34           |
| <i>TD-Fe (nM)</i> | 2.2  | 1.0                   | 45         | 5    | 0.7  | 22           |

distribution was observed in the central Atlantic with a mean value of 34 pM, which was slightly below the mean ocean value of 40 pM (5° N to 26° S); and, (4) The Western South Atlantic is characterised by high TD-Co concentrations, which increase in a southerly direction from ~40 pM to 73 pM (mean TD-Co = 53 pM) between 29° S and 52°S.

5.3.3. *TD-Ni distribution in Atlantic sub surface waters*

The total dissolvable metal measurements have been defined in the previous section. Concentrations of total dissolvable Ni (TD-Ni) in surface waters (at 7 m depth) has been plotted along with mean TD-Ni concentration, and the upper and lower SD boundaries (Fig. 5.6). The SD and mean TD-Ni were calculated from the surface water TD-Ni data

Figure 5.6 Total dissolvable Ni distribution in Atlantic surface waters (7 m depth). The mean oceanic Ni concentration (nM) has been plotted in addition to the standard deviation.



series. However, TD-Ni values in excess of 5 nM were excluded from the calculation as these values were considered unusually high for open ocean environments (mean TD-Ni = 2.57 nM, SD = 0.73, n = 29). In contrast to the strong variations in the concentration of TD-Co, TD-Ni showed a more homogenous distribution in Atlantic surface waters. The most notable feature observed in the TD-Ni distribution was a clear trend of TD-Ni enrichment in the South West Atlantic (TD-Ni = 2.2 nM at 35° S to 6.5 nM at 55° S).

#### *5.3.4. TD-Al and TD-Fe distribution in the Atlantic*

The total dissolvable Al (TD-Al) and total dissolvable Fe (TD-Fe) distributions are plotted with their mean concentration and SD (Fig. 5.7 and 5.8). In order to obtain mean oceanic concentration for TD-Al and TD-Fe values in excess of previously reported open ocean maximum concentrations were excluded from the calculations (Table 5.c e.g. values in excess of 50 nM (TD-Al) and 5 nM (TD-Fe). TD-Al, TD-Fe and TD-Co show similar surface water profiles with coinciding maxima. Briefly, TD-Fe and TD-Al exhibits: (1) Low concentrations in the region of the eastern north Atlantic between ca 42° N to 24° N; (2) Strong enrichment off the Northwest African coast (ca 20° N to 5° N); (3) Surface water enrichment in the Southwest Atlantic (TD-Fe = 4.5 nM, TD-Al = 48 nM at 50° S). The TD-Ni profile does not shows similarity with TD-Al, TD-Fe and TD-Co with the exception of enhanced concentrations in the region of the Southwest Atlantic (ca 29° S and 52° S).

#### *5.3.5. Ortho-phosphate, Nitrite, Silicate and Chlorophyll-a distributions in the Atlantic*

The behaviour of dissolved nutrients (Ortho-phosphate, Nitrite and Silicate) in open ocean systems is linked to the metabolic cycle of primary producers. Surface waters (<200 m depth) can become depleted in nutrients as they are rapidly scavenged by phytoplankton

Figure 5.7 Total dissolvable Al distribution in Atlantic surface waters (7 m depth). The mean oceanic Al concentration (nM) has been plotted in addition to the standard deviation.

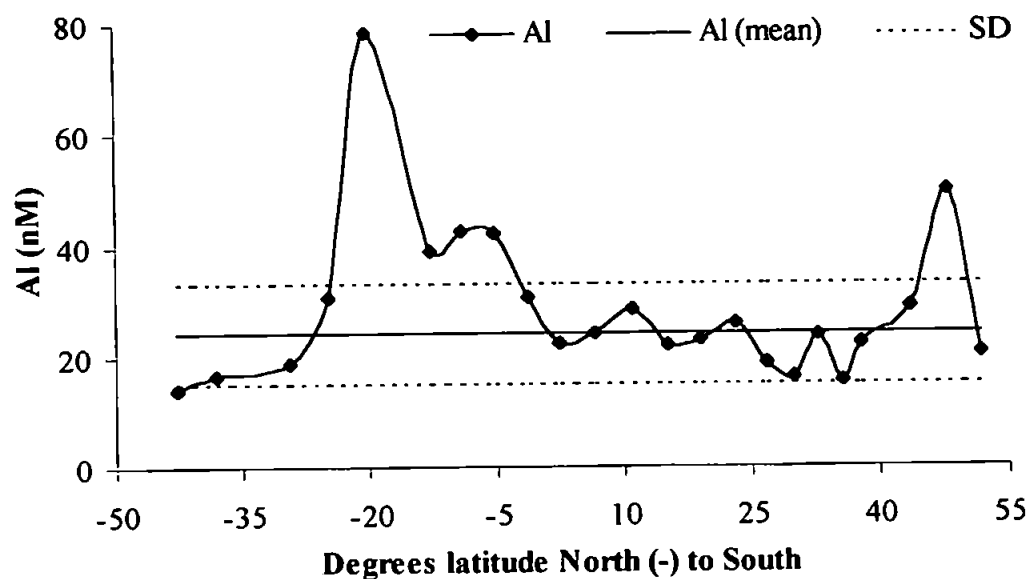
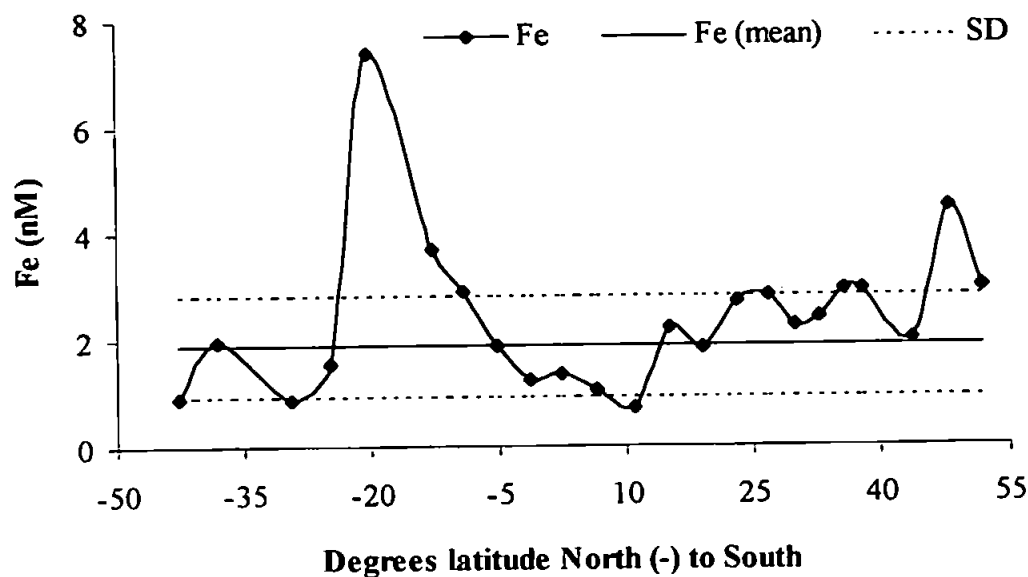


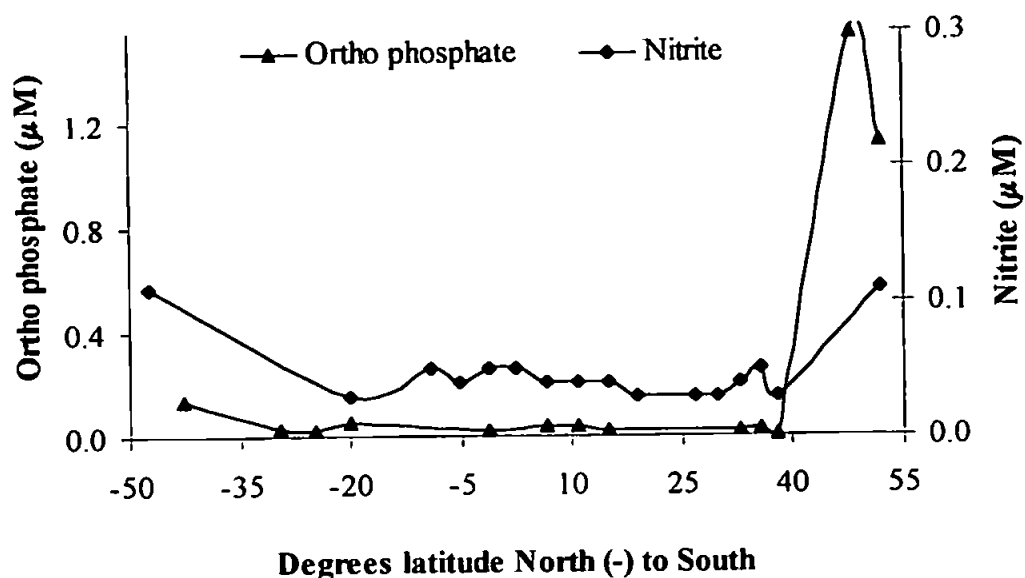
Figure 5.8 Total dissolvable Fe distribution in Atlantic surface waters (7 m depth). The mean ocean Fe concentration has been plotted in addition to the standard deviation.



(Saager *et al.*, 1992). Supply of nutrients to surface waters comes from bottom water upwelling and degeneration of biomass (Hydes *et al.*, 1986; Saager *et al.*, 1997). Furthermore, the majority of biomass is concentrated within photosynthesising organisms. The measurement of chlorophyll-a can give a good indication of the standing stock of primary producers.

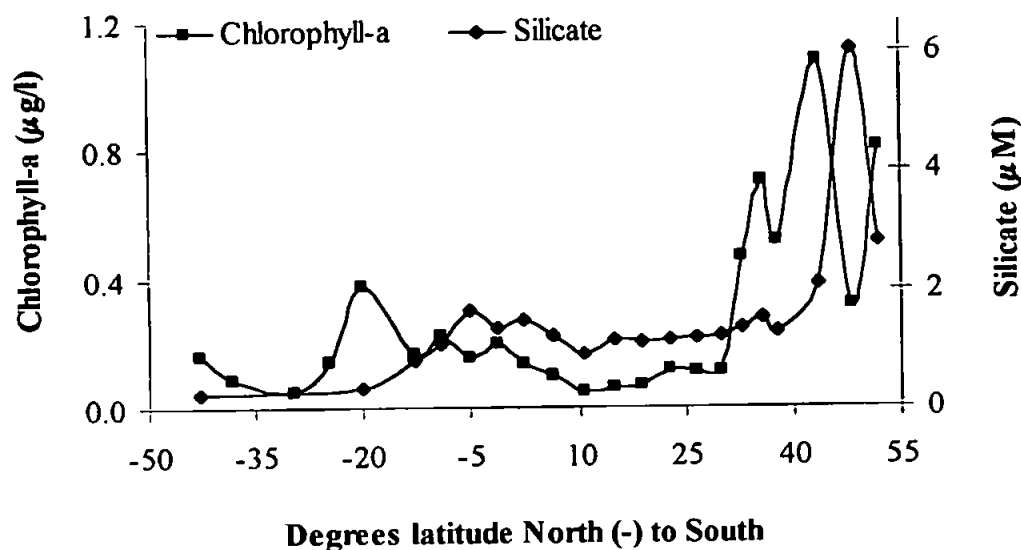
Mean oceanic concentrations of nitrite and ortho phosphate were  $0.03 \mu\text{M}$  ( $n = 24$ ) and  $0.13 \mu\text{M}$  ( $n = 24$ ) respectively (Fig. 5.9). Their concentration profiles suggest surface water depletion in all but the high latitude zones (between  $50^\circ \text{N}$  to  $47^\circ \text{N}$  and  $29^\circ \text{S}$  and  $52^\circ \text{S}$ ). In these zones the concentration of ortho phosphate and nitrite showed an increase (ortho phosphate =  $\sim 1.5 \mu\text{M}$ ,  $48^\circ \text{S}$ , nitrite =  $\sim 0.12 \mu\text{M}$ ,  $47^\circ \text{N}$  and  $52^\circ \text{S}$ ). Similarly, chlorophyll-a showed enrichment at high latitudes and chlorophyll-a enrichment was observed close to the Northwest coast of Africa ( $20^\circ \text{N}$   $20^\circ \text{W}$ ) (Fig. 5.10). Silicate exhibited low

Figure 5.9 Ortho phosphate and nitrite concentrations of Atlantic surface waters (7 m depth).



concentrations (ca 0.1  $\mu\text{M}$ ) in the North Atlantic ( $42^\circ\text{ N}$  to  $24^\circ\text{ N}$ ) and in the central Atlantic ( $5^\circ\text{ N}$  to  $26^\circ\text{ S}$ ) silicate levels increased to a mean value of 1.3  $\mu\text{M}$ .

Figure 5.10 Chlorophyll-a and silicate concentrations of Atlantic surface waters (7 m depth).



5.3.6. Physical oceanography

In addition to the salinity, temperature and SPM measurements, which were conducted in situ (Fig. 5.11 and 5.12), monthly averaged satellite sea surface temperature (SST) and monthly averaged chlorophyll density satellite observations were utilised to identify potentially different water masses and upwelling zones (Legechis, 1978; Olson *et al.*, 1988) (Fig. 5.1, Fig. 5.13 and Fig. 5.14). The SST images were the most recent available (22-10-95 to 20-10-95). Since ocean SST exhibits low inter-annual variation and the observations were conducted during the same season, these images were useful for our

Figure 5.11 Surface water (7 m depth) salinity and temperature values of sampling localities in the Atlantic Ocean.

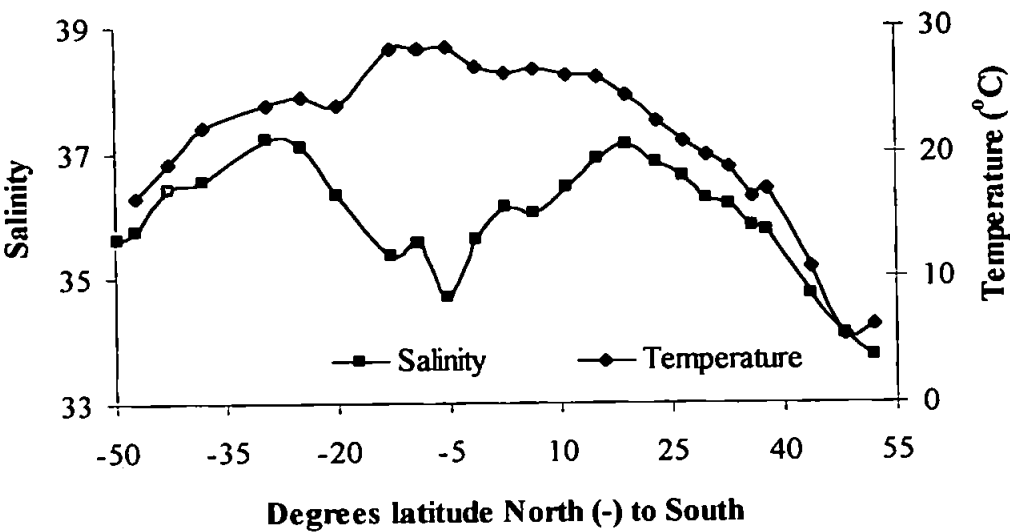
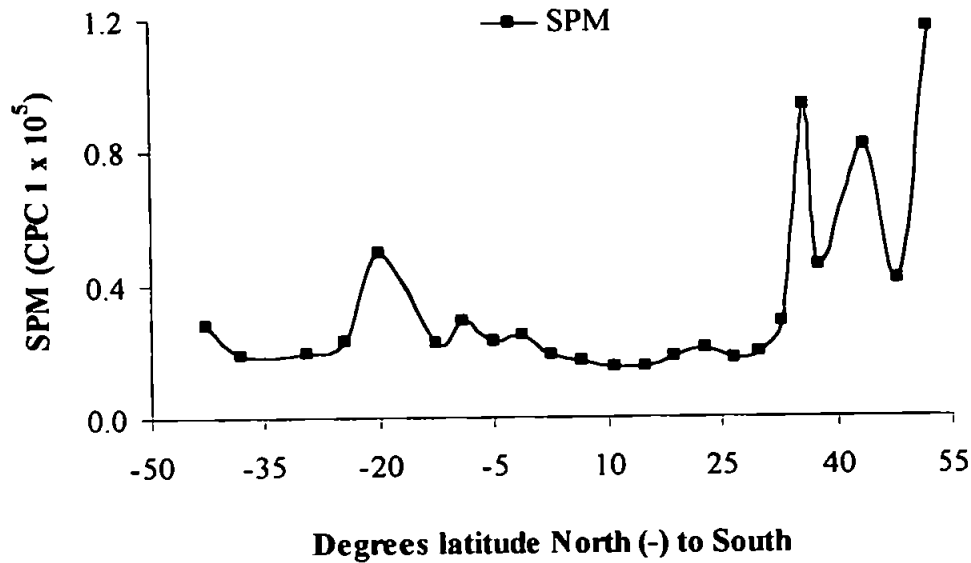


Figure 5.12 Depth of water column and inferred surface water (7 m depth) SPM encountered at sampling locations in the Atlantic Ocean.



5.13 Mixed layer (0 to 200 m depth) mean daily primary production (chlorophyll). Satellite image taken from SeaWif, Global Ocean Studies (GOS) for the period of April 1996 and October 1996.

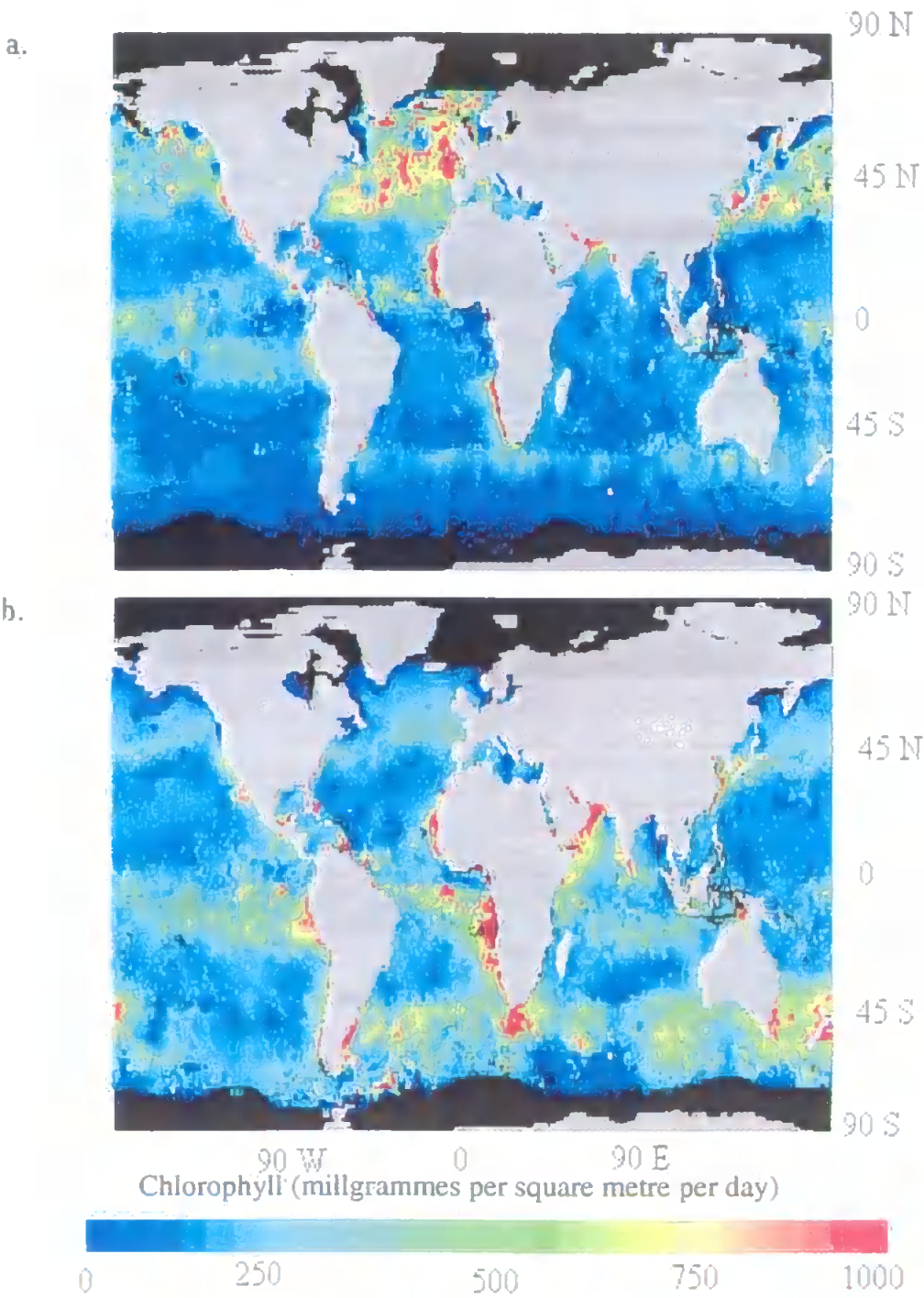


Figure 5.14 NOAA AVHRR images of the Brazil confluence region for (a) 11-10-1984 and (b) 11 -02-1985. A temperature scale is provided along side each image (warm waters in red; cool waters in blue).



purposes. Similarly, the ocean chlorophyll density images were not from the period of sampling and give an indication of the chlorophyll distribution experienced during April and October, which are expected to be seasonally similar (Antaoine *et al.*, 1996; Eppley, 1972; Sathyendranath *et al.*, 1995). From the SST images it was possible to identify 5 regions of potentially different water bodies which the AMT-3 transect passed through. Water masses and their boundaries in the North and South Atlantic have also been identified by Legeckis, (1978).

#### *5.3.7 Trace metal (TD-Co, TD-Ni, TD-Fe and TD-Al), nutrient and hydrographic measurements in the upper mixed layer (0 to 200 m depth)*

Samples were collected from depths of up to 200 m at 5 stations in the Atlantic Ocean (Fig. 5.15 to 5.19). The upper most 200 m of the water column is known as the upper mixed layer and is the zone of strongest advective mixing caused by wind action. Furthermore, the upper mixed layer experiences the highest light intensities hence most biological productivity is concentrated in the upper 200 m of the water column. The activity of phytoplankton and bacteria in the upper water column has profound effects on nutrient and trace metal concentrations either by direct assimilation, complexation of metals with dissolved organic exudates or by adsorption processes (Saager *et al.*, 1997; Westerlund and Ohman, 1991; Yeats *et al.*, 1995; Tappin *et al.*, 1993; Hydes *et al.*, 1986; Morely *et al.*, 1993). Nutrients are commonly depleted in the upper mixed layer, as are some trace metals (Fe, Co, Zn, Ni, Mn and Cu), which exhibit nutrient like behaviour in open ocean environments with surface depletion and enhanced concentrations in deeper waters (Gordon *et al.*, 1998; Saager *et al.*, 1992; Knauer *et al.*, 1982).

Station 273 (24° N 21°W) was located at 42° N 24° N (Northeast Atlantic open ocean gyre). Station 274 (20° N 20° W) was located in the Northwest African upwelling region (20° N to 5° N). Two depth profiles (stations 281, 6° S 29° W and 285, 22° S 36° W) were

Figure 5.15 Water characteristics of the upper mixed layer (0 to 200 m depth) at station 273 (24° N 21 ° W). (a) Al and Co, (b) Fe and Ni, (c) Silicate and phosphate, (d) Chlorophyll-a and nitrite, (e) salinity and (f) temperature.

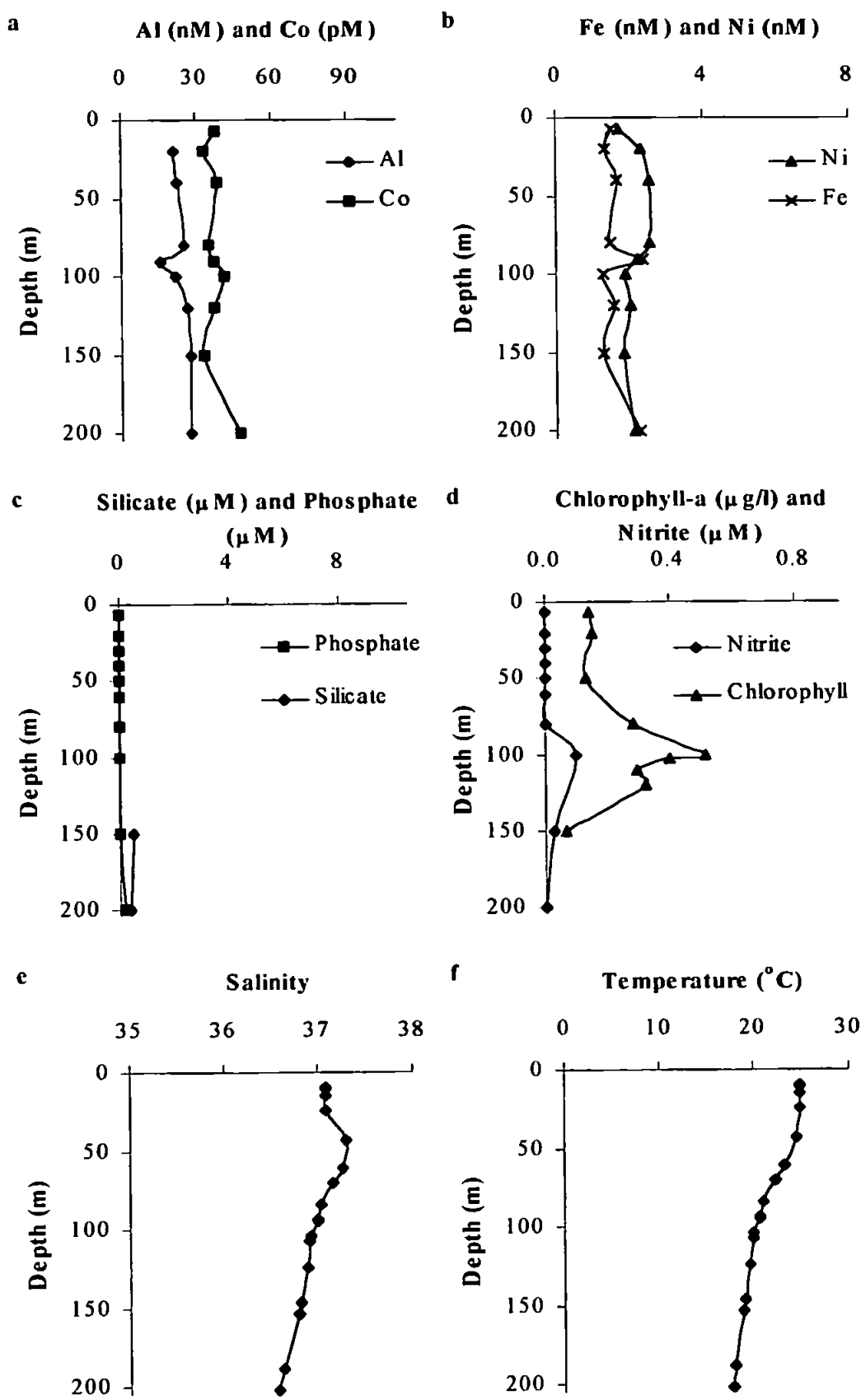


Figure 5.16 Water characteristics of the upper mixed layer (0 to 200 m depth) at station 274 (20° N 20° W). (a) Al and Co, (b) Fe and Ni, (c) Silicate and phosphate, (d) Chlorophyll-a and nitrite, (e) salinity and (f) temperature.

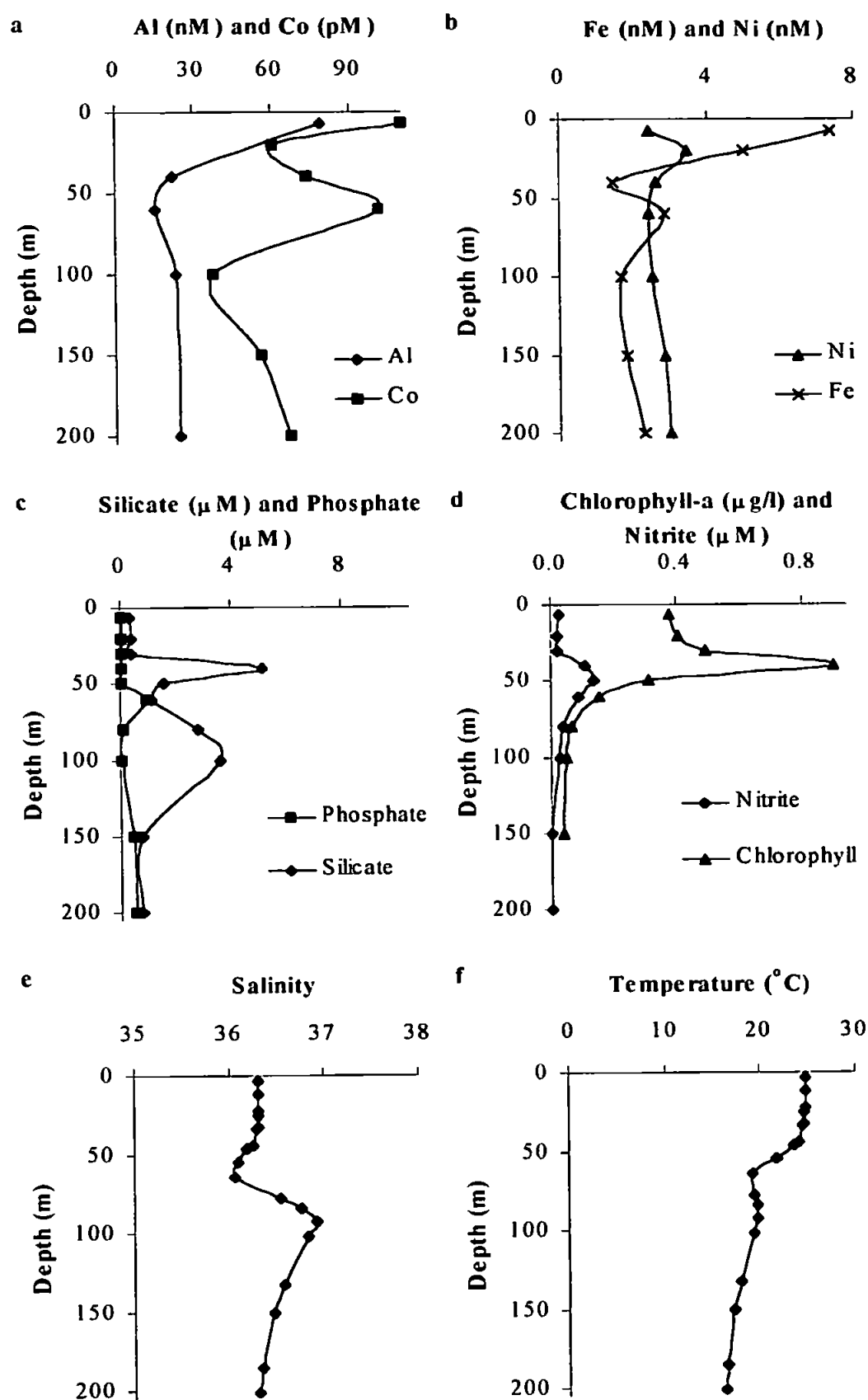


Figure 5.17 Water characteristics of the upper mixed layer (0 to 200 m depth) at station 281 (6° S 29° W). (a) Al and Co, (b) Fe and Ni, (c.) Silicate and phosphate, (d) Chlorophyll-a and nitrite, (e) salinity and (f) temperature.

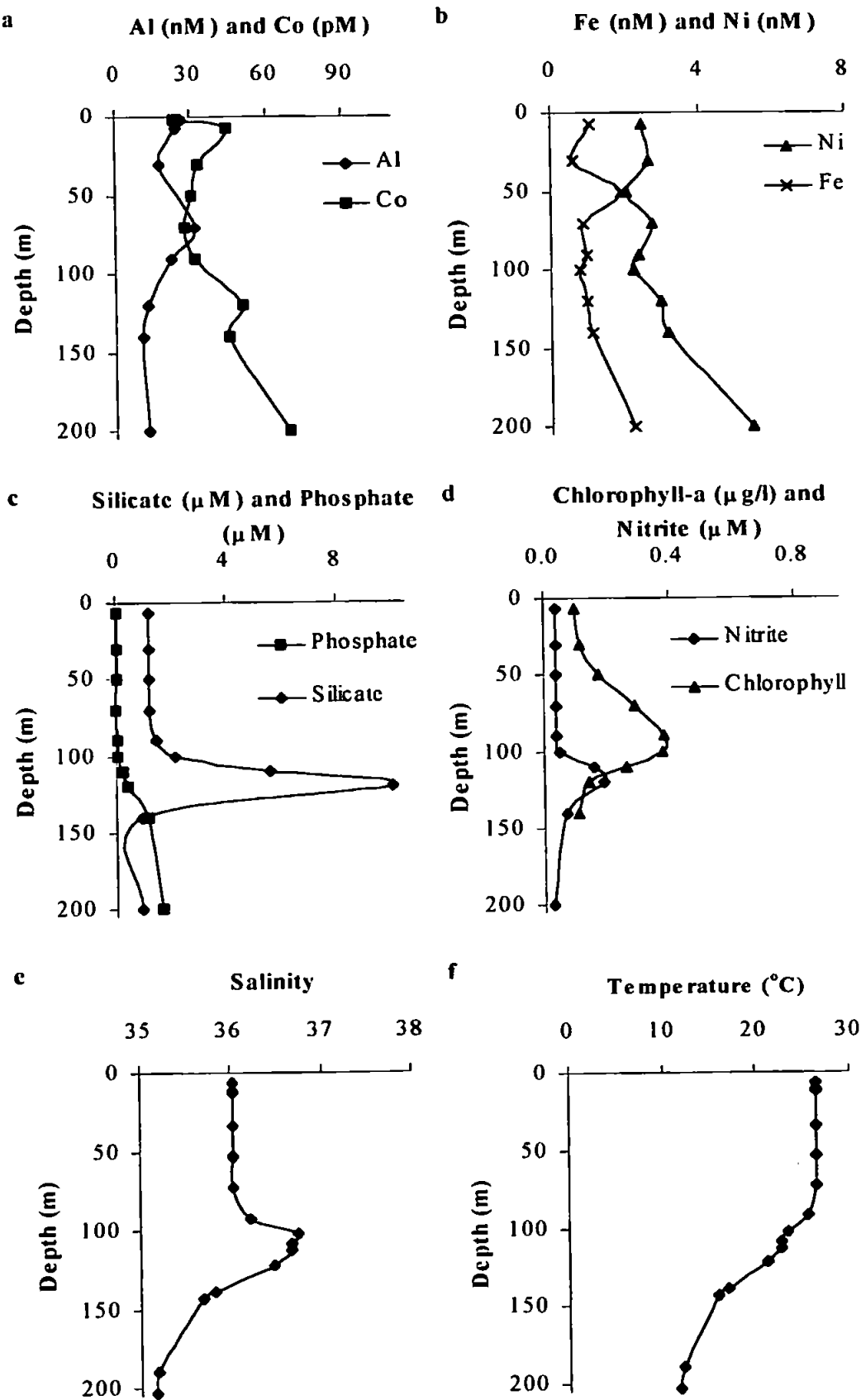


Figure 5.18 Water characteristics of the upper mixed layer (0 to 200 m depth) at station 285 (23° S 37° W). (a) Al and Co, (b) Fe and Ni, (c) Silicate and phosphate, (d) Chlorophyll-a and nitrite, (e) salinity and (f) temperature.

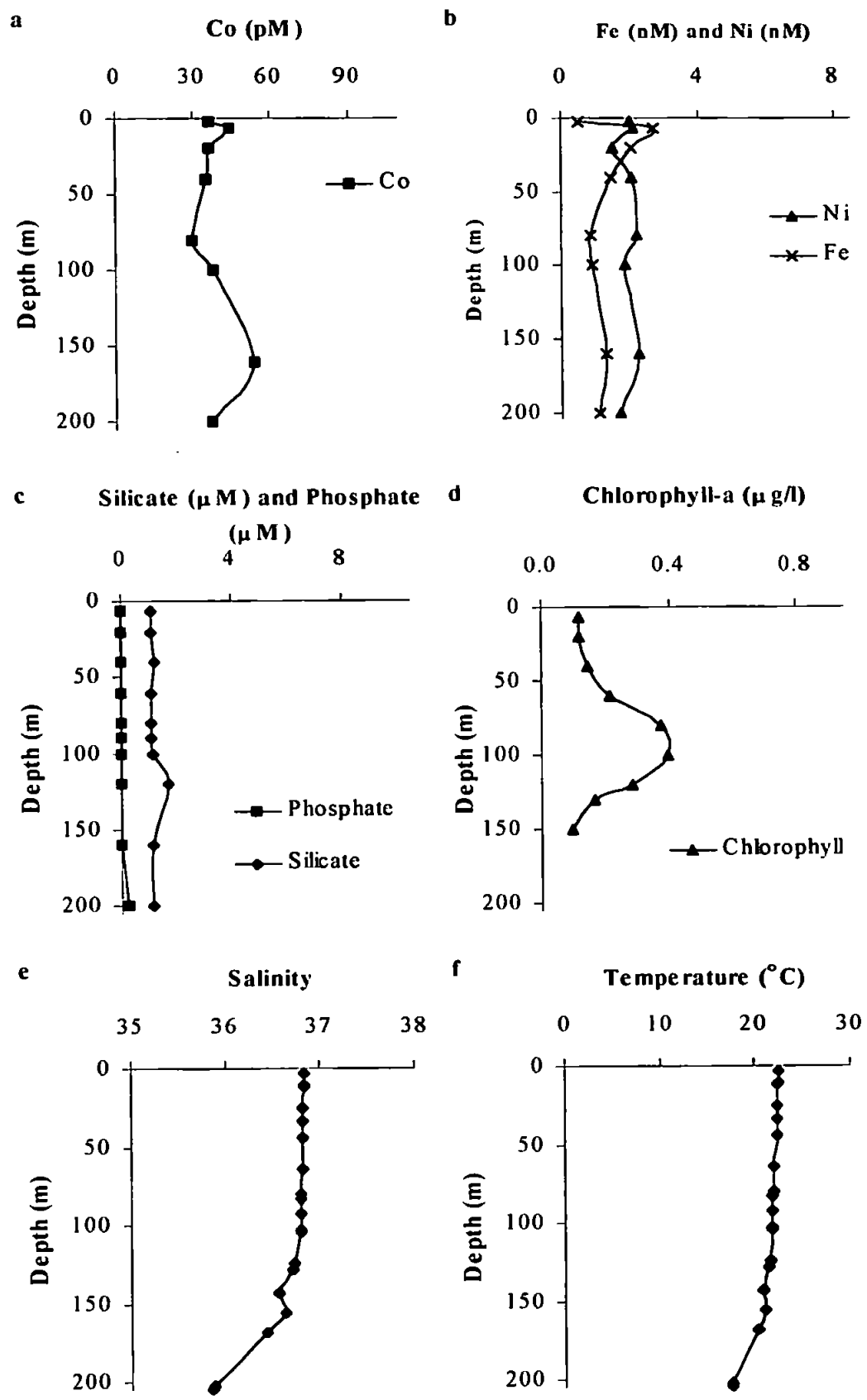
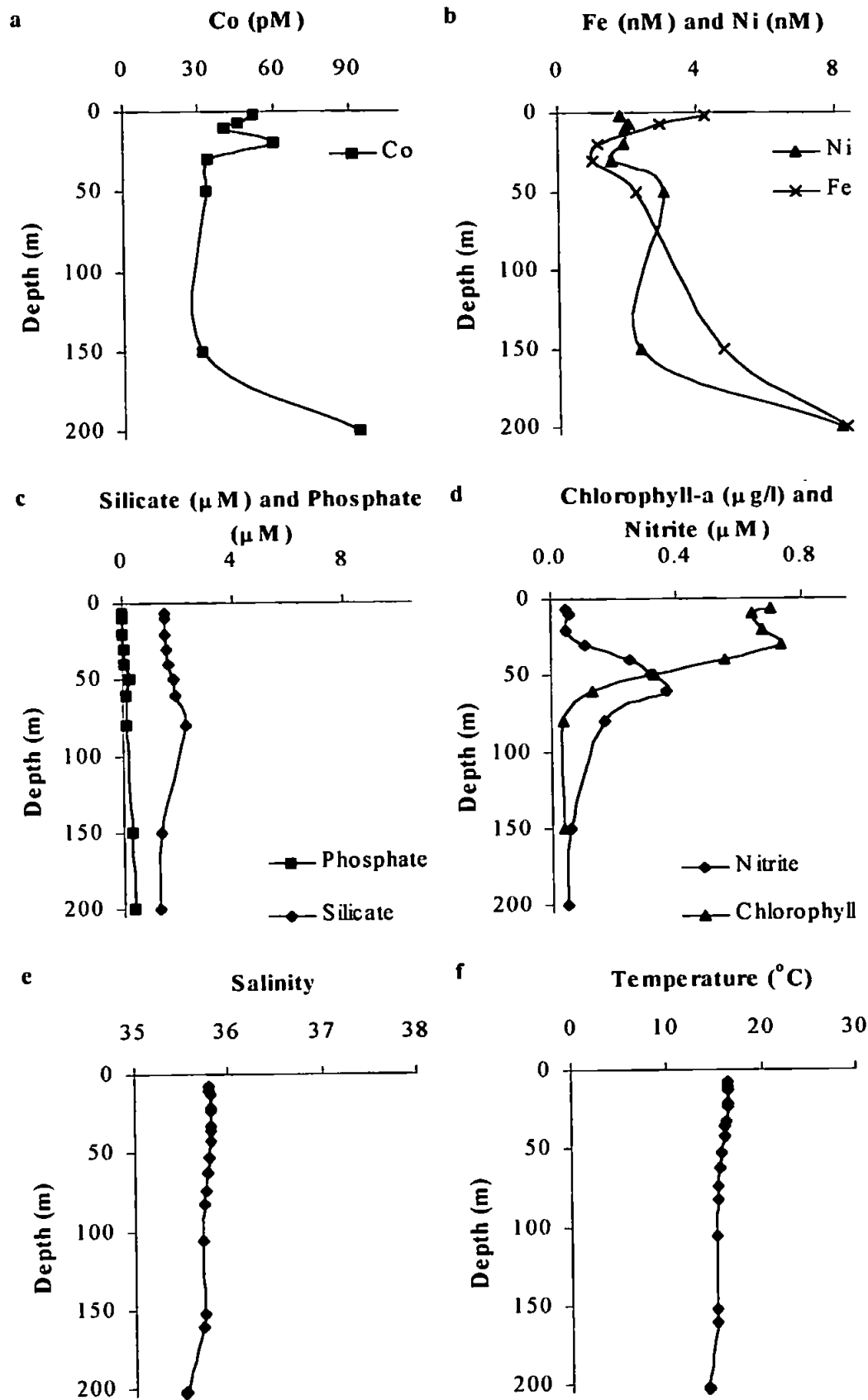


Figure 5.19 Water characteristics of the upper mixed layer (0 to 200 m depth) at station 289 (36° S 49° W). (a) Co, (b) Fe and Ni, (c) Silicate and phosphate, (d) Chlorophyll-a and nitrite, (e) salinity and (f) temperature.



obtained in the Central and South West Atlantic (province 4, 5° N to 26° S). Station 289 (35° S 49° W) was situated at the confluence between the Falkland Island current and the Brazilian current (29° S to 52° S). Figures 5.15, 5.16, 5.17, 5.18 and 5.19, present trace metal, nutrient and hydrographic measurements performed on samples collected from CTD depth casts undertaken at station; 273, 274, 281, 285 and 289, respectively.

## 5.4 Discussion

### 5.4.1 Comparison with other open oceanic studies

Table 5.d summaries dissolved trace metal (Co, Ni, Fe and Al) concentrations in surface waters of the world's oceans. These data show that open oceanic trace metal concentrations are relatively constant in the surface waters. TD-Co concentrations reported in this chapter were consistent with previous TD-Co studies in open ocean waters (Tappin *et al.*, 1993; Yeats, 1993; Westerlund and Ohman, 1991). Similarly, TD-Ni concentrations were in agreement with previously reported values for the North and South Atlantic (TD-Ni = ~2-3 nM Yeats *et al.*, 1995; Tappin *et al.*, 1993; Martin and Thomas, 1994; Westerlund and Ohman, 1991; Yeats, 1993; Saager *et al.*, 1997).

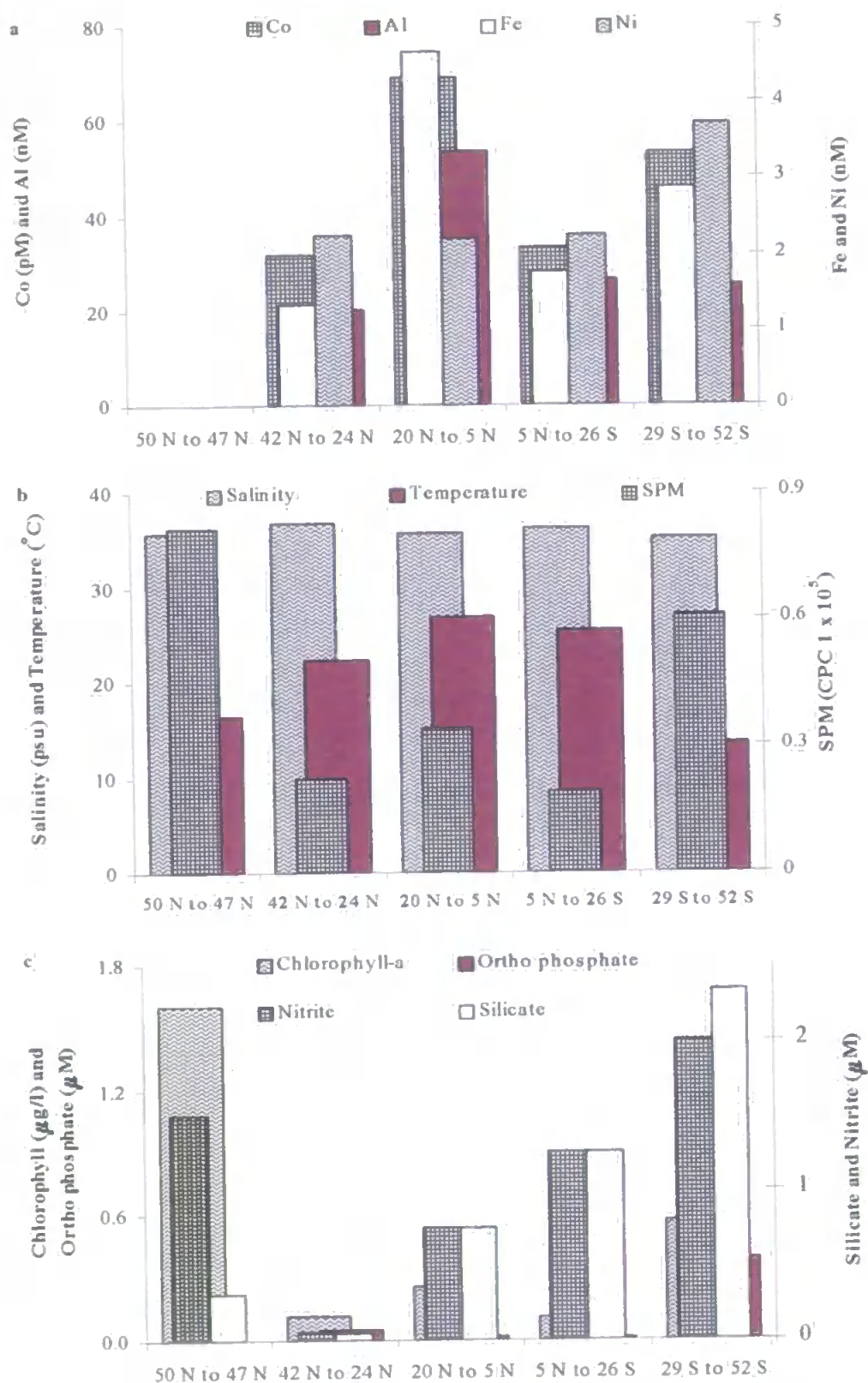
### 5.4.2. The distribution of Ni and Co in the Atlantic Ocean

The surface Atlantic water masses were characterised using the combined hydrographic, satellite, trace metal and nutrient data (Fig. 5.20). The chemical and hydrographic features of the provinces are described below and summarised in Table 5.e. The provinces may have encompassed more than one water mass, and hence represent regions where the water chemistries (e.g. trace metals; nutrients) and physical variables (e.g. water temperature; SPM) were similar. The boundaries are representative for autumn 1996 as the samples

Table 5.d Trace metal (Co, Ni, Fe and Al) concentrations in the world surface oceanic waters.

| Location                                | Source                         | Co<br>(pM) | Ni<br>(nM) | Fe<br>(nM) | Al<br>(nM) |
|-----------------------------------------|--------------------------------|------------|------------|------------|------------|
| <i>North and South Atlantic</i>         | This study                     | 42         | 2.4        | 2.2        | 24         |
| <i>North Atlantic</i>                   | Landing <i>et al.</i> , (1995) | 40         | 2.5        | 1.5        |            |
| <i>Atlantic</i>                         | Yeats <i>et al.</i> , (1995)   |            | 2.5        |            |            |
| <i>Northeast Atlantic</i>               | Hydes <i>et al.</i> , (1986)   |            | 2.4        |            | 10         |
| <i>Northeast Atlantic</i>               | Saager <i>et al.</i> , (1997)  |            | 1.7 to 3   |            |            |
| <i>Northeast Atlantic SW Approaches</i> | Tappin <i>et al.</i> , (1993)  | 240        | 3.3        |            |            |
| <i>Weddell Sea, Antarctic</i>           | Westerlund and Ohman, (1991)   | 30 to 40   | 6 to 7     |            |            |
| <i>Indian Ocean</i>                     | Morley <i>et al.</i> , (1993)  | 45         | 2.1        | 1.7        |            |
| <i>Indian Ocean</i>                     | Saager <i>et al.</i> , (1992)  |            | 2.5        |            |            |
| <i>Equatorial Pacific</i>               | Gordon <i>et al.</i> , (1998)  | 20         | 2.7        | 0.07       |            |

Figure 5.20 Averaged surface water characteristics of Atlantic Ocean divided into provinces based on water chemical and physical similarities: (a) TD-metals, (b) hydrographic information and (c) nutrient concentrations.



| Province                               | Location       | Oceanographic Features                       | Station    | TD-Fe (nM)       | TD-Co (nM)       | TD-Ni (nM)      | TD-Al (nM)     | Silicate (μM)    | Ortho Phosphate (μM) | Nitrite (μM)     | Chlorophyll-a (μg/l) | SPM (CPC 1 x 10 <sup>5</sup> ) | Salinity | Temp (°C) |
|----------------------------------------|----------------|----------------------------------------------|------------|------------------|------------------|-----------------|----------------|------------------|----------------------|------------------|----------------------|--------------------------------|----------|-----------|
| <i>South West Approaches</i>           | 50° N to 47° N | Continental Shelf edge                       | 266 to 268 | N/A              | N/A              | N/A             | N/A            | 0.31             | N/A                  | 1.5              | 1.6                  | 0.81                           | 36       | 16        |
| <i>North East Atlantic</i>             | 42° N to 24° N | Open ocean Gyre                              | 269 to 273 | 1.32<br><b>L</b> | 31.9<br><b>L</b> | 2.2             | 20<br><b>L</b> | 0.05<br><b>L</b> | 0.05                 | 0.06<br><b>L</b> | 0.11                 | 0.22                           | 37       | 22        |
| <i>West African Margin</i>             | 20° N to 5° N  | Mauritanian Upwelling                        | 274 to 277 | 4.66<br><b>H</b> | 69.0<br><b>H</b> | 2.2<br><b>L</b> | 54<br><b>H</b> | 0.75             | 0.02<br><b>L</b>     | 0.75             | 0.26                 | 0.34                           | 36       | 27        |
| <i>Central and South West Atlantic</i> | 5° N to 26° S  | Open ocean Gyre                              | 278 to 286 | 1.76             | 33.2             | 2.2             | 27             | 1.25             | 0.01                 | 1.25             | 0.11                 | 0.19                           | 36       | 25        |
| <i>Falkland Island Current</i>         | 29°S to 52° S  | Brazilian and Falkland Island Current mixing | 287 to 299 | 2.86             | 53.4             | 3.7<br><b>H</b> | 25             | 2.33<br><b>H</b> | 0.39<br><b>H</b>     | 2<br><b>H</b>    | 0.57                 | 0.61                           | 35       | 14        |

**L** = Lowest mean

**H** = Highest mean

Table 5.e Mean chemical and physical characteristics of Atlantic surface water provinces.

were collected within one month and as such would be comparable considering the seasonal changes of the surface ocean. Seasonal factors influence the bio chemical variables of the water masses, especially at high latitudes and hence temporal variability in the boundaries between the provinces identified could exist. The distribution of nutrients and trace metals in the 5 regions of the Atlantic Ocean identified in Table 5.e are discussed below.

#### 1. The South West Approaches (50° N to 47° N).

No trace metal sampling was carried out in this region (Table 5.e) during our survey, however, the region has been extensively studied (Saager *et al.*, 1997; Hydes *et al.*, 1986; Tappin *et al.*, 1993). This region is characterised by enhanced concentrations of trace metals, nutrients, chlorophyll-a and SPM and low temperature and salinity. The high trace metal and nutrient concentrations could be accounted for by the close proximity to continental Europe and it's associated anthropogenically derived metals and nutrients, and nearby European continental shelf. It has been reported that bottom water currents upwelling at the edge of the European shelf cause disturbance of benthic shelf sediments and results in major inputs of nutrients and trace metals to the region (Tappin *et al.*, 1993; Saager *et al.*, 1997). A boundary for the southern extent of this province was drawn at ca 47° N, the existence of this boundary was supported by the satellite SST and chlorophyll images which show depleted chlorophyll concentrations and higher temperatures to the south.

#### 2. North East Atlantic Oligotrophic Gyre (42° N to 24° N)

Mean TD-Co and TD-Ni concentrations in province 2 (Table 5.e) were 31.9 pM and 2.2 nM respectively. Hydes *et al.*, (1986) studied trace metal (Ni = 2.4 nM and Al = 10 nM) and nutrient (ortho phosphate = 0.08 µM and silicate = 0.7 µM) concentrations in the region and their values were in agreement with those obtained from this study (TD-Ni =

2.2 nM, TD-Al = 20 nM, ortho phosphate = 0.05  $\mu$ M and silicate = 0.05  $\mu$ M; Hydes *et al.*, 1986). McCartney, (1992) and Tsuchiya *et al.*, (1992) have previously identified the Northeast Atlantic open ocean gyre system. The surface waters in this system are characterised by low nutrient, chlorophyll-a, SPM and trace metal concentrations and high salinity and temperature (Table 5.e). The region is isolated from landmasses and therefore, inputs of aeolian material is low thus unlikely to enhance metal and nutrient concentrations. The net inputs of metals and nutrients were likely to be very low and surface waters could become depleted due to biological uptake and particle scavenging. Metal and nutrient enrichment could be achieved by lateral mixing of the surface waters, however, mixing of water masses of different density and temperatures occurs very slowly and therefore the increase of metals and nutrients achieved by lateral mixing is likely to be low.

### 3. North West African margin (20° N 5° N)

TD-Co and TD-Ni concentrations of surface oceanic waters in the vicinity of North West Africa were 69.0 pM and 2.2 nM respectively (Table 5.e). The AMT-3 transect passed close to the African continental landmass where high inputs of atmospheric particulate material have been observed (Powell *et al.*, 1995; Helmers and Schrems, 1995; Saager *et al.*, 1997). Field observations indicated that at station 274 (20° N 20° W) there was a visible high abundance of aeolian material, and the deck of the ship was covered a film of dust (personal communication, A. Bowie). Similarly, Powell *et al.*, (1995) observed enhanced aeolian deposition and a corresponding TD-Fe maximum during a sampling campaign in the same area (TD-Fe ~7 nM, SPM ~600  $\mu$ g/l). Furthermore, for this area Duce and Tindale, (1991) calculated an annual particle deposition rate of 1000 mg/m<sup>2</sup> yr, which is high for open ocean systems. This observation may explain the enhanced concentration of trace metals observed in this region (up to TD-Co = 110 pM, TD-Fe = 7.38 nM and TD-Al = 78.5; Figs. 5.5, 5.7 and 5.8). In contrast, the TD-Ni concentration

remained unchanged at station 274, which is probably due to the nature of the particulate material. Indeed, Yeats *et al.*, (1993) analysed corresponding filtered and unfiltered water samples and concluded that measurable Ni concentrations were not significantly different. Since no sample filtration was undertaken during our study, it was not possible to estimate the potential contribution of particulate metal to the TD-metal measurements. In addition to the enhanced trace metal concentrations, elevated concentrations of chlorophyll-a were observed in this region. The region is considered part of the Northwest African upwelling system and this could account for the high productivity (Powell *et al.*, 1995; Yeats *et al.*, 1995; Saager *et al.*, 1997). However, enhanced nutrient concentrations (nitrite  $\sim 0.5 \mu\text{M}$ , ortho phosphate =  $1.0 \mu\text{M}$ , silicate =  $1.5 \mu\text{M}$ , Powell *et al.*, 1995), which are commonly associated with regions of upwelling were not observed.

The boundaries of the North West African Margin region were decided after consultation of the water chemistry data, and the SST and Chlorophyll satellite images (Fig. 5.1 and 5.13). These images show a monthly averaged composite. The region is characterised by elevated temperatures and chlorophyll concentrations that support the boundaries identified from the chemical analysis and underway temperature and salinity measurements.

#### 4. Central and South West Atlantic ( $5^\circ \text{N}$ to $26^\circ \text{S}$ )

Mean TD-Co and TD-Ni concentrations were  $33.2 \mu\text{M}$  and  $2.2 \text{ nM}$ , respectively. The province comprises surface waters of the central Atlantic. Samples taken from stations 278 ( $05^\circ \text{N } 24^\circ \text{W}$ ) and 279 ( $01^\circ \text{N } 25^\circ \text{W}$ ) were the most remote regions from continental landmasses visited. Consequently, very low inputs of terrestrially derived nutrients and metals were expected. The system was characterised by very low concentrations of trace metals and nutrients (table 5.e). The chlorophyll-a concentrations measured from the discrete samples and the satellite chlorophyll images indicate very low productivity (chlorophyll-a =  $0.11 \mu\text{g/l}$ , Figs. 5.10 and 5.13). The system is similar to province 2 in

terms of its water characteristics (Table 5.e) and both systems have been described as open ocean gyres.

#### 5. Falkland Island Current (29° S to 52° S)

This region has three important hydrographic features that are best identified using SST images (Fig. 5.1, 5.14 and Table 5.e). An important feature in the region is the discharge from the river Plate, which flows in a northward direction and close to the coastline. The cruise track shows that sampling was not undertaken in this area hence, the discharge from the river Plate would probably have had little effect on the chemistry of the sampled waters. The mixing processes between the Brazilian current (to the north) and the Falklands current are characterised by numerous eddies in a wide zone (~400 km). This is shown in Figure 5.14, with the northward flowing cold low salinity waters of the Falkland current mixing with the warm high salinity waters of the Brazilian current that flow in a southerly direction. The measurements of water chemistries in this zone show a high spatial variability, which is probably related to the nature of the water mixing. TD-Ni and TD-Co for this region show a positive relationship with salinity ( $R^2 = 0.8$  and  $1.0$  respectively, where  $n = 7$ , at the 99 % confidence interval), indicating relatively conservative mixing between the high metal low salinity waters of the Falkland current with the low metal-high salinity waters of the Brazilian current. TD-Ni and TD-Co were enriched in the Falkland Island current (TD-Co = 53.4 pM, TD-Ni = 3.7 nM, Table 5.f). The nutrient (nitrite, ortho phosphate, silicate), chlorophyll-a, TD-Al and TD-Fe distributions showed a high spatial variability, which supports the notion of a highly convoluted mixing of the two water masses. The relationships between these variables and salinity is shown in Table 5.f. The satellite sea surface chlorophyll production estimates indicate high rates of productivity (Fig. 5.14). Uptake by primary producers could have influenced the distribution of nutrients and possibly Fe.

Table 5.f Relationship between TD-Co, TD-Ni, TD-Al, TD-Fe, silicate, ortho phosphate and nitrite with salinity at the Falkland Island current and Brazilian current confluence

| <i>Element</i>                     | <b>TD-Co<br/>(pM)</b> | <b>TD-Ni<br/>(nM)</b> | <b>TD-Al<br/>(nM)</b> | <b>TD-Fe<br/>(nM)</b> | <b>Chlorophyll-a<br/>µg/l</b> | <b>Silicate<br/>µM</b> | <b>Ortho<br/>phosphate<br/>µM</b> | <b>Nitrite<br/>µM</b> |
|------------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-------------------------------|------------------------|-----------------------------------|-----------------------|
| <i>R<sup>2</sup></i>               | 1.0                   | 0.8                   | 0.3                   | 0.3                   | 0.2                           | 0.7                    | 0.9                               | 0.9                   |
| <i>Confidence<br/>interval (%)</i> | 99                    | 98                    |                       |                       |                               | 95                     | 99                                | 99                    |
| <i>Number</i>                      | 7                     | 7                     | 7                     | 7                     | 7                             | 7                      | 5                                 | 5                     |
| <i>Abundance</i>                   | 53<br>± 13            | 3.7<br>± 1.7          | 25<br>± 12            | 2.9<br>± 0.8          | 0.57 ±<br>0.32                | 2.3<br>± 1.8           | 0.6<br>± 0.7                      | 0.05<br>± 0.03        |

#### 5.4.3 Behaviour of trace metals and nutrients in the Atlantic upper mixed layer (< 200 m)

The sampling locality (station 273) was situated in the Northeast Atlantic open ocean gyre (province 2, 42° N to 24° N), which compares well with the characterisation of the province based on the surface waters (section 5.4.2.2). Figure 5.15 shows enhanced salinity and temperature values in the surface waters (mean values of S = 36.98; temperature = 21.44 °C for the 0 to 200 m depth interval). A decrease in salinity and temperature was observed towards the bottom of the profile (S = 36.58, temperature = 17.78 °C at 200 m depth). A salinity maximum was observed at 43 m depth, which coincided with the sharp decrease in temperature. Low salinities (37.09 psu) were observed in the upper water column (<25 m) where temperatures were highest (24.77 °C). The low salinities observed in the upper water column could be explained by dilution caused by rainfall. Indeed, the sampling location is situated close to the Tropic of Cancer (23°26' N), a region of high rainfall. The surface waters (<60 m) are depleted in nutrients (silicate, nitrite, and ortho

phosphate =  $<0.01 \mu\text{M}$ ). However, the nitrite maximum ( $0.1 \mu\text{M}$  at 100 m depth) is accompanied by enhanced chlorophyll-a concentrations. Trace metal concentrations were homogeneously distributed throughout the water column (TD-Al (nM) =  $23 \pm 4.2$ , TD-Co (pM) =  $38 \pm 4.4$ , TD-Ni (nM) =  $2.2 \pm 0.3$  and TD-Fe (nM) =  $1.67 \pm 0.4$ ).

The results of analysis of samples collected at station 274 ( $20^\circ \text{N } 20^\circ \text{W}$ ) are presented in Figure 5.16. Salinity measurements show a sharp discontinuity at  $\sim 60 \text{ m}$ , where salinity increases from 36.26 psu at 44 m to 36.91 at 92 m. The salinity discontinuity was accompanied by a change in the temperature gradient ( $24.06^\circ \text{C}$  at 44.13 m and  $19.72^\circ \text{C}$  at 92.83 m). This observation suggests two water masses may have been present. The maximum chlorophyll-a concentration ( $0.91 \mu\text{g/l}$ ) observed at 40 m depth was above the salinity discontinuity. Silicate and nitrite maximas coincided with the maxima in chlorophyll-a, with the ortho phosphate maximum occurring below the chlorophyll-a maximum. Silicate and ortho phosphate exhibited a secondary increase at ca. 100 m depth and this could be accounted for by remineralisation of silicate and ortho phosphate owing to the breakdown of biomass. Enhanced TD-Al, TD-Co and TD-Fe concentrations in the surface 50 m of the water column were observed (TD-Al = 75 nM, TD-Co = 110 pM and TD-Fe = 7.4 nM). This could be explained by inputs of airborne particulate material (section 5.4.2.3). TD-Co and TD-Fe minima's (TD-Co = 60 pM at 20 m and TD-Fe = 1.4 nM at 40 m) broadly coincided with the chlorophyll-a maximum concentration, which could be due to uptake of these trace metals by photosynthesising organisms (Gorden *et al.*, 1998; Knauer *et al.*, 1982). In contrast, there was very little variation in the TD-Ni concentrations throughout the water column (TD-Ni =  $2.8 \pm 0.4 \text{ nM}$ ). The slight enrichment of TD-Ni towards the bottom of the water column (TD-Ni = 2.5 nM, 3.0 nM at 7 m and 200 m depth respectively) suggested that Ni was possibly released from decaying biota.

Station 281 ( $6^\circ \text{S } 29^\circ \text{W}$ ) was located in the centre of the south Atlantic Oligotrophic gyre (province 4, Table 5.e), and was the most remote location away from continental land

masses. Trace metal, nutrient and hydrographic depth profiles are presented in Figure 5.17. From the salinity profile (Fig. 5.16) it is possible to identify a sharp discontinuity at ~100 m depth ( $S = 36.03$  at 76 m,  $36.75$  at 102 m and  $35.70$  at 143 m). Maximum abundance of chlorophyll-a ( $0.38 \mu\text{g/l}$ ) was observed at 100 m depth, nutrient concentrations were highest abundance at ca 120 m depth and the chlorophyll-a maxima was slightly shallower (ca 100 m depth) than the nutrient maxima. The maximum concentration of chlorophyll-a at this locality implies very low levels of primary production (chlorophyll-a =  $0.39 \mu\text{g/l}$ ), which is consistent with the previous description of the province based on the surface water hydrographic and chemical characteristics (section 5.3.4.4). The trace metal concentrations were lower than their average ocean concentrations (TD-Al =  $19.9 \text{ nM}$ , TD-Ni =  $2.9 \text{ nM}$  TD-Co =  $39.5 \text{ nM}$  and TD-Fe =  $1.2 \text{ nM}$ , Table 5.c). TD-Co, TD-Ni and TD-Fe show a slight enrichment toward the bottom of the water column, which could be due to release of metals from degenerating biomass.

Station 285 ( $23^\circ \text{ S } 37^\circ \text{ W}$ ) was situated in the same province as the previous depth cast (station 281). Indeed, the concentration and distribution of trace metals and nutrients were very similar (Fig. 5.18). The salinity and temperature distributions suggest that waters in the surface 130 m were reasonably well mixed ( $S = 36.83$  and temperature =  $22.46^\circ \text{ C}$  at 3 m depth, and  $S = 36.63$  and temperature =  $21.08^\circ \text{ C}$  at 155 m depth). In addition, TD-Co, TD-Fe and TD-Ni exhibited homogeneity and concentrations fluctuated around mean values  $39 \pm 7 \text{ (pM)}$ ,  $1.4 \pm 0.7 \text{ (nM)}$  and  $1.97 \pm 0.3 \text{ (nM)}$  respectively. As a result of the remoteness of the location the system probably received very low inputs of trace metals and nutrients from aeolian deposition.

Station 289 was located close to the confluence of the Brazilian and Falkland Island water currents (section 5.4.2.5; province 5). The two water currents can be distinguished by their contrasting chemical and physical characteristics. Figure 5.12 shows a satellite image of surface water chlorophyll production. High levels of chlorophyll were observed in both the satellite image and in the discrete samples that were collected. The chlorophyll-a

maximum (0.73  $\mu\text{g/l}$ ) was located in shallow waters (0 to 30 m depth). Silicate, ortho phosphate and nitrite (1.55  $\mu\text{M}$ , 0.02  $\mu\text{M}$  and 0.05  $\mu\text{M}$  respectively) exhibited low concentrations in the upper water column (0 to 30 m depth). Enhanced TD-Fe and TD-Co concentrations were noticed in the surface waters (7 m depth), which suggests that TD-Co and TD-Fe distributions may have been influenced by atmospheric inputs. A minimum in TD-Fe (1 nM) was observed at shallow depths (30 m), coinciding with the chlorophyll-a maxima, and this suggests uptake of Fe by phytoplankton. Fe behaviour has been previously linked to the biological cycle of marine organisms, which is among the essential micronutrients required for life (Gorden *et al.*, 1998; Knauer *et al.*, 1982). Another feature of the trace metal profiles is the enhanced concentrations of TD-Ni, TD-Co and TD-Fe at ca. 200 m depth. This could be due to the recycling of metals from degrading organic material in the lower water column. The relatively high salinity and temperature of the waters suggest that their primary source was the Brazilian current.

A bulk characterisation of the water chemistry in the mixed layer (<200 m) depth profiles is presented in Table 5.g. Briefly, stations 273, 281 and 285 are characterised by low trace metal and nutrient concentrations, where the chlorophyll-a ( $\sim 0.42 \mu\text{g/l}$ ) maxima is observed at relatively deep depths ( $\sim 100$  m). In contrast, stations 274 and 289 exhibit high trace metal and chlorophyll-a ( $\sim 0.8 \mu\text{g/l}$ ) concentrations at shallow depths (30 to 40 m), which suggests that in areas of nutrient and trace metal depletion, photosynthesising organisms are less productive in the surface waters.

## **5.5 Additional Atlantic trace metal analysis**

In addition to the TD-Co and TD-Ni measurements discussed earlier, trace metal analysis was undertaken on surface water samples that were collected during a second Atlantic

|         | TD-Co (pM)  |                   | TD-Ni (nM)   |                   | TD-Fe (nM)   |                   | TD-Al (nM)  |                   | PO <sub>4</sub> (μM) | SiO <sub>2</sub> (μM) | NO <sub>2</sub> (μM) | Chlorophyll-a<br>μg/l |
|---------|-------------|-------------------|--------------|-------------------|--------------|-------------------|-------------|-------------------|----------------------|-----------------------|----------------------|-----------------------|
| Station | Mean        | Cmax<br>Depth (m) | Mean         | Cmax<br>Depth (m) | Mean         | Cmax<br>Depth (m) | Mean        | Cmax<br>Depth (m) | Cmax<br>Depth (m)    | Cmax<br>Depth (m)     | Cmax<br>Depth (m)    | Cmax<br>Depth (m)     |
| 273     | 38<br>± 4.4 | 47<br>200         | 2.2<br>± 0.3 | 2.6<br>40         | 1.7<br>± 0.4 | 2.4<br>90         | 23<br>± 4.2 | 28<br>200         | 0.21<br>200          | 0.5<br>150            | 0.1<br>100           | 0.51<br>100           |
| 274     | 72<br>± 25  | 110<br>7          | 2.8<br>± 0.4 | 3.5<br>20         | 3.2<br>± 2.2 | 7.4<br>7          | 33<br>± 26  | 79<br>7           | 1.0<br>60            | 5.2<br>40             | 0.5<br>50            | 0.9<br>40             |
| 281     | 40<br>± 14  | 69<br>200         | 2.9<br>± 1   | 5.5<br>200        | 1.2<br>± 0.5 | 2.2<br>200        | 20<br>± 7.5 | 32<br>70          | 1.6<br>200           | 10<br>120             | 0.2<br>120           | 0.4<br>110            |
| 285     | 39<br>± 7   | 54<br>160         | 2.0<br>± 0.3 | 2.3<br>160        | 1.4<br>± 0.7 | 2.7<br>7          | N/A         | N/A               | 0.3<br>200           | 1.8<br>120            | N/A                  | 0.4<br>100            |
| 289     | 49<br>± 20  | 93<br>200         | 2.8<br>± 2.2 | 8.2<br>200        | 3.5<br>± 2.5 | 8.3<br>200        | N/A         | N/A               | 0.4<br>200           | 2.3<br>80             | 0.4<br>60            | 0.7<br>30             |

Table 5.g Overview of trace metal and nutrient concentrations at 5 stations in the Atlantic Ocean. Cmax = maximum concentration; mean = mean value for 0 to 200 m depth interval.

meridional transect (AMT-6). In contrast to the AMT-3 survey, which travelled from the Southampton (UK) to the Falkland Island (UK), AMT-6 travelled between Cape Town (South Africa) and Southampton (UK). Analyses of TD-Ni and TD-Co were performed according to the procedures described in section 5.2.1 and 5.2.2, and are thus directly comparable to measurements undertaken on the AMT-3 samples. At the time of writing it was not possible to access other water chemistry information to compare with our Ni and Co measurements. However, the TD-Ni and TD-Co measurements have been plotted against latitude and are presented in Figure 5.22 and 5.23 respectively.

The mean concentration of TD-Ni ( $2.5 \pm 0.9$  nM) is comparable to the mean concentration identified from the AMT-3 campaign ( $2.4 \pm 0.7$  nM). Similarly, TD-Co (TD-Co =  $57 \pm 23$  pM) were in agreement with the values obtained from the AMT-3 voyage (TD-Co =  $42 \pm 14$  pM). Without the supporting data series it is not possible to make a thorough interpretation of the Ni and Co data series. In contrast to the AMT-3 voyage, the AMT-6 expedition travelled between Cape Town (South Africa) and Southampton (United Kingdom) during June 1998. Therefore, the cruises followed different routes during different seasons. Despite the differences between sampling locations in the Atlantic and sampling seasons, the data sets show that both total dissolvable Co and (especially) Ni were well mixed in the Atlantic Ocean. However, without the supporting data series it is not possible to undertake detailed comparisons between the Ni and Co data series for AMT-3 and AMT-6.

## 5.6 Conclusions

This chapter has demonstrated that adsorptive cathodic stripping voltammetry (AdCSV) can be used to produce a unique high quality trace metal data set for open oceanic waters. There is a limited data on Co and Ni concentrations and distributions in the Atlantic Ocean,

Figure 5.21 Total dissolvable Co distribution in Atlantic surface waters (7 m depth). The mean ocean Co concentration has been plotted.

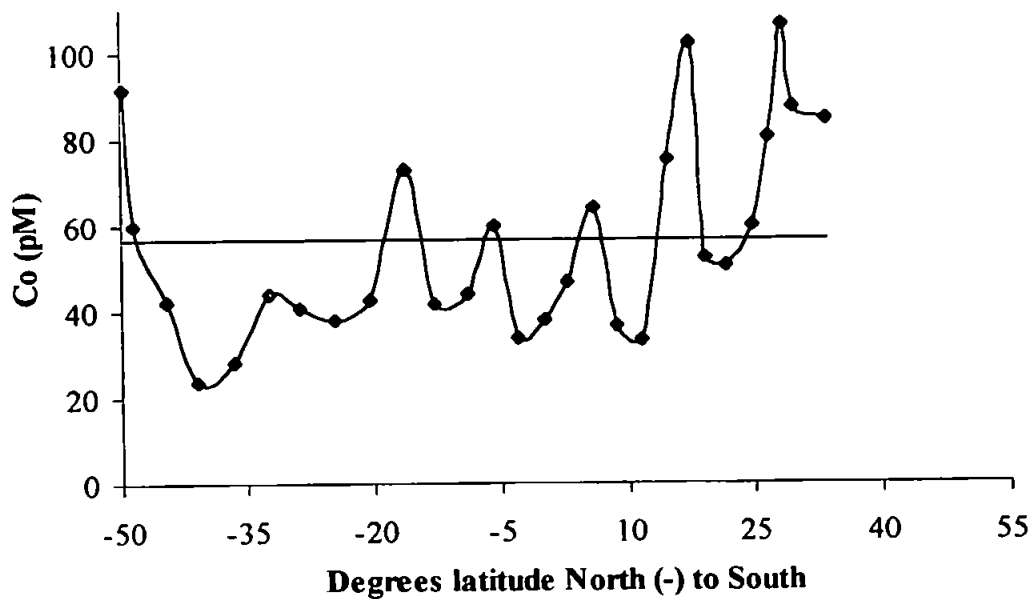
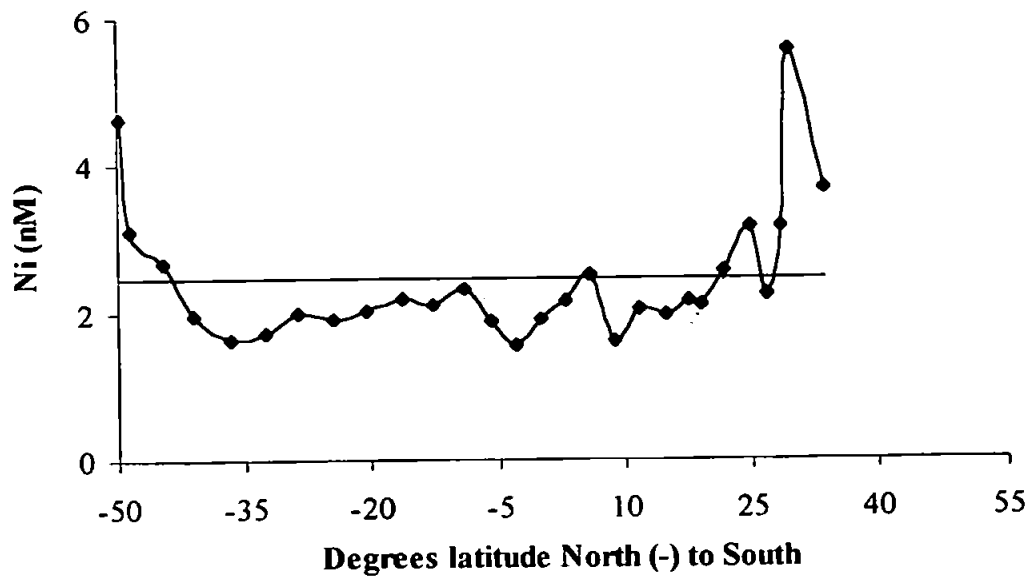


Figure 5.22 Total dissolvable Ni distribution in Atlantic surface waters (7 m depth). The mean ocean Ni concentration has been plotted.



and the data obtained from the AMT-3 and AMT-6 surveys will aid future open ocean research into Co and Ni behaviour.

TD-Ni exhibited a relatively homogeneous distribution in the Atlantic Ocean and concentrations were consistent with previous open ocean studies (TD-Ni  $\sim 2.5 \pm 0.7$  nM; Table 5.d). TD-Ni showed no correlation with chlorophyll-a, nutrients and was unaffected by enhanced rates of aeolian deposition and variability in SPM concentrations, which suggests that Ni exhibited relatively conservative behaviour in the Atlantic Ocean. However, TD-Ni exhibited enrichment by conservative mixing between the relatively Ni depleted (TD-Ni =  $\sim 2.2$  nM) Brazilian current and the Ni enriched (TD-Ni =  $\sim 6.5$  nM) Falkland Island current (29° S to 52° S).

TD-Co exhibited inhomogeneous distribution in the Atlantic and concentrations varied between 20 pM and 110 pM, which were comparable to previous findings (Table 5.d). It was possible to elucidate a strong enrichment of TD-Co off the North West African coast which was associated a region of enhanced aeolian deposition. Lowest TD-Co values were observed in the most remote oceanic regions and were probably due to the uptake and scavenging by phytoplankton and particles and the low rate of replenishment either by atmospheric deposition or oceanic mixing. In the South Atlantic (29° S to 52° S) TD-Co exhibited similar behaviour to TD-Ni and similarly can be characterised by conservative mixing between the relatively TD-Co depleted (TD-Co =  $\sim 40$  pM) Brazilian water mass and the enriched (TD-Co =  $\sim 70$  pM) Falklands current.

The investigation into the distribution of TD-Co and TD-Ni with depth (up to 200 m) generally showed uptake in the upper 100 m of the water column and enrichment with depth, which could indicate a link with phytoplankton activity. It was not possible to discern the mechanisms responsible to the removal of Co and Ni in the upper 100 m. However, uptake by direct/indirect assimilation during the phytoplankton growing phase and release as a result of to their decomposition could account for Co and Ni depletion at shallow depths (0 m to 100 m) and their enrichment in deeper waters (150 m to 200 m).

## 6. Conclusion

In order to advance the understanding of the behaviour of trace metals in estuarine environments marine chemists must develop novel approaches for the analysis of estuarine water and SPM samples. During the course of this study an automated on line dissolved Ni monitor with AdCSV detection was developed and validated for estuarine studies. Using this novel approach measurements were attained throughout the estuarine salinity range ( $S = 0$  to  $\sim 35$ ) of the highly dynamic macro tidal environment of the Tamar estuary (Whitworth *et al.*, 1998; Chapter 2). Each sample was fully calibrated by the automated system used during this study, resulting in high quality dissolved Ni data. The calibration approach was especially important in estuarine conditions with strong and rapid variations in the samples chemical composition. These conditions may result in erroneous metal concentration determinations when external calibration procedures are applied. The main advantages of the Ni monitor was its ability to perform high resolution dissolved Ni measurements (4-6 measurements per hour). High frequency measurements are essential for pollution and geochemical studies in estuaries owing to the highly variable chemistry of the systems. The application of the transportable estuarine metal monitor was successful and the system could, therefore, form a useful analytical tool for water quality monitoring organisations.

The automated AdCSV Ni monitor can be readily modified to measure other trace metals (including Zn, Co, Cu, V, Cr, Cd and Pb) by changing the reagents and voltammetric conditions. Furthermore, the metal species selectivity of AdCSV makes this technique suitable for trace metal speciation analysis. The *in situ* approach developed during this study would ideally suit metal speciation studies because the near immediate analysis upon sampling minimises any shift in the chemical equilibrium between the various physico chemical forms of trace metals present in natural waters.

Development of a novel method to assess the non lattice bound trace metal concentration of estuarine SPM was also undertaken during the initial stages of the study (Chapter 2). The methodology utilised EDTA (0.05 M) as the added extraction reagent. EDTA acts as a metal complexing ligand and has a well defined binding strength and the leaching technique provides information about the nature and strength of the sorption sites on particles. This approach is analogous to the ligand competition techniques used for determination of trace metal complexation by dissolved organic ligands in natural waters (Gerringa *et al.*, 1996; Campos and van den Berg, 1994). Following analytical developments the EDTA technique was successfully applied to samples from the Scheldt Estuary. Assessment of the contribution of biogeochemically available trace metals to the total particulate metal concentration in SPM can be performed when a total digestion using HF and HNO<sub>3</sub> compliments the extraction scheme. Advantages of the EDTA (0.05 M) extraction protocol included (1) a low requirement of SPM (minimum SPM concentration = 15 mg), (2) simplicity of application, (3) minimal sampling handling requirement, hence low inherent risk of sample contamination, and (4) no post trace metal extraction re-adsorption artifacts (within 72 h) (Rendell *et al.*, 1980).

Trace metal total dissolved and dissolved chemical speciation (AdCSV labile) measurements of Co, Ni, Cu and Zn were undertaken in the Tamar Estuary (United Kingdom). The generated data set is unique as it covers a long sampling period (3 years; 11 surveys between 12-02-1996 to 13-01-1999) (Chapter 3). Furthermore, it is the first reported study for the Tamar Estuary with a detailed trace metal speciation approach.

Despite differences in Co, Ni, Zn and Cu concentration and temporal variability their behaviour was similar and can be characterised by three persistent features that are summarised below:

1. Removal of metals in the low salinity ( $S = 0$  to  $\sim 5$ ), high turbidity region ( $SPM = 100$  to  $850$  mg/l), which was probably due to adsorption of metals onto the surface of particulate material. In addition, removal of organically complexed metals (especially Zn) was observed at low salinities ( $S = 0$  to  $\sim 10$ ).
2. Enrichment of Co, Ni, Cu and Zn was observed in the mid estuary ( $S = 5$  to  $25$ ) and was accounted for by the infusion of sediment interstitial waters and/or desorption of metals as a result of a re-distribution of cation competition for adsorption sites on SPM and dissolved complexation of particulate metals by e.g. chloride.
3. Relatively conservative mixing behaviour in the lower estuary ( $S = \sim 25$  to  $\sim 35$ ) with metal concentrations falling to low concentrations near typical for coastal seawaters owing to the dilution with relatively metal depleted seawater.

AdCSV Co, Cu and Ni speciation measurements indicated that the high salinity ( $S = \sim 30$  to  $\sim 35$ ) waters collected from Plymouth Sound generally contained the highest fractions of organically complexed metals. In contrast, in the upper estuary, organically complexed Zn was removed from solution with increasing salinity and a small fraction of relatively stable organic Zn complexes were persistent throughout the estuary. Davis, (1984) and Paulson *et al.*, (1995a, b) reported that dissolved organic compounds (e.g. humic substances and fulvic acids), which can form complexes with dissolved metals, may flocculate in the low salinity zone ( $S = 0$  to  $\sim 10$ ) as a result of an increasing ionic strength. Hence, it is suggested that an additional mechanism for the depletion of Zn in the low salinity region of estuaries could be the flocculation of organically complexed Zn.

To further characterise the Cu-organic complexation, measurements of Cu natural ligand conditional stability constants and natural ligand concentrations were undertaken in samples collected during two surveys in the Tamar estuary. These data indicated the presence of high concentrations of Cu complexing ligands with high Cu ligand conditional stability constants in low salinity waters ( $S = 0$  to  $5$ ,  $\text{Log}_{10} K_{\text{CuL}} = \sim 14.3$ ,  $\text{Cu}_L = \sim 200$  neq

$\text{Cu } \text{l}^{-1}$ ;  $S = \sim 35$ ,  $\text{Log}_{10} K_{\text{CuL}} = \sim 13.4$ ,  $\text{Cu}_L = 50 \text{ neq Cu } \text{l}^{-1}$ ). Furthermore, the strong complexing ligands were removed from solution in the low salinity zone, which suggests that the flocculation of organic material in the low salinity zone could be an important mechanism for the removal of Cu in the Upper Tamar Estuary. A positive relationship was observed between the strength of Cu complexing ligands ( $\text{Log}_{10} K_{\text{CuL}}$ ) and total dissolved Cu concentration, which could indicate that strong complexing ligands are important for to the buffering of dissolved Cu concentrations in this estuary in this estuary.

In addition to investigation of the behaviour and distribution of trace metals in the Tamar Estuary, an axial transect survey was undertaken on the Scheldt Estuary (Belgium) during December 1996 (Chapter 4). In contrast to Tamar Estuary, the Scheldt Estuary is characterised by a pronounced dissolved oxygen gradient that may persist into the winter months in the upper estuary. This is explained by anthropogenic inputs of nutrients and discharges of organic rich wastewater followed by enhanced rates of microbiological degradation (Wollast and Peters, 1978; Wollast, 1988). Total and labile (AdCSV; filtered and non filtered) dissolved Co, Ni, Zn and Cu were analysed in samples collected in the Scheldt Estuary. Complimentary measurements of total and EDTA (0.05 M) extractable particulate Cu, Zn, Ni and Mn concentrations were evaluated to investigate the change in metal partitioning between the particulate and dissolved phases. It was apparent that dissolved Cu and Zn exhibited a similar behaviour and distribution in the Scheldt Estuary, where concentrations were enhanced in the upper estuary, probably due to oxygenation of sulphidic sediments and its mixing with overlying water. Furthermore, mid estuarine inputs of Zn and Cu were observed, which were explained by mobilisation of particulate metals owing to complexation by dissolved ligands e.g. chloride and infusion of anoxic sediment interstitial waters. Dissolved and particulate Zn and Cu concentrations exhibited down stream dilution ( $S = \sim 20$  to  $\sim 35$ ) with relatively metal depleted seawater.

Maximum concentrations of 0.05 M EDTA exchangeable particulate Cu, Ni and Zn broadly coincided with the POC maxima, indicating that organic coating on SPM may be an important factor influencing adsorption of these metals from the dissolved phase. The decrease in concentration of Cu natural complexing ligands and decrease in conditional stability constants ( $S = 0$  to  $\sim 10$ ) indicates that Cu could become removed in the low salinity region ( $S = 0$  to  $\sim 10$ ) owing to the flocculation of dissolved organic Cu complexing ligands ( $S = 0$  to  $5$ ,  $\text{Log}_{10} K_{\text{CuL}} = \sim 15.6$ ,  $\text{Cu}_L = \sim 200 \text{ neq Cu l}^{-1}$ ;  $S = \sim 35$ ,  $\text{Log}_{10} K_{\text{CuL}} = \sim 14.4$ ,  $\text{Cu}_L = 80 \text{ neq Cu l}^{-1}$ ). Ni and Co were not as strongly implicated with organic complexation by dissolved ligands as Zn and Cu.

An additional limited study involved the measurement of AdCSV labile Co, Ni, Zn and Cu in unfiltered waters from the Scheldt Estuary. Such studies have not previously been reported for estuarine waters. The measurement of unfiltered labile metals gave an indication of the redistribution of metals between the dissolved and particulate phases. For example, in the upper estuary the labile Cu ( $\text{Cu}_{\text{flab}}$ ) concentration was equal to the labile unfiltered Cu concentration, which indicates that the concentration of rapidly exchangeable particulate Cu ( $\text{Cu}_{\text{lab}}$ ) was not measurable in the upper estuary. In contrast, the  $\text{Cu}_{\text{lab}}$  values were up to double the concentration of  $\text{Cu}_{\text{flab}}$  in the mid estuary and this indicates the possible adsorption of rapidly exchangeable Cu onto SPM in the mid estuary. The measurement of Co, Ni, Zn, and Cu in unfiltered waters was undertaken on-board ship, which suggests that unfiltered measurements of metals could be more widely undertaken in estuarine studies yielding novel measurements of metal partitioning between the dissolved and particulate phase.

A study of dissolved Ni and Co concentrations in samples collected from the North and South Atlantic was undertaken (Chapter 5). In contrast to the estuarine environment, Co and Ni were present at very low concentrations in open oceanic waters of the North and South Atlantic (Ni ca 2.5 nM and Co ca 0.04 nM). Chapter 5 contains the first reported

measurements of Ni and Co from an axial transect of the Atlantic Ocean between Southampton (United Kingdom) and the Falkland Islands (United Kingdom) and demonstrated that a unique high quality trace metal data series may be generated using AdCSV. There is a limited database for baseline Co and Ni concentrations and distributions in the Atlantic Ocean and the data obtained from the AMT surveys will aid future open ocean research into Ni and Co behaviour in the Oceans.

TD-Ni exhibited a relatively homogeneous distribution in the Atlantic Ocean and concentrations were consistent with previous open ocean studies (TD-Ni  $\sim 2.5 \pm 0.7$  nM). In the surface waters (7 m depth), TD-Ni showed no correlation with chlorophyll-a, nutrients and was unaffected by enhanced rates of aeolian deposition and variability in SPM concentrations. This suggests that Ni exhibited relatively conservative behaviour in the Atlantic Ocean. However, TD-Ni exhibited enhanced concentrations through conservative mixing between the relatively Ni depleted (TD-Ni =  $\sim 2.2$  nM) Brazilian current with the Ni enriched (TD-Ni =  $\sim 6.5$  nM) Falkland Island current (29° S to 52° S).

TD-Co exhibited inhomogeneous distribution in the Atlantic and concentrations varied between 20 pM and 110 pM, which was comparable to previous findings. A strong enrichment of TD-Co was apparent off the North West African coast which attributed to an enhanced aeolian deposition in this region. Lowest TD-Co values were observed in the most remote oceanic regions and were probably due to the uptake and scavenging by phytoplankton and particles and the low rate of replenishment by atmospheric deposition. In the South Atlantic (29° S to 52° S) TD-Co exhibited similar behaviour as TD-Ni and similarly, can be characterised by conservative mixing between the relatively TD-Co depleted (TD-Co =  $\sim 40$  pM) Brazilian water mass with the enriched (TD-Co =  $\sim 70$  pM) Falklands current.

The investigation of the distribution of TD-Co and TD-Ni with depth (up to 200 m) generally showed uptake in the upper 100 m of the water column and enrichment with depth, which could indicate a link with phytoplankton activity. It was not possible to

discern the mechanisms responsible to the removal of Co and Ni in the upper 100 m. However, uptake by direct/indirect assimilation during the phytoplankton growing phase and release owing to their decomposition could account for Co and Ni depletion at shallow depths (0 m to 100 m) and their enrichment in deeper waters (150 m to 200 m).

This thesis has demonstrated the suitability of AdCSV to the analysis of samples throughout estuarine and open ocean environments. Furthermore, the data series gained through this research will form a useful addition to the overall trace metal databases for estuarine and open ocean systems.

## 6.1 Future Research

Further research is required in the area of dissolved Co and the chemical speciation of Co in seawater. There is a gap in our understanding of the distribution and behaviour of dissolved Co in estuarine, coastal and open ocean waters. In particular, chemical speciation studies of dissolved and particulate Co could resolve the question of the role of Co as a limiting micro nutrient for phytoplankton growth in open oceanic waters.

Further seasonal investigations of dissolved and particulate metals in the Tamar estuary could aid the assessment of long term (>10 years) trends in trace metal speciation and distribution. The Tamar is an ideal site for seasonal investigations of this nature as the Tamar is accessible and a wealth of high quality data is already available for this system. The data generated from this investigation into dissolved speciation of trace metals in estuaries could be incorporated into existing estuarine computer modelling techniques (e.g. ECOS) and could help further developments of trace metal estuarine modelling software. Parallel studies of the rate of adsorption and desorption of trace metals between the dissolved and particulate phase based on end member mixing experiments would further refine modes of trace metal behaviour in estuaries.

The application of ligand competition methodologies to the study of particulate metal partitioning could yield valuable information regarding particulate trace metal affinities. This could be achieved by using a range of metal complexing ligands with well defined constraints with respect to the competition for trace metals between the added ligand and the particles. The methodology presented in chapter 2 could be applied to evaluate the potential for application of other metal complexing ligands to particulate trace metal studies.

Seasonal investigations of chemical speciation of trace metals in estuaries are required to improve our understanding of trace metal partitioning in these systems. A better

understanding of the character of dissolved metal complexing ligands could enhance our understanding of trace metal toxicity to estuarine and marine phytoplankton.

The development of an automated *in situ* metal monitor that can be deployed for prolonged periods (days to weeks) will be valuable for studies of complex marine systems. The monitors could be deployed in geographic remote regions thereby eliminating the need for high cost and often laborious monitoring studies involving discrete sampling and analysis.

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