

**COMPLEXATION AND PARTICLE-WATER INTERACTIONS  
OF NICKEL IN ESTUARIES**

**M. MARTINO**

**Ph.D. 2000**

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Signed.....*Mamika Marjine*.....  
Date.....*2<sup>nd</sup> June 2000*.....

*This thesis is dedicated to Nonno Bartolo, Nonna Franca and to my parents.*

*“Considerate la vostra semenza:  
fatti non foste a viver come bruti,  
ma per seguir virtute e conoscenza”*

*“Consider your origin:  
you were not made to live in brutish ignorance,  
but to follow knowledge and intelligence”*

*(Dante Alighieri, Inferno, Canto XXVI, 118-120)*

**COMPLEXATION AND PARTICLE-WATER INTERACTIONS  
OF NICKEL IN ESTUARIES**

by

**MANUELA MARTINO**

A thesis submitted to the University of Plymouth  
in partial fulfilment for the degree of

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Faculty of Sciences

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## Complexation and particle-water interactions of nickel in estuaries

Manuela Martino

### ABSTRACT

The speciation and particle-water interactions of Ni were investigated in three estuaries with contrasting pollution levels, hydrodynamics and geochemical characteristics. Samples of water and sediments were collected seasonally from the Tamar, Tweed and Mersey Estuaries. The chemical speciation of dissolved Ni was determined by adsorptive cathodic stripping voltammetry (ACSV), and the sorptive behaviour of Ni was studied under simulated estuarine conditions using  $^{63}\text{Ni}$  coupled to liquid scintillation counting.

A relatively high particle reactivity was observed only in the Tamar Estuary, where ACSV-non labile Ni was removed in the low salinity region, followed by addition of ACSV-labile Ni in the mid-estuarine region. The largely conservative behaviour of dissolved Ni in the Tweed Estuary was attributed to the combination of rapid flushing and low suspended particles concentration. In the Mersey Estuary, dissolved Ni (and Co, Zn, Cd and Pb) often showed positive deviations from conservative behaviour, which were attributed to anthropogenic and/or geochemical inputs. The fraction of ACSV-non labile Ni behaved differently in the three estuaries, with a sharp decrease from 90 to 30% from freshwater to seawater in the Tamar, scatter between 30 and 70% in the Tweed, and relatively constant values of 50-70% in the Mersey. These differences are interpreted within the context of different hydrodynamics and geochemistry of the three estuaries. Speciation modelling showed that between 30 and 70% of dissolved Ni in the Tweed, and between 50 and 70% in the Mersey, was bound to a class of strong ligands ( $\log K'_{\text{NiL}} = 19.0 \pm 0.4$  and  $18.7 \pm 0.5$ , respectively), which were saturated by the ambient concentrations of Ni throughout the estuaries, suggesting that the ligands are highly specific towards Ni.

Irradiation of riverwater samples with UV light (believed to remove dissolved organic matter) significantly enhanced Ni uptake onto estuarine suspended particulate matter, with an increase in the  $^{63}\text{Ni}$  distribution coefficients ( $K_{\text{ds}}$ ) of up to 10 fold. Conversely, the addition of synthetic humic acids to UV-treated riverwater decreased significantly the  $^{63}\text{Ni}$   $K_{\text{ds}}$ . Complexation of Ni by dissolved natural ligands also affected the progression of sorptive reactions, with a system response time (i.e. the time required to achieve 63% of the sorptive equilibrium) between 1.6 and 8.9 hours.

The results from this study suggest that the low particle reactivity generally exhibited by Ni during estuarine mixing is due to its ability to complex strongly with dissolved natural ligands (truly dissolved organic or colloidal organic/inorganic), and therefore resist adsorption onto particles.

## 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.

This study was financed with the aid of a studentship from the University of Plymouth.

A programme of advanced studies was undertaken, which included guided reading in topics relating to environmental and estuarine geochemistry. Training was given in clean sampling and sample handling techniques, and in a range of analytical methodologies including the voltammetric determination of trace metals at nanomolar concentrations. Training was also given in the safe use of radioactive isotopes and the analysis of  $^{63}\text{Ni}$  radiotracers using liquid scintillation counting.

Relevant scientific seminars and conferences were regularly attended at which work was often presented, external institutions were visited for consultation purposes, and scientific papers were prepared for publication.

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Southampton Oceanographic Centre, University of Southampton, Progress in Chemical Oceanography II meeting, 17-18 September 1997. Poster presentation: Speciation and partitioning of nickel in the Tweed Estuary.

Marine Biological Association, Plymouth, 3 October 1997. Plymouth Marine Fund autumn seminars series. Oral presentation: Biological oceanography at the Bermuda Biological Station for Research.

University of Southampton, UK Oceanography '98 meeting, 7-11 September 1998. Poster presentation: Speciation and partitioning of nickel in the Mersey Estuary.

Royal Institution of Chartered Surveyors, London. NERC Environmental Diagnostics meeting, 20 January 1999. Oral presentation: Speciation and water-particle interactions of nickel in the Mersey Estuary.

Edge Hill University College, Ormskirk, 8-9 April 1999. ECSA meeting: The coasts and Estuaries of north-west England. Oral presentation: Speciation and water-particle interactions of nickel in the Mersey Estuary.

Department of Environmental Sciences, University of Plymouth, 1997-1999. A number of oral presentations have been given throughout the PhD project.

### Courses and external contacts:

A graduate Course in Biological Oceanography was attended at the Bermuda Biological Station for Research, 26<sup>th</sup> July-16<sup>th</sup> August 1997.

Meetings were held with colleagues from CCMS (Plymouth Marine Laboratory) and the Environment Agency North-West, for fieldwork planning and discussion of data.

Signed...*Maureen Blenkinsop*...  
Date...*2nd June 2000*...

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# CHAPTER 1

## INTRODUCTION

Estuaries play a fundamental role in the biogeochemical cycling of trace metals, by modifying their chemical speciation (Bourg, 1988; van den Berg, 1993), water-particle interactions (Millward, 1995; Turner, 1996), and ultimately, their net particulate and dissolved fluxes from land to the oceans (Chiffoleau et al., 1994; Dai et al., 1995; Millward and Glegg, 1997). An understanding of the processes affecting the transport and distributions of contaminants within an estuary (together with information on the state of the estuary, its water quality and biota) is fundamental for water quality management, and for assessing the impact and predicting the fate and dispersion of contaminants. The behaviour of trace metals in natural waters is, however, extremely complex, due to the high number of interactions with different components of the aquatic medium. Trace metals in natural waters can occur in a variety of physico-chemical forms (i.e. species), which determine their behaviour and the extent of interaction with the components of different environmental compartments. Different metal species may have, for example, different bioavailability, toxicity and tendency to react with solid substrates, and ultimately, different residence times in the aquatic environment (Stumm and Morgan, 1996; Moran et al., 1996; Gustaffson and Gschwend, 1997). The determination of metal speciation in the aquatic environment is, therefore, essential for understanding the rate and extent of biological and geochemical processes the metal is involved in (Wood et al., 1995; Tessier and Turner, 1995).

This study focuses on nickel, a metal of concern in the aquatic environment, owing to its toxicity (Oliveira and Antia, 1986; Florence et al., 1994) and ability to bioaccumulate in living organisms (Wang and Wood, 1984). Few studies have focussed on the speciation and particle-water interactions of Ni in estuaries (Nimmo, 1987; Liu et al., 1998; Turner et al., 1998), and the factors and processes affecting its geochemical behaviour in estuaries



are still largely unknown. This is the first study carried out to explore the estuarine geochemistry of Ni by comparing its behaviour in estuaries with contrasting metal contamination, hydrodynamics, physical and geochemical characteristics. Three English estuaries (fully described in Section 2.1) were selected for this study: the Tamar (characterised by historical contamination by metal mining and high turbidity), the Tweed (a relatively pristine environment, with low turbidity and short flushing time), and the Mersey (affected by heavy industrial and domestic sewage discharges, high turbidity and a long flushing time). The study will focus on: (i) the factors governing the dissolved speciation of Ni and its water-particle interactions in estuaries, and (ii) the effect of complexation with dissolved organic ligands on Ni sorptive behaviour on estuarine mixing. It will then attempt to identify some of the common and contrasting factors affecting the biogeochemical behaviour of Ni in estuaries.

The information generated from this study will contribute to the development of estuarine water quality models for predicting the fate of Ni in estuaries under a variety of environmental conditions, and, in particular, those caused by climate change and anthropogenic modifications in land use patterns. Estuaries and coastal environments are under severe threat both on a global and local scale, due to global warming risk and socio-economic pressure (Nicholls and Mimura, 1998). Coastal zone management and protection of water resources threatened by natural and anthropogenic pressures are at present among the fundamental issues addressed within the European Union (European Commission, 1997) and in the U.K. (Edwards et al., 1997; Environment Agency, 1999). Changes in the hydrological cycle may affect precipitation patterns (Tsonis, 1996), which have already been shown to cause an increase in river flow, flooding and soil erosion in winter, and reduced river flows during summer (e.g. Tweed river catchment: Fox and Johnson, 1997; Marsh and Sanderson, 1997). The rise in global temperatures and sea level can alter substantially the salinity and temperature distributions, sediment loads and biological activity in estuaries (Jones, 1994; Sherif and Singh, 1999; Environment Agency, 1999). In

addition, estuarine and coastal areas have for long been subject to intense socio-economic pressure and exploitation, such as urban and industrial developments, discharge of industrial and domestic waste, dredging of sediments, commercial fishing, land reclamation and substantial alteration of river flow by creation of water barrages (Environment Agency, 1999). All of the above factors may significantly affect the fluxes, transport and fate of trace metals in estuaries, by modifying sediment (and associated metals) transport, deposition and resuspension patterns, freshwater flows, salt water intrusion limit, flushing times of dissolved constituents, water-particle reaction rates. The understanding of the factors and mechanisms affecting trace metal behaviour in estuaries is therefore fundamental for predicting the impact of environmental changes.

## 1.1 The estuarine environment

### 1.1.1 WATER AND SEDIMENT DYNAMICS IN ESTUARIES

The most comprehensive definition of an estuary has probably been given recently by Dyer (1997): “an estuary is a semi-enclosed coastal body of water which has free connection to the open sea, extending into the river as far as the limit of tidal influence, and within which sea water is measurably diluted with fresh water derived from land drainage”. The most common classification of estuaries is that based on salinity distribution (Dyer, 1997). In estuaries the mixing of freshwater and seawater takes place with a pattern mainly determined by the relative contributions of river flow and tidal amplitude. Some examples of estuaries with contrasting characteristics are given in Table 1.1. Where the river flow dominates the tidal flow, like in the Rhine Estuary, a salt wedge is formed by the seawater intruding underneath the riverwater, which gives rise to a very sharp halocline. In macrotidal estuaries where the tidal flow is dominant on the river flow (e.g. the Mersey and Severn Estuaries) the whole water column is mixed efficiently, thus generating a uniform vertical salinity profile. In estuaries where river and tidal flows are comparable, partial stratification occurs (e.g. the Tamar Estuary).

**Table 1.1.** Physical characteristics of the Tamar, Tweed, Mersey, Rhine and Severn Estuaries. SPM = suspended particulate matter.

	Tamar	Tweed	Mersey	Rhine	Severn
Tidal excursion (km)	31 <sup>a</sup>	13 <sup>b</sup>	50 <sup>c</sup>	40 <sup>a</sup>	190 <sup>p</sup>
Catchment area (km <sup>2</sup> )	917 <sup>d</sup>	4390 <sup>c</sup>	5000 <sup>f</sup>		10 <sup>4p</sup>
Mean river flow: annual; summer/ winter (m <sup>3</sup> s <sup>-1</sup> )	22; 7/40 <sup>d</sup>	80; 30/140 <sup>g</sup>	40; 30/50 <sup>f</sup>	2200 <sup>a</sup>	10 <sup>3p</sup>
Mean tidal range, springs/ neaps (m)	4.7/2.2 <sup>a</sup>	4.1/2.5 <sup>b</sup>	8.2/4.6 <sup>a</sup>	1.9/1.5 <sup>a</sup>	13.2/9.8 <sup>f</sup>
Stratification	partly mixed <sup>b</sup>	Partly mixed/ salt wedge <sup>b</sup>	well mixed <sup>i</sup>	salt wedge <sup>a</sup>	well mixed <sup>p</sup>
Flushing time: min/max (days)	7/14 <sup>j</sup>	0.5/1 <sup>b</sup>	20/50 <sup>k</sup>	2 <sup>a</sup>	100-200 <sup>p</sup>
SPM (mg l <sup>-1</sup> ): min/max	<5/2000 <sup>l</sup>	2/30 <sup>c</sup>	50/700 <sup>m</sup>	20-100 <sup>a</sup>	2000 <sup>p</sup>

<sup>a</sup>Grabemann et al (1997); <sup>b</sup>Uncles and Stephens (1996); <sup>c</sup>Taylor (1986); <sup>d</sup>Environment Agency data (1999); <sup>e</sup>Balls (1994); <sup>f</sup>National Rivers Authority (NRA, 1995); <sup>g</sup>Uncles and Stephens (1997); <sup>h</sup>Uncles and Stephens (1990); <sup>i</sup>Jones (pers. comm., 1998); <sup>j</sup>Millward and Turner (1995); <sup>k</sup>Jones (1978); <sup>l</sup>Ackroyd et al (1986); <sup>m</sup>this study; <sup>n</sup>Campbell et al. (1988); <sup>p</sup>Mantoura and Woodward (1983); <sup>q</sup>Paalman and van der Weijden (1992); <sup>r</sup>Allen and Duffy (1998).

An important hydrodynamic parameter in estuaries is the flushing time. This is defined as the time necessary to replace the volume of freshwater in the estuary at a rate equal to that of the river flow (Millward and Turner, 1995). Estuarine flushing time can vary considerably within an estuary, depending on its hydrodynamic regime. For example, seasonal variations in precipitation patterns can substantially modify the river flow and therefore also the flushing time (e.g. Table 1.1). The flushing time is a fundamental parameter in controlling trace metal reactivity in estuaries (Morris, 1990; Millward and Turner, 1995), as it determines the residence time of chemical components in the estuarine environment, and therefore controls the progression of heterogeneous chemical reactions. The flushing time of the low salinity region of an estuary is particularly important, because this is a region of enhanced trace metal reactivity (Morris, 1986). Therefore, for small estuaries with a rapidly flushed low salinity region (e.g. minutes to hours for the Tamar: Liu et al., 1998), the progression of heterogeneous chemical reactions may be a function of the relative magnitude of the flushing time and response time for sorptive reactions (e.g. the time required to reach 63% of the sorptive equilibrium: Honeyman and Santschi,

1988). Quasi-conservative behaviour has been observed for Ni in the Tamar Estuary during high river flow conditions in winter, because of the fast flushing time, whilst persistent removal occurred in the turbidity maximum zone (TMZ) during low-flow summer conditions, when the flushing time and the response time have similar values (Liu et al., 1998).

The concentration of suspended matter in estuaries is highly variable (Table 1.1) as materials undergo continuous deposition-resuspension cycles under the effect of tidal motion. Estuaries are zones of net sediment deposition (Morris et al., 1986; Dyer, 1997; Millward and Glegg, 1997), because of landward transport of coarse marine material, and a combination of tidal movements and estuarine circulation, which tend to accumulate finer terrestrial material (silt and clays, < 63  $\mu\text{m}$  size). Therefore estuaries can act as a trap for particles, whose residence time in the estuary may be much longer (typically years to decades: e.g. Bale et al., 1985; Millward and Turner, 1995; Kraepiel et al., 1997; Millward and Glegg, 1997) than that of the estuarine water (typically days or weeks: Table 1.1). The internal cycling of fine-grained sediments is of major importance in the retention and cycling of particle-bound trace metals in estuaries (e.g. Morris et al., 1986; Millward and Glegg, 1997; Zwolsman et al., 1993), as trace metals have been found to associate preferentially with fine-grained particles in estuaries, owing to their high specific surface area and therefore high number of active surface sites (Duinker, 1983; Millward et al., 1990; Turner et al., 1994; Regnier and Wollast, 1993).

Estuarine suspended particulate matter (SPM) originates from multiple sources (Bale et al., 1989; Millward and Turner, 1995): terrestrial (plant debris, rock weathering products such as quartz and other clay minerals); marine (eroded coastal sediments, shell remains, organic material of biological origin); generated *in-situ* (flocculated humics and Fe and Mn oxyhydroxides, biogenic material); anthropogenic (airborne, industrial and domestic discharges). Estuarine suspended aggregates are distributed in a range of sizes (operationally defined as between 0.2  $\mu\text{m}$  and a few mm: Dyer, 1986), with the majority of

fundamental particles (inorganic clay-sized minerals) measuring less than 4  $\mu\text{m}$  in diameter (Fennessy et al., 1994; Dyer and Manning, 1999). A large fraction of the estuarine particulate matter exists as amorphous aggregates, or flocs (Chen et al., 1994; Fennessy et al., 1994; Manning and Dyer, 1999). These large (150  $\mu\text{m}$ -several mm) and fragile flocs are formed by the flocculation of fine-grained, cohesive sediment (van Leussen, 1999; Dyer and Manning, 1999). The size and concentration of flocs is largely variable both on a temporal and spatial scale, and is mainly a function of SPM concentration and tidal shear (Law et al., 1997; van Leussen, 1999). It is believed that flocculation is enhanced at low shear, whereas a higher turbulence causes floc disaggregation and breakdown (Dyer and Manning, 1999). This is supported by in-situ estuarine particle sizing measurements carried out in the Tamar Estuary during tidal cycles, which revealed an increase in concentration of larger aggregates ( $> 250 \mu\text{m}$ ) at slack water, whilst material with smaller particle size ( $< 100 \mu\text{m}$ ) was apparent at peak current velocities, when the turbulent shear is stronger (Bale et al., 1989; Dyer and Manning, 1999). An important fraction of the particle population in estuaries are colloids, unsettleable particles in the size range between few nm (or  $\sim 1000$  Da) and 0.2-1  $\mu\text{m}$  (Buffle and Leppard, 1995; Wen et al., 1997; 1999), which are operationally included in the dissolved phase, and cannot be detected by the available in-situ instruments. Colloids are "dynamic" particles, continuously generated, removed from solution and transferred through the particle-size spectrum by coagulation and breakup of humic substances, biopolymers, Fe and Mn oxyhydroxides, and aluminosilicates (Stumm, 1993; Muller, 1996a; Gustaffson and Gschwend, 1997; Wen et al., 1997), probably with mechanisms similar to those responsible for floc aggregation and disaggregation. Owing to their large specific surface area and high reactivity, colloids may play a fundamental role in trace metal transport and cycling in estuaries (Sañudo-Wilhelmy et al., 1996; Wen et al., 1999).

The seawater-freshwater interface can be an area of enhanced tidally-controlled resuspension of bed sediments, which, coupled with tidal pumping of particles from down-

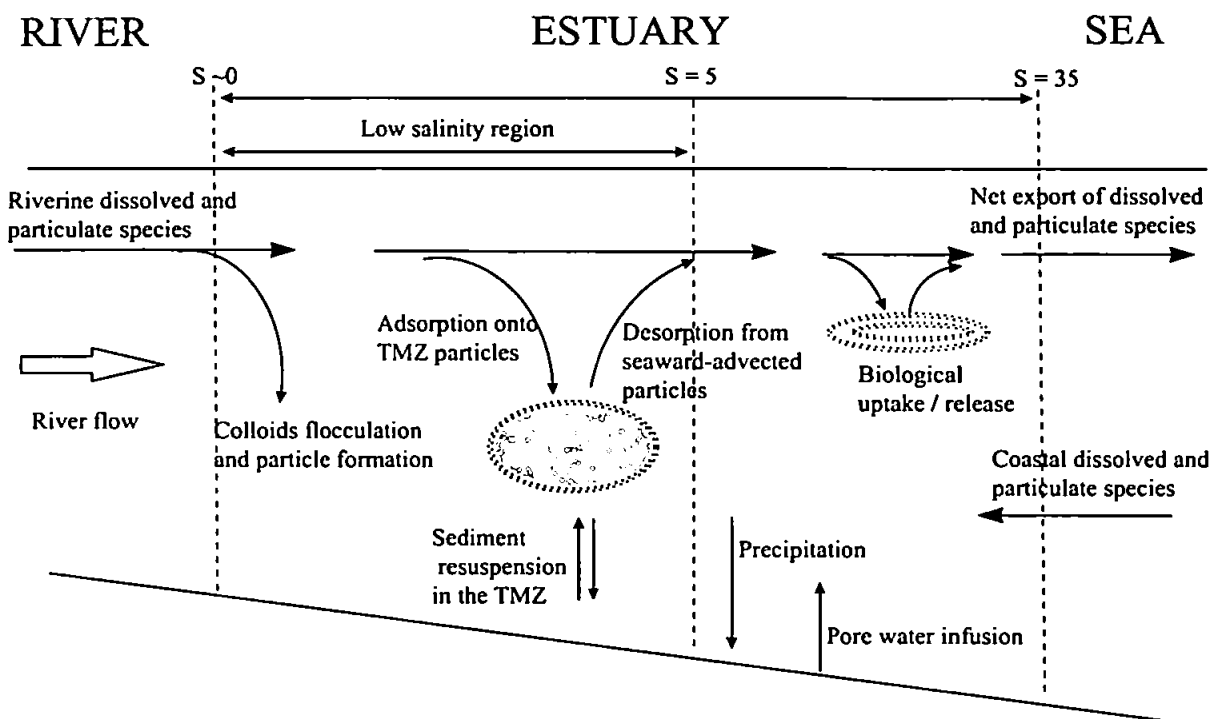
estuary, can give rise to a TMZ (Bale et al., 1985). Suspended particles in the TMZ have been shown to have a smaller diameter (20-25  $\mu\text{m}$  in the Tamar: Bale et al., 1989) and higher specific surface areas (Millward et al., 1990) than the overall estuarine particle population. The causes for these specific properties of TMZ suspended particles are probably a combination of (i) disaggregation of resuspended particles due to tidal shear (Bale et al., 1985), (ii) selective retention processes (Bale et al., 1989); (iii) precipitation of newly formed Fe and Mn oxy-hydroxides (Millward et al., 1990). The TMZ is therefore an area of high trace metal reactivity, due to the scavenging properties and high concentrations of the SPM (Millward et al., 1990).

### 1.1.2 PHYSICO-CHEMICAL PROCESSES IN ESTUARIES

Estuaries are highly dynamic environments where mixing of riverwater with seawater induces gradients in ionic strength, pH, dissolved oxygen, temperature and particle character and concentration. Fluctuations in the above parameters are experienced daily (tidally) and seasonally, and induce a variety of biogeochemical processes which can strongly affect the chemical speciation and reactivity of trace metals in the estuarine environment (Bourg, 1988). A diagram of the factors and processes affecting trace metal reactivity in estuaries is shown in Figure 1.1.

Seawater and riverwater have a very different chemical composition. The concentration of inorganic components in seawater is generally higher than in riverwater (Table 1.2). While the composition of the major components and pH of seawater are virtually constant (because the rate of mixing of oceanic waters is faster than the rate of removal or supply of the components themselves), the composition of riverwater depends on the chemical composition of the weathered rocks and on the nature of the river catchment. This is reflected in the estuarine pH gradient, which is positive for low alkalinity riverwater, or negative for high alkalinity riverwater (Table 1.2). Much lower riverine pH values may occur in areas affected by acid mine drainage (Braungardt et al., 1998). Gradients in major ionic components and pH influence the inorganic speciation of

trace metals in estuaries, and promote desorption from particles, flocculation of organic and inorganic colloids, and co-precipitation with newly-formed iron oxyhydroxides (Millward and Moore, 1982; Bourg, 1987).



**Figure 1.1.** Principal estuarine physico-chemical processes and factors affecting trace metal transport and reactivity. “Dissolved” represents the  $<0.45 \mu\text{m}$  fraction and includes truly dissolved and colloidal trace metal species.

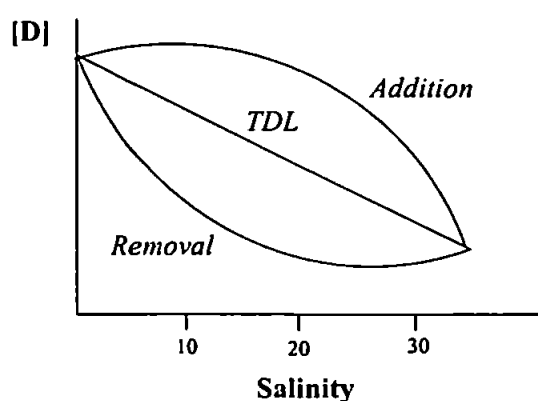
**Table 1.2.** Concentration of major inorganic constituents of standard seawater (SSW), high (HARW) and low alkalinity (LARW) riverwater. From: Dyrssen and Wedborg (1980).

Constituent, mol L <sup>-1</sup> (*)	SSW	HARW	LARW
Na <sup>+</sup>	0.47932	0.00030	0.00030
K <sup>+</sup>	0.01045	0.000065	0.000065
Mg <sup>2+</sup>	0.05439	0.00020	0.000030
Ca <sup>2+</sup>	0.01053	0.00057	0.000087
Cl <sup>-</sup>	0.55862	0.00020	0.00020
SO <sub>4</sub> <sup>2-</sup>	0.02889	0.00015	0.00015
Carbonate alkalinity	0.0024	0.0014	0.0001
HCO <sub>3</sub> <sup>-</sup>	0.00186	0.00136	0.0001
CO <sub>3</sub> <sup>2-</sup>	0.000275	0.000018	$9.4 \times 10^{-8}$
pH	8.12	8.43	7.3
Ionic strength	0.7	0.004	0.001
Salinity	35	0.144	0.041

\* except carbonate alkalinity (eq L<sup>-1</sup>), pH and salinity.

Nutrients (N, P, Si) and dissolved organic matter concentrations are usually higher in riverwater than in seawater, due to anthropogenic (fertiliser and sewage discharges) or natural (leaching of humic substances from soils) sources. High nutrient loads, coupled to low turbidity, may support high estuarine primary production, which can result in removal of trace metals in estuaries with a long flushing time (Luoma et al., 1998). Organic matter is known to occur in a wide range of particle sizes, from organic macromolecules, to colloidal humic substances and coatings on particles (Buffle, 1988), which generally have the ability of binding trace metals (Sections 1.3.2-1.3.4): the fate of organic matter (conservative dilution or flocculation) is therefore fundamental in determining that of the associated trace metals.

Particulate and dissolved (i.e. truly dissolved and colloidal) trace metals, being associated with different components, are subject to different physico-chemical processes and transport mechanisms, which will ultimately determine their fate in the aquatic environment (Figure 1.1). Some dissolved species are simply diluted by physical mixing and are carried to the sea (conservative behaviour), whereas other species are involved in *in-situ* biogeochemical processes, resulting in addition or removal of a constituent (non-conservative behaviour) from the dissolved phase (Figure 1.2). The extent of the addition/removal will depend, among several factors, on the concentration and physico-chemical nature of the suspended particles (Millward and Turner, 1995), and on the flushing time of the estuary (Millward, 1995).



**Figure 1.2.** Estuarine mixing behaviour for a dissolved constituent, [D]. TDL = theoretical dilution line for conservative behaviour (After Liss, 1976).



Addition of trace metals to the dissolved phase may be the result of desorption from seaward-advected particles (Chiffoleau et al., 1994; Kraepiel et al., 1997), pore-water infusion (Morris et al., 1982a; Ackroyd et al., 1986; Laslett and Balls, 1995), or anthropogenic inputs (Campbell et al., 1988). While trace metal desorption from seaward-advected particles occurs as a result of increased competition for the adsorption sites by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , and/or complexation by  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  (Bourg, 1987; Comans and van Dijk, 1988), pore water infusion takes place upon tidal disturbance of bottom sediments with subsequent injection of metal-rich pore waters into the water column (Laslett and Balls, 1995).

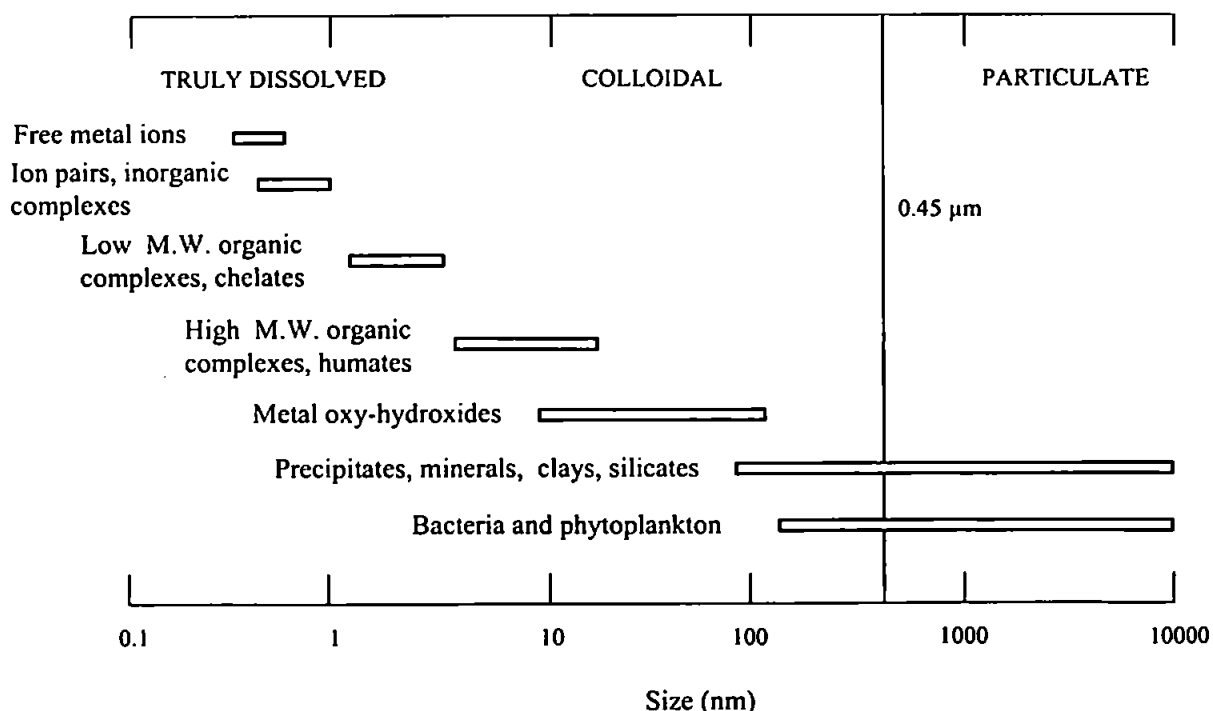
Removal of dissolved constituents may result from adsorption onto suspended particles (Ackroyd et al., 1986), co-precipitation with organic or inorganic matter during flocculation of colloids (Sholkovitz and Copland, 1981) and of newly formed Fe oxyhydroxides (Millward and Moore, 1982), or uptake by biota (Luoma et al., 1998). Flocculation of (colloidal) Fe and Mn hydrous oxides and humic acids occurs in the presence of seawater cations which act to destabilise the surface charge of the colloids (Sholkovitz and Copland, 1981). Moreover, fresh Fe hydroxides may precipitate when Fe-rich acidic mine streams enter the low salinity region of estuaries, or upon tidal disturbance of bed sediment with injection of  $\text{Fe}^{2+}$  (Millward and Moore, 1982). Uptake by aquatic biota is a fundamental mechanism for trace metal cycling in the aquatic environment. Interaction of trace metals with living bacteria and phytoplankton occurs through binding at the cell surface followed by transfer into the cell across the membrane (Morel et al., 1991). In estuaries the complexity of transport processes makes it difficult to discriminate biological processes from physico-chemical ones; moreover trace metal removal will only occur when the water turnover time is slow enough for biological uptake processes to be effective (Luoma et al. 1998).

Deviations from the theoretical dilution line may occur also for conservative constituents if temporal variations in their end-member concentrations occur over

timescales similar to or shorter than their estuarine residence time (Cifuentes et al.,1990). Variations in river flow can affect the riverine concentration of dissolved constituents entering an estuary (by either diluting or increasing their concentration: Neal et al., 1997), but also, together with changes in tidal state, can affect the estuarine flushing time (Morris, 1990). Therefore, the mixing behaviour of a conservative component may depend on the complex interplay of river flow, estuarine flushing time and variability in end-member concentrations.

## 1.2 Trace metal speciation: theoretical considerations

It is well known that the determination of trace metal physico-chemical speciation is essential in order to predict their bioavailability, behaviour and impact in aquatic systems (Sunda, 1988; Stumm and Morgan, 1996). Trace metal species can occur in the aquatic environment in a continuum of sizes, from true solution to colloidal and particulate phases (Figure 1.3); this distribution is the result of the interaction with a large number of



**Figure 1.3.** Size-distribution of trace metal species (after Morris, 1983). The vertical line represents the conventional pore size used to discriminate between dissolved and particulate phases. M.W. = molecular weight.

inorganic components and poorly-characterised organic components (Buffle, 1988; Stumm and Morgan, 1996). However, despite the progress in analytical techniques during the last 20 years, it is still not possible to detect all individual species of trace metals, and models have been developed which allow the estimation of trace metal speciation on the basis of measured or postulated stability constants. A number of speciation codes have been optimised for specific applications: for example, MINEQL+ (Schecher and McAvoy, 1992) allows modelling of reactions in the truly dissolved phase; WHAM (Tipping, 1994) and SCAMP (Lofts and Tipping, 1998) are designed specifically for calculating speciation in presence of dissolved and adsorbed humic substances and of particulate metal oxides.

Accurate models are now available for describing and predicting the inorganic speciation of trace metals in natural waters, because the chemical composition and stability constants for species formation of the electrolytic components of seawater are well known. However, there is still a fundamental lack of knowledge of the chemical composition and binding strength of natural dissolved organic matter and natural particulate matter. Therefore models describing the interaction of trace metals with these natural components are under current development, and their ability to predict speciation outside the conditions of experimental measurement is still a challenge (Turner, 1995).

At the basis of chemical speciation model studies is the assumption that the system under study is in equilibrium (Tipping et al., 1998). This is a reasonable assumption for a system composed of inorganic species only, as it is well known that most inorganic complexation reactions reach equilibrium quickly (Turner, 1995). The assumption may not be always true for trace metal interactions with organic ligands and particle surfaces, because of the generally slow complexation properties of natural organic ligands (Hering and Morel, 1988a; 1989) and slow migration into the crystalline structure of particles (Nyffeler et al., 1984).

### 1.2.1 METAL COMPLEXATION IN THE DISSOLVED PHASE

Calculations for describing trace metal speciation in the truly dissolved phase are based on established thermodynamic theory (Stumm and Morgan, 1996), and will be summarised here only briefly. In the following discussion, ionic charges are omitted for simplicity.

At a given ionic strength, the overall stoichiometric stability constant for the equilibrium reaction between a metal (M) and n ligands (L) for the formation of the n<sup>th</sup> order complex ML<sub>n</sub> :



is defined by:

$$\beta_n = [ML_n] / [M] [L]^n \quad (1.2)$$

and is related to the thermodynamic stability constant for reaction (1.1) by:

$$\beta_n = \beta_n^\circ \gamma_M \gamma_L^n / \gamma_{ML_n} \quad (1.3)$$

where  $\beta_n^\circ$  is the overall thermodynamic stability constant for the formation of ML<sub>n</sub>, and  $\gamma_M$ ,  $\gamma_L$  and  $\gamma_{ML_n}$  are the activity coefficients of the respective species. Their dependence on the ionic strength can be described by a Debye-Hückel type equation. Mass balance equations describe the distribution of the metal M among its different species:

$$[M]_T = [M] + \sum_{i,j} [ML_{ij}] \quad (1.4)$$

where ML<sub>ij</sub> is the i<sup>th</sup> order complex (i=1...n) with the ligand L, and j is the number of ligand types (e.g. Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>...). Similar mass balances can be defined for the ligands. Combination of equations (1.2) and (1.4) yields:

$$[M]_T = [M] + \sum_{i,j} \beta_{ij} [M] [L_j]^i \quad (1.5)$$

If the values of  $[M]_T$ ,  $[L]$  and  $\beta_{ij}$  are known, then equation (1.5) can be solved for  $[M]$  and therefore  $[ML_i]$  can be calculated for all species. For systems with a high number of components, a set of equations of the type (1.5) has to be solved and this is usually accomplished with the aid of computer software such as MINEQL+ (Schecher and McAvoy, 1992). This program will be used for modelling the species distribution of dissolved Ni in the Tweed and Mersey Estuaries in Chapter 5. Equation (1.5) can also be written as:

$$[M]_T = [M] \sum_j \alpha_{Mj} \quad (1.6)$$

where  $\alpha_{Mj}$  is the  $\alpha$ -coefficient, or side-reaction coefficient, for the reaction of M with the  $j^{\text{th}}$  ligand or group of ligands:  $\alpha$ -coefficients are defined as the ratio of the metal concentration which is complexed by a particular ligand or group of ligands over the free metal ion concentration (Ringbom and Still, 1972). Generally, the  $\alpha_M$  coefficients can be calculated from knowledge of medium composition and stability constants for the formation of the metal species (van den Berg and Nimmo, 1987; Gledhill and van den Berg, 1994). However, usually the side-reactions of the natural ligands cannot be determined, and information on the reaction of a metal with a natural ligand can only be provided by conditional stability constants:

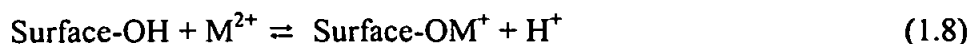
$$K' = \beta / \alpha_L = [ML] / [M] [L'] \quad (1.7)$$

The conditional stability constant above is defined for specific conditions of pH, ionic strength and composition of the aquatic medium.

### 1.2.2 SURFACE COMPLEXATION

A number of models have been developed to describe the interaction of trace metals with well-defined particle surfaces, like Fe, Al and Mn oxides (Dzombak and Morel, 1990; Lofts and Tipping, 1998). Such models, which go under the generic name of "surface complexation models" (SCM), and extensively reviewed by Dzombak and Morel

(1990), describe the interaction of trace metals with the particle surfaces in terms of competition of the metal and the proton for the adsorption sites on the particle surface, under the effect of the net electric charge at the surface. Therefore for the reaction at the surface:



the corresponding surface complexation constant is given by a covalent and an electrostatic component:

$$K_{\text{surface}} = K_{\text{int}} K_{\text{elect}} \quad (1.9)$$

In equation (1.9),  $K_{\text{int}}$  is the intrinsic conditional stability constant for reaction (1.8), which is considered analogous to reactions in the dissolved phase, and  $K_{\text{elect}}$  represents the interaction between the binding ion and the electrostatic potential at the surface (Turner, 1995). The various surface complexation models differ in the relative weight of the chemical and electrostatic components, and in the models which relate the surface potential to the surface charge (Tessier, 1992; Turner, 1995).

The application of models such as the SCM to the interaction of trace metals with natural particles is, however, not straightforward. A successful modelling of trace metal adsorption processes onto natural particle surfaces is in fact limited by the lack of knowledge of the particle surface heterogeneous chemical composition and binding capacity of each physico-chemical component (Millward, 1995).

### 1.2.3 SORPTION MODELLING: THE DISTRIBUTION COEFFICIENT CONCEPT

A more practical way to describe water-particle interactions of trace metals in natural systems is via the use of the distribution coefficient  $K_d$  (Olsen et al., 1982):

$$K_d = P / D \quad (1.10)$$

where  $P$  is the concentration in the particulate phase (w/w) and  $D$  is the concentration in the dissolved phase (w/v). Distribution coefficients are conditional with respect to salinity,

pH, temperature, particle concentration and chemical nature, and speciation of the metal in the dissolved phase (Bourg, 1987; Duursma and Carrol, 1996). The use of  $K_{ds}$  for modelling purposes is based on the following assumptions: (i) equilibrium between the dissolved and particulate phases; (ii) low concentration of the adsorbed trace metal compared with the number of the adsorption sites; (iii) homogeneous particle population; (iv) no dissolved organometallic species (Bourg, 1987; Millward, 1995; Benoit, 1995).

Distribution coefficients may be derived from the partitioning of radioactive tracers added to the samples (e.g. Jannasch et al., 1988; Turner et al., 1992a; Barbeau and Wollast, 1994), or from field observations of dissolved and particulate constituents (e.g. Balls, 1989; Turner et al., 1992b; Elbaz-Poulichet et al., 1996; Paucot and Wollast, 1997). Field  $K_d$  calculations are based on partial or total trace metal extraction techniques, which lack selectivity (Tack and Verloo, 1995) and often are strong enough to remove trace metals that are associated with binding sites within the matrix structure: these metals are not actually available for exchange, and as a result, field  $K_{ds}$  can be up to two orders of magnitude higher than radiotracer  $K_{ds}$  (Duursma and Carroll, 1996; also shown in Tables 1.8 and 1.9). Field  $K_{ds}$ , therefore, do not necessarily represent equilibrium distributions of trace metals between phases (Bourg, 1987), but are useful tools in water quality modelling, as they can be used for assessing temporal changes in the fraction of trace metals associated with dissolved and particulate phases in aquatic environments subject to anthropogenic inputs (Balls, 1989). On the other hand, the empirical determination of  $K_{ds}$  through the use of radiotracers accounts only for exchange reactions at the surface, which are those of interest in water-particle interaction processes.

The main criticism of the use of  $K_{ds}$  is that they are dependent on the water chemistry and surface properties of the system under study, and there may be kinetic constraints on their use. As a consequence,  $K_{ds}$  cannot be extrapolated to environments where other geochemical conditions prevail (Tessier, 1992). Despite this drawback,  $K_{ds}$  are an useful tool in comparing the relative affinity of trace metals for particles and solution

for a given system (Tipping et al., 1998), and in the diagnostic modelling of trace metal reactivity and distributions in aquatic environments (Wood et al., 1995; Liu et al., 1998).

### 1.3. Trace metal species in the aquatic environment

#### 1.3.1 INORGANIC SPECIATION – THE TRULY DISSOLVED SPECIES

The main inorganic ligands believed to complex trace metals in natural waters are  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  and  $\text{OH}^-$  (Turner et al., 1981; Byrne et al., 1988). The inorganic composition of seawater and riverwater is considerably different (Table 1.2), and as a consequence, the inorganic speciation of trace metals varies from fresh water to seawater. Table 1.3 shows the speciation of some trace metals in high and low alkalinity riverwater, and Table 1.4 in seawater (Turner et al., 1981). For all metals, the free ion is the dominant species in freshwater at pH 6, whilst at pH 9 the carbonate species are more important for Co, Cu and Ni, and the hydroxide for Zn. In seawater, Ni, Co and Zn are mainly present as the free metal ion and as chloride complexes, whilst the carbonate complex is the fundamental inorganic Cu species.

**Table 1.3.** The inorganic speciation of dissolved trace metals in low alkalinity riverwater (pH 6) and high alkalinity riverwater (pH 9, in brackets), as % of total dissolved metal. Data from Turner et al. (1981).

Metal	Free	MOH <sup>+</sup>	MCl <sup>+</sup>	MSO <sub>4</sub>	MCO <sub>3</sub>
Ni <sup>2+</sup>	98 (8)	* (2)	* (*)	2 (*)	* (90)
Co <sup>2+</sup>	98 (20)	* (7)	* (*)	2 (*)	* (73)
Cu <sup>2+</sup>	93 (*)	1 (3)	* (*)	2 (*)	4 (96)
Zn <sup>2+</sup>	98 (6)	* (78)	* (*)	2 (*)	* (16)

\* = species contributing less than 1%; - = species not considered in the calculations.

**Table 1.4.** The inorganic speciation of dissolved trace metals in seawater (pH 8.2) as % of total dissolved metal. Data from Turner et al. (1981).

Metal	Free	MOH <sup>+</sup>	MCl <sup>+</sup>	MSO <sub>4</sub>	MCO <sub>3</sub>
Ni <sup>2+</sup>	47	1	34	4	14
Co <sup>2+</sup>	58	1	30	5	6
Cu <sup>2+</sup>	9	8	3	1	79
Zn <sup>2+</sup>	46	12	35	4	3

\* = species contributing less than 1%; - = species not considered in the calculations.



### 1.3.2 COMPLEXATION WITH NATURAL ORGANIC LIGANDS

In natural waters a variable fraction of trace metals can be associated with natural or anthropogenically derived organic matter, which plays an important role in controlling the metal bioavailability (Morel et al., 1991; Mackey and Zirino, 1994). Dissolved organic matter in natural waters includes a wide variety of compounds, most of which have low concentrations and have not been well characterised (Morel, 1983; Buffle, 1988). Additionally, the chemical composition of the organic ligands pool is likely to vary over temporal and spatial scales (Buffle, 1988). It is therefore difficult to assign stability constants of general applicability for the formation of complexes with trace metals, and hence model metal-organic ligand interactions. However it is possible for stability constants to be calculated using different analytical techniques, but they are conditional with respect to the pH and ionic strength of the samples, as the side-reactions of the ligands are not known (e.g. Bruland, 1989; van den Berg and Nimmo, 1987; Donat et al., 1994).

There have been a number of studies on trace metal complexation with well-defined, low-molecular weight organic ligands which are known to occur in natural waters (e.g. Daniele et al., 1985; Turner and Whitfield, 1987), and thermodynamic stability constants for the formation of a wide variety of such metal-ligand complexes have been compiled by Martell and Smith (1974, 1977) and by Smith and Martell (1975). These ligands, however, are believed not to be important in the complexation of trace metals in natural waters, because of a combination of relatively weak trace metal binding constants and low specificity (Morel, 1983).

Trace metal complexation by aquatic humic and fulvic acids has been extensively studied (e.g. Mantoura et al., 1978; Turner et al., 1986; Hering and Morel, 1988b; Warwick and Hall, 1992; Mandal et al., 1999). Humic and fulvic acids (generally known as humic substances) are complex polyelectrolytes with a variable degree of aromaticity, a high and variable fraction of carboxylic, alcoholic and phenolic groups, and a refractory nature (Turner, 1995). Riverine humic substances are known to be derived from the

decomposition of terrestrial plants, whilst marine humic substances are believed to be formed *in situ* from the condensation, polymerization and partial oxidation of lipids, carbohydrates and amino-acids (Morel, 1983; Buffle, 1988). They are believed to form 70-90% of the DOC in natural waters (Buffle, 1988), and therefore are thought to play an important role in trace metal complexation (Hering and Morel, 1988b). Humic and fulvic acids form trace metal complexes of moderate to high strength, with log  $K'$  values generally in the range 2-10 (e.g. Warwick and Hall, 1992; Hering and Morel, 1988b). However, often metal-humic interaction studies have been carried out after severe manipulation of the water samples in order to preconcentrate and/or extract the humic material from the original samples. Processes like precipitation, redissolution, preconcentration by rotary evaporation may irreversibly modify the nature and chemical reactivity of the original ligands (Shuman et al., 1990) and may lead to contamination and/or losses of trace constituents.

Voltammetric methods, i.e. adsorptive cathodic stripping voltammetry (ACSV) and anodic stripping voltammetry (ASV), are well-suited for the determination of the chemical speciation of dissolved trace metals in natural waters, and have the advantage of high sensitivity and minimal manipulation of the samples (van den Berg, 1991; Mota and Correia Dos Santos, 1995). ACSV has been extensively used to study the chemical speciation of several metals, and in some studies, complexes with log  $K'$  values well above 10 have been detected (e.g. van den Berg and Nimmo, 1987; Zhang et al., 1990; Gledhill and van den Berg, 1994). The method is based on the addition of a known amount of a ligand which competes with the natural ligands for complexing the metal. The metal fraction which is directly measured (ACSV-labile) is that complexed by the added ligand, and includes the free, inorganically bound metal, and some fraction of the metal bound in natural (organic truly dissolved or organic/inorganic colloidal) complexes (Donat et al., 1994). The ACSV-labile metal is therefore operationally defined, as its concentration depends on the relative magnitudes of the  $\alpha$ -coefficients (see Section 1.2.1) of the metal

complexes with the natural and added ligands ( $\alpha_{ML}$  and  $\alpha_{MAL}$ , respectively). Probably the main limitation of ACSV is that only the complexes whose  $\alpha_{ML}$  lie within 1-2 decades above and below  $\alpha_{MAL}$  (which identifies the detection window) can be detected accurately (Zhang et al., 1990). Therefore, all complexes with  $\alpha_{ML} \ll \alpha_{MAL}$  are detected as labile, even if they may form complexes of moderate to strong stability.

$C_{18}$ -solid phase extraction has extensively been used to operationally isolate metal-organic complexes with a non-polar, hydrophobic nature in natural waters (Donat et al., 1986; Mackey and O'Sullivan, 1990; Yoon et al., 1999). For example, Donat et al. (1986) showed that up to 30% of total dissolved Cu, and up to 10% of total dissolved Zn, Ni, Cd, Mn and Pb in the Central North Pacific Ocean are isolated by this method. However, at least for Cu, Zn, and Ni, these complexes are believed to constitute only a fraction of the naturally-occurring metal-organic complexes in sea water as voltammetric studies have shown that >80% of Cu (Donat et al., 1994), >98% Zn (Bruland, 1989), and 25-30% of Ni (Nimmo, 1987; Donat et al., 1994) are organically complexed in seawater.

The main uncertainty of trace metal complexation studies concerns the physico-chemical nature of the ligands themselves (Butler, 1998; Moffett and Brand, 1996; Wells et al., 1998). Characterisation of the chemical structure of natural metal-binding ligands is extremely difficult owing to the very low concentrations in which these ligands occur in natural waters (typically of the order of nM: van den Berg and Nimmo, 1987; Moffett, 1995). It has been suggested that many of these high-affinity ligands may be of biological origin, and are produced by phytoplankton as a response to ambient concentrations of trace metals (for a review, see Butler, 1998). Therefore, conditions more favourable for growth are created either by mitigating metal toxicity (Gonzalez-Davila, 1995; Moffett and Brand, 1996; Gledhill et al., 1999), or by increasing the bioavailability of the metal (Rue and Bruland, 1997). The strong ligands observed to bind Ni and Co have been suggested to have a porphyrin-type structure, originating from degradation of chlorophyll (Zhang et al.,

1990; Achterberg et al., 1997): however, there is no evidence to support this hypothesis and further research is necessary.

Mackey and Zirino (1994) proposed a different model for organic complexation of trace metals in natural waters. According to their model, trace metals in seawater are present in colloids of 10-100 nm diameter (the “onion”) made of layers of marine humic substances held together by hydrogen bonds and by trace metals through coordination bonds. The metal availability therefore is determined by the sterical hindrance of the metals trapped in the “onion” layers which are not readily exchangeable. The authors suggest that the model can explain the slow reaction kinetics observed for trace metals such as Zn, Ni, Co and Pb in seawater. The onion model has been recently challenged by Wells et al. (1998), who showed that metals are bound to ligands whose nature differs for individual metals. The role of such ligands as metal buffers (Moffett and Brand, 1996) or as intermediates in scavenging processes (Wen et al., 1997), or both (Wells et al., 1998), still remains a subject open to investigation.

### 1.3.3 THE COLLOIDAL FRACTION OF TRACE METALS

Historically an operational distinction has been made between “dissolved” and particulate phases by filtration through 0.45  $\mu\text{m}$  pore size filters. However, owing to the advance in ultrafiltration techniques, in the last decade it has been established that organic and inorganic matter (and associated trace metals) exist in a continuum from truly dissolved (< 1 nm) to macroscopic state (Figure 1.2), and the importance of the colloidal phase has been established (Morel and Gschwend, 1987; Honeyman and Santschi, 1988; Stumm, 1993; Mackey and Zirino, 1994; Gustafsson and Gschwend, 1997; Wells et al., 1998). Colloids have been operationally defined as particles, which have the physical and chemical properties of solids, but which do not settle under the effect of gravity (Gustafsson and Gschwend, 1997). Colloids are important in determining the biogeochemistry and transport of trace metals in aquatic systems (Benoit et al., 1994; Moran et al., 1996; Santschi et al., 1997; Wells et al., 1998), as the colloidal and truly

dissolved trace metal fractions often have different geochemical behaviour (Martin et al., 1995). Muller (1996b) used ASV to determine the conditional stability constants for Cu, Pb and Cd complexation by natural ligands in the dissolved, colloidal and truly dissolved phases. The strong similarities obtained for the log  $K'$  values in all the three phases suggested the presence of a limited number of metal-binding ligands with similar binding strength but with a wide size range across the different fractions.

#### 1.3.4. PARTICLE-WATER INTERACTIONS AND SPECIATION OF PARTICULATE METALS

The interaction of trace metals with particulate matter has a fundamental role in controlling dissolved trace metal concentration in estuaries and in aquatic environments in general (Dzombak and Morel, 1987). There are a number of particulate components, which can, in principle, contribute to the sorptive capacity of natural particulate matter.

The inorganic particles of major importance for trace metal adsorption are Fe and Mn oxyhydroxides: these occur in aquatic systems as colloids, discrete particles, or as coatings onto mineral particles. Oxyhydroxides of Fe and Mn are characterised by high specific surface areas (SSA) of the order of 200-400 m<sup>2</sup> g<sup>-1</sup> (Crosby et al., 1983; Millward et al., 1990), which confers them high adsorptive properties and high affinity for trace metals (Drever, 1988). In contrast to Fe and Mn oxyhydroxides, clay minerals have a small trace metal scavenging capacity due to their low SSA (e.g. 12 m<sup>2</sup> g<sup>-1</sup> for kaolinite: Millward et al., 1990), and they are believed to be more important as nucleation centres for Fe and Mn oxides precipitation and for organic coating in estuarine waters (Forsgren et al., 1996). Adsorption of trace metals onto hydrous oxide surfaces is a pH-dependent process. Generally trace metals show very low tendency to adsorb at low pH, due to competition of protons for surface sites, whilst they are strongly adsorbed at high pH, as a result of the increase of the negative charge developed on the particle surface by deprotonation. This transition occurs over a narrow pH range known as the adsorption edge (Stumm, 1992), which is different for different metals, substrates and solutions (Dzombak and Morel,

1987). For Ni, the adsorption edge generally lies in the pH range 5-7 (Bryce et al., 1994; Coughlin and Stone, 1995).

It has been shown that suspended particles in natural waters are negatively charged due to the adsorption of organic material, mainly of humic origin (Hunter and Liss, 1979; Muller, 1996a), which provides carboxylic and phenolic groups for complexation reactions with metal ions (Davis, 1982). It has been suggested that surface binding on colloids (or particles) coated with organics, rather than reactions with simple inorganic surfaces, generally controls the distribution of trace metals between dissolved and particulate phase (Balistrieri et al., 1981).

Adsorption of trace metals onto particles has usually been studied using well-defined synthetic substrates and model solutions (e.g. Bryce et al., 1994; Coughlin and Stone, 1995). However, natural particles are a complex mixture of coexisting phases of different origin and chemical composition, and their combined effect on trace metal adsorption can be rather different from what may be observed for individual phases (Adediran and Kramer, 1987; Zachara et al., 1994), especially in the presence of organic coatings on particles (Lofts and Tipping, 1998). This is why an empirical  $K_d$  approach is often favoured when studying metal reactivity in natural waters (Wood et al., 1995; Liu et al., 1998).

#### 1.4 Nickel in the aquatic environment

Nickel is a metal of the first transition series, and in the elemental state has an electronic configuration  $[\text{Ar}] 3d^8 4s^2$ . Its aqueous chemistry is based on the ion  $\text{Ni}^{2+}$ , which is the most common oxidation state in nature for this metal (Greenwood and Earnshaw, 1984). In aqueous solution, the free metal ion is present as  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ , while its complexes are usually square planar or octahedral. Nickel has been defined as the slowest reacting transition metal of biological interest (Price and Morel, 1991). The slow complexation kinetic of Ni with a variety of organic ligands has been attributed to the slow exchange of

Ni co-ordination water (Morel et al., 1991; Mandal et al., 1999).

Nickel occurs in crude oils, oil shales, coals and sedimentary rocks as Ni<sup>2+</sup> complexes in geological metalloporphyrins (Pretorius et al., 1993) ultimately originating from chlorophyll-*a* (Pretorius, 1994). The main anthropogenic Ni sources in the environment are fossil fuel burning and mining activities (McIlveen and Negusanti, 1994). The total (dissolved + particulate) atmospheric and riverine Ni inputs to the world ocean have been evaluated as 0.37-0.49×10<sup>9</sup> and 0.33×10<sup>9</sup> mol L<sup>-1</sup> yr<sup>-1</sup>, respectively (Duce et al., 1991; Martin and Thomas, 1994).

Nickel is a micronutrient required for phytoplankton growth: as with many trace metals, it has a stimulatory effect at low concentrations (Price and Morel, 1991) but can inhibit growth at high concentrations (Oliveira and Antia, 1986). It has been shown that phytoplankton growth rate is inversely correlated to the concentration of free Ni<sup>2+</sup> ion, and is independent on total Ni concentration (e.g. Spencer and Nichols, 1983; Watras et al., 1985). Price and Morel (1991) have shown that phytoplankton growing on urea as a sole N source require Ni<sup>2+</sup> at concentrations at least above 1 nM in order to achieve optimal growth rate, as Ni is a cofactor in the enzyme urease. The toxic threshold for phytoplankton growth has been shown to be > 1 μM Ni<sup>2+</sup> (Spencer and Nichols, 1983): this concentration is, however, unlikely to occur in most marine and freshwater environments (except for some systems affected by acid mine drainage: e.g. Braungardt et al., 1998).

#### 1.4.1. INORGANIC AND ORGANIC NI SPECIATION

A summary of the inorganic speciation of dissolved Ni in natural waters calculated from equilibrium models is shown in Tables 1.3 and 1.4. In seawater, inorganic Ni is believed to occur mainly as the free, hydrated ion, and as carbonate and chloride complexes (Turner et al., 1981; Byrne et al., 1988). In freshwater, the dominant species is either the free ion or the carbonate complex, depending on the pH of the system, whilst all other species are negligible.

Mantoura et al (1978) used gel filtration chromatography to determine the conditional stability constants of Ni complexes with humic materials extracted from a variety of aquatic environments. The values obtained were in the range  $\log K' = 4.2-5.5$  (pH 8.0; Ionic strength 0.02 M). The authors included the Ni-humic complex conditional stability constants in a speciation model for estuarine waters, and showed that only 1% of dissolved Ni was complexed by the humic material in riverwater, whilst this fraction became negligible in seawater. However, Donat et al. (1986), using the C<sub>18</sub> solid phase extraction (SPE) method, showed that up to 10% of total dissolved Ni was complexed to hydrophobic, humic-like organic material in the central North Pacific Ocean. Martin et al. (1994) showed that up to 28% of dissolved Ni in the Venice Lagoon was bound to hydrophobic organic ligands which were believed to be released by the macroalga *Ulva*. Moreover, voltammetric studies (Nimmo, 1987; van den Berg and Nimmo, 1987; Nimmo et al., 1989; Donat et al., 1994) showed that 20-50% of Ni is bound to a class of extremely strong ligands in natural waters (Table 1.5). The conditional stability constants determined for these complexes were in the range of  $\log K' = 17.3-18.7$ , which are 12 orders of magnitude higher than those reported by Mantoura et al. (1978) for seawater (Table 1.5). The validity of the values obtained by Mantoura et al. (1978) may be questioned, owing to the heavy sample manipulation (Shuman et al., 1990). However, although Ni complexes with  $\log K'$  values lower than those detected by ACSV may occur in natural waters, they would not be detected by this technique, because of its limited detection window (between  $10^{8.8}$  and  $10^{11.1}$  for salinity between 2 and 35 and added competing ligand of 0.2 mM: van den Berg and Nimmo, 1987).

Donat et al. (1994) used chelating resin column partitioning (based on ion exchange onto Chelex-100) coupled to graphite furnace atomic absorption spectrometry (CRCP-GFAAS) to determine the chemical speciation of Ni with a detection window centred around the inorganic alpha coefficient of Ni ( $\alpha_{Ni^{2+}} = 1.6-1.8$  in the conditions of their study). The authors found evidence for a class of ligands with  $\log K' > 11$ , with a concentration



**Table 1.5.** A comparison of the results of Ni chemical speciation studies in natural waters.

Analytical method	Sample	log $K'_{NiL}$	% Ni "complexed"	Reference
Gel filtration chromatography	Various aquatic environments	4.2-5.5	< 1 (model prediction)	Mantoura et al. (1978)
C <sub>18</sub> SPE	North Pacific		<10	Donat et al. (1986)
C <sub>18</sub> SPE	Venice Lagoon		< 28	Martin et al. (1994)
ACSV	Tamar Estuary		20-80	Nimmo (1987)
ACSV	Beaulieu Estuary		20-60	Turner et al. (1998)
ACSV	Irish Sea	17-18	20-45	Nimmo (1987)
ACSV	English Channel	17.4-18.4	50	Nimmo (1987)
ACSV	Menai Straits	17.8-18.2	35	van den Berg and Nimmo (1987)
ACSV	Liverpool Bay	17.8-18.7	30-40	Nimmo et al. (1989)
ACSV	North Atlantic		20-30	Nimmo (1987)
ACSV	San Francisco Bay	> 17	35-50	Donat et al. (1994)
CRCP-GFAAS	San Francisco Bay	> 11	30-40	Donat et al. (1994)

within 15% of those determined by ACSV: this agreement suggested the presence of only one class of Ni-binding ligands, although no information could be obtained for ligands with  $\log K' < 11$ . All of the studies carried out by Nimmo (1987), van den Berg and Nimmo (1987), Nimmo et al. (1989), and Donat et al. (1994) showed that the ligands appeared to be saturated by the ambient Ni concentrations. All the voltammetric determinations indicate that in natural waters, 20-50% of Ni is bound to a single class of ligands with high values of conditional stability constants. These complexes may or may not correspond to those detected by C<sub>18</sub> SPE: the narrow detection windows of these techniques is such that they only allow the determination of a fraction of Ni-natural complexes. Whether the complexes detected by ACSV are in the truly dissolved or in the colloidal phase, and what the chemical nature of the ligands is, remains unknown.

#### 1.4.2. NICKEL IN SEAS, RIVERS AND ESTUARIES

Dissolved Ni (< 0.45  $\mu\text{M}$ ) has a nutrient-type distribution in oceanic waters, with depletion at surface and regeneration in intermediate and deep water, with concentrations ranging from 2-3 nM at the surface to 5-6 and 10-12 nM at depth for the north Atlantic and north Pacific Oceans, respectively (Saager et al., 1997; Noriki et al., 1998). Nickel concentrations in coastal waters are generally higher than in oceanic waters, owing to the

proximity of land-based sources. Some examples are shown in Table 1.6 with Ni concentrations varying between 1 and 70 nM in estuarine plumes.

Martin and Windom (1991) reported a world riverine average of 8 nM for dissolved Ni, and some examples of riverine concentrations of Ni are shown in Table 1.6. When comparing the data shown in Table 1.6, it should be kept in mind that differences in concentrations not only reflect different pollution levels, but also natural variations in river chemistry and catchment source rocks. Whilst dissolved Ni background concentrations of 3-4 nM have been reported for unpolluted rivers (Boyle et al., 1982; Windom et al., 1991; Guieu et al., 1996), values of hundreds of nM have been observed in polluted European estuaries (Comber et al., 1995; Paucot and Wollast, 1997), and as high as thousands of nM in rivers affected by acid mine drainage (a range of 1.6-6.9  $\mu\text{M}$  has been reported for the Tinto and Odiel rivers by Braungardt et al., 1998).

**Table 1.6.** End-member concentrations (nM, except otherwise indicated) and reactivity of dissolved Ni (<0.45  $\mu\text{m}$ ) in world estuaries and UK coastal seas. REM = riverine end member ( $S < 1$ ); MEM = marine end member ( $S > 27$ ).

Estuary	REM	MEM	Behaviour	Reference
World Average	8			Martin and Windom (1991)
Amazon	3-4	1	conservative	Boyle et al.(1982)
Beaulieu	82	15	conservative	Turner et al. (1998)
Danube	15	10	conservative	Guieu et al. (1998)
Forth	10-15	5	addition	Laslett and Balls (1995)
Gironde	7	5	addition	Kraepiel et al. (1997)
Huelva	1.6-6.9 $\mu\text{M}$	5.13	conservative/addition	Braungardt et al. (1998)
Humber	140-190	70	addition	Comber et al. (1995)
Lena	4	5	addition	Guieu et al. (1996)
Maeklong	3-8	5	addition	Windom et al. (1991)
Mersey	110-170	40-50	addition	Comber et al. (1995)
Mississippi	20	2	conservative	Shiller and Boyle (1991)
Ob	21-24	3-5	conservative	Dai and Martin (1995)
Rhône	27	5	conservative	Elbaz-Poulichet et al. (1996)
San Francisco Bay	17	7	addition	Sañudo-Wilhelmy et al. (1996)
Savannah	3	5	addition	Windom et al. (1991)
Scheldt	120-170	20	conservative	Paucot and Wollast (1997)
Seine	60	8	addition	Chiffolleau et al. (1994)
Tamar	35	5	removal/addition	Morris et al. (1986)
Tay	7	4	removal/addition	Owens and Balls (1997)
Yenisey	8.8-9.4	3-5	addition	Dai and Martin (1995)
English Channel		3.8 $\pm$ 0.8		Tappin et al. (1993)
Central North Sea		2-6		Tappin et al. (1995)
Irish Sea		6-7		Achterberg and van den Berg (1996)

The concentrations of particulate Ni in suspended matter of some world estuaries and marine particulate matter are shown in Table 1.7. Nickel concentrations in the particulate phase are highly variable, reflecting different origins (marine or terrestrial), physico-chemical composition, and contamination levels of the particles. The “background” trace metal concentration itself may be very variable, reflecting the composition of the drainage basin rocks and of marine-derived particles (Windom et al., 1989). A direct comparison of the particulate Ni data in Table 1.7 for different estuaries should therefore be undertaken with caution.

**Table 1.7.** Concentrations of particulate Ni ( $\mu\text{mol g}^{-1}$ ) in estuarine suspended particulate matter (SPM) and in marine particulate matter. All concentrations are determined after total digestion of particulate samples.

Compartment	REM	MEM	Reference
<b>Estuarine SPM</b>			
World Average	1.53		Martin and Windom (1991)
Gironde	0.75-1.0	0.8-1	Kraepiel et al. (1997)
Humber		0.7-0.9	Laslett (1995)
Lena	0.45	0.3	Martin et al. (1993)
Mersey		0.3-1	Laslett (1995)
Rhône	0.87	0.75-1.0	Elbaz-Poulichet et al. (1996)
Scheldt	0.9-1.1	0.4-0.8	Zwoisman and van Eck (1999)
Seine	0.3-0.4	0.5-1.0	Chiffoleau et al. (1994)
Tweed		0.8-1.2	Laslett (1995)
<b>Sea</b>			
English Channel		0.3-0.4	Laslett (1995)
North Sea		0.2-1.1	Laslett (1995)
Irish Sea		0.2-0.6	Laslett (1995)
Sinking particles (Northeast Atlantic Ocean)		0.2-0.4	Kuss and Kremling (1999)
Deep-sea clays		3.4	Martin and Whitfield (1983)
Fe-Mn nodules		75-170	Dymond et al. (1984)

Martin and Windom (1991) reported an average riverine particulate Ni concentration of  $1.53 \mu\text{mol g}^{-1}$ , which is high compared to most of the other rivers in Table 1.7. This could be due to sampling and analytical contamination artefacts, because the world average includes values obtained when there was no or little awareness of “clean” sample handling and analytical procedures. Recently determined concentrations in European estuaries have been shown to be generally in the range  $0.3-1 \mu\text{mol g}^{-1}$  (Chiffoleau et al., 1994; Paucot and Wollast, 1997; Martin et al., 1993; Kraepiel et al.,

1997). Nickel has often been shown to be associated preferentially with the detrital, refractory phase of riverine and estuarine lithogenic suspended particles (Martin et al., 1993; Chiffoleau et al., 1994; Campbell et al., 1988; Comber et al., 1995). Metals trapped in the detrital phase are far from the particle-water interface and therefore largely unreactive. However, several authors have suggested a preferential association with Fe and Mn oxides and oxyhydroxide phases, the latter either as coating on or as discrete particles (James et al., 1993; Comber et al., 1995; Sands et al., 2000). Positive correlation of Ni with Mn has also been observed in estuarine particulate matter in the Tweed (Laslett, 1995), Forth (Laslett and Balls, 1995), Rhine-Meuse (Paalman and van der Weijden, 1992), and Scheldt (Zwolsman and van Eck, 1999) Estuaries. This suggests that, to some degree, the Ni geochemical cycle is coupled with those of Fe and Mn, as Ni is co-precipitated with Fe and Mn in oxygenated waters (Balistrieri and Murray, 1986). The same scavenging capacity of Fe and Mn is at the origin of the high Ni concentrations in the deep-sea clays and pelagic Fe-Mn nodules (Table 1.7).

There is no universal pattern for the behaviour of dissolved Ni in estuaries, i.e. Ni behaviour is estuary-specific (Table 1.6). Conservative behaviour and addition are generally observed for Ni, whilst removal has only been reported for the Tamar (Morris et al., 1986) and Tay (Owens and Balls, 1997). However, some of the behaviours reported in Table 1.6 have been derived on the basis of a single or restricted number of surveys, which would not allow seasonal variability in the behaviour of Ni to be established (for example, the effect of biological uptake during phytoplankton blooms). Moreover, a very limited number of sites were sampled on certain surveys, with only one or two samples collected in the low salinity region of the estuaries (e.g. Comber et al., 1995, for the Mersey and Humber estuaries). Estuarine low salinity regions are however known to be zones of enhanced trace metal reactivity (Morris, 1986; Ackroyd et al., 1986; Liu et al., 1998), and a low sampling frequency would not allow the identification of removal or addition processes occurring in this highly reactive region (Ackroyd et al., 1986).

The removal of Ni in the low salinity region of the Tamar Estuary is well documented (Morris, 1986; Nimmo, 1987; van den Berg et al., 1991), and recently it has also been reported for the Tay Estuary (Owens and Balls, 1997). In the turbidity maximum zone (TMZ), the combination of (i) high concentrations of suspended particulate matter (up to 5 mg l<sup>-1</sup>), (ii) its depletion in particulate trace metals, (iii) its high specific surface area (Millward et al., 1990), all contribute to the removal of Ni. The addition exhibited by Ni seawards from the Tamar TMZ has been attributed to desorption from metal-enriched particles which are carried downstream from the TMZ and across the fresh-seawater interface (Morris, 1986; Liu et al., 1998).

The main geochemical processes believed to cause Ni addition to the dissolved phase are desorption from particulate matter (Li et al., 1984a; Morris, 1986; Liu et al., 1998; Kraepiel et al., 1997) and remobilization from bottom sediments (Laslett and Balls, 1995). Desorption of Ni from particulate matter is believed to occur when fine suspended particles are advected seawards across the freshwater-seawater interface. The increase in salinity can cause desorption via two mechanisms: (i) an increase in competition for the adsorption sites by Ca<sup>2+</sup> and Mg<sup>2+</sup>; and/or (ii) an increase in complexation of the metal by Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> (Morris, 1986; Li et al., 1984a; Hegeman et al., 1992; Paalman et al., 1994). These explanations are supported by laboratory experiments (Liu, 1996; Liu et al., 1998) which show that Ni, previously adsorbed onto estuarine SPM from riverwater, is released from particles upon an increase in salinity.

Remobilization from bottom sediments has been invoked by Laslett and Balls (1995) to explain the addition of Ni to the dissolved phase in the Forth Estuary. The authors believe that Ni, scavenged during precipitation of the insoluble Fe and Mn oxides in oxic conditions, is then released into the pore waters when Fe and Mn are reduced to the more soluble forms during bacterial degradation of organic matter. Upon tidal disturbance of bed sediments, the pore waters rich in Ni are then injected into the water column.

The lack of reactivity of Ni in estuaries has been often attributed to its preferential

association with the crystalline, refractory phase of the particulate matter (Chiffoleau et al., 1994; Campbell et al., 1988; Martin et al., 1993; Comber et al., 1995). More recently, the conservative behaviour of Ni in estuaries has been attributed to its low particle reactivity (Turner et al., 1998), which may be the result of its strong affinity for dissolved natural ligands (van den Berg and Nimmo, 1987).

#### 1.4.3. NICKEL SPECIATION AND PARTICLE-WATER INTERACTIONS IN ESTUARIES

Only a few studies have determined the chemical speciation of Ni in estuaries (Nimmo, 1987; van den Berg et al., 1991; Turner et al., 1998). The ACSV non-labile fraction of Ni has been shown to range between 20 and 80% in the Tamar Estuary (Nimmo, 1987; van den Berg et al., 1991), and between 20 and 60% in the Beaulieu Estuary (Turner et al., 1998). The results from van den Berg et al. (1991) indicated that the non-labile fraction of Ni behaved conservatively upon estuarine mixing, whilst the labile fraction was more reactive and exhibited removal at low salinity and addition in the mid-estuarine region. The same behaviour for labile Ni in the Tamar Estuary was observed by Nimmo (1987). It therefore appears that the particles in the TMZ provide abundant adsorption sites for the free or weakly bound Ni, but not for the more strongly bound non-labile Ni. On the other hand, Turner et al. (1998) observed a largely conservative behaviour of total and ACSV-labile Ni in the Beaulieu, an estuary characterised by high natural DOC concentrations (in contrast to the Tamar Estuary: Miller, 1999), and attributed it to a combination of low SPM concentrations and low particle-affinity of Ni. The latter was partly attributed to the strong association of Ni with dissolved natural ligands which was suggested would prevent Ni adsorption onto particles. The above observations indicate that the reactivity of Ni in estuaries is controlled, at least partly, by its complexation with dissolved organic matter. However, the study of Turner et al. (1998) was carried out in an estuary characterised by extremely high concentrations of natural humic acids, a feature which is not representative of the other estuaries where conservative behaviour of Ni has been reported (Table 1.6). No comparative studies have been carried out on the effect of

natural/anthropogenic dissolved organic matter in estuaries with contrasting physico-chemical and hydrological characteristics.

Little information is available on the nature and physical state of Ni-binding ligands. The fraction of dissolved Ni associated with colloids has been shown to vary from <2% in San Francisco Bay Estuary (Sañudo-Wilhelmy et al., 1996) to 20-50% in Galveston Bay (Wen et al., 1999), and 10-60% in the Ob and Yenisey estuaries (Dai and Martin, 1995). The good correlation between colloidal organic carbon and colloidal Ni shown for the Ob and Yenisey Estuaries (Dai and Martin, 1995) and for Galveston Bay (Wen et al., 1999) suggested that Ni-bearing colloids in the above estuaries have an organic nature. On the other hand, Powell et al. (1996) suggested that Ni was associated with Fe-oxyhydroxide colloids and/or with organic matter coating onto the Fe-oxyhydroxide surface in the Ochlockonee Estuary. Colloidal Ni has been shown to have either a refractory nature (Dai and Martin, 1995) or marked reactivity, with removal or formation of colloids throughout the estuarine mixing zone (Powell et al., 1996; Wen et al., 1999). In the Ochlockonee Estuary, "dissolved" Ni is conservative, but transition from the colloidal to the truly dissolved phase (< 1 kD) occurs with increasing salinity, probably due to desorption from colloidal Fe-oxyhydroxides (Powell et al., 1996). Conversely, dissolved Ni has been shown to occur mainly in the truly dissolved fraction in the Rhône Estuary (Dai et al., 1995), the Venice Lagoon (Martin et al., 1995) and San Francisco Bay Estuary (Sañudo-Wilhelmy et al., 1996). From the above studies, it seems that Ni shows a wide degree of association with both the truly dissolved and colloidal phases, and also different reactivity, probably due to the different nature of the ligands which bind the metal in the different estuaries. However, in these and other studies, Ni seems to have a relatively low particle affinity with respect to other metals, as shown by the  $K_{ds}$  in Tables 1.8 and 1.9. For the same metal, both field and radiotracer  $K_{ds}$  may vary by more than one order of magnitude, reflecting the differences in particle concentration and physico-chemical composition among different estuaries, but also the variations in salinity and pH. The

magnitude of the field and radiotracer  $K_d$ s generally follows the order:

$$\text{Fe} > \text{Pb} > \text{Zn} \sim \text{Cu} > \text{Ni} \sim \text{Cd}$$

Whilst the high values for Fe and Pb reflect their strong particle affinity (and for Fe also its occurrence as a fundamental constituent of estuarine particulate matter), the lower values for Zn, Cu, Ni, and Cd are probably also a consequence of their dissolved phase chemistry. Whilst the dissolved phase speciation of Cd in estuarine waters is known to be strongly affected by chloro-complexation (Comans and van Dijk, 1988), Zn, Ni and Cu form moderately strong chloro-complexes (Turner et al., 1981), but strong organic complexes (van den Berg and Nimmo, 1987; van den Berg et al., 1987) which have been suggested to keep the metals in solution (van den Berg et al., 1987; Comber et al., 1995; Turner et al.,

**Table 1.8.** A comparison of field distribution coefficients for Ni and other trace metals in estuaries. All values were obtained using total particulate dissolution techniques.

Metal	log $K_d$					
	Galveston Bay <sup>a</sup>	San Francisco Bay <sup>b</sup>	Scheldt <sup>c</sup>	Seine <sup>d</sup>	Mersey <sup>e</sup>	European coastal waters <sup>f</sup>
Ni	4.23 ± 0.11	5.1 ± 0.3	3.5-34.2	4.2-4.4	3.7-4.4	4.0-4.5
Cd	4.41 ± 0.32		3.9-6.3	3.9-4.0	4.4-5.1	3.5-5.0
Cu	4.11 ± 0.13	4.7 ± 0.4	4.2-5.7	4.5-4.7	4.7-5.0	4.0-5.0
Fe	6.92 ± 0.46	6.8 ± 1.1				
Pb	5.31 ± 0.27			6.1-6.3	5.0-5.4	5.0-7.0
Zn	5.28 ± 0.22	5.5 ± 0.4	4.3-5.2	4.4-4.7	4.4-4.6	4.0-5.0

References: <sup>a</sup>Wen et al. (1999); <sup>b</sup>Sañudo-Wilhelmy et al. (1996); <sup>c</sup>Paucot and Wollast (1997); <sup>d</sup>Chiffoleau et al. (1994); <sup>e</sup>Comber et al. (1995); <sup>f</sup>Balls (1989).

**Table 1.9.** A comparison of distribution coefficients obtained from radiotracer experiments for Ni and other trace metals in estuaries.

Metal	log $K_d$						
	Beaulieu <sup>a</sup>	Scheldt <sup>b</sup>	Humber <sup>c</sup>	Hudson <sup>e</sup>	Sabine-Neches <sup>f</sup>	Puget Sound <sup>g</sup>	Southern North Sea <sup>h</sup>
Ni	2.8 - 3.7	3.1-3.8	2.5-3.1 <sup>d</sup>				
Cd			2.9-3.5	3.6-4.2			2.1-3.0
Cu						4.4	
Fe				5.3-5.8			
Pb					3.4-4.6		
Zn			3.9-4.0	3.2-4.1			3.3-3.7

References: <sup>a</sup>Turner et al. (1998); <sup>b</sup>Barbeau and Wollast (1994); <sup>c</sup>Turner et al. (1993); <sup>d</sup>values for the Humber coastal zone: Sands (1997); <sup>e</sup>Li et al. (1984a); <sup>f</sup>Baskaran et al. (1997); <sup>g</sup>Paulson et al. (1994); <sup>h</sup>Turner et al. (1992a).



1998). Several authors have investigated the importance of trace metal complexation by natural ligands in affecting their sorptive behaviour in natural waters (van den Berg et al., 1987; Paulson et al., 1994), but only a few studies have investigated the role of natural DOC on the sorptive behaviour of Ni (Gerringa, 1990; Gerringa et al., 1991; Garnier et al., 1997), and only one study has been reported for estuarine waters (Turner et al., 1998).

### 1.5 Aims of the study

From previous studies on Ni reactivity in natural waters, it appears that its behaviour is governed by the competitive effects of complexation and adsorption. Both of these effects are fundamental in determining its bioavailability, fate and transport in the aquatic environment. However, no comprehensive, comparative study has been carried out so far to identify common and contrasting factors that determine the estuarine behaviour of Ni.

The aims of this study are, therefore, to:

- investigate the estuarine processes which affect the distributions of total dissolved Ni and ACSV species thereof, and its particle-water interactions, through field studies on Ni reactivity in estuaries with contrasting hydrological, physico-chemical and pollution characteristics (namely, the Tweed, Mersey and Tamar Estuaries);
- examine the effect of the estuarine master variables and degree of complexation with natural ligands on the sorption of Ni on estuarine particles;
- model the speciation and particle-water interactions of Ni from the field and laboratory data.

## CHAPTER 2

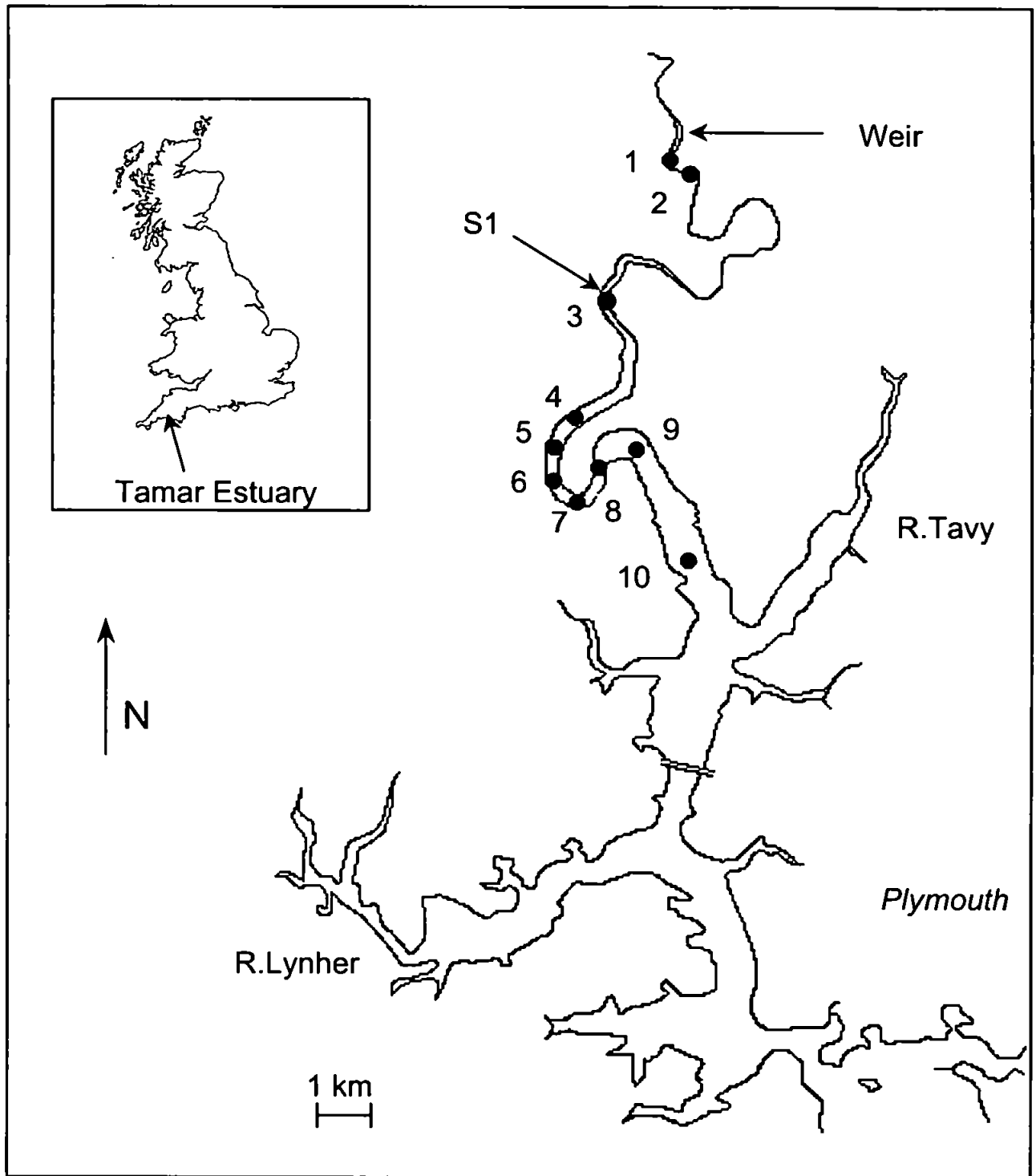
### SAMPLING AND ANALYTICAL METHODOLOGIES

The work carried out on the Tamar, Tweed and Mersey Estuaries has been divided into field studies and process-orientated laboratory studies. While the field studies aimed to examine the seasonal variability in the distributions and chemical speciation of dissolved Ni in the three estuaries, the process-orientated studies aimed to identify some of the factors affecting the estuarine sorptive behaviour of Ni, focussing on the effect of complexation with organic ligands in the dissolved phase. Additional process-orientated studies were carried out with samples collected on the Beaulieu Estuary, Southern England, as this estuary is characterised by high concentrations of natural humic acids (Turner et al., 1998).

#### 2.1 The study areas

##### 2.1.1. THE TAMAR ESTUARY

The Tamar Estuary (Figure 2.1) drains a rural area, with forestry and farming as principal land uses. Extensive mining of tin, copper, arsenic, lead and silver was carried out in the catchment area up until the 19<sup>th</sup> century (Kavanagh et al., 1997). The residues from the mining activities resulted in unvegetated spoil tips which are therefore open to aeolian and hydrogeological erosion (Kavanagh et al., 1997). Numerous metal-rich streams still drain into the estuary, resulting in relatively high estuarine concentrations of dissolved trace metals (including Ni). The estuary is characterised by extensive intertidal mud flats, mainly composed of silt and clay (90-95% in the upper estuary and 60-70% near the mouth: Stephens et al., 1992). Tidally-induced resuspension of bed sediment gives rise to a pronounced turbidity maximum in the low salinity region of the estuary (Grabemann et al., 1997; Uncles et al., 1994). The specific surface areas (i.e. the surface area per unit mass, SSA) of the suspended particulate matter (SPM) are in the range 8-22 m<sup>2</sup>g<sup>-1</sup>, with the highest values being detected at the turbidity maximum zone (Millward et al., 1990). This



**Figure 2.1.** Location of the Tamar Estuary and the sampling stations. Also indicated is the site of sediment collection (S1) for radiotracer experiments.

is a highly reactive area where persistent removal of Ni, Zn, and Cu has been observed (Ackroyd et al., 1986; Morris, 1986; Morris et al., 1986). The ability of the turbidity maximum zone (TMZ) particles to remove trace metals has been attributed to the combination of: (i) high SPM concentration (Millward and Turner, 1995); (ii) high SSA (Millward et al., 1990); and (iii) continuous tidal pumping from down-estuary of particles relatively depleted in trace metals (Morris, 1986; Morris et al., 1986).

### 2.1.2. THE TWEED ESTUARY

The Tweed Estuary (Figure 2.2) is considered one of the least polluted estuaries of the UK, with a largely rural river catchment, a low population density and little industrial activity (Robson and Neal, 1997). Land use is mostly agricultural, with large areas of grassland, woodland and heather/peatland, with soil rich in iron and peat/humus. Extensive agricultural activity since 1970 and strong soil erosion are believed to be the cause of high nutrient enrichment that supports high primary productivity in the estuary (Balls, 1994; Clayton, 1997). Observations by Uncles and Stephens (1996) over a spring-neap tidal cycle suggest that the salinity stratification of the estuary depends on the tidal state and freshwater inflow, with highly stratified conditions prevailing at neap tides, and partially mixed conditions prevailing on the late flood at spring tides. The estuary is characterised by a rapid flushing time of one or two tides, depending on the spring-neap tidal state and river flow (Uncles and Stephens, 1996). The estuarine bed is composed of gravel and small stones, with only isolated areas of mud, which results in low SPM concentrations of 2-30 mg l<sup>-1</sup> (Uncles and Stephens, 1997). The combination of rapid flushing times and low SPM content suggests that particle-water interactions may not be significant. Therefore, for dissolved components with slow reaction kinetics (in comparison with the flushing times) a conservative behaviour can be expected on estuarine mixing (Morris, 1990). This is consistent with the observation made by Balls (1994) that phosphate mixing behaviour in the Tweed is conservative.

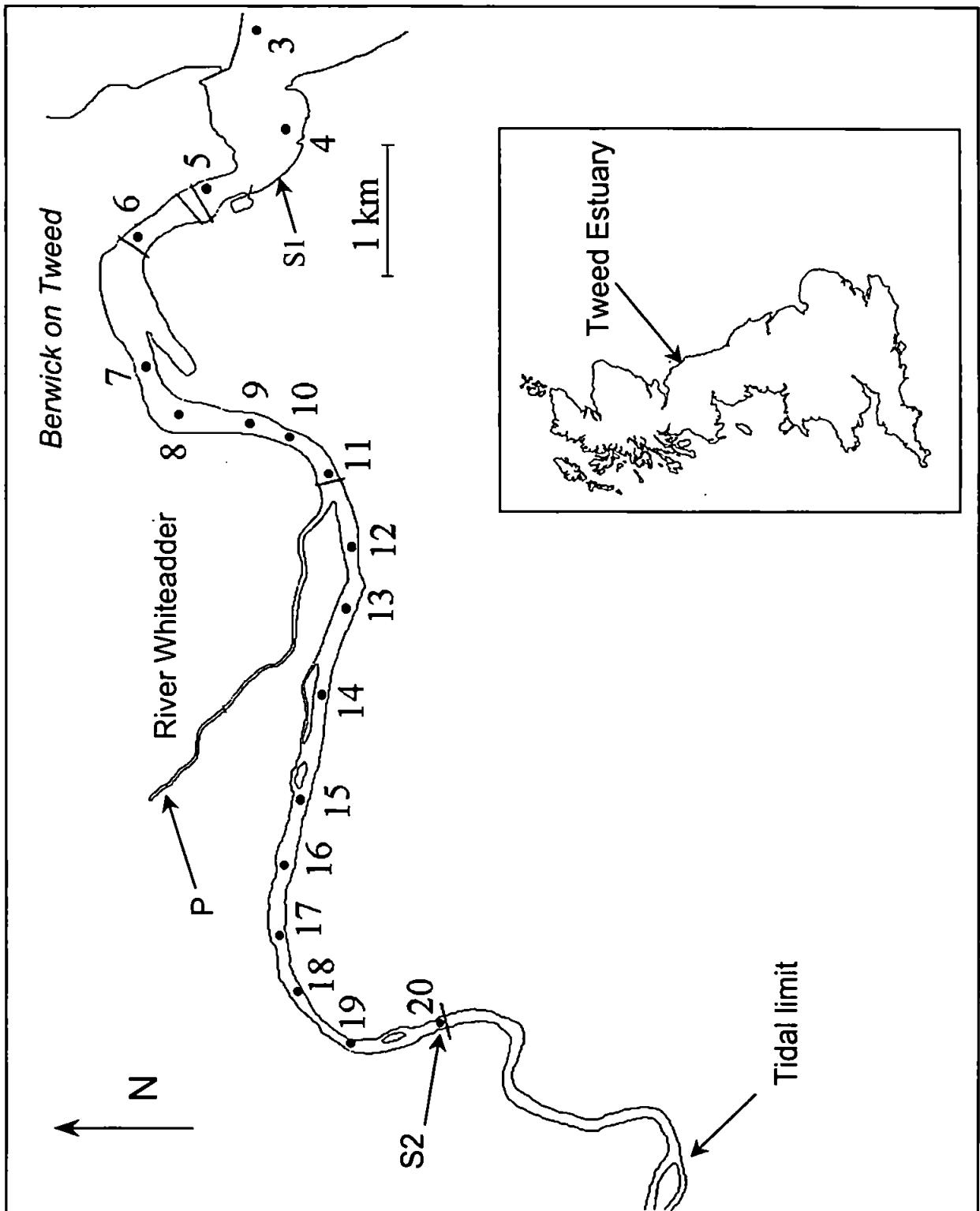


Figure 2.2. Location of the Tweed Estuary and the sampling stations. P is the sampling station on the Whiteadder. Also indicated are the sites of sediment collection, S1 and S2, for radiotracer experiments.

### 2.1.3. THE MERSEY ESTUARY

The Mersey (Figure 2.3) has for decades been considered one of the most polluted estuaries in Europe (Campbell et al., 1988; NRA, 1995): for more than two centuries, it has received the untreated domestic and industrial effluents from a densely populated and heavily industrialised catchment. Trace metals inputs into the estuary have gradually decreased during the last 20 years (Taylor, 1986; Campbell et al., 1988; Comber et al., 1995; Laslett, 1995), due to improved treatment works of industrial and domestic effluents (NRA, 1995). However, the estuary is still considered to have poor water quality and several tidal and non-tidal point sources of trace metals exist (NRA, 1995). The estuary can be divided into four main sections. The upper estuary is a narrow channel that extends for 17 km from the weir to Runcorn; here 20-60% of the surface sediments are composed of silt, with the rest being sand (Harland and Riddle, 1997). Below Runcorn, the estuary broadens in the inner estuary, a shallow basin 20 km long and up to 4.8 km wide, characterised by extensive intertidal mud flats and salt marshes. The position of these banks has been constantly changing during the last decades, causing the sediments to act as sinks or reservoirs, by either locking up or releasing pollutants in the estuary (NRA, 1995). Downstream of Eastham the estuary becomes a straight and narrow channel (~ 1 km wide), with depths of about 30 m and strong tidal currents (up to  $3 \text{ m s}^{-1}$ ; Campbell et al., 1988) that inhibit sediment deposition. The outer estuary is an area of sediment deposition; training walls have been built for 16 km outwards of New Brighton, and are continuously dredged to keep the channel navigable. The strong tidal currents give rise to significant sediment resuspension, that is most pronounced during spring tides in the upper estuary, where a turbidity maximum zone (TMZ) is observed (NRA, 1995). The mean specific surface area (SSA) of the suspended particles is  $9.6 \pm 2.4 \text{ m}^2\text{g}^{-1}$  and is relatively constant through the whole estuary (Millward et al., 1990). This value is lower than the mean SSA reported for other estuaries by the same authors, and does not show any increase in the TMZ area, suggesting that trace metal removal processes may not be significant.

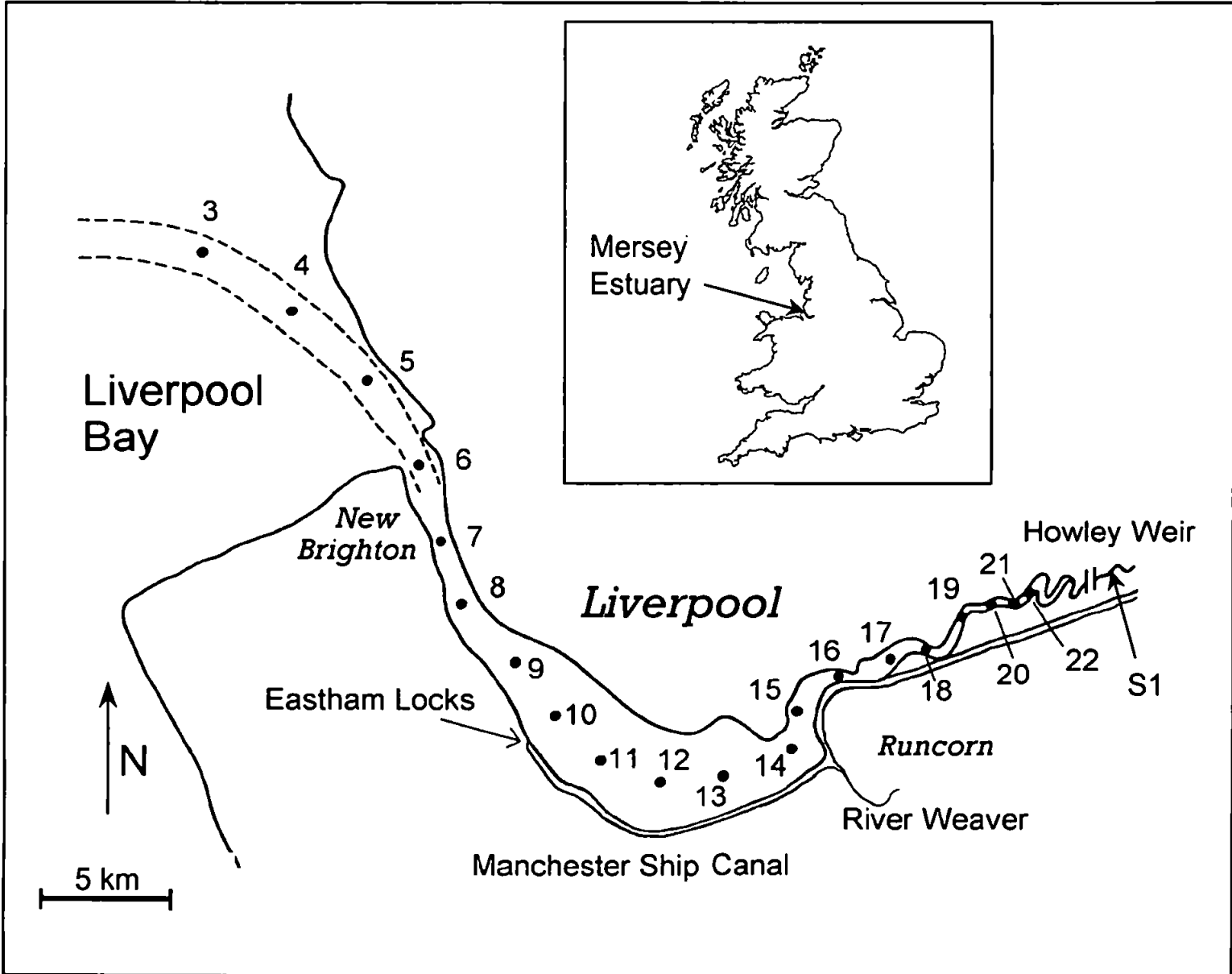


Figure 2.3. Location of the Mersey Estuary and the sampling stations. S1 is the sampling station for riverwater samples, and also the site of sediment collection for radiotracer experiments.

## 2.2. Field studies

The principal aim of the field studies was to examine the speciation, distribution, and behaviour of dissolved Ni within the Tamar, Tweed and Mersey Estuaries. A flow diagram illustrating the general strategy of the surveys is shown in Figure 2.4, whilst a summary of all the field survey details is shown in Table 2.1. Salinity, temperature, pH and dissolved oxygen were monitored throughout all the surveys, and concentrations of suspended particulate matter (SPM) and dissolved organic carbon (DOC) were also determined. Water samples were collected for the determination of total dissolved and ACSV labile Ni. Complexing capacity titrations were carried out during one survey each on the Tweed and Mersey Estuaries, in order to determine the concentration of Ni-complexing ligands and the conditional stability constants for their interaction with Ni. Total dissolved Co, Cu, Cd, Pb and Zn were determined for the Mersey Estuary surveys as part of the NERC Environmental Diagnostics Programme. As part of the same programme, Mersey particulate trace metals were determined by other members of the Plymouth University Marine Chemistry Group. Water and sediment samples were also collected for process-orientated studies using  $^{63}\text{Ni}$  (Section 2.3).

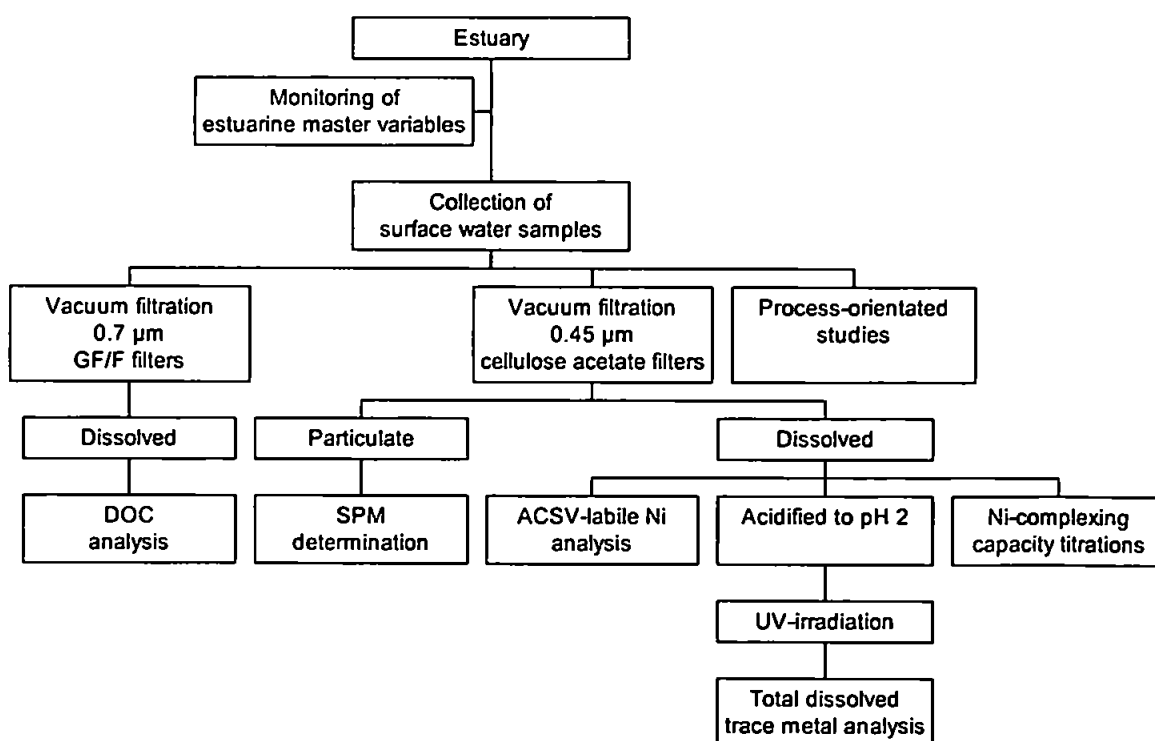


Figure 2.4. Flow diagram illustrating the strategy of the study.



**Table 2.1.** Summary of the field surveys, hydrological conditions, monitored master variables and samples collected. Q = mean river flow; S = Salinity; T = Temperature; DO<sub>2</sub> = Dissolved Oxygen; n = number of samples; CC = complexing capacity titrations; HW = High water.

Estuary	Season (Date)	Q (m <sup>3</sup> s <sup>-1</sup> )	Survey	Tidal state	S	T	pH	DO <sub>2</sub>	n	DOC	ACSV-labile Ni	dissolved trace metals	CC
Tamar	Autumn (14-Oct-96)	4.25	axial transect	HW-springs	✓	✓	✓	✓	10		✓	Ni	
Tweed	Winter (10-Nov-96)	89.6	axial transect	HW-springs	✓	✓	✓	✓	13	✓	✓	Ni	
"	Winter (12-Nov-96)	200.3	tidal cycle	springs	✓	✓	✓	✓	7			Ni	
"	Spring (5-June-97)	27.7	axial transect	HW-springs	✓	✓	✓	✓	9	✓	✓	Ni	
"	Autumn (22-Sept-98)	34.9	axial transect	HW-springs	✓	✓	✓	✓	19	✓	✓	Ni	✓
Mersey	Winter (16-Dec-97)	28.5	axial transect	HW-springs	✓	✓	✓	✓	11	✓	✓	Ni, Co, Cu, Cd, Pb, Zn	
"	Spring (30-Mar-98)	47.0	axial transect	HW-springs	✓	✓	✓	✓	18	✓	✓	Ni, Co, Cu, Cd, Pb, Zn	
"	Summer (25-Jun-98)	29.1	axial transect	HW-springs	✓	✓	✓	✓	21	✓	✓	Ni, Co, Cu, Cd, Pb, Zn	
"	Autumn (20-Oct-98)	82.3	axial transect	HW-springs	✓	✓	✓	✓	20	✓	✓	Ni, Co, Cu, Cd, Pb, Zn	✓

### 2.2.1. SAMPLING CAMPAIGNS

All surveys were carried out on spring tides, (i) in order to allow boat access over a wider length of the estuaries, and (ii) to eliminate the effect of tidal state when comparing estuarine distributions. For all surveys, the estuarine master variables were measured with calibrated instruments whose details are reported in Appendix 1. A total of eight axial transects were carried out at high water on the Tamar, Tweed and Mersey estuaries, each covering the widest possible salinity range.

Only one survey was carried out on the Tamar Estuary, as the distributions, speciation and water-particle interactions of Ni in the estuary have been extensively studied (Morris, 1986; Nimmo, 1987; van den Berg, et al., 1991; van den Berg, 1993; Liu et al., 1998; Whitworth, 1999).

Three surveys were carried out on the Tweed Estuary between November '96 and September '98. Two of the surveys were carried out on board the LOIS research vessel *Tamaris* as part of the LOIS RACS(C) Core Programme (November '96 and June '97). Axial transects were carried out on 10 November '96 and 5 June '97 using the LOIS semi-rigid inflatable boat. The master variables were provided courtesy of the LOIS programme. On 22 September '98 the axial transect was carried out on a glass-fibre boat. During the November '96 survey, an additional water sample was collected on the Whiteadder River (site P, Figure 2.2), and eight water samples were collected during a tidal cycle at station 5 (Figure 2.2). During the June '97 survey, additional marine and riverine end-member water samples were collected daily at stations 3, 4, and 20 (Figure 2.2).

Four axial transects were carried out on the Mersey Estuary on board the Environment Agency (EA) vessel *Seajet* (16 December '97; 30 March '98; 25 June '98) and rib *Seafury* (20 October '98). The March, June and October '98 surveys were carried out jointly with the EA, as part of their monthly monitoring programme. The December '97 survey, had to be abandoned at station 11 due to adverse weather conditions, and another

four samples were collected from the shore (corresponding to stations 16, 19, and 22, and at 2 km below the weir). Additional freshwater samples were collected from 100 m above the weir on each survey (Site S1, Figure 2.3).

## 2.2.2. EQUIPMENT PREPARATION FOR FIELD STUDIES

All preparation of equipment for surveys, and sample collection, handling and analysis was carried out using trace metal clean procedures. Disposable plastic gloves were used throughout all equipment handling, high purity reagents and high-purity water (purified by reverse-osmosis, Milli-RO, 18 M $\Omega$  cm, and then by ionic exchange, Milli-Q, Millipore) were used. When necessary, work was carried out under a Class-100 laminar flow hood.

Sampling and storage bottles for trace metals samples (Nalgene, high-density polyethylene, HDPE) were soaked in detergent (Decon, 5%) for 48 hours, then rinsed thoroughly with Milli-Q water and soaked for one week in 6 M HCl (BDH GPR). The bottles were then rinsed with Milli-Q water and soaked in 2 M HNO<sub>3</sub> (BDH AnalaR) for one week. They were finally rinsed thoroughly and filled with Milli-Q water, then acidified to pH < 2 by addition of concentrated HCl (BDH AristaR, 500  $\mu$ l for 500 ml bottles), and double sealed in plastic bags until required for use. Cellulose acetate filters (Sartorius 0.45  $\mu$ m pore size, 47 mm diameter) were soaked for 24 hours in 0.05 M HCl (BDH AristaR), then rinsed thoroughly with Milli-Q water and allowed to dry overnight under a laminar flow hood. They were then individually placed in acid-washed (1 M HCl, BDH AnalaR) petri-dishes, and then placed in a dessiccator and weighed until they reached constant weight. Two Nalgene 500 ml, polysulphone filtration units were soaked in 1 M HCl (BDH AnalaR) for 48 hours, then they were thoroughly rinsed with Milli-Q water and then double sealed in plastic bags until required for use.

A Millipore glass filtration unit and glass bottles for the collection and storage of DOC samples were soaked in detergent (Decon 5%) for 48 hours, then rinsed thoroughly

with Milli-Q water and ashed in a muffle furnace for 8 hours at 450 °C. They were then wrapped in combusted Al foil and stored until required for use. Glass fibre filters (Whatman GF/F, 0.7 µm pore size, 47 mm diameter) were ashed in an muffle furnace at 450 °C for 8 hours and wrapped in combusted Al foil until required for use.

### 2.2.3. SAMPLE COLLECTION AND TREATMENT

Sub-surface water samples were collected by immersing the closed sampling bottles directly under the surface. The bottles were then opened under the surface in order to avoid surface microlayer contamination. All containers were handled with disposable plastic gloves, and all bottles were rinsed three times with the samples before sample collection.

For the Tweed surveys, the samples were filtered immediately after collection in a clean cabinet that was constructed from clean polythene sheets (on board *Tamaris* for the November '96 and June '97 surveys, and in a Transit van for the September '98 survey). For the other surveys, samples were filtered under a class-100 laminar flow hood back at the laboratory in Plymouth or in the Life Sciences Department at the University of Liverpool. Filtration of the samples was carried out in order to isolate the “dissolved” fraction and therefore allow a comparison of the results with previous work on trace metals in estuaries. Therefore in this work the term “dissolved” is used to operationally identify substances passing through a 0.45 µm filter, i.e. truly dissolved and colloidal material. However, dissolved trace metals concentration in the filtrate may be underestimated because of filter clogging caused by colloids (Horowitz et al., 1996). It has been shown that such filtration artefacts are most pronounced for dissolved Al and Fe, but may affect also the concentration of dissolved Ni, Cu and Zn (Horowitz et al., 1996). In this study, it was attempted to limit these filtration artefacts by (i) using always the same make of filters, and (ii) changing filters when a decrease in filtration rate was noticed. All samples for trace metal analyses were filtered through cellulose acetate filters (Sartorius, 0.45 µm pore

size) using clean equipment as described in Section 2.2.2. The first 100 ml of the filtrate was always discarded. The remaining filtrate was divided into several aliquots: 300 ml were collected into acid-clean HDPE bottles and acidified to pH < 2 with concentrated HCl (BDH AristaR, 300 µl for 300 ml samples), while 10 ml aliquots were collected, in triplicate, in polystyrene (Sterilin) tubes, and treated for dissolved labile Ni analyses as detailed in the section 2.2.4.1. Additional 500 ml aliquots were filtered during the Tweed September '98 and Mersey October '98 surveys for Ni complexing capacity determinations: these samples were stored frozen and unacidified. All operational blanks consisted of Milli-Q water filtered and treated exactly as the samples. All the filters were rinsed with Milli-Q water and stored in acid-washed petri-dishes for determination of suspended particulate matter (SPM) and for particulate trace metal analyses (Mersey survey only).

Samples for DOC analyses were filtered using clean equipment as described in section 2.2.2. The filtrate was collected in glass bottles with ground-glass stoppers, acidified with concentrated H<sub>3</sub>PO<sub>4</sub> (BDH AristaR, 300 µl for 100 ml of sample), wrapped in aluminium foil and stored at 4 °C until analysis (Tupas et al., 1994). The operational blank consisted of Milli-Q water treated exactly as the samples. Concentrations of DOC in the H<sub>3</sub>PO<sub>4</sub> reagent were always below the detection limit.

#### 2.2.4. DISSOLVED TRACE METALS ANALYSIS

In this work, voltammetric methods were used to determine the concentrations of total dissolved Ni, Co, Cu, Cd, Pb and Zn, and the interaction of Ni with natural ligands.

Adsorptive cathodic stripping voltammetry (ACSV) is based on the addition of a complexing ligand to the water sample, with subsequent formation of an electroactive complex which adsorbs on the surface of a hanging mercury drop electrode (HMDE). A potential scan is then carried out and the resulting reduction current is proportional to the amount of adsorbed metal (van den Berg, 1991). Anodic stripping voltammetry (ASV) is

based on the plating of the metals onto the HMDE, followed by a potential scan whereby the metal is stripped back into solution: the resulting oxidation current is proportional to the amount of plated metal (van den Berg, 1989).

Dissolved trace metals (Ni, Co, Cu, Cd, Pb and Zn) were determined using either a  $\mu$ -Autolab (Ecochemie) voltammeter connected to a Metrohm 663VA mercury drop electrode, or an Autolab (Ecochemie) voltammeter connected to a PAR 303A mercury drop electrode. Total and labile dissolved Ni, and total dissolved Co, Cu, Cd, and Pb were determined by ACSV after the addition of a complexing ligand and a pH buffer. Total dissolved Zn was determined by ASV at pH 3. Analytical conditions and reagents used for each metal analysis are given in Table 2.2.

**Table 2.2.** Analytical conditions used for the determination of dissolved trace metals. In brackets, the working concentrations of reagents in the sample are shown.

	Ni, Co	Cu, Cd, Pb	Zn
Technique	ACSV	ACSV	ASV
Complexing ligand	DMG (0.2 mM)	Oxine (0.1 mM)	-
Buffer	H <sub>3</sub> BO <sub>3</sub> (0.01 M) / NH <sub>4</sub> OH (0.0033 M)	HEPES (0.01 M)	-
pH	8.3	7.8	3
Reference	van den Berg and Nimmo (1987); Zhang et al. (1990)	van den Berg (1987)	van den Berg (1989)

Manipulation of samples and reagents was carried out under a Class-100 laminar flow hood. All reagents were purchased from BDH and Sigma, and were of AristaR analytical grade. A stock solution of 0.1 M dimethyl-glyoxime (DMG) was prepared in quartz-distilled methanol. A pH buffer solution containing 1.0 M boric acid and 0.33 M NH<sub>4</sub>OH was UV-irradiated prior to use to remove organic compounds that would interfere with the Ni determinations (M. Gledhill, pers. comm., 1996). A 0.1 M stock aqueous solution of oxine (8-hydroxyquinoline) was prepared in 0.15 M HCl; 0.01 M oxine solutions were prepared by dilution of the 0.1 M stock. A 1 M buffer solution of N-2-hydroxyethylpiperazine-N'-2-ethane sulphonic acid (HEPES) was prepared in 0.5 M

NH<sub>4</sub>OH. The reagents did not need any further purification, as assessed by analysis of Milli-Q blanks. Standard solutions of Ni, Co, Cu, Cd, Pb and Zn were prepared by dilution of atomic absorption (Spectrosol, BDH) stock solutions, and acidified to pH 2 with HCl.

#### *2.2.4.1. Sample preparation for labile Ni analysis*

In this study, labile Ni is operationally defined as the dissolved Ni fraction that reacts with 0.2 mM DMG, and is measured at equilibrium upon competition between the added ligand and natural complexing ligands. Immediately after filtration, three 10 ml samples for labile Ni measurements were transferred into polystyrene vials (Sterilin); 100 µl of 1 M borate buffer and 20 µl of 0.1 M DMG (final concentrations 0.01 M and 0.2 mM, respectively) were added, and the samples were allowed to equilibrate for ~36 hours to account for the slow dissociation kinetics of the Ni-natural ligand complexes. This equilibration time was chosen after examining the kinetic of ligand exchange between DMG and the natural ligands for the Tweed and Mersey Estuaries.

#### *2.2.4.2. Sample preparation for total dissolved trace metal analysis*

For the determination of total dissolved trace metals, the acidified samples were UV-irradiated for four hours with a 400 W high-pressure Hg-vapour lamp after the addition of 20% H<sub>2</sub>O<sub>2</sub> (30 µl to 30 ml of sample). The UV-irradiation process breaks down the organic-metal complexes and removes interference of organic surfactants (Achterberg and van den Berg, 1994). For Ni, Co, Cu, Cd and Pb analyses, 10 ml of sample were added to the voltammetric cell to which the ligand, pH buffer and 50% NH<sub>4</sub>OH (BDH AristaR or isothermally distilled, for sample neutralization) were previously added (Table 2.2). Samples for Zn analyses were obtained by a 1 to 10 dilution in Milli-Q of the acidified samples. Dilution was necessary because carry-over was observed between samples owing to the high concentrations of Zn (120-250 nM) in the original samples.

### 2.2.4.3. Analysis of dissolved trace metals

After the addition of reagents and sample to the voltammetric cell, the solution was purged for 180 seconds with water-saturated nitrogen to remove dissolved oxygen. Four Hg drops were discarded after which a new Hg drop was extruded and the deposition of the metal on the drop started whilst stirring the solution. The instrumental conditions adopted are given in Table 2.3. The deposition time was varied accordingly to the metal concentration in the samples. The stirrer was stopped, and the solution was allowed to become quiescent for 5-10 seconds, after which the voltammetric scan was carried out. At least three scans were carried out on each aliquot. The relative standard deviation of replicate scans was typically below 10%. The scans were repeated after each of two metal standard additions in order to calibrate the sensitivity. The average analytical precision for individual metal determinations are shown in Table 2.4. For each sample, at least two analyses were carried out: additional aliquots were analysed if the spread between the two measurements was more than 10%. Blanks, detection limits and linear ranges are presented in Table 2.4. The instrumental detection limits were calculated as three times the standard deviation of five or six trace metal determinations of Atlantic Ocean water samples.

**Table 2.3.** Instrumental conditions used for the determination of dissolved trace metals.

Parameter/condition	Ni	Co	Cu	Cd	Pb	Zn
Purging time (s)	180	180	180	180	180	180
Deposition potential <sup>a</sup> (V)	-0.8	-1.0	-0.8	-1.1	-1.1	-1.35
Deposition time (s)	10-30	10-60	10-20	40-60	40-60	10-40
Equilibration potential <sup>a</sup> (V)	-0.8	-1.0	-0.2	-0.4/-0.45	-0.4/-0.45	-1.25
Equilibration time (s)	5-10	5-10	5-10	10	10	5-10
Scan initial potential <sup>a</sup> (V)	-0.8	-0.8	-0.2	-0.4/-0.45	-0.4/-0.45	-1.25
Scan final potential <sup>a</sup> (V)	-1.2	-1.2	-0.8	-0.8	-0.8	-0.8
Scan waveform	SQW <sup>b</sup>	SQW <sup>b</sup>	SQW <sup>b</sup>	SQW <sup>b</sup>	SQW <sup>b</sup>	SQW <sup>b</sup>
Scan frequency (Hz)	10	50	50	50	50	50
Step potential (mV)	4.88	4.88	3.66	3.66	3.66	3.66
Modulation amplitude (mV)	10	20	20	25	25	25

<sup>a</sup> vs. Ag/AgCl (saturated AgCl in 3 M KCl) electrode; <sup>b</sup>square wave.



**Table 2.4.** Analytical conditions for trace metal determinations.

Parameter	Ni	Co	Cu	Cd	Pb	Zn
Average analytical precision (%)	7.1 (labile) 4.8 (total)	4.1	3.9	8.2	7.0	4.4
Detection limit (nM)	0.3	0.05	0.3	0.1	0.3	0.3
Blank (nM)	0.1-0.3	n.d. <sup>a</sup>	0.3	n.d. <sup>a</sup>	n.d. <sup>a</sup>	n.d. <sup>a</sup>
Contamination from the filtration process (nM)	0.2-0.3	n.d. <sup>a</sup>	n.d. <sup>a</sup> -1.5	n.d. <sup>a</sup>	n.d. <sup>a</sup>	2-4
Minimum linear range (deposition time, s)	5-470 (10)	1-230 (10)	10-240 (10)	1-30 (60)	1-30 (60)	5-300 (20)

<sup>a</sup> n.d.: non detectable with 120 seconds deposition.

The accuracy of the technique was assessed by replicate analyses of Certified Reference Material (CRM) CASS-3 (coastal water) and SLRS-2 (river water), supplied by the Canadian National Research Council (Table 2.5). The CRM aliquots, already supplied acidified to pH 1.6, were UV-irradiated and analysed using the procedure described in the previous section. The results of the analyses indicate that there is a good agreement with the certified values for all metals except for the SLRS-2 value for Cd, which was overestimated probably because of contamination of the sample.

**Table 2.5.** Analysis of CRM CASS-3 and SLRS-2 (nM). n = number of determinations; certified values are in brackets. Errors represent two standard deviations.

CRM	Ni	Co	Cu	Cd	Pb	Zn
CASS-3	5.8 ± 1.0 n=6	0.51 ± 0.28 n=6	8.0 ± 1.5 n=6	0.35 ± 0.13 n=5	n.d.	22.4 ± 2.5 n=6
	(6.6 ± 1.0)	(0.7 ± 0.15)	(8.1 ± 1.0)	(0.27 ± 0.04)	(0.06 ± 0.02)	19 ± 3
SLRS-2	19.8 ± 1.4 n=5	0.85 ± 0.08 n=5	40.2 ± 3.5 n=6	0.56 ± 0.12 n=7	0.64 ± 0.03 n=4	49.6 ± 2.8 n=5
	(17.5 ± 1.7)	(1.0 ± 0.2)	(43.4 ± 2.7)	(0.25 ± 0.04)	(0.62 ± 0.05)	(50.9 ± 2.3)

### 2.2.5. NICKEL COMPLEXING CAPACITY TITRATIONS

The complexing capacity titrations were carried out with samples collected along axial transects of the Tweed Estuary (September '98 survey) and the Mersey Estuary (October '98 survey). For each sample titration, fifteen aliquots of 10 ml were pipetted into polystyrene cups into which DMG and borate buffer (final concentrations 0.2 mM and 0.01

M, respectively) and varying aliquots of Ni had been previously added. The amounts of Ni added to the samples varied depending on the initial concentration of the samples: for the Tweed samples, which had total Ni concentrations below 10 nM, the Ni additions were in the range 0-50 nM, while for the Mersey Estuary the Ni additions varied from 0-100 nM to 0-200 nM. The cups were conditioned for 2-3 hours (in order to minimise adsorption onto cup walls) and the samples were thrown away; fresh reagents, Ni standards and samples were then pipetted into the cups and were allowed to equilibrate at room temperature for 36 hours prior to measurement. For each titration, the aliquots were then transferred to the voltammetric cell in order of increasing concentration, and at least three scans were carried out for each aliquot. The data treatment for the titration results is described in Appendix 2.

#### 2.2.6. DISSOLVED AND PARTICULATE ORGANIC CARBON ANALYSIS

Dissolved organic carbon was determined immediately upon return to Plymouth using an automatic Shimadzu Total Organic Carbon-5000 analyser (University of Plymouth). The instrument was calibrated in the range 0-20 mg C l<sup>-1</sup> with standard solutions of Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> for inorganic carbon and potassium hydrogen phthalate for total carbon.

Particulate organic carbon was estimated by the loss on ignition method (LOI) for the Mersey December '97 survey only. The filters were ashed at 450 °C and the percentage weight loss determined. However, this method overestimates the organic content of the particles up to four times, due to the accompanying loss of water associated with clay lattices (Dankers and Laane, 1983).

### 2.3. Process-orientated studies

The process-orientated studies carried out with samples collected in the three estuaries are summarised in Table 2.6. The adsorption of Ni was studied as a function of salinity, time, DOC concentration, and equilibration time of <sup>63</sup>Ni with filterable ligands. In addition, an uptake kinetics experiment was carried out with samples from the Beaulieu

Estuary (Southern England), in order to investigate the effect of high natural DOC concentration on sorption processes. For the Mersey Estuary, the effect of salinity on previously incubated particles was also examined in desorption experiments.

**Table 2.6.** Summary of the radiotracer experiments carried out.

Estuary	Experiment			
	Salinity gradient	Uptake kinetics	Incubations with unfiltered samples	Desorption kinetics and seawater leaches
Tamar	✓	✓		
Tweed	✓	✓	✓	
Mersey	✓	✓	✓	✓
Beaulieu		✓		

The partitioning of Ni between dissolved and particulate phases was studied using the pure  $\beta$ -emitter  $^{63}\text{Ni}$  ( $E_{\text{max}} = 0.067 \text{ MeV}$ ;  $t_{1/2} = 92 \text{ years}$ ; Colle and Zimmerman, 1996). The method is based on the assumption that the radioactive Ni added to the sample behaves chemically in the same way as the stable Ni, and that the addition of a sub-nanomolar amount of radiotracer to the sample does not perturb the pre-existent chemical equilibria (Anderson et al., 1987). In this study, the activity of  $^{63}\text{Ni}$  was determined by liquid scintillation counting (Goulding, 1986). In this technique, an aqueous sample is mixed with a liquid scintillation cocktail (LSC) which contains an aromatic solvent (usually toluene or 1,4 dioxane), a surfactant (which allows the sample to be miscible with the organic solvent), and one or more fluorescent solutes. The radiation emitted by  $^{63}\text{Ni}$  is captured by the  $\pi$ -electrons of the solvent, re-emitted and captured by the fluorescent solutes, which re-emit the radiation at a wavelength that is efficiently detected by a photomultiplier.

### 2.3.1. EQUIPMENT PREPARATION FOR RADIOCHEMICAL EXPERIMENTS

All bottles, carboys, filters and filtration units for collection, filtration and storage of water samples for radiotracer experiments were cleaned as detailed in Section 2.2.2. In

addition, the following procedures were carried out.

A glass filtration unit (Millipore, for 25 mm diameter filters) and 60 ml, Nalgene polycarbonate (PC) bottles were soaked in detergent (Decon 5%) for 24 hours, rinsed with Milli-Q water and soaked in 1 M HCl (BDH AnalaR) for 48 hours. They were then rinsed thoroughly with Milli-Q water and dried in a laminar flow hood. Plastic pots with snap-on lids and plastic scoops for the collection of surface sediment samples were acid washed in 10 % HCl and sealed in plastic bags until required for use. For the June '97 Tweed survey only, PC filters (Sartorius, 0.2  $\mu\text{m}$  pore size, 47 mm diameter) were soaked in 0.05 M HCl for 5 hours, rinsed thoroughly with Milli-Q water and dried overnight under a laminar flow hood in individual acid-washed petri-dishes. A Nalgene, 250 ml polysulphone filtration unit was soaked in 1 M HCl (BDH AnalaR) for 48 hours, then rinsed thoroughly with Milli-Q water and double sealed in plastic bags until required for use. A standard solution of  $0.210 \pm 0.003 \text{ MBq ml}^{-1}$  of  $^{63}\text{Ni}$  was obtained by dilution of a carrier-free, stock solution of  $411 \text{ MBq ml}^{-1}$  in 0.08 M HCl (Amersham International). The specific activity of the standard solution was checked weekly by counting in triplicate  $20 \mu\text{l}$  of solution in 5 ml LSC (Ultima Gold, Canberra Packard), on a Beckman 6500 liquid scintillation counter. All reagents used in the radiotracer experiments were of BDH AnalaR analytical grade.

### 2.3.2. SAMPLING AND SAMPLE TREATMENT FOR SALINITY EFFECT AND KINETIC EXPERIMENTS

Surface sediments were collected on the Tamar Estuary on 21 May 1998 on an intertidal mud flat during low tide (site S1, Figure 2.1); water samples were collected 300 m above the weir (riverine end member, REM) and offshore Plymouth (marine end member, MEM) on the same date.

The Tweed samples were collected on two occasions. During the November '96 survey, a surface sediment sample was collected at low tide on a small mud bank on 11 November (Site S1, Figure 2.2); REM and MEM samples were collected, respectively, at station 5 during ebb tide (Salinity < 0.3), and at the pier mouth (salinity 30.0) on 12

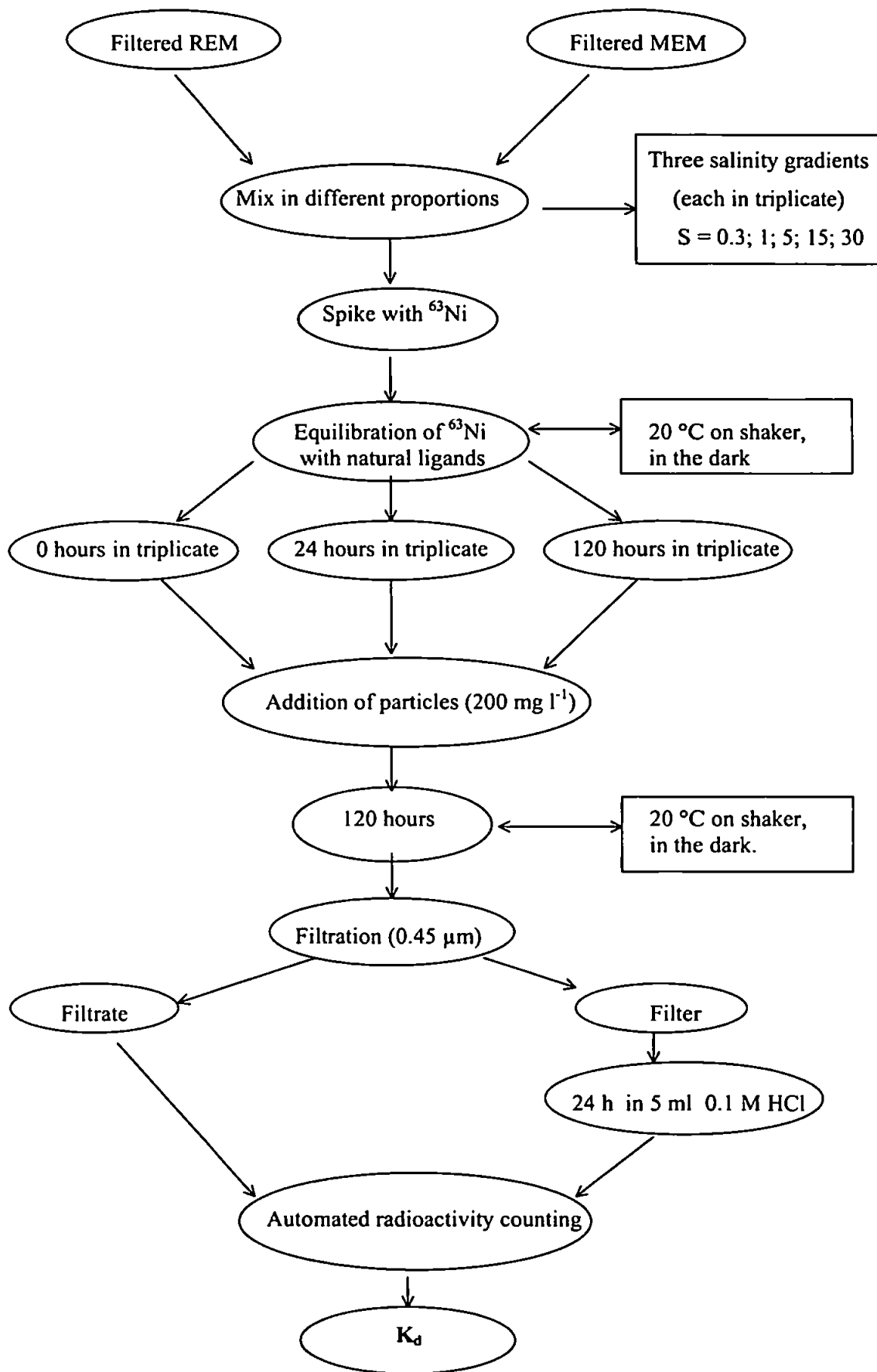
November. During the September '98 survey, a sediment sample and a REM were collected from shore at Station 20 (Site S2, Figure 2.2) on 22 September.

The Mersey samples were collected on 6 March '99. Surface sediment and REM samples were collected 100 m above the weir (site S1), while a MEM sample was collected on the same day at Station 6 (Figure 2.3).

All samples described above were collected in acid-washed, 5 litres carboys, and acid-washed polyethylene sediment pots. Additional water samples were collected at the same time for DOC, salinity, temperature and pH analyses. After collection, samples were stored cool in the dark until return to the laboratory in Plymouth. Water samples were filtered using a 500 ml polysulphone filtration unit and cellulose acetate filters (Sartorius 0.45  $\mu\text{m}$  pore size). The filtrate was collected in HDPE bottles and stored in the dark at 4°C until use (usually within a few days from collection). Surface sediment samples were wet-sieved through a 63  $\mu\text{m}$  nylon mesh using native river water, and the slurries were collected in acid-washed plastic pots. The SPM concentration of the slurries was calculated by filtering in triplicate 10 ml of suspension through 0.45  $\mu\text{m}$  pore size, pre-weighed Sartorius cellulose acetate filters. The slurries were stored in the dark at 4 °C. Specific surface area, POC, and particulate Fe, Mn, Al, Ca and Mg (available to 0.05 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25% v/v  $\text{CH}_3\text{COOH}$ ), were analysed on freeze-dried samples according to established techniques (Millward et al., 1990), and details are reported in Appendix 3.

### 2.3.3. SALINITY GRADIENT

This experiment, shown schematically in Figure 2.5 was carried out to assess the multiple effects of salinity and of natural ligand complexation kinetics on the sorptive behaviour of nickel.  $^{63}\text{Ni}$  was pre-equilibrated with filterable natural ligands in solutions at different salinities for 0, 24 and 120 hours, before addition of particles and incubation for 5 days. Filtered end members were mixed in different proportions in 1-litre, acid-washed



**Figure 2.5.** Flow diagram showing the procedure adopted for the salinity gradient experiments. REM=Riverine end-member; MEM=marine end-member.

HDPE bottles to create a salinity gradient (0, 3, 15, 50, 100 % seawater). Polycarbonate bottles were conditioned for 3 hours with the samples, then the solutions were discarded and the bottles were filled again with 40 ml of sample, and each was spiked with 20  $\mu\text{l}$  of  $0.210 \pm 0.003 \text{ MBq ml}^{-1}$  of  $^{63}\text{Ni}$  stock solution. Three different salinity gradients were created (each in triplicate), allowing  $^{63}\text{Ni}$  to pre-equilibrate with the natural filterable ligands for 0, 24 and 120 hours. After this time, the samples were spiked with the concentrated slurry to achieve a final SPM concentration of  $200 \text{ mg l}^{-1}$ , and were incubated for 5 days at  $20 \text{ }^\circ\text{C}$  in the dark on a shaker. The pH of the samples was monitored at daily intervals and the variations were always within 0.2 pH units throughout the 5-day incubations. The samples were then filtered through pre-weighed cellulose acetate filters (Sartorius  $0.45\mu\text{m}$  pore size, 25 mm diameter) in a Millipore glass filtration unit. Filters were rinsed with Milli-Q water, dried overnight at  $40 \text{ }^\circ\text{C}$ , re-weighed and then digested in 5 ml of 0.1 M HCl (BDH AnalaR) for 24 hours (Nolting et al., 1996). The choice of 0.1 M HCl as a leach was driven by the incompatibility of the liquid scintillation cocktail with aqueous solutions of higher acidity, as stated by the LSC cocktail manufacturer. Filtrates and filter digests were added to the liquid scintillation cocktail (1 ml solution to 4 ml cocktail) and their activities were counted on a Beckman 6500 liquid scintillation counter. Distribution coefficients were then calculated applying equation 1.10. Blanks consisted of samples with no SPM added. Mass balances showed that the recovery of  $^{63}\text{Ni}$  was usually between 95% and 105%, indicating (i) no significant loss of  $^{63}\text{Ni}$  by wall adsorption, and (ii) that 0.1 M HCl can be considered as a “total digest” for adsorbed  $^{63}\text{Ni}$ . The analyses of replicate samples gave relative standard deviations of less than 5% .

#### 2.3.4. UPTAKE KINETICS

Uptake of  $^{63}\text{Ni}$  was studied with riverwater samples as a function of time, DOC concentration and pre-equilibration time of  $^{63}\text{Ni}$  with filtered natural ligands prior to the addition of particles. This experiment was also carried out with samples collected on the Beaulieu Estuary, which is characterised by high concentrations of natural humic acids

(Turner et al., 1998).

For each different estuary, three 60 ml aliquots of REM were transferred into acid-washed PC bottles. An additional sample was obtained after UV-irradiation to remove natural organic ligands. The bottles were allowed to condition for 3 hours, then the samples were discarded and the bottles were filled again with 60 ml samples. The samples were spiked with 30  $\mu\text{l}$  of  $0.210 \pm 0.003 \text{ MBq ml}^{-1}$  of  $^{63}\text{Ni}$  stock solution, and equilibrated for 0, 24 and 120 hours (only 0 hours for the UV-irradiated sample) at 20 °C prior to the addition of particles ( $\sim 200 \text{ mg l}^{-1}$  SPM). Blanks were run at the same time without SPM. The samples were placed on a shaker, at 20 °C in the dark. The pH of the samples was monitored at daily intervals. Aliquots of 5 ml were withdrawn after 1, 4, 8, 24, 48 and 120 hours, filtered and processed as detailed in section 2.3.3.

In order to test further the effect of complexation of Ni by filterable organic ligands, additional uptake kinetic experiments were carried out with the Tamar samples. In the first, 12.5  $\text{mg l}^{-1}$  of commercial humic acids (Aldrich chemical) were added to UV-irradiated filtered river water, the pH was adjusted by addition of 0.1 M NaOH, and the samples were processed as above. Synthetic humic acids have been used in this study as “model” dissolved organic ligands in solution, although it is understood that they are believed not to be representative of the humic acids found in natural waters (Malcolm and MacCarthy, 1986). In the second experiment, 200  $\text{mg l}^{-1}$  SPM were added to 1 l of Tamar river water in a pre-conditioned Teflon beaker; a control was run without SPM addition. The samples were stirred with a Teflon-coated magnetic stirrer and 50 ml aliquots were withdrawn at time intervals. Ni sorptive kinetics were studied by monitoring stable dissolved total and ACSV-labile Ni.

### 2.3.5. DESORPTION KINETICS

These experiments were carried out only with Mersey samples. Sixty ml acid-washed PC bottles were filled with Mersey REM samples, the bottles were conditioned for



3 hours and the samples were discarded. The bottles were then filled up again with 60 ml samples and spiked with 30  $\mu\text{l}$  of  $0.210 \pm 0.003 \text{ MBq ml}^{-1}$  of  $^{63}\text{Ni}$  stock solution. They were then allowed to equilibrate for 120 hours prior to the addition of SPM ( $200 \text{ mg l}^{-1}$ ) to three of the bottles (3 other non-spiked samples being the particle-free blanks). The samples were then incubated for 120 hours at  $20 \text{ }^\circ\text{C}$ , on a shaker. A spike of concentrated triple-strength artificial seawater was then added to each sample (and blanks), to achieve final salinities of 1, 2, and 5. The relative variation in the final sample volumes was less than 5%. The pH of the samples was monitored at daily intervals throughout the experiments. Aliquots of 5 ml were withdrawn after 1, 4, 8, 24, 48 and 120 hours (after the seawater spike), filtered, and treated as detailed in section 2.3.3.

A “continuous” adsorption-desorption experiment was carried out using a larger REM sample, in which the salinity was gradually increased from freshwater to 1, 2 and 5. Two 1-litre, PC bottles were conditioned with Mersey REM for 3 hours; the samples were discarded and the bottles filled again with 1-litre samples. The samples were spiked with 500  $\mu\text{l}$  of  $0.210 \pm 0.003 \text{ MBq ml}^{-1}$  of  $^{63}\text{Ni}$  stock solution, and allowed to equilibrate for 5 days. An SPM spike was then added to one of the pots to achieve a final concentration of  $200 \text{ mg l}^{-1}$ . Ten 5 ml aliquots were withdrawn (after 30 minutes, 1, 2, 3, 4, 6, 8, 24, 48, 120 hours); the salinity was then increased to  $S = 1$ , and 4 aliquots were withdrawn after 1, 3, 7, 24 hours; the salinity was increased again to  $S = 2$  and after a day to  $S = 5$ , with withdrawal of 4 and 6 aliquots, respectively. The pH of the samples was monitored at daily intervals throughout the experiments. The withdrawn aliquots were filtered and treated as detailed in section 2.3.3.

#### 2.3.6. INCUBATIONS WITH UNFILTERED SAMPLES

Incubations with unfiltered samples were carried out with Mersey samples (March, June and October '98 surveys) immediately back at the laboratory in Plymouth, whilst *in-situ* incubations with unfiltered samples were carried out on the June '97 Tweed survey.

### 2.3.6.1. Tweed

*In-situ* incubations were carried out with water samples at 3 different sites (stations 5, 9, 16, Figure 2.2) along the Tweed Estuary during the June survey, in collaboration with Dr. P.J. Shaw (Southampton University). Temperature, pH and salinity of the samples were monitored. The SPM concentration of the samples was calculated by filtering 10 litres of the same sample through 0.4  $\mu\text{m}$  PC filters. Water samples for stable dissolved Ni analyses were also collected at each incubation site. At each station, water samples were collected in nine 60 ml PC bottles, and each was spiked with 60  $\mu\text{l}$  of  $0.210 \pm 0.003 \text{ MBq ml}^{-1}$  of carrier-free  $^{63}\text{Ni}$  stock solution (Amersham International). Three of the samples were poisoned with  $\text{HgCl}_2$  (300  $\mu\text{l}$  of 3% w/v to 100 ml sample) to determine the non-biological uptake. Polycarbonate bottles were chosen for their good optical properties in the UV-VIS range (Sands, pers. comm. 1997). Samples were incubated in triplicate in the following conditions: (i) alive-light; (ii) alive-dark; (iii) poisoned-dark. The alive-light bottles were placed on a rig and immersed below the water surface, exposed to the light for 13 hours. The rigs were then retrieved and placed overnight in a dark container (to avoid any contact with light) at seawater temperature. All the other bottles were placed in a dark plastic bag and immersed under the water surface with a heavy weight for 24 hours. Further details of the incubation setup are reported in Shaw et al. (1998). A parallel experiment was carried out with the water samples collected at station 16, in which filtered riverwater, that had been equilibrated overnight with  $^{63}\text{Ni}$  (therefore allowing complexation of  $^{63}\text{Ni}$  by natural ligands), was added to another set of samples, which were then treated in the same manner as before. All samples were then filtered through 0.2  $\mu\text{m}$  pore size PC filters (Barbeau and Wollast, 1994): the filtrate was acidified to pH 2 with concentrated HCl. The filters were rinsed with Milli-Q water and stored in petri-dishes; they were then digested for 24 hours with 5 ml of 0.1 M HCl. The filtrate and digests were added to the liquid scintillation cocktail, and counted on a Beckman 6500 liquid scintillation counter.

### 2.3.6.2. Mersey

During the March, June and October '98 surveys, samples were collected for determination of five-day  $K_d$ s (i.e. after 5 days equilibration) on unfiltered, untreated samples. Additional samples were incubated after poisoning with  $HgCl_2$  (in order to evaluate potential biological effects).

During the March survey it was decided to carry out the incubations with samples collected at all stations in order to assess, on a first instance, the levels and patterns likely to be found in the estuary. In order to minimise any modification of the samples caused by biological activity, it is important to carry out experiments involving particle-water interactions as soon as possible after sample collection (Jenne, 1995). For this reason, all the incubation experiments were carried out at the same time and immediately upon return to the laboratory (one day after sample collection). However, the drawback of this approach was that only a limited number of samples can be incubated at the same time, and therefore the March experiments were not carried out in replicate. In order to assess the reproducibility of the method, the June and October incubations were carried out on a smaller number of samples at selected stations in triplicate.

Acid-washed PC bottles were conditioned with the samples for two hours, before being filled with 40 ml of fresh sample and spiked with 20  $\mu$ l of  $0.210 \pm 0.003$  MBq  $ml^{-1}$  of carrier-free  $^{63}Ni$  stock solution: the pH value was not altered by the spike. The samples were incubated for five days at 20°C on a shaker. The samples were filtered through pre-weighed cellulose acetate filters (Sartorius, 25 mm diameter, 0.45  $\mu$ m pore size), using an acid-washed Millipore glass filtration unit. Filters were allowed to dry overnight and reweighed, and then were sequentially digested with 5 ml seawater (Santschi et al., 1984; Turner et al., 1992a) for 5 hours and then 0.1 M HCl (Nolting et al., 1996) for 24 hours. This scheme gives an operational measure of the speciation of adsorbed Ni: i.e. exchangeable and leachable (Turner et al., 1992a). The filtrate and digests were then treated as detailed in section 2.3.3.

## CHAPTER 3

### FIELD STUDIES: Ni REACTIVITY IN ESTUARIES

The results from the surveys on the Tamar, Tweed and Mersey Estuaries are presented in this chapter. Dissolved (total and ACSV labile and non-labile) Ni distributions are discussed and compared with literature data. The behaviour and reactivity of Ni in the Mersey Estuary is compared and contrasted with those of Co, Cu, Cd, Pb and Zn in the same estuary.

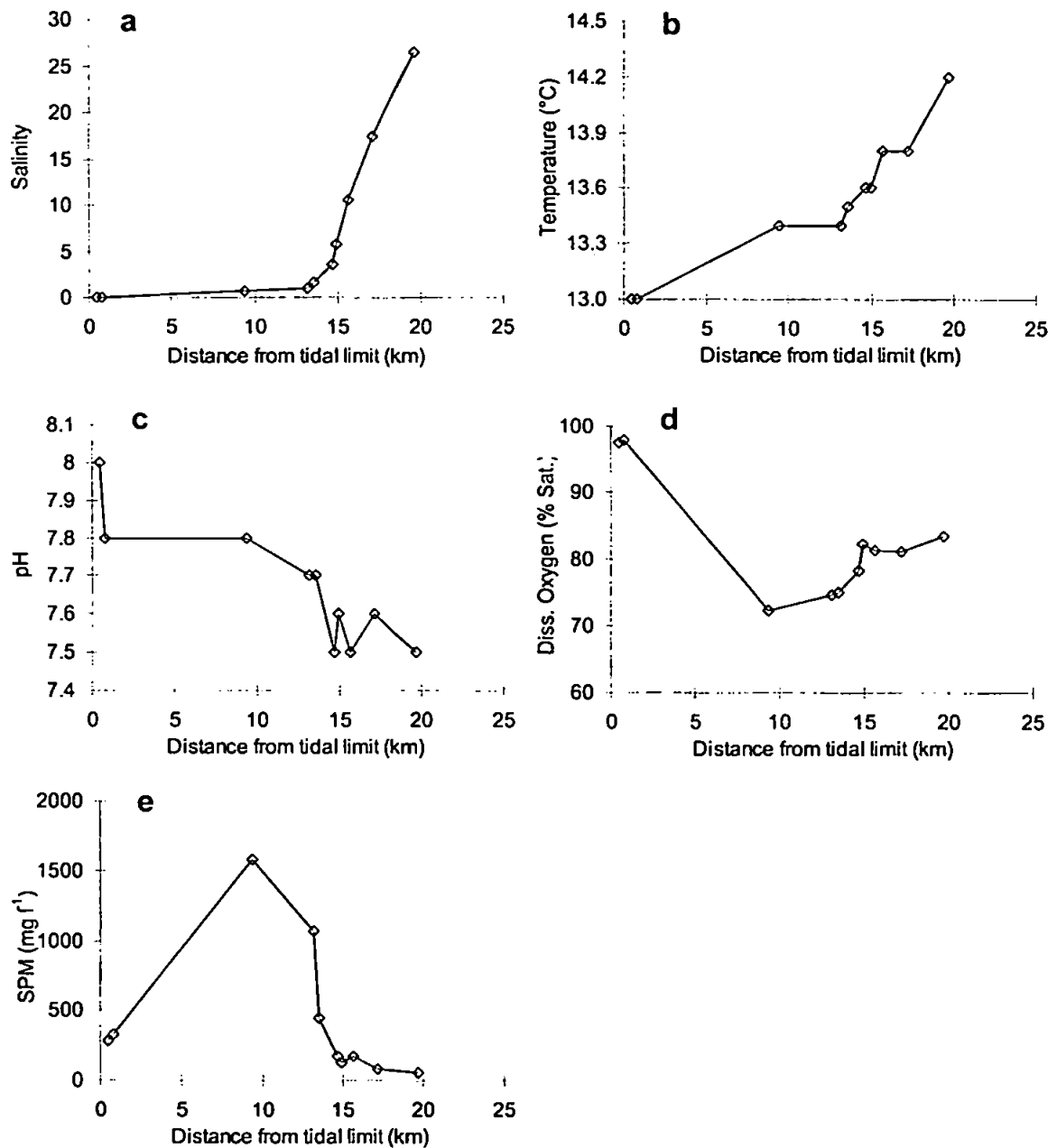
Where necessary, in the salinity-dependence diagrams, data have been plotted on a combined scale of salinity/distance from the point of saline intrusion. Throughout the chapter, all the error bars in the graphs represent either the spread between two measurements or one standard deviation of at least three replicates, unless otherwise specified. Hereafter, the term *particulate* will be used for components with a size  $> 0.45 \mu\text{m}$ , and the term *dissolved* will be used for components with a size  $< 0.45 \mu\text{m}$ . The term *Ni-complexing ligands* will be used to indicate specifically those ligands that bind Ni in complexes that are in the ACSV-non labile form. These ligands may be truly dissolved organic ligands or organic/inorganic colloids, and of natural or anthropogenic origin. For ease of reading, the terms “labile” and “non-labile” will be used to represent the dissolved ACSV labile and ACSV non-labile Ni fractions.

#### 3.1. The Tamar Estuary

##### 3.1.1. TAMAR ESTUARY MASTER VARIABLES

Salinity, temperature, dissolved oxygen, pH and suspended particulate matter (SPM) for samples collected along the October '96 axial transect are plotted in Figure 3.1 as a function of distance from the tidal limit. Temperature is lower in the river ( $13^{\circ}\text{C}$ ) and increases as the warmer seawater from the English Channel enters the estuary ( $14.2^{\circ}\text{C}$ ). The highest SPM concentration ( $1600 \text{ mg l}^{-1}$ ) defines the peak of the turbidity maximum

zone (TMZ), which is located in the low salinity region of the estuary, at the freshwater-seawater interface. The dissolved oxygen minimum coincides with the TMZ, and is due to bacterial degradation of organic matter suspended in the TMZ (Morris et al., 1982b).



**Figure 3.1.** Master variables recorded on the Tamar Estuary axial transect in October '96. (a) salinity; (b) temperature; (c) pH; (d) dissolved oxygen; (e) SPM.

### 3.1.2. DISSOLVED Ni IN THE TAMAR ESTUARY

Total and labile dissolved Ni for the axial transect are plotted as a function of salinity in Figure 3.2a. Total Ni varied between 46 nM (in river water) and 31.4 nM (the most seawards sample, S = 26.4), while labile Ni varied from 6 nM to 20 nM. The total Ni concentrations in this study are comparable to the ones observed by other workers for the same estuary (Table 3.1).

Total dissolved Ni shows removal followed by addition in the low salinity region (S < 4), in agreement with literature data (Morris, 1986; Morris et al., 1986; Nimmo, 1987; van den Berg et al, 1991; Liu et al., 1998). At salinity above 4, however, total dissolved Ni appears to decrease linearly with salinity. This observations suggest an enhanced reactivity

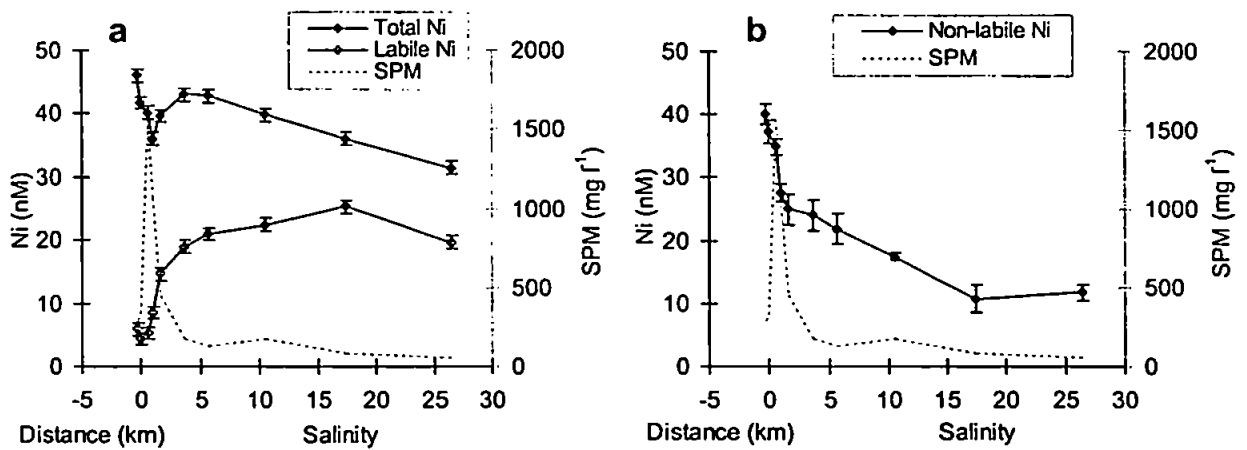


Figure 3.2. (a) Dissolved total and labile Ni, and (b) non-labile Ni in the Tamar Estuary.

Table 3.1. Ranges in total dissolved Ni concentrations (nM) in the Tamar River, Estuary and in the English Channel (subsurface samples).

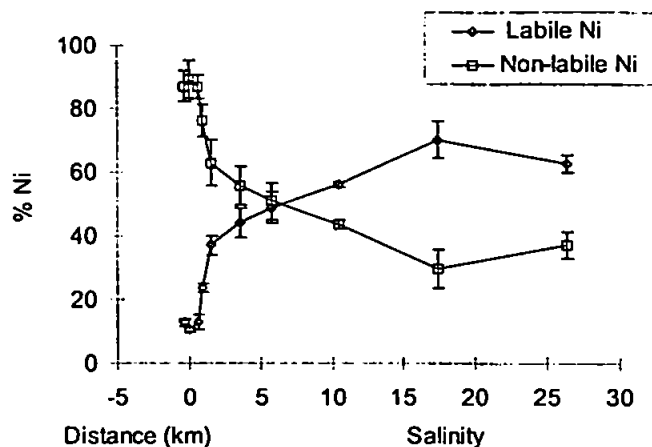
Study area	Total Ni	Behaviour	Reference
River	30-40		Millward, unpublished data (1983-1984)
Estuary	31.4-46	Removal/addition	This study
Estuary	12.3-70.2	Removal/addition	Nimmo (1987)
Estuary	38-64	Removal/addition	van den Berg et al. (1991)
Estuary	5.1-43	Removal/addition	Morris et al. (1986)
Estuary	15-40	(not appropriate for tidal cycle data)	Whitworth et al.(1998)
English Channel	3.8 ± 0.8*		Tappin et al. (1993)

\*This value represents the average Ni concentration for three seasons ( November – December '85: 3.8 ± 0.8 nM ; May '86: 3.8 ± 0.7 nM; July-August '86: 3.8 ± 0.7 nM).

of Ni in the low salinity region, whilst its behaviour at higher salinity seems to be governed by physical dilution.

The total dissolved Ni distribution can be interpreted in terms of the behaviour of its components: labile and non-labile Ni. The non-labile Ni (Figure 3.2b) is calculated as the difference between the measured total and labile dissolved Ni. The two Ni fractions seem to follow two different geochemical behaviours. Labile Ni increases seaward, from 6 to 20 nM, whilst non-labile Ni decreases from 40.1 to 11.1 nM. The observed removal of total dissolved Ni in the low salinity region is most likely due to the decrease of non-labile Ni, as there is no evidence of removal of labile Ni. The removal of non-labile Ni at low salinity can be explained in terms of flocculation of Ni-complexing colloidal material at the onset of the salinity gradient (Sholkovitz and Copland, 1981).

In contrast, the addition displayed by total Ni between salinity 1 and 4 mirrors the increase in labile Ni, whereas the non-labile Ni shows a decrease. Addition of labile Ni in the low salinity region (also reported by Nimmo, 1987 and van den Berg et al., 1991) is probably due to desorption from seaward-advected particles (Morris et al., 1986), but also to conversion from the non-labile fraction (see below). At salinity > 4, total dissolved Ni decreases in a conservative fashion, whilst labile Ni increases, resulting from a change in speciation with re-equilibration of Ni between the two fractions within the dissolved phase (Figure 3.3). An increase in the labile Ni fraction at the expense of the non-labile Ni fraction can be expected on the basis of thermodynamic considerations, due to increased Ni complexation by chloride (Turner et al, 1981), and displacement of Ni from the strong complexing ligands by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . The kinetics of Ni complexation with/dissociation from natural ligands is known to be slow (Morel et al., 1991; Price and Morel, 1991; Mandal et al., 1999). However, the flushing time of the estuary (7-14 days: Millward and Turner, 1995) is probably long enough to allow for the above re-equilibration processes to take place in the outer estuary.



**Figure 3.3.** Percentages of labile and non-labile Ni as a function of salinity in the Tamar Estuary.

The behaviour of Ni species in the low salinity region contrasts with observations by Nimmo (1987) and van den Berg et al. (1991), who showed that the removal of labile Ni in the TMZ is more important relative to that of non-labile Ni. In this study removal of labile Ni is not observed, as in the low salinity region the majority of Ni (90%) is in the non-labile form. However, laboratory experiments carried out using Tamar samples and  $^{63}\text{Ni}$  suggest that complexation with natural ligands prevents Ni scavenging onto particles (Section 4.3.1.1). It is therefore suggested that Ni removal in the low salinity region is caused by flocculation of colloidal material and associated Ni (rather than by adsorption of non-labile Ni onto SPM), whilst addition of (labile) Ni at higher salinity is due to a combination of desorption from seaward-advected particles and re-equilibration with the non-labile fraction.

## 3.2. The Tweed Estuary

### 3.2.1. TWEED ESTUARY MASTER VARIABLES

Figure 3.4 shows the surface master variables recorded along the axial transects of the estuary in November '96, June '97 and September '98. Owing to the high river flow in November '96, only the seawards 4 km of the estuary had salinity values above 0.1, while in June '97 and September '98 salt water penetrated further up-estuary. The pH in the



upper estuary is significantly higher in June '97 than in the other seasons, a phenomenon often observed in the Tweed Estuary which has been attributed to autotrophic activity (Clayton, 1997). Dissolved oxygen data are only available for a limited number of samples for the June survey, as the oxygen probe of the YSI 6000 analyser malfunctioned, but the

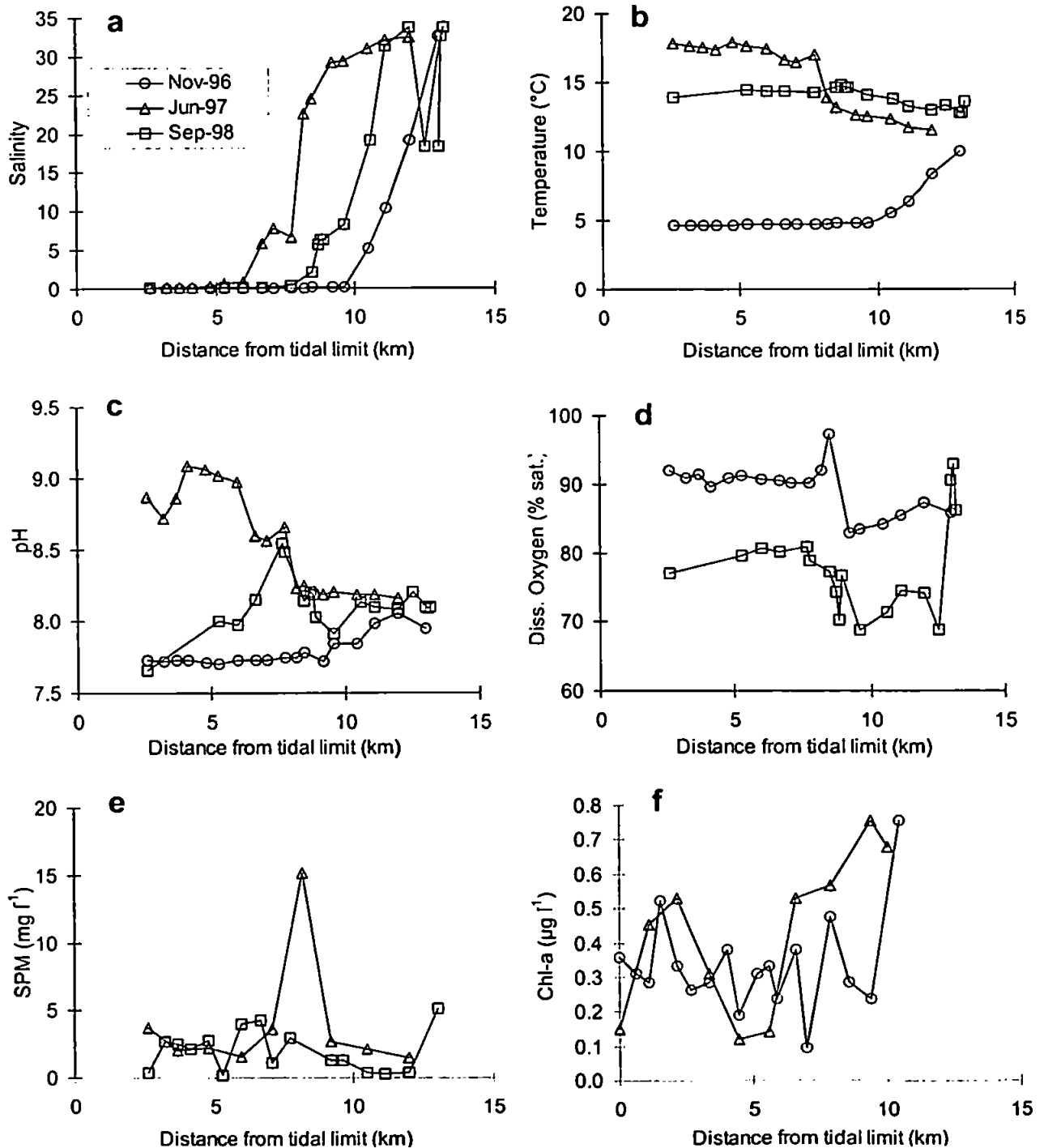


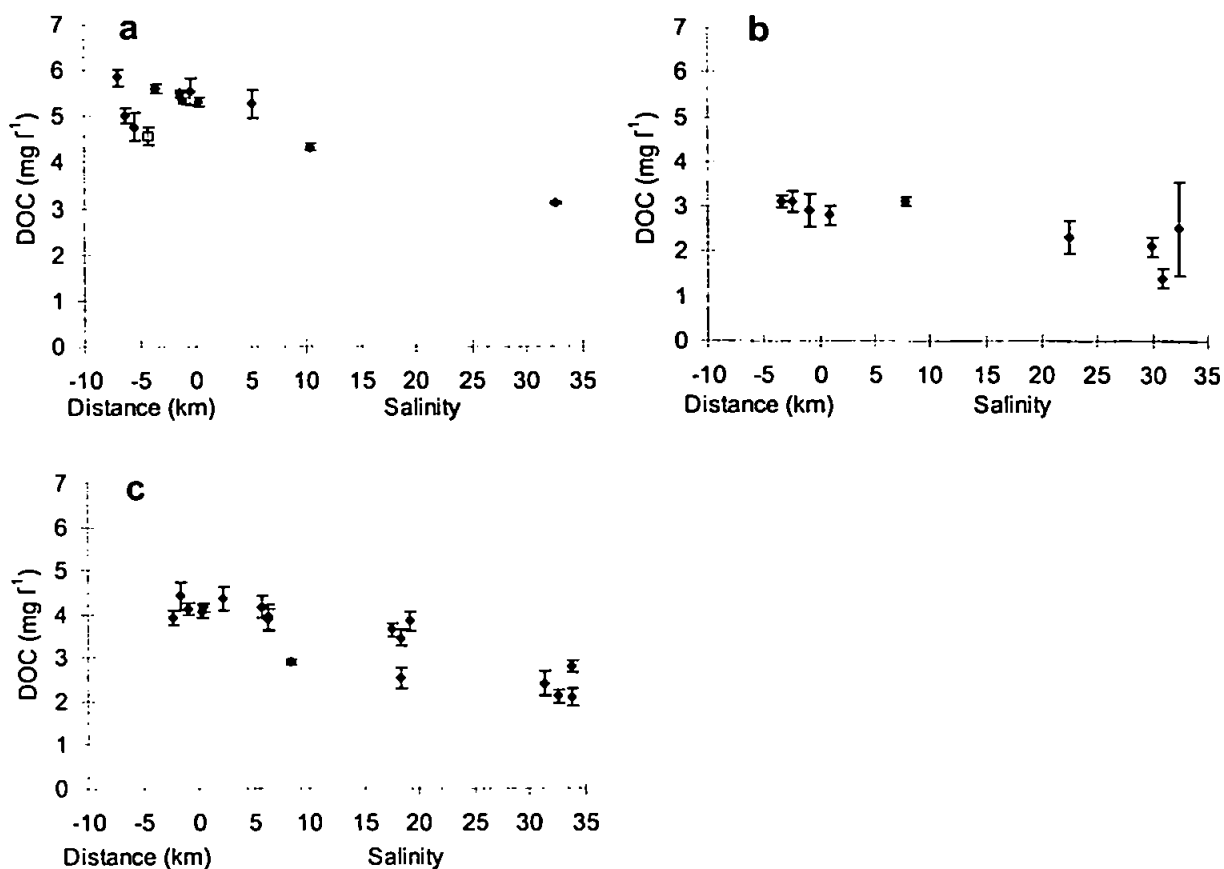
Figure 3.4. Master variables recorded on the Tweed Estuary axial transects in November '96, June '97, and September '98. (a) salinity; (b) temperature; (c) pH; (d) dissolved oxygen; (e) SPM; (f) chlorophyll-a.

data available for the riverine end member on the 3<sup>rd</sup> and 4<sup>th</sup> June '97 (103.5 and 143.3 % saturation, respectively) suggest high levels of photosynthesis (Clayton, 1997). The chlorophyll-a data, however, do not show a correspondent increase in phytoplankton biomass in June '97 compared to December '96, probably because of tidal flushing of phytoplankton. Alternatively, the increase in pH may result from benthic photosynthesis, due to the presence of extensive beds of aquatic macrophytes (Clayton, 1997). The mid-estuarine dissolved oxygen sag is probably due to high biological activity degrading organic material from nearby sewage outlets. The concentration of SPM were generally very low, in the range 0.2-4 mg l<sup>-1</sup> in December '96 and 1.5-15 mg l<sup>-1</sup> in June '97. The increase in SPM at salinity 20 in June is probably due to turbulence on mixing of the Tweed and Whiteadder water masses.

Figure 3.5 shows DOC as a function of salinity/distance for the Tweed surveys. The DOC values in November '96 (3.1-5.8 mg l<sup>-1</sup>) are higher than those in June '97 (1.3-3.1 mg l<sup>-1</sup>) and September '98 (2.1-4.4 mg l<sup>-1</sup>). Higher DOC levels in winter can be explained by the increased runoff from land that transports soluble organic matter (humic substances) from the soil into the river and estuary (Alvarez-Salgado and Miller, 1998). Although the data show some degree of scatter, the DOC appears to behave reasonably conservatively in all surveys, in agreement with observations for most other UK estuaries (Table 3.2).

**Table 3.2.** End-member concentrations of dissolved organic carbon (mg l<sup>-1</sup>) for the Tweed Estuary and other U.K. estuaries. MEM: Marine-End-Member (S > 30); REM: Riverine-End-Member (S < 0.3).

Estuary	MEM	REM	Distribution	Reference
Tweed	1.3-3.1	3.1-5.8	conservative	This study
Mersey	1.0-2.7	9.7-10.6	conservative	This study
Tamar	1.3	5.7	conservative /addition	Miller (1999)
Humber	0.96-1.32	3.6-7.12	conservative/addition	Alvarez-Salgado and Miller (1998)
Beaulieu	1.2 -2.3	9-18	removal	Turner et al. (1998)
Severn	0.7-2.2	3.1-7.8	conservative	Mantoura and Woodward (1983)

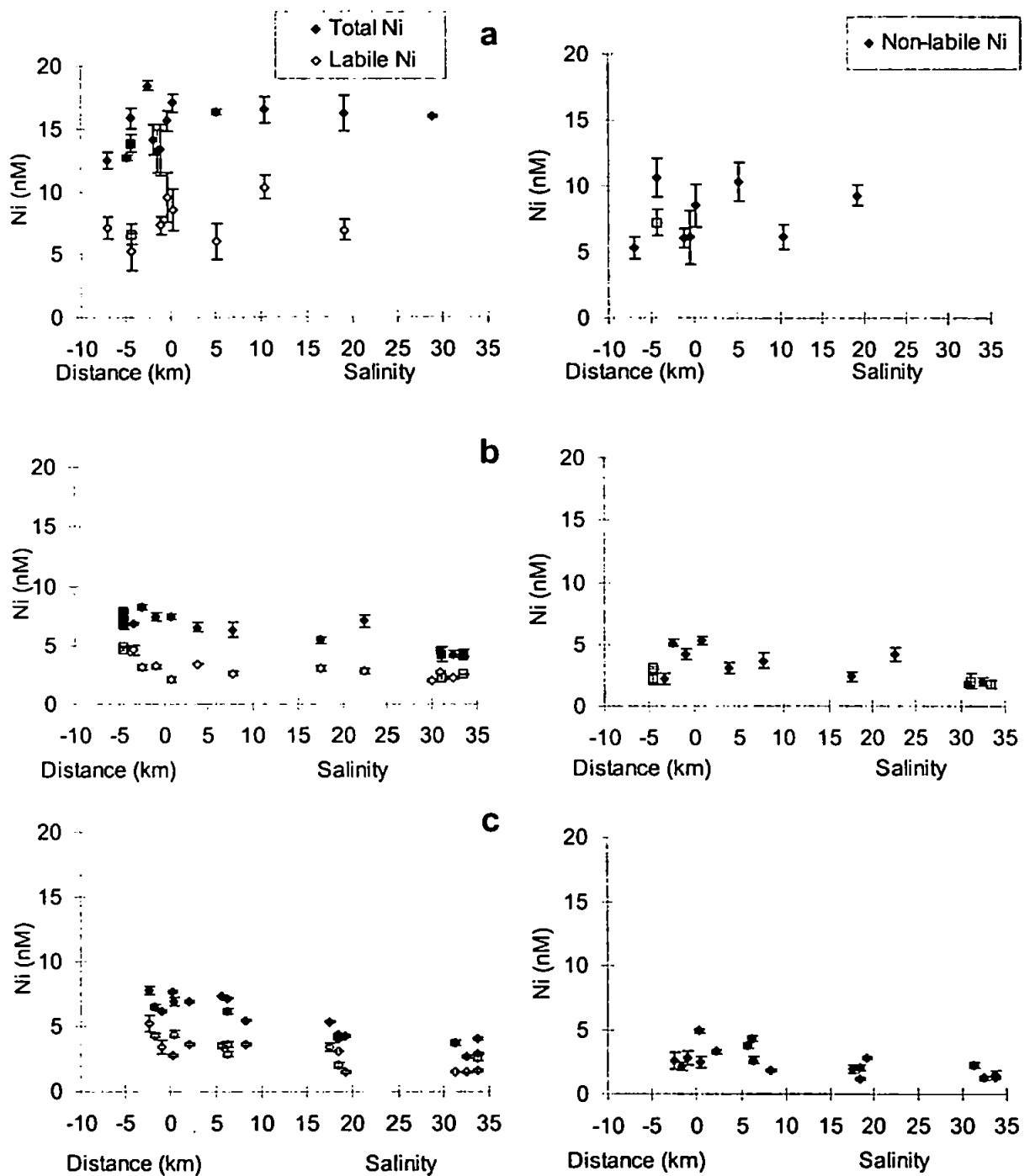


**Figure 3.5.** Dissolved organic carbon in the Tweed Estuary for the (a) November '96, (b) June '97, and (c) September '98 surveys. The square in (a) at 4 km from the point of saline intrusion represents the sample collected on the Whiteadder tributary (Site P, Figure 2.2).

### 3.2.2. DISSOLVED Ni IN THE TWEED ESTUARY

Total and labile dissolved Ni for the axial transects are plotted as a function of salinity/distance in Figure 3.6. Total dissolved Ni concentrations range between 11 and 18 nM in November '98, between 3.5 and 8.2 nM in June '97 and between 2.5 and 7.8 nM in September '98. These values are in agreement with those previously reported for the Tweed River, Estuary and plume (Table 3.3).

The total dissolved Ni concentrations in the riverine end member under baseflow conditions (i.e. those observed during the June '97 and September '98 surveys) are comparable with those of the least polluted world estuaries (Table 1.1). However during the November '96 survey, Ni concentrations are around 10 nM higher than in the other seasons. A plot of the riverine end-member Ni concentrations versus the mean daily river



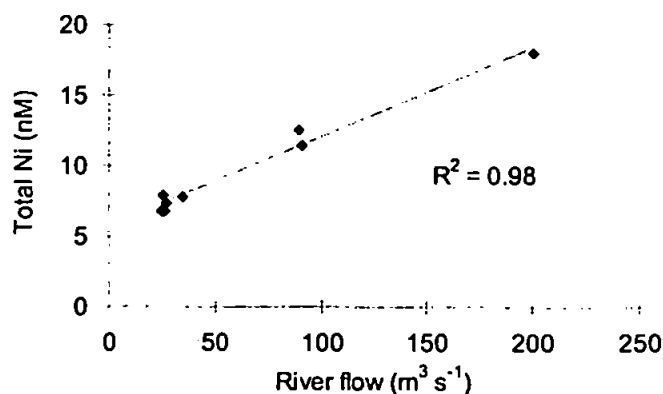
**Figure 3.6.** Dissolved total and labile Ni (left), and non-labile Ni (right) in the Tweed Estuary for the (a) November '96, (b) June '97, and (c) September '98 surveys. The squares in (a) represent a sample collected on the Whiteadder tributary (Site P in Figure 2.2): full square: total Ni; open square: labile Ni (left) and non-labile Ni (right). Full and open squares in (b) represent riverine and marine end-member samples collected on different days during the June survey.

flow for all the surveys (Figure 3.7) suggests that river flow is the cause of variable riverine end-member Ni concentration. This effect has been observed for other trace metals and was attributed to microparticulate soil material which is washed into the Tweed River by surface runoff during stormflow events (Robson and Neal, 1997; Neal et al., 1997). These microparticulates (i.e. colloids), composed of clays and Fe, Al and Mn oxyhydroxides (and associated trace metals), by passing through the conventional 0.45  $\mu\text{m}$  pore size filters are actually accounted for in the “dissolved” phase. The higher Ni concentrations observed throughout the estuary in November '96 are consistent with the higher river flow occurring during the same survey. Moreover, during the anchor station in November, on the day of stronger runoff ( $200 \text{ m}^3\text{s}^{-1}$ ), higher concentrations of dissolved

**Table 3.3.** Ranges in total dissolved Ni concentrations (nM) in the Tweed River, Estuary, plume and in the Northern North Sea (subsurface samples).

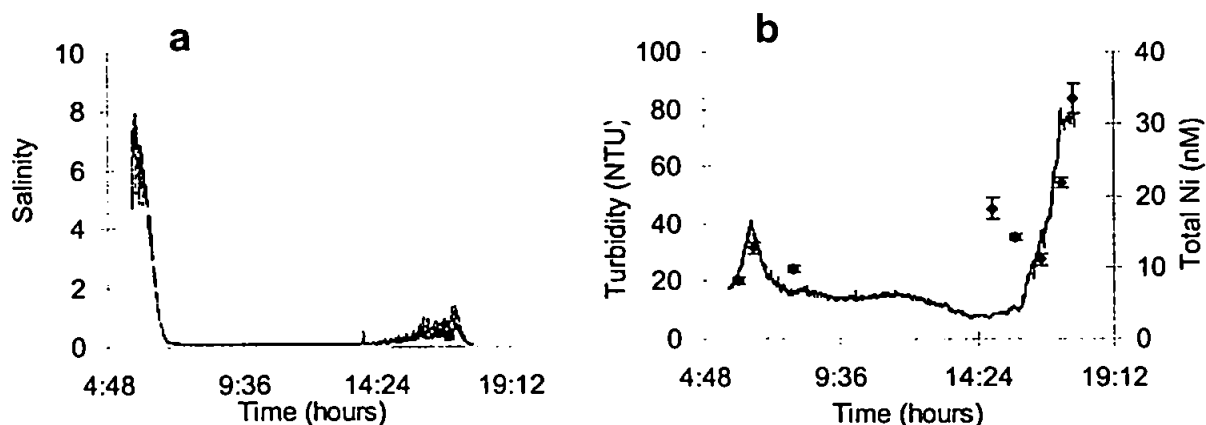
Study area	Total Ni	Behaviour	Reference
River	< 17		Robson and Neal (1997)
Estuary	2.5-18	Conservative/addition	This work
Estuary	2-34	Conservative/addition	Tappin, pers. comm. (1998)
Outer Estuary	7.9-15 <sup>a</sup>		Laslett (1995)
Outer Estuary	3.8-5.8 <sup>b</sup>		Laslett (1995)
Plume	3.1-3.6		Tappin et al. (1995)
Northern North Sea	1.9-6.0		Tappin et al. (1995)

<sup>a</sup>Data for Summer '91; <sup>b</sup>data for Summer '92.



**Figure 3.7.** Riverine total dissolved Ni versus mean daily Tweed river flow.

Ni, up to 33.5 nM, were found, which also corresponded to a sharp increase in turbidity during the ebb tide (as revealed by the on-line nephelometric measurements carried out by the Plymouth Marine Laboratory: Figure 3.8).



**Figure 3.8.** (a) Salinity and (b) total dissolved Ni (diamonds) and turbidity in arbitrary nephelometric turbidity units (solid line) for the November '96 anchor station on the Tweed Estuary. Low water: 08:30; high water: 15:03.

All the estuarine total Ni distributions can be largely defined by conservative mixing. Conservative behaviour has also been observed for phosphate in the Tweed Estuary by Balls (1994). A lack of particle reactivity for Ni has been reported for other estuaries (Shiller and Boyle, 1991; Elbaz-Poulichet et al., 1996; Paucot and Wollast, 1997; Turner et al., 1998) and has often been attributed to short residence times of waters compared to slow kinetics of water-particle interactions (Shiller and Boyle, 1991; Elbaz-Poulichet et al., 1996). During winter, the riverine concentration of dissolved Ni increases from around 12 nM to 18 nM towards the point of saline intrusion, probably due to the nearby sewage outlet. Alternatively, the peak in the low salinity region can result from temporal variations in the riverine total Ni concentration in response to changes in river flow: Loder and Reichard (1981) and Cifuentes et al. (1990) have shown that for variations in end-member concentrations occurring within timescales similar or smaller than the estuarine flushing time, the mixing curve may not be linear, even under conservative or non-reactive mixing conditions.

Labile Ni is in the range 5.2-13 nM for the November '96 survey, 2-4.8 for the June '97 survey, and 1.5-5.2 nM for the September '98 survey. The calculated non labile Ni concentrations (Figure 3.6) range between 3-10.8 nM in November '96, 1.8-5.1 nM in June '97, and 1.3-4.9 nM in September '98. These are the first data on Ni speciation in the Tweed Estuary.

Although labile Ni increases with salinity in November '96 and decreases in June '97 and September '98, the ratio of labile over total Ni is scattered between the values of 20 and 70%, and does not show any consistent trend with salinity for any of the transects (Figure 3.9). This behaviour is in contrast with that observed in the Tamar Estuary, where a substantial change in the dissolved Ni speciation was observed with increasing salinity (Figure 3.3). The lack of any specific trends in the labile Ni fraction in the Tweed Estuary is probably due to the fact that the flushing time of the estuary is too fast for any re-

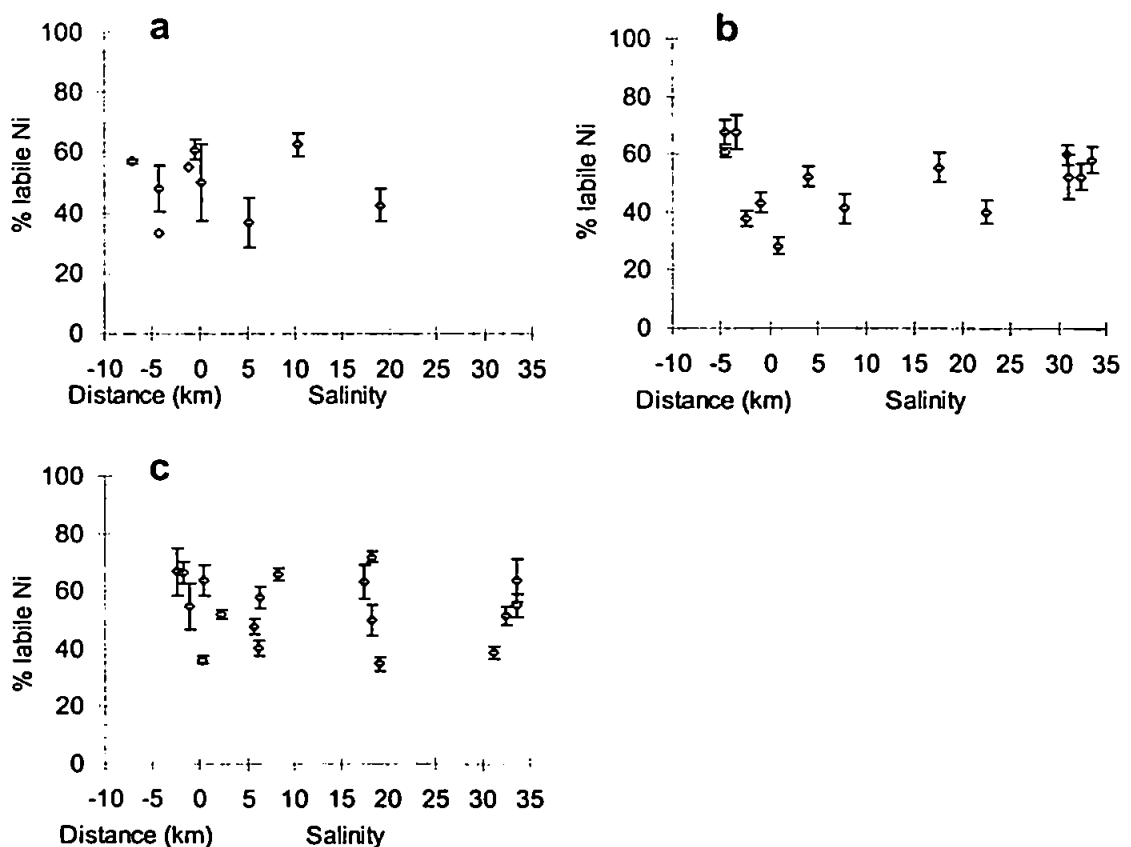


Figure 3.9. Percentage of labile Ni as a function of salinity in the Tweed Estuary. (a) November '96; (b) June '97; (c) September '98.

equilibration reaction between the two fractions to take place within the estuary, and the species therefore reflect variations in the speciation of the riverine end-member. Moreover, the low concentrations encountered in this study cause higher relative analytical errors in calculated parameters such as the fraction of labile Ni, which may mask subtle environmental trends.

Figure 3.10 shows the relationship between the fraction of non-labile Ni and the DOC. The DOC is higher in November '96 than in the other seasons, however the fraction of non-labile Ni does not show any clear dependence on the DOC concentration: this suggests that perhaps Ni is bound to a specific fraction of ligands and is not affected by variations of the "bulk" of the dissolved organic matter (Santschi et al., 1997). More specifically, since the increase in DOC in winter is probably due to pedogenic organic matter originating from terrestrial plant degradation (Alvarez-Salgado and Miller, 1998), it

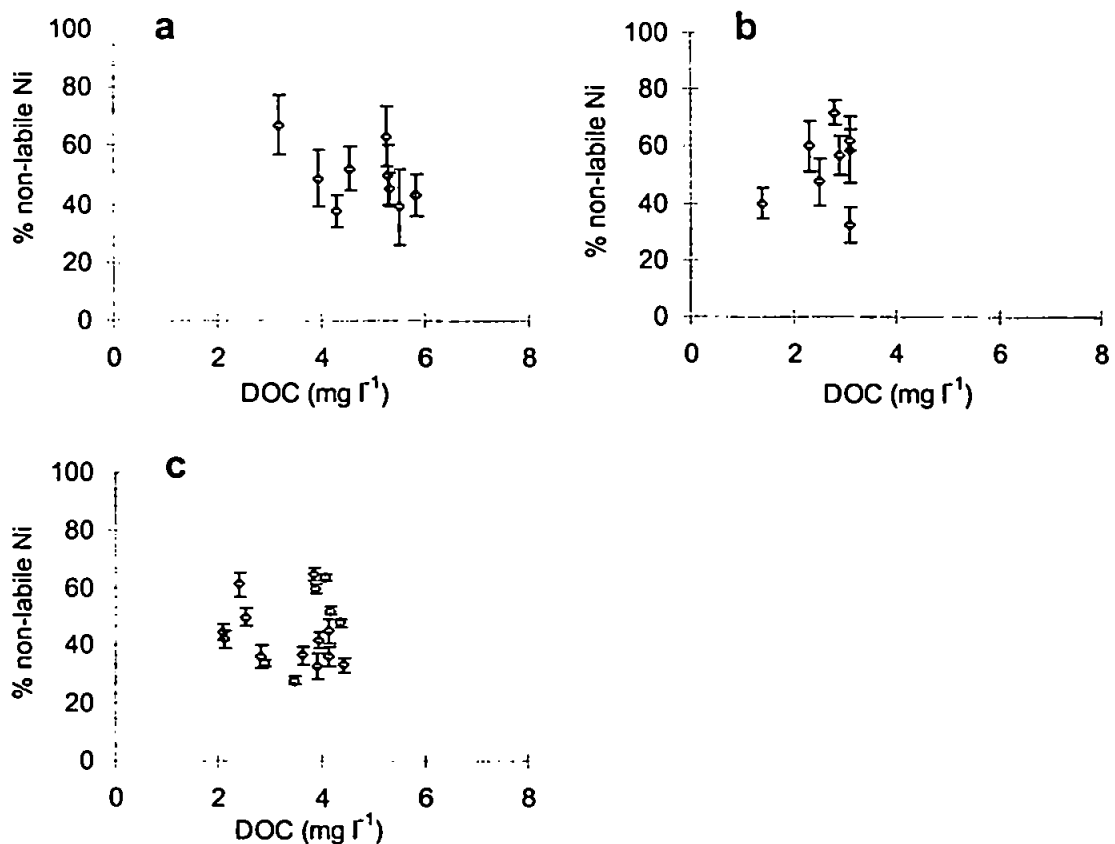


Figure 3.10. Percentage of non-labile Ni as a function of DOC in the Tweed Estuary. (a) November '96; (b) June '97; (c) September '98.



may be argued that this fraction of organic matter does not affect the complexation of dissolved Ni, and that ligands of different origin are responsible for its observed complexation. Achterberg et al. (1997) suggested that the organic complexation of Ni observed in Esthwaite Water during the summer months was due to organic material of probable autochthonous origin, i.e. generated *in-situ* by primary production. Intense phytoplankton blooms are known to occur in the Tweed Estuary (Clayton, 1997), but the occurrence of Ni-complexing ligands of biogenic origin cannot be proved on the basis of the available data.

### 3.2.3. NICKEL COMPLEXING LIGANDS IN THE TWEED ESTUARY

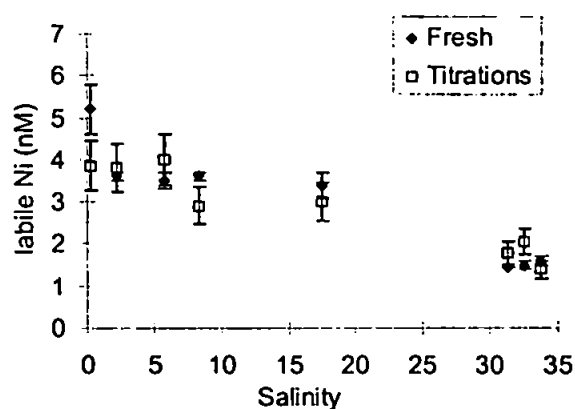
In this section, the results of the complexing capacity determinations carried out with Tweed samples for the September '98 transect are discussed. It should be emphasised that the ACSV technique adopted in this study only allows the determination of a fraction of the whole complexing capacity of the water body (Donat et al., 1994). The values of the stability constants used in this study for the evaluation of  $\alpha_{\text{Ni}(\text{DMG})_2}$  were determined by van den Berg and Nimmo (1987) for a range of salinities: at the concentration of DMG used in this study (0.2 mM), the detection window lies between  $10^{8.8}$  and  $10^{10.8}$  (salinity 32.5) and between  $10^{9.1}$  and  $10^{11.1}$  (salinity 2). The theoretical basis for the titration calculations is given in Appendix 2.

The effect of freezing the samples for the complexing capacity determinations was evaluated by comparing the labile Ni measured in the frozen and non-frozen samples (Figure 3.11). A paired *t-test* showed that there is no significant difference between the labile Ni measured in the two sets of samples, with a calculated t-value of 0.44 against a critical value of 2.45 ( $P < 0.05$ ;  $n=8$ ).

The results of the complexing capacity determinations for Ni in the Tweed Estuary are shown in Table 3.4. These are the first data reported for Ni complexing capacity and conditional stability constants in freshwater and brackish water. The results show that Ni is

bound to a class of extremely strong ligands, with average conditional stability constants of  $\log K' = 19.0 \pm 0.4$ . The values of the conditional stability constants are nearly one order of magnitude higher than those reported by van den Berg and Nimmo (1987) and Nimmo et al. (1989) for seawater samples (Table 3.5). However, there are insufficient data to establish whether there are systematic variations in the values of the stability constants as a function of salinity.

The ligand concentration (Figure 3.12) decreases with increasing salinity, from 4 nM in freshwater to 2.1-2.8 nM in seawater. Ligand concentrations are lower than the total Ni concentrations throughout the estuary. The calculation of Ni speciation in the original



**Figure 3.11.** Labile Ni for the fresh and defrosted (titration) samples in the Tweed Estuary during the September '98 survey.

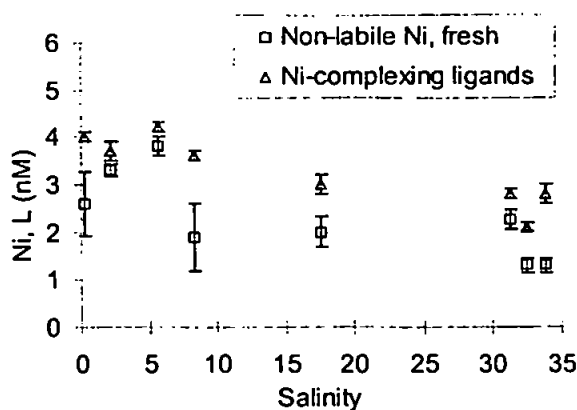
**Table 3.4.** Results of the complexing capacity titrations for the Tweed Estuary.  $C_L$  = concentration of Ni-complexing ligands (nM). All titrations were carried out on defrosted samples. Total dissolved Ni concentrations (nM) are also reported.

Station	Salinity	$Ni_{Total}$	$C_L$	$\log K'_{NiL}$
15	0.3	$7.8 \pm 0.3$	$4.0 \pm 0.1$	$19.5 \pm 0.4$
10	2.2	$6.9 \pm 0.1$	$3.7 \pm 0.2$	$18.8 \pm 0.2$
9	5.7	$7.30 \pm 0.01$	$4.2 \pm 0.1$	$18.6 \pm 0.2$
7	8.3	$5.5 \pm 0.7$	$3.6 \pm 0.1$	$19.4 \pm 0.3$
8	17.5	$5.4 \pm 0.1$	$3.0 \pm 0.2$	$19.4 \pm 0.6$
5	31.3	$3.7 \pm 0.2$	$2.8 \pm 0.1$	$19.3 \pm 0.5$
4	32.5	$2.8 \pm 0.1$	$2.1 \pm 0.1$	$18.5 \pm 0.2$
3	33.8	$2.9 \pm 0.1$	$2.8 \pm 0.2$	$18.8 \pm 0.2$

water samples (for these calculations the reader is referred to Appendix 2) indicates that the Ni-complexing ligands are saturated by the ambient Ni concentrations, in agreement with the findings by Nimmo (1987), van den Berg and Nimmo (1987), and Donat et al., (1994) for oceanic and coastal waters.

**Table 3.5.** Comparison of conditional stability constants reported in literature for Ni complexation by natural ligands.

Sample	Salinity	[DMG]	$\log K'_{NiL}$	Reference
Tweed Estuary	0.3-33.8	0.2 mM	$19.0 \pm 0.4$	This study
Mersey Estuary	0.3-32.5	0.2 mM	$18.7 \pm 0.5$	This study
Liverpool Bay	> 32.5	0.2 mM	17.7-18.7	Nimmo et al. (1989)
Menai Strait	32.5	0.5 mM	$17.8 \pm 0.1$	van den Berg and Nimmo (1987)
English Channel	34.5	0.1 mM	$17.3 \pm 0.1$	van den Berg and Nimmo (1987)
San Francisco Bay	27.8-31.7	0.1 mM	> 17	Donat et al. (1994)



**Figure 3.12.** Nickel complexing ligands and non-labile Ni in the Tweed Estuary during the September '98 survey.

The concentration of the Ni-complexing ligands is significantly higher than that of the non-labile Ni. A paired *t-test* for a difference between the two sets of concentrations resulted in a calculated *t* value of 5.32 against a critical value of 2.36 ( $P < 0.05$ ,  $n = 8$ ). This suggests that the addition of DMG causes the release of Ni from the NiL complexes, however this observation is in contrast with those from the Mersey Estuary (Section 3.3.3) and other coastal waters (van den Berg and Nimmo, 1987). The explanation for these contrasting observations may lie in the low concentrations of Ni and Ni-complexing

ligands observed in this study: this may be a consequence of the relatively high uncertainties associated with calculated parameters such as the non-labile Ni and ligand concentrations, which are derived from measured parameters, rather than directly measured.

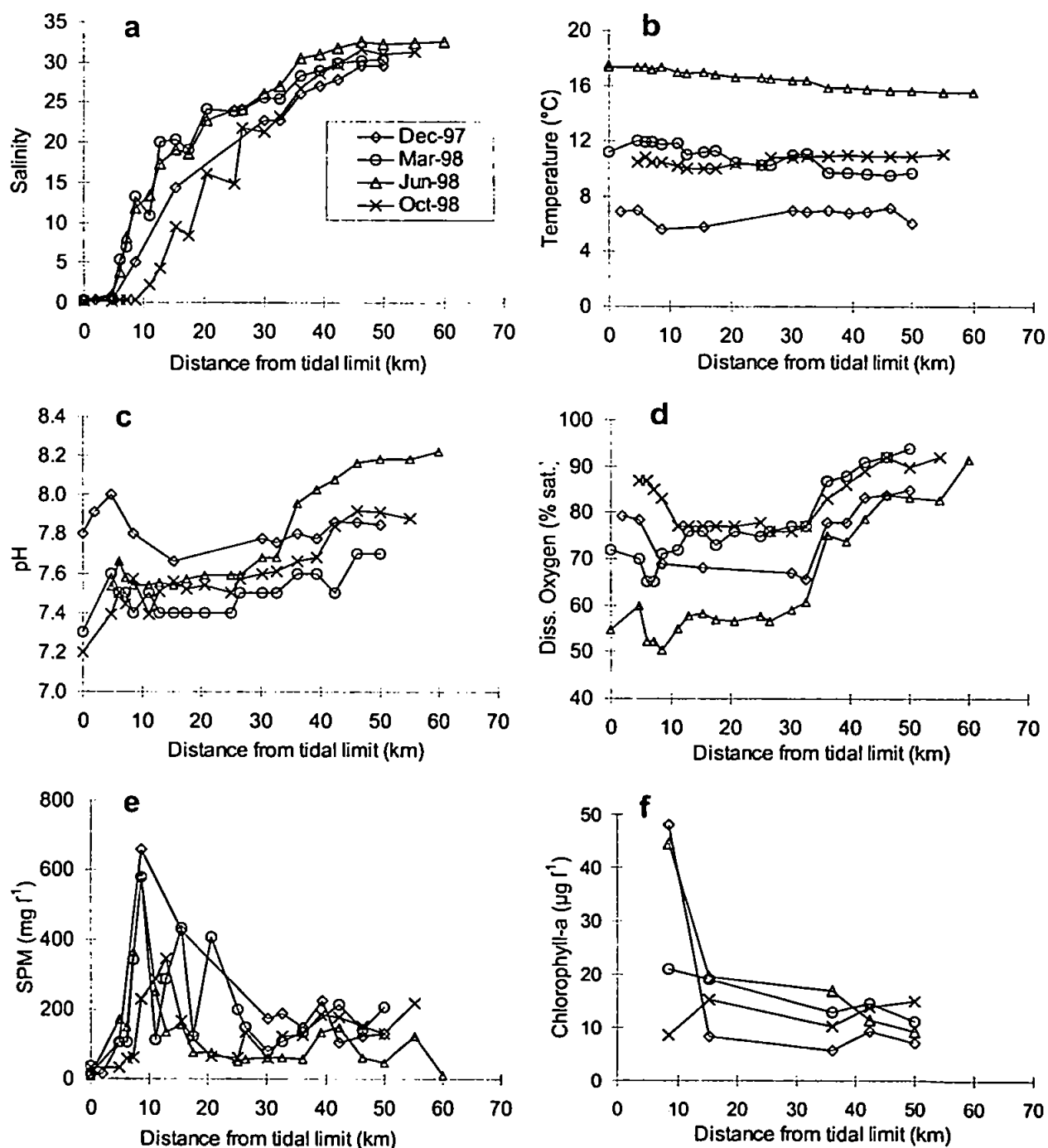
There is no significant positive correlation between the Ni-complexing ligands and the DOC ( $r^2 = 0.26$ ,  $n = 8$ ,  $P < 0.05$ ), which further suggests that variations in Ni-complexing ligand concentrations are not affected by those in the bulk of the DOC (Section 3.2.2).

### 3.3. The Mersey Estuary

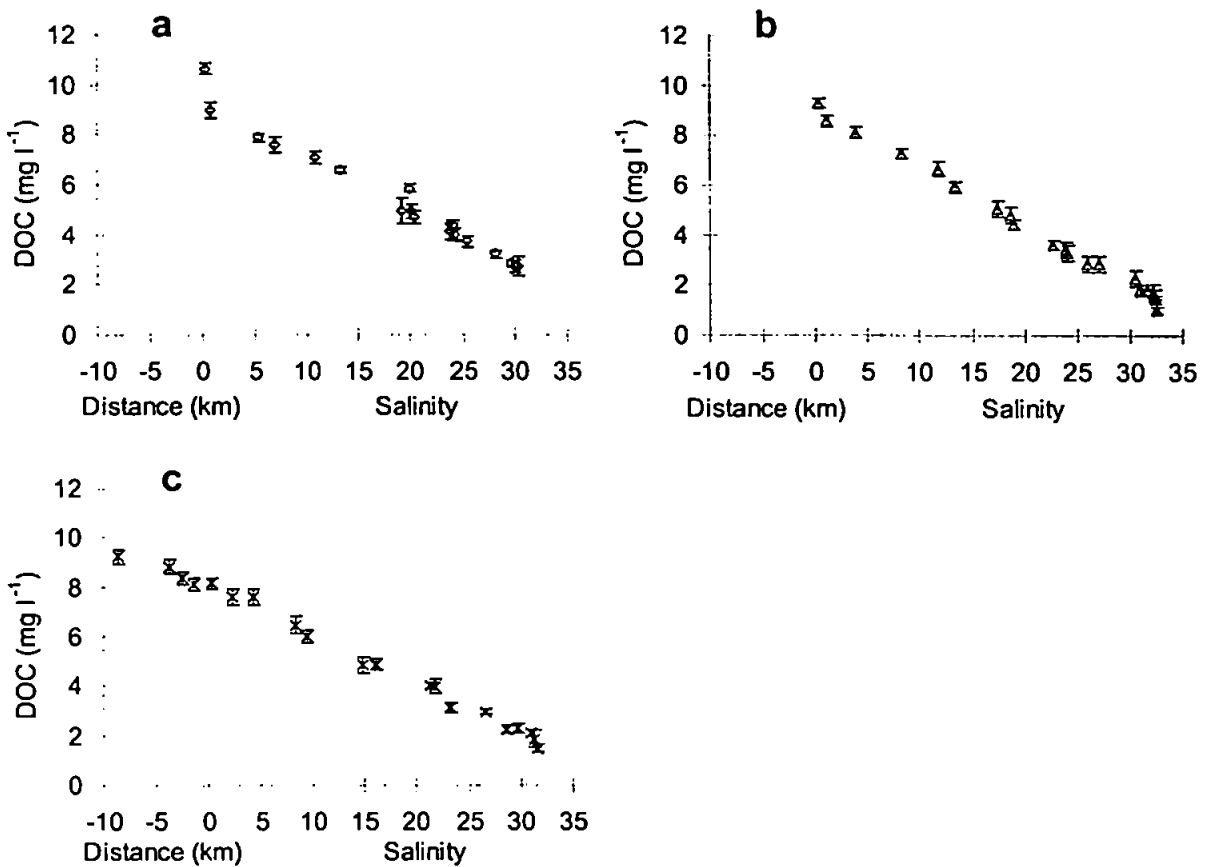
#### 3.3.1. MERSEY ESTUARY MASTER VARIABLES

Figure 3.13 shows the surface master variables and chlorophyll-a plotted versus distance from the tidal limit. Seasonal variations can be seen for temperature, dissolved oxygen and pH. A turbidity maximum, with SPM loads up to  $700 \text{ mg l}^{-1}$ , is situated at about 9 km below the tidal limit. The TMZ is shifted seawards during October '98, due to the higher river flow characterising this survey. The broad oxygen sag, observed in all seasons, is due to bacterial degradation of the organic load from effluent discharges, and from tidally-resuspended, organic-rich, bottom sediments (NRA, 1995). The smaller sag, apparent at low salinity during the March and June surveys, is associated with the TMZ (Morris et al., 1982b). A decrease in pH, due to bacterial respiration, occurs together with of the oxygen sag. Except for a "hot spot" at 8.6 km in December '97 and June '98, chlorophyll-a is relatively constant throughout the estuary in all seasons, as photosynthetic activity is generally inhibited by high turbidity (NRA, 1995). Dissolved organic carbon is plotted versus salinity in Figure 3.14. The Mersey DOC concentrations are comparable to those of the Beaulieu Estuary (Table 3.2); however, in contrast to the Beaulieu (which is rich in natural dissolved organic matter: Turner et al., 1998), it is likely that a relatively high fraction of the Mersey DOC is of anthropogenic origin, owing to the discharge of

domestic and industrial effluents in the River Mersey. The DOC behaves in a conservative fashion in all seasons, as also observed in the Tweed Estuary (Figure 3.5), but shows no seasonality.



**Figure 3.13.** Master variables recorded on the Mersey Estuary axial transects in December '97, March '98, June '98, and October '98. (a) salinity; (b) temperature; (c) pH; (d) dissolved oxygen; (e) SPM; (f) chlorophyll-a. The chlorophyll-a data (courtesy of the EA) were acquired on the same surveys, except for the December '97 data, which were acquired on a survey carried out on the previous day by the EA.



**Figure 3.14.** Dissolved organic carbon in the Mersey Estuary for the (a) March '97, (b) June '98, and (c) October '98 surveys.

### 3.3.2. DISSOLVED NICKEL IN THE MERSEY ESTUARY

Total, labile and non-labile Ni are plotted versus salinity in Figure 3.15. Concentrations of total dissolved Ni range from about 9 nM to 230 nM, with freshwater values ranging between 51 and 203 nM. The differences in freshwater concentrations can be attributed to variations in anthropogenic inputs in the River Mersey and river flow. The observed inverse relationship between river flow and total dissolved Ni concentrations (Figure 3.16) may be attributed to Ni inputs from point-sources which are diluted at increased river flow. This is in contrast with observations carried out on the Tweed Estuary, where the increased river flow caused an increase in the total dissolved Ni concentration (Figure 3.7, Section 3.2.2). The different behaviour of total dissolved Ni with river flow can probably be attributed to very different river catchments: whilst the Tweed drains a largely agricultural region, which is more prone to soil erosion during

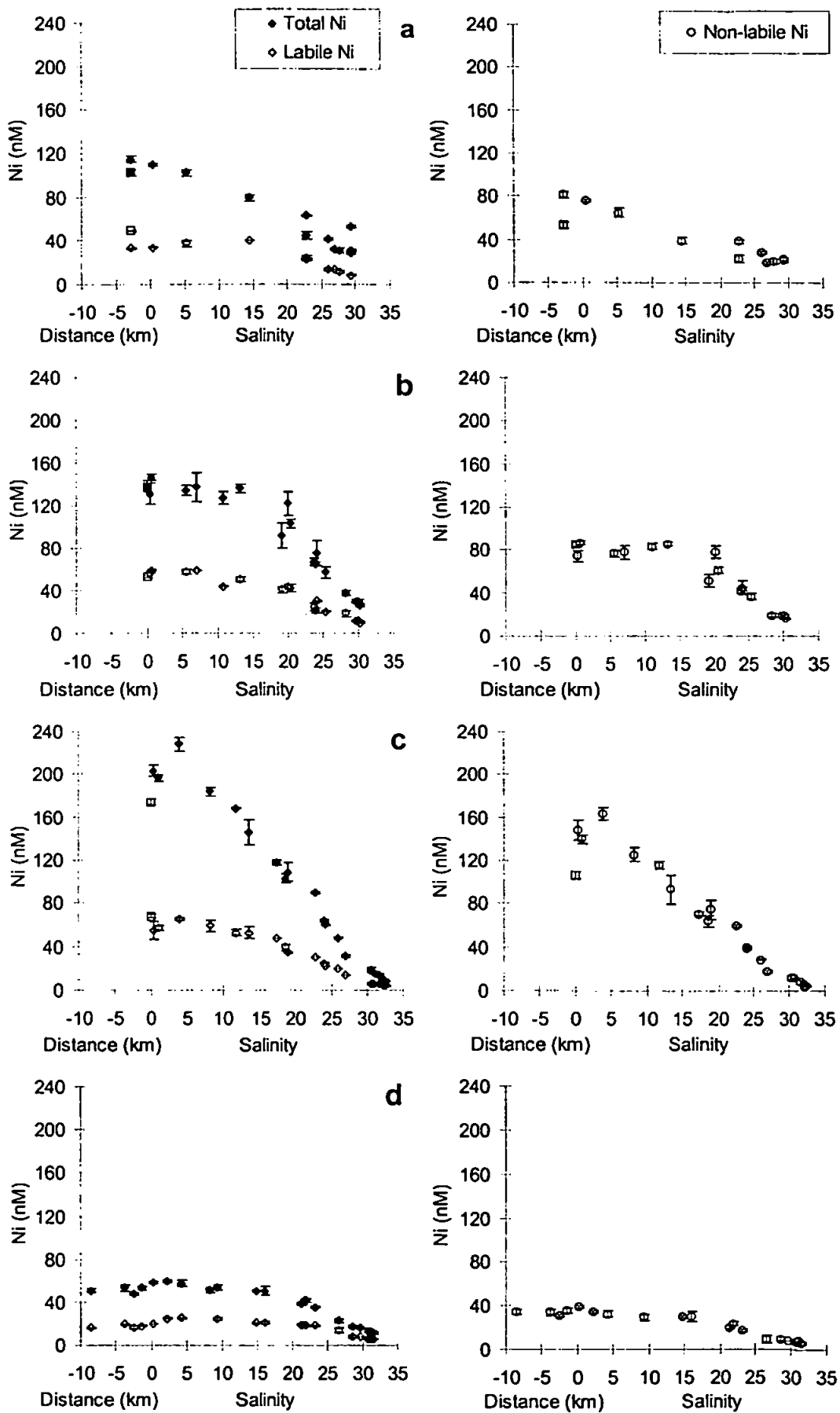
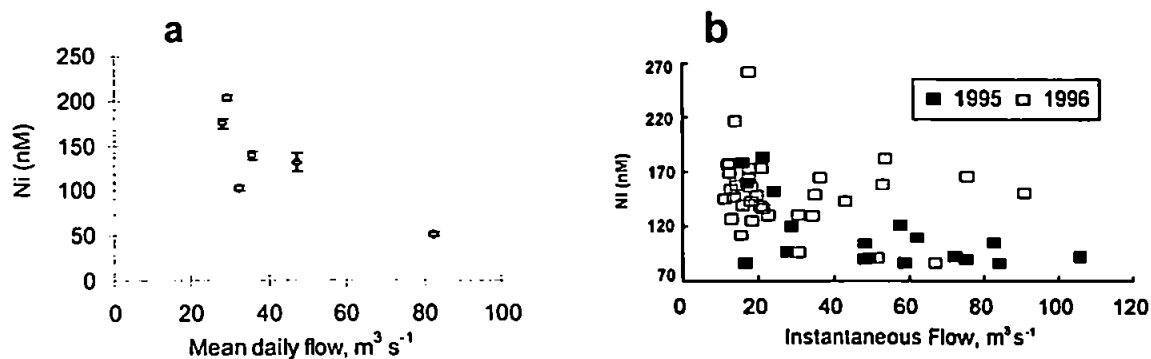


Figure 3.15. Dissolved total and labile Ni (left), and non-labile Ni (right) in the Mersey Estuary for the (a) December '97, (b) March '98, (c) June '98, and (d) October '98 surveys. Riverine samples represented by squares (Figures 3.15 a, b, c) were collected on the day previous to or following the survey.



**Figure 3.16.** Relationship between riverine total dissolved Ni and river flow in the Mersey River at Howley Weir. (a) this study; (b) Environment Agency data for the period 1995-1996. In (a), the highest and lowest flow values correspond to the October '98 and June '98 surveys, respectively.

stormflow conditions, the Mersey drains a heavily industrialised catchment, with anthropogenic metal point sources prevailing over natural ones.

Labile, non-labile and total dissolved Ni generally exhibit positive deviations from conservative mixing. The inputs may be due to one or more of the following: (i) anthropogenic sources; (ii) pore water infusion upon tidal disturbance of bed sediments; (iii) desorption from seaward-advected SPM and/or from resuspended contaminated sediments. Although the geochemical source of Ni cannot be established with certainty, it is likely that at least some of the inputs are of anthropogenic origin. For example, the Ni peaks at salinity ~28 (December '97) and 20 (March '98) are likely to represent inputs from the Manchester Ship Canal, which discharges into the estuary at 32.6 km from the weir. Previous studies on Ni distributions in the Mersey Estuary have shown that dissolved Ni has either a conservative behaviour or shows positive deviations from conservative mixing in the upper estuary (Table 3.6). Campbell et al. (1988), on the basis of dissolved and particulate Ni data from a series of surveys during the period 1980-1984, concluded that geochemical processes were a negligible source of dissolved Ni compared to anthropogenic inputs in the upper estuary. These authors believed that the inputs of Ni above and below the weir were both continuous and pulsed, and identified a manufacturer



**Table 3.6.** Ranges in total dissolved Ni concentrations (nM) in the Mersey River, Estuary, plume and in the Irish Sea (subsurface samples).

Study area	Total Ni	Behaviour	Reference
River	85-270		EA <sup>a</sup> unpublished data (1999)
River	51-203		This study
Estuary	9-228	Conservative/addition	This study
Estuary	30-200	Conservative	Jones (1978)
Estuary	25-200	Addition	Campbell et al. (1988)
Estuary	40-170	Addition	Comber et al. (1995)
Outer Estuary	14-160 <sup>b</sup>		Laslett (1995)
Outer Estuary	15-85 <sup>c</sup>		Laslett (1995)
Liverpool Bay	6-22		Nimmo et al. (1989)
Liverpool Bay	6-14		Achterberg and van den Berg (1996)
Irish Sea	4-15		Laslett (1995)

<sup>a</sup>Environment Agency; <sup>b</sup>Data for Summer '91; <sup>c</sup>data for Summer '92.

of the catalyst Raney Ni as one of the major sources of Ni into the estuary (discharging about 1.6 km below the tidal limit). However, Raney Ni production stopped around 1989, and it was replaced by Ni oxide on alumina substrate which was manufactured until 1998. Nickel is currently being used as a hydrogenation catalyst in the edible oil and fat industry at different industrial sites along the estuary, but discharges from these sources are probably not significant, as the effluents are all treated (A. Wither, Environment Agency North-West, pers. comm.). However, owing to the heavily industrialised and urbanised nature of the estuarine banks, other localised inputs of Ni from anthropogenic sources should not be excluded.

For each survey, plots of labile Ni as function of the total dissolved Ni exhibit a linear relationship (Figure 3.17). The slopes of the plots are shown in Table 3.7, and range between 0.315 and 0.40. The lower value obtained for the June slope indicates a higher fraction of non-labile Ni in the estuary, which may be related to the presence of ligands of different origin. The value of the slopes obtained in this study are considerably lower than those obtained by Nimmo (1987) and Nimmo et al. (1989) for Liverpool Bay (salinity > 30), possibly because of a higher proportion (relatively to Ni) of Ni-complexing ligands in the Mersey Estuary compared with adjacent coastal waters. The results shown in Figure

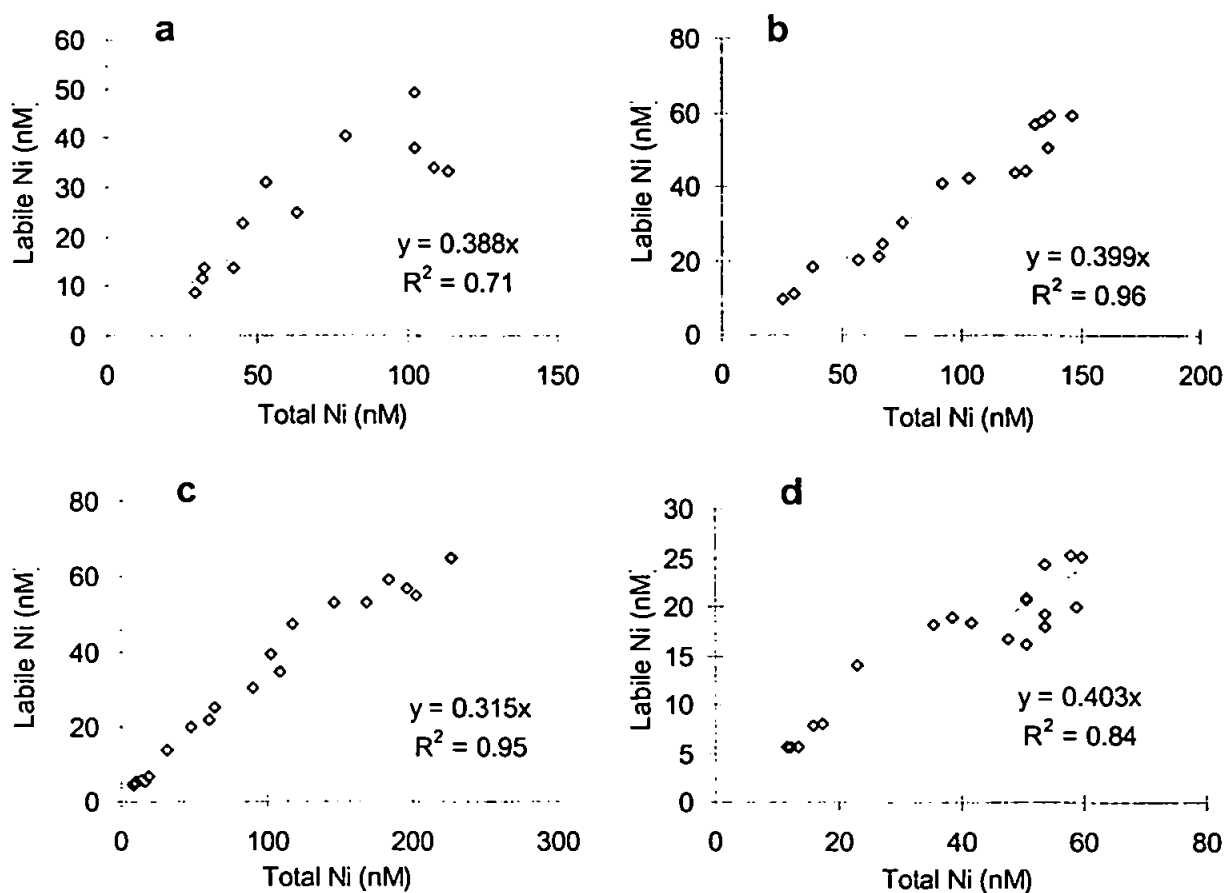


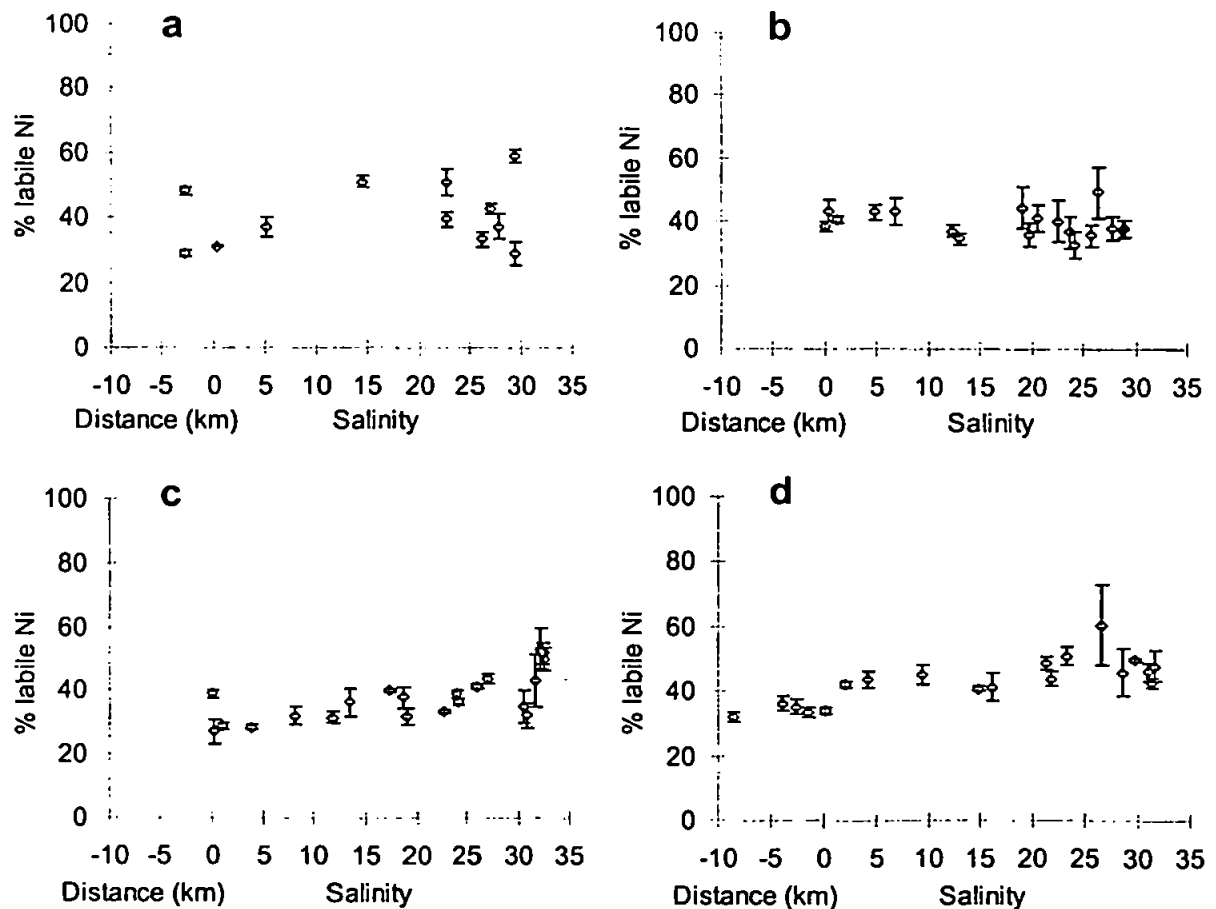
Figure 3.17. Labile Ni as a function of total dissolved Ni in the Mersey Estuary in (a) December '97, (b) March '98, (c) June '98, and (d) October '98.

Table 3.7. Results of linear regression of labile Ni versus total dissolved Ni for the Mersey surveys (this study) and Liverpool Bay (Nimmo et al., 1989). All regressions were forced through the origin of the axis.

Survey	Slope	$r^2$ (P < 0.05)	number of samples	Reference
December '97	$0.39 \pm 0.03$	0.71	12	This study
March '98	$0.40 \pm 0.09$	0.96	18	This study
June '98	$0.315 \pm 0.009$	0.95	21	This study
October '98	$0.40 \pm 0.01$	0.84	19	This study
May '85	$0.65 \pm 0.03$		27	Nimmo et al. (1989)
September '85	$0.57 \pm 0.03$		(*)	Nimmo et al. (1989)

(\*) Not reported.

3.17 suggest equilibrium between the labile and non labile fractions within the hydrodynamic timescales of the estuary. The flushing time of the Mersey Estuary has been estimated as 32 days (Jones, 1978) under average river flow conditions: this would allow sufficient time for the two fractions to reach equilibrium, and for any additional input in the estuary to be re-distributed between the two fractions. The relationship between labile and total Ni in Figure 3.17 indicates that the fractions of labile and non-labile are roughly constant through the estuary. This can be better seen when plotting the percentage of labile Ni on a salinity / distance scale (Figure 3.18). The percentage of labile Ni is relatively constant between 30 and 50% (or increases slightly) throughout the estuary, and shows little seasonality. This behaviour is different from that observed in the Tamar (where the percentage of labile Ni increased from 10 to 60% with increasing salinity: Figure 3.3) and



**Figure 3.18.** Percentage of labile Ni as a function of salinity in the Mersey Estuary in (a) December '97, (b) March '98, (c) June '98, and (d) October '98.

in the Tweed (where it was scattered between 20 and 70% and showed no consistent trend with salinity). The results in Figure 3.18 suggests the presence of Ni-complexing ligands with a high affinity for Ni, and with a lower affinity for Ca and Mg, in contrast to those observed in the Tamar Estuary (Section 3.1.2).

### 3.3.3. NICKEL COMPLEXING LIGANDS IN THE MERSEY ESTUARY

As for the Tweed, the samples for the Mersey complexing capacity titrations were frozen, and the effect of freezing was evaluated from the comparison of the labile Ni measured in the frozen (titration) and fresh samples (Figure 3.19). The data clearly show that above salinity ~ 15 there is no significant difference (a paired *t*-test resulted in a calculated  $t=0.11$  against a critical value of 3.18,  $P<0.05$ ,  $n=5$ ), whilst below salinity ~15 the labile Ni content is underestimated by up to 60% in the frozen samples. This suggests that loss of labile Ni has occurred in some of the titration samples, which may cause an error on the estimation of the complexing ligand concentrations ( $C_L$ , see below).

The loss of labile Ni can be attributed to wall adsorption, in which case the actual total Ni is lower in the titration (frozen) samples than in the “fresh” samples. Assuming that loss of labile Ni onto walls is the only effect of freezing (i.e. no labile Ni is lost to the

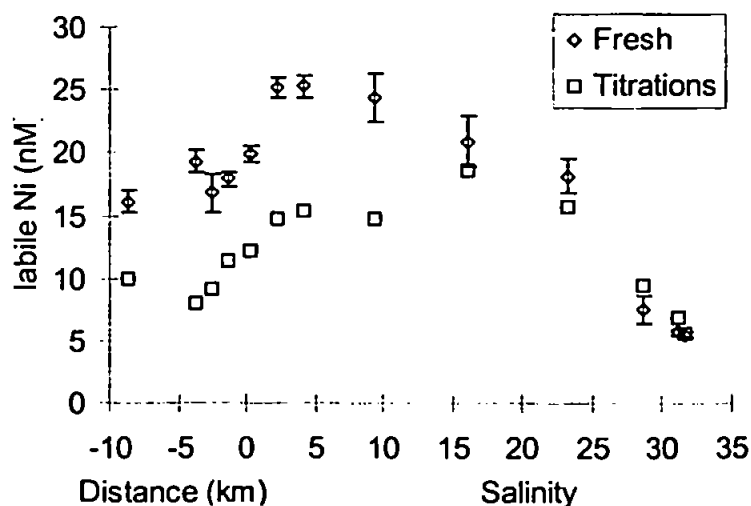


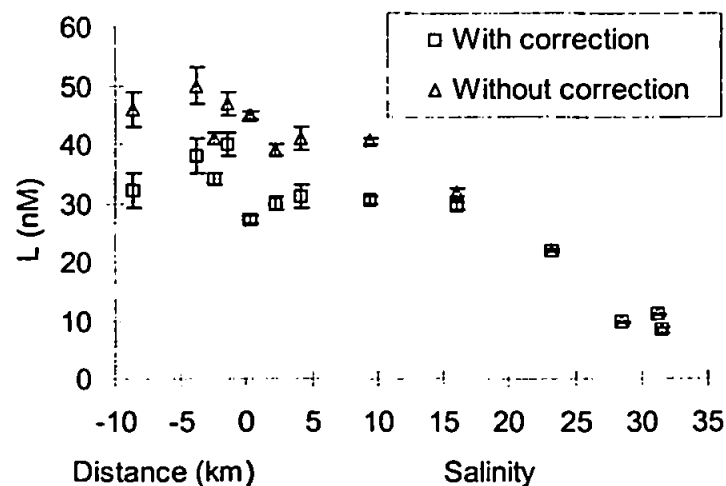
Figure 3.19. A comparison of labile Ni from the analyses of fresh and frozen (titration) samples. Mersey Estuary, October '98 survey.

non-labile fraction), then the total dissolved Ni in the frozen samples can be estimated as the sum of labile Ni from the frozen samples and non-labile Ni from the fresh samples. This value of total Ni can then be used for calculating  $C_L$ . The results of the Ni complexing capacity titrations are shown in Table 3.8 and Figure 3.20 with and without the correction for wall adsorption. The latter effect did not influence the values of the conditional stability constants, which are the same with and without the correction.

**Table 3.8.** Results of the complexing capacity titrations for the Mersey Estuary.  $C_L$  = concentration of Ni-complexing ligands (nM). Total dissolved Ni concentrations (nM) are also reported. All titrations were carried out on defrosted samples from the October '98 survey.

Station	Salinity	Ni <sub>Total</sub>	$C_L$	log $K'_{NiL}$	Ni <sub>Total</sub> corrected <sup>b</sup>	$C_L$ corrected <sup>b</sup>
Weir (REM)	0.2	51 ± 2	46 ± 3	18.3 ± 0.2	45 ± 2	32 ± 3
22	0.2	54 ± 4	50 ± 3	18.5 ± 0.3	42 ± 4	38 ± 3
21	0.3	48 ± 1	41 ± 1	18.6 ± 0.2	40 ± 1	34 ± 1
20	0.3	54 ± 3	47 ± 2	18.4 ± 0.2	47 ± 3	40 ± 2
19	0.3	59 ± 2	44.9 ± 0.8	> 18.5 <sup>a</sup>	51 ± 2	27.2 ± 0.8
18	2.2	59.6 ± 0.8	39 ± 1	> 18.5 <sup>a</sup>	49 ± 1	30 ± 1
17	4.2	58 ± 3	41 ± 2	> 18.4 <sup>a</sup>	48 ± 3	31 ± 2
16	9.4	54 ± 2	40.6 ± 0.5	> 18.6 <sup>a</sup>	44 ± 2	30.5 ± 0.5
14	16.1	51 ± 4	31.8 ± 0.6	> 18.7 <sup>a</sup>	51 ± 4	29.6 ± 0.6
10	23.2	36 ± 1	21.9 ± 0.4	18.5 ± 0.2	36 ± 1	21.9 ± 0.4
8	28.6	17.5 ± 1.5	9.7 ± 0.2	18.5 ± 0.1	17.5 ± 1.5	9.7 ± 0.2
6	31.6	11.7 ± 1.0	8.4 ± 0.4	18.0 ± 0.1	11.7 ± 1.0	8.4 ± 0.4
4	31.2	13.5 ± 0.4	11.0 ± 0.3	17.8 ± 0.1	13.5 ± 0.4	11.0 ± 0.3

<sup>a</sup> For these samples,  $\alpha_{NiL}$  was above the analytical detection window. Although this does not affect the determination of  $C_L$ , only a minimum estimate of log  $K'_{NiL}$  can be given (Donat et al., 1994). <sup>b</sup>These are the values of total Ni and  $C_L$  after estimated correction for wall adsorption is made.



**Figure 3.20.** Ni-complexing ligands in the Mersey Estuary, October '98 survey.

The conditional stability constants (Table 3.8) range between 17.8 and >18.7: these values are similar to those observed by van den Berg and Nimmo (1987) for English coastal waters, and the lowest values of  $K'_{NiL}$  occurs for the high salinity sample, in good agreement with the values of 17.8-18.2 reported for the Irish Sea by the same authors. Despite ligand concentrations calculated for the two sets differing by up to 40%, in both cases they are lower than the total Ni concentrations. Moreover, for both sets of  $C_L$  and total Ni values, the speciation in the original sample indicates that the ligands are saturated by the ambient Ni concentrations (see Appendix 2 for calculations): the fraction of total dissolved Ni which is bound to these ligands is equal to the concentration of the ligands throughout the estuary. The saturation of the ligands with Ni at all salinities, together with the roughly constant ratios of labile to total Ni (Figure 3.18) suggest that these ligands have a higher affinity for Ni than for Ca and Mg (in contrast with observations in the Tamar Estuary, where the non-labile Ni fraction decreased with increasing salinity). The lack of a broad seasonality in the labile versus total Ni plots (Figure 3.17) also suggests that these ligands are a persistent feature in the Mersey Estuary.

For the samples corrected for wall adsorption, the ligand and the non-labile Ni concentrations do not differ significantly throughout the whole salinity range (Figure 3.21): in this case the paired *t*-test gives a calculated *t* value of 0.04 which is smaller than the critical *t* value of 2.18 ( $P < 0.05$ ,  $n = 13$ ). This observation is in agreement with previous findings by Nimmo (1987) and van den Berg and Nimmo (1987), and suggests that the knowledge of the non-labile Ni concentration can yield to an indirect estimate of this fraction of the Ni-complexing capacity in the Mersey Estuary.

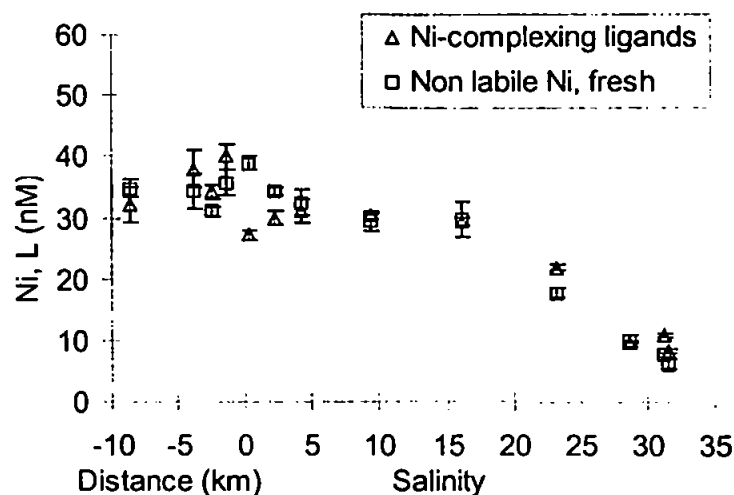


Figure 3.21. Ni-complexing ligands and non-labile Ni after correction for wall adsorption in the titration calculations. Mersey Estuary, October '98 survey.

### 3.3.4. DISSOLVED CO, ZN, CU, CD AND PB IN THE MERSEY ESTUARY

In this section, the observed distributions of dissolved Co, Zn, Cu, Cd and Pb for the four axial transects carried out on the Mersey Estuary are reported and discussed. The concentration ranges in total dissolved trace metals in the Mersey Estuary are shown in Table 3.9. A comparison of total dissolved trace metal concentrations from this study with other world's estuaries suggests that the Mersey is highly contaminated with respect to pristine estuaries such as the Lena (Guieu et al., 1996). Total dissolved trace metals in the Mersey Estuary are of the same order of magnitude (Zn, Cu, Pb and Cd) or more than one order of magnitude (Co) as in the highly contaminated Scheldt and Seine Estuaries.

Table 3.9. Ranges in concentrations (nM) of total dissolved Co, Zn, Cu, Cd and Pb in the Mersey Estuary, and in other world estuaries.

Estuary	Co	Zn	Cu	Cd	Pb	Reference
Mersey	0.76-40.6	49-314	24-89	0.29-2.2	0.31-6.0	This study
Scheldt	0.45-1.42 <sup>a</sup>	50-400	5-50	<2		Paucot and Wollast (1997)
Seine	0.5-3.5	25-200	8-35	0.2-2.5	0.3-1.8	Chiffoleau et al. (1994)
Gironde		10-30	6-20	0.2-1.1	0.1-0.3	Kraepiel et al. (1997)
Lena		1-5	6-16	0.1-0.4	0.05-0.5	Guieu et al. (1996)
Galveston Bay	0.5-3	2-7	4-16	0.05-0.8	0.02-0.13	Wen et al. (1999)

<sup>a</sup>Data from Zhang et al. (1990)

### 3.3.4.1. Cobalt

Total dissolved Co (Figure 3.22) shows positive deviations from conservative behaviour in all seasons. These are the first data on total dissolved Co concentrations in the Estuary, as there are no published dissolved Co data, and the metal is not part of the EA monthly monitoring programme. Lower Co concentrations occur in October '98 compared to the other seasons, probably due to the higher river flow, which has a dilution effect on the metal point-sources both above the weir and in the upper estuary.

A persistent and localised Co input occurs in the low salinity region. The occurrence of the Co peaks in proximity of the TMZ in all seasons, and the fact that in October '98 the Co peak is shifted seawards together with the TMZ, suggests that the Co input is not geographically localised, but it occurs in association with sediment resuspension in the TMZ. Chiffoleau et al. (1994) suggested that in the Seine Estuary Co,

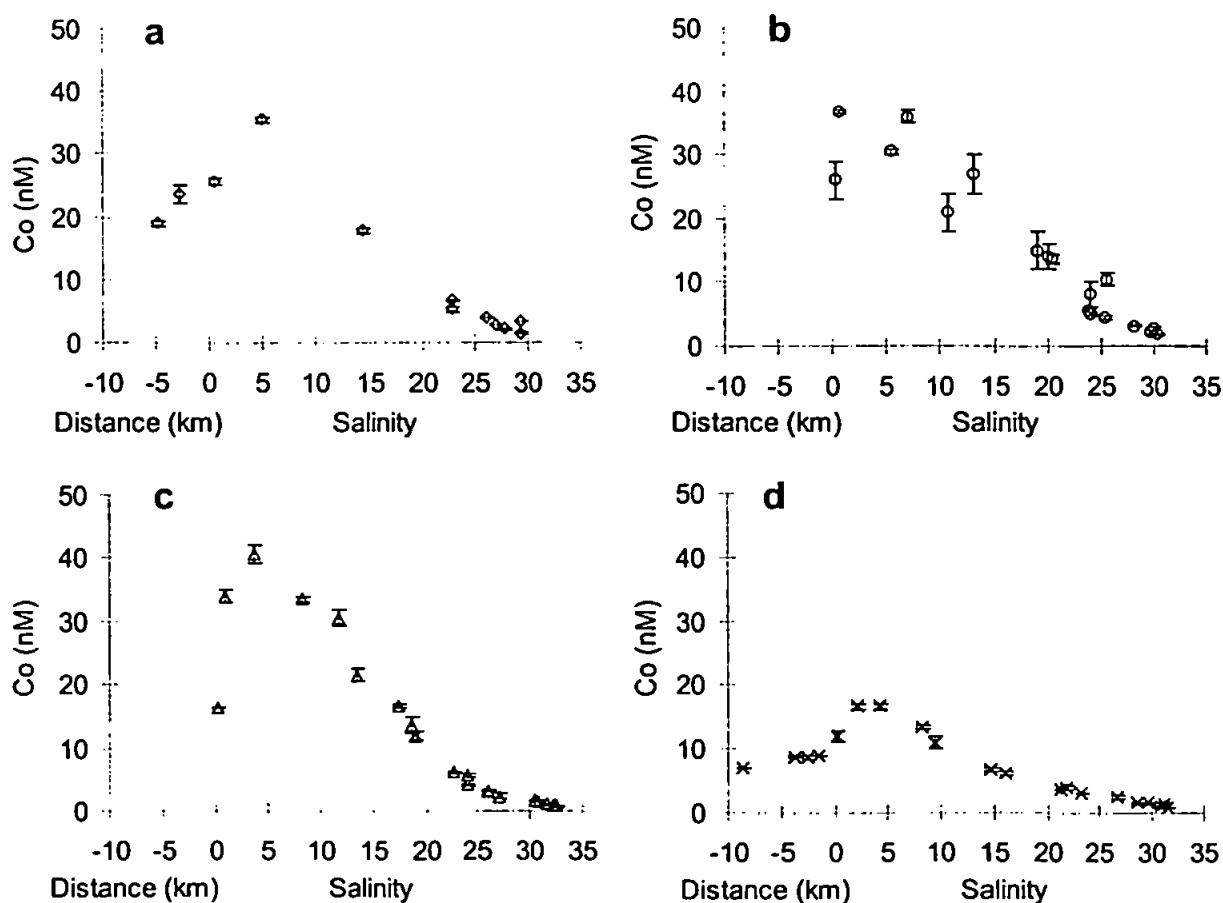


Figure 3.22. Total dissolved Co in the Mersey Estuary in (a) December '97, (b) March '98, (c) June '98, and (d) October '98.



scavenged together with insoluble Mn(IV) in oxic conditions, is released into the pore waters during the reductive solubilization of Mn(IV). Sediment pore waters enriched in Co and Mn(II) are then injected into the water column upon tidal resuspension of bed sediments in the TMZ occurring during spring tides. The coupling of the geochemical cycles of dissolved Co and Mn has often been observed (Balistrieri and Murray, 1986; Sundby et al., 1986; Lienemann et al., 1997), and may be a feature of the Mersey Estuary.

### 3.3.4.2. Zinc

Total dissolved Zn (Figure 3.23) varies between 50 and 315 nM in the estuary, and exhibits positive deviations from conservative behaviour in all seasons. The values reported in this study generally well agree with those by Comber et al. (1995) for the Mersey Estuary, who reported Zn concentrations in the range 110-260 nM for a 1991-1992

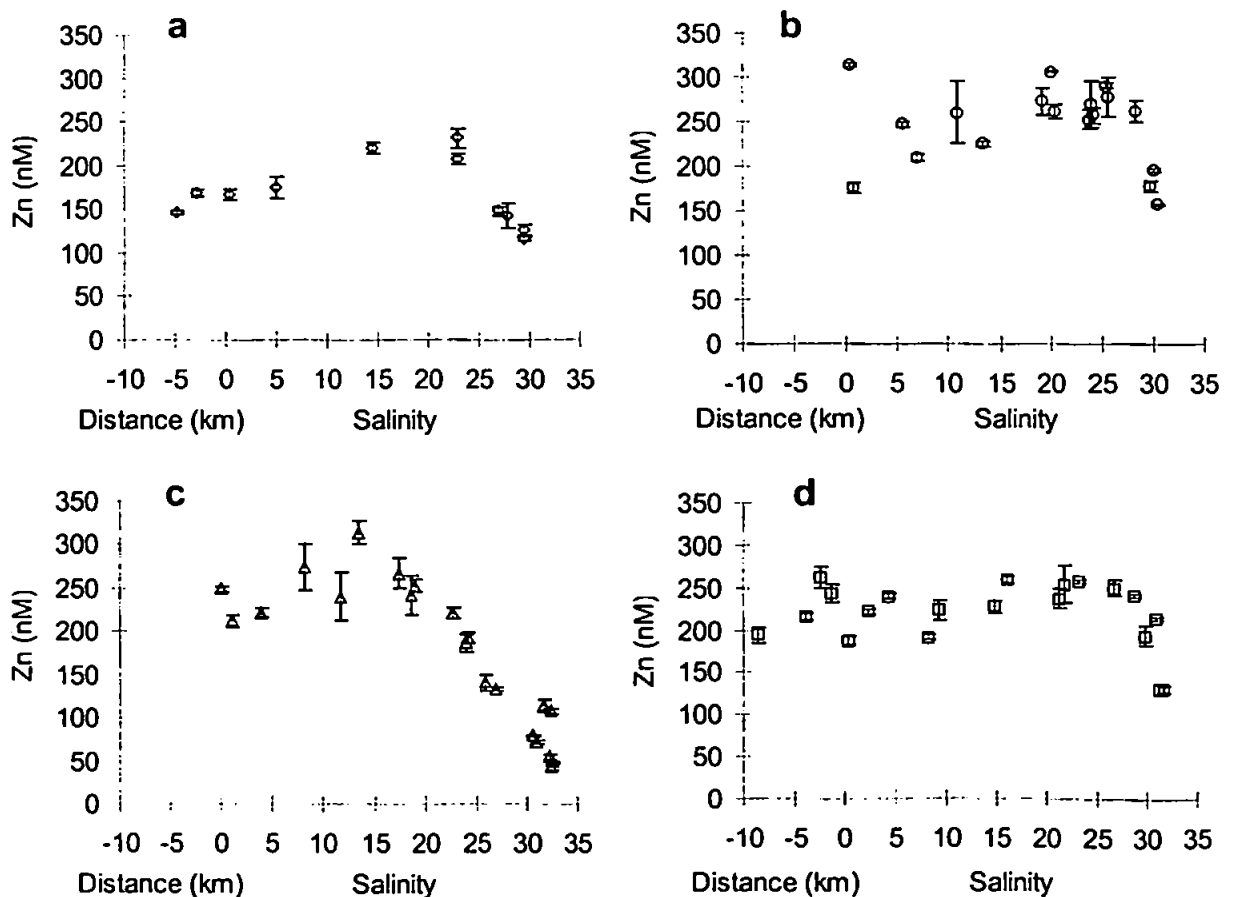


Figure 3.23. Total dissolved Zn in the Mersey Estuary in (a) December '97, (b) March '98, (c) June '98, and (d) and October '98.

study. The end-member concentrations observed in this study are also in good agreement with the values for the period 1980-1983 reported by Campbell et al. (1988); however these authors reported much higher mid-estuarine concentrations, with peaks up to 850 nM, which were attributed to discharge of industrial and domestic effluents between stations 6 and 10 (Figure 2.2). The decrease in Zn inputs to the mid estuary since the work of Campbell et al. (1988) is likely due to the reduced industrial use of zinc and to improved industrial and domestic effluent treatment works (NRA, 1995). However, the Zn trends reported in this study are consistent with those of Campbell et al. (1988), with broad mid-estuarine maxima, located in the salinity range 15-20. Seaward of the maxima, Zn decreases linearly with salinity. The location of the maxima in correspondence of the stretch between Eastham and New Brighton (where a number of domestic/industrial discharges are located, including the Manchester Ship Canal), suggests that the mid-estuarine additions are caused by anthropogenic Zn inputs being carried up-estuary by the incoming tide. Alternatively, the positive deviations of Zn from conservative behaviour may be attributed to desorption from seaward-advected particles or from resuspended contaminated bed sediments (Ackroyd et al., 1986; Paucot and Wollast, 1997; Chiffoleau et al., 1994).

#### 3.3.4.3. *Copper*

Copper concentrations vary between 23 and 89 nM for all surveys (Figure 3.24), in good agreement with the range 16-75 nM reported by Comber et al. (1995). These authors also reported removal of Cu in the low and mid estuarine region, and attributed it to the high scavenging capacity of the Mersey SPM. In this study Cu exhibits a more complex behaviour. Conservative behaviour occurs in June '98; the salinity plots of December '97, March '98 and October '98 show removal in the salinity range 0-15, followed by addition at salinity 15-25, and then conservative dilution at higher salinity. Removal of Cu could be due to adsorption onto estuarine SPM, as it has been shown that Cu has a high affinity for

surface organic ligands (e.g. Gerringa, 1990, Paulson et al., 1994). Addition of Cu in the salinity region 20-25 could be due to solubilisation and pore-water infusion occurring during degradation and recycling of particulate organic matter (Church, 1986; Gaillard et al., 1986), and/or desorption from seaward-advected sediments (Chiffoleau et al., 1994). The position of the Cu maxima at high salinity corresponds to that of the maxima of Zn, suggesting a common source for both metals in the outer estuary.

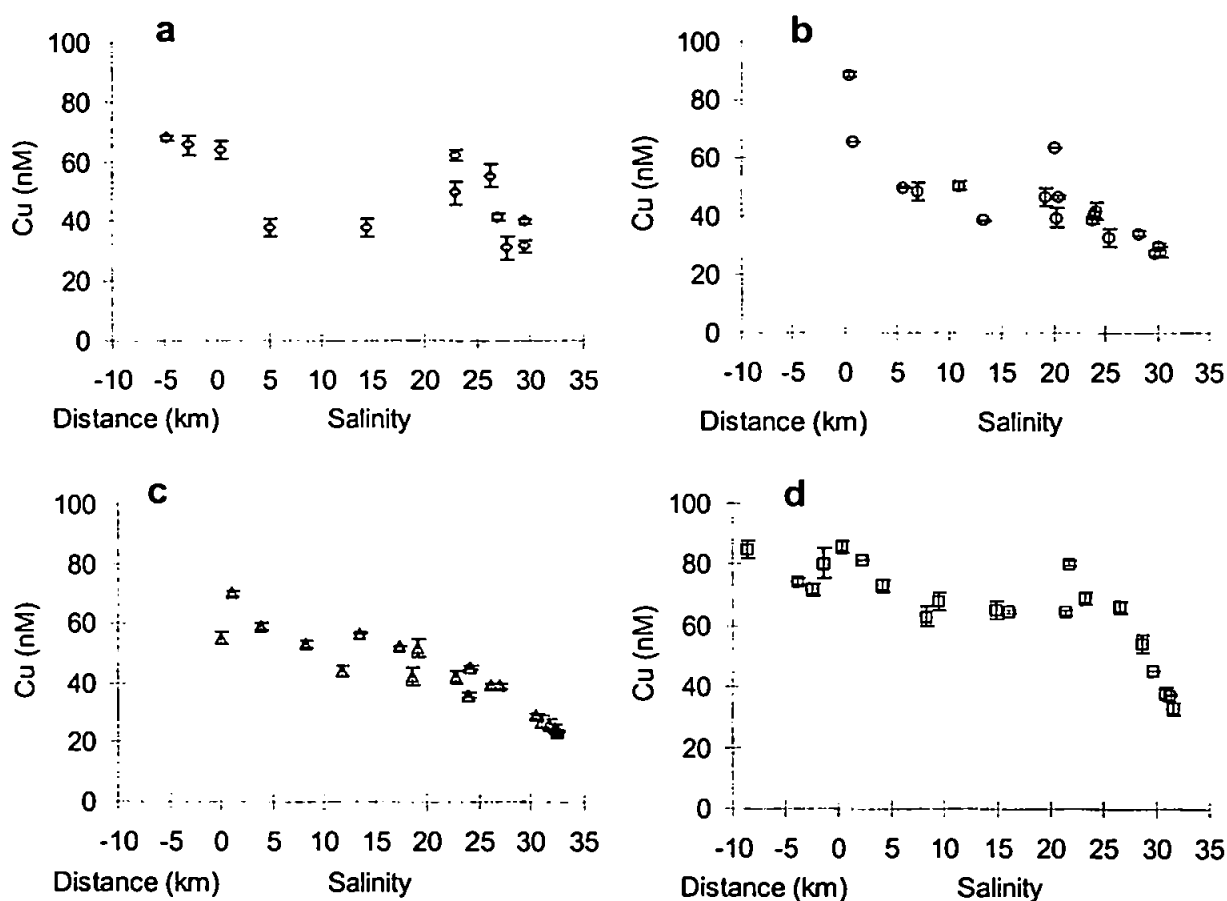


Figure 3.24 Total dissolved Cu in the Mersey Estuary in (a) December '97, (b) March '98, (c) June '98, and (d) October '98.

#### 3.3.4.4. Cadmium

Total dissolved Cd generally varies between 0.3 and 2.3 nM, and exhibits positive deviations from conservative behaviour in all seasons (Figure 3.25). Two “anomalous” data points with concentrations of 4.4 and 3.7 nM were observed, respectively, in December '97 and March '98: these high concentrations may be due to sample

contamination, however anthropogenic inputs cannot be excluded, owing to the industrialised nature of the estuarine catchment. A high scatter characterises the December '97 and March '98 distributions, which makes it difficult to interpret the data for these two seasons. However, all distributions show positive deviations from conservative behaviour. Desorption of Cd from seaward-advected particles is well-documented (Chiffoleau et al., 1994; Guieu et al., 1996; Kraepiel et al., 1997; Paucot and Wollast, 1997), and has been attributed to the formation of the thermodynamically stable chloro-complexes due to the increase in chloride concentration upon freshwater-seawater mixing (Comans and van Dijk, 1988).

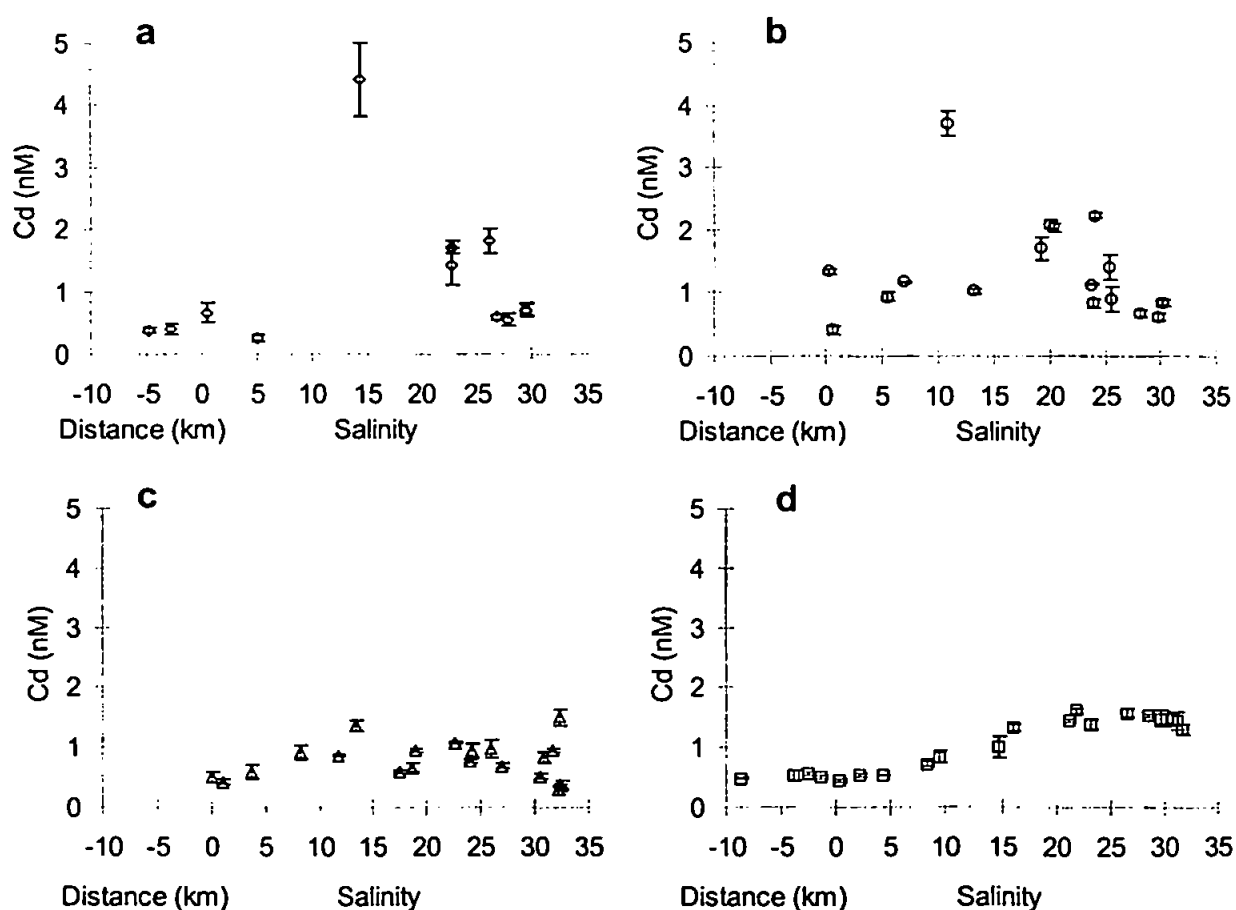


Figure 3.25. Total dissolved Cd in the Mersey Estuary in (a) December '97, (b) March '98, (c) June '98, and (d) October '98.

### 3.3.4.5. Lead

Total dissolved Pb concentrations range between 0.3 and 6.0 nM (Figure 3.26). A significant source of Pb to the estuary is from a manufacturer of tetra-alkyl lead compounds: this discharge is known to contain water-soluble organic Pb species (NRA, 1995). The Pb versus salinity profiles show addition in all seasons, with broad mid-estuarine maxima in December '97, March and June '98 located in the salinity range 5-15. In October '98, the Pb peak is less pronounced than in the other seasons: this effect may be due to a "dilution" effect (as observed for Co) due to the higher river flow occurring during this survey. The Pb peaks are probably due to industrial discharges, but may also be caused by desorption from resuspended contaminated sediments.

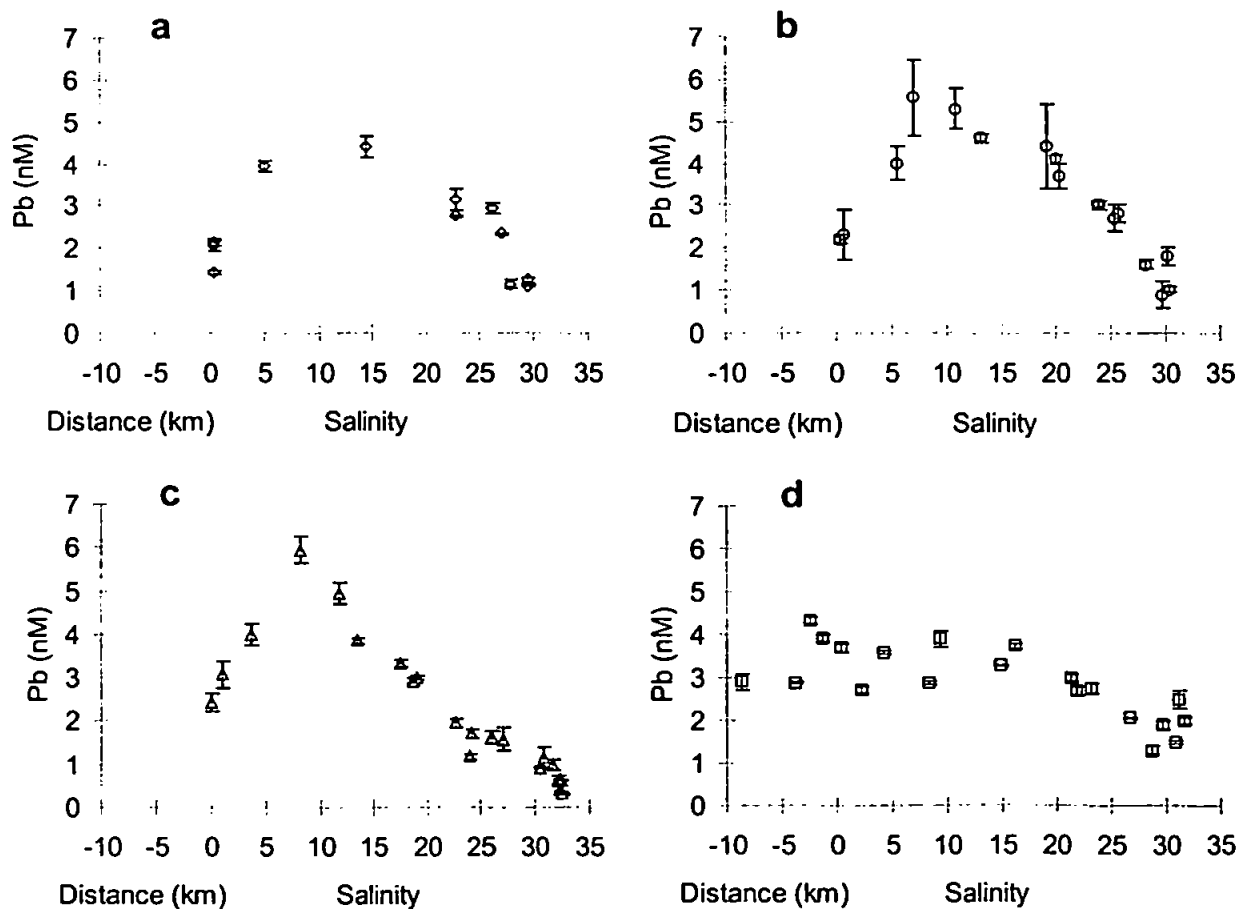


Figure 3.26. Total dissolved Pb in the Mersey Estuary in (a) December '97, (b) March '98, (c) June '98, and (d) October '98.

#### 3.3.4.6. Summary

All dissolved trace metals show to some extent positive deviations from conservative behaviour. The inputs may be due to one or more of the following: (i) anthropogenic sources; (ii) remobilization from interstitial waters; (iii) desorption from seaward-advected SPM or from resuspended contaminated bed sediments. Among all metals, Cu is the only one which exhibits removal in the estuary, probably as a result of adsorption onto SPM. The variety of metal inputs to the estuary does not allow the identification with certainty of the origin of the observed peaks in the metal distributions, and it is possible that inputs from domestic and industrial effluents throughout the estuary “mask” the signal of geochemical reactions. Moreover, the metals exhibit maxima at different values of salinity. For example, Co and Pb maxima are located at salinity ~5 and 10-15, respectively, whilst Zn, Cu and Cd peaks occur at salinity >15. This, together with the different reactivity of the metals, suggests metal sources to the estuary of different nature. The metal distributions generally do not show a pronounced seasonal variability. Co and Pb are the only metals which exhibit a decrease in the extent of the maxima during the high-flow October '98 conditions: this effect is due to the occurrence of the Co and Pb peaks in the upper estuary, which are diluted due to the increased river flow. Cobalt exhibits a significant positive correlation with Ni in all seasons ( $r^2=0.74-0.88$ ,  $P<0.05$ ), suggesting a common source of the two metals in the remobilised, upper estuarine bed sediments.

#### 3.3.5. PARTICULATE NI IN THE MERSEY ESTUARY

All particulate trace metal data reported in this section were kindly supplied by Ms. Sarah Watts (University of Plymouth). The seasonal distributions of particulate Ni (as available to 1 M HCl) are shown in Figure 3.27 as a function of salinity. The highest concentrations of particulate Ni occur in freshwater, where they vary between  $430 \text{ nmol g}^{-1}$  (October '98) and  $3270 \text{ nmol g}^{-1}$  (December '97). Lower and fairly uniform concentrations

occur throughout the mid- and outer estuary in all seasons ( $320 \pm 110 \text{ nmol g}^{-1}$ ), and marine-end member concentrations vary between  $220 \text{ nmol g}^{-1}$  (December '97) and  $330 \text{ nmol g}^{-1}$  (March '98).

Particulate Ni concentrations are compared with those previously reported for the Mersey Estuary and coastal zone in Table 3.10. Although it is not possible to draw a direct comparison owing to the different acid extraction techniques adopted, it seems that estuarine Ni concentrations have declined since the 1980-1981 study of Campbell et al. (1988), probably because the production (and waste discharge) of Ni-based catalysts has ceased.

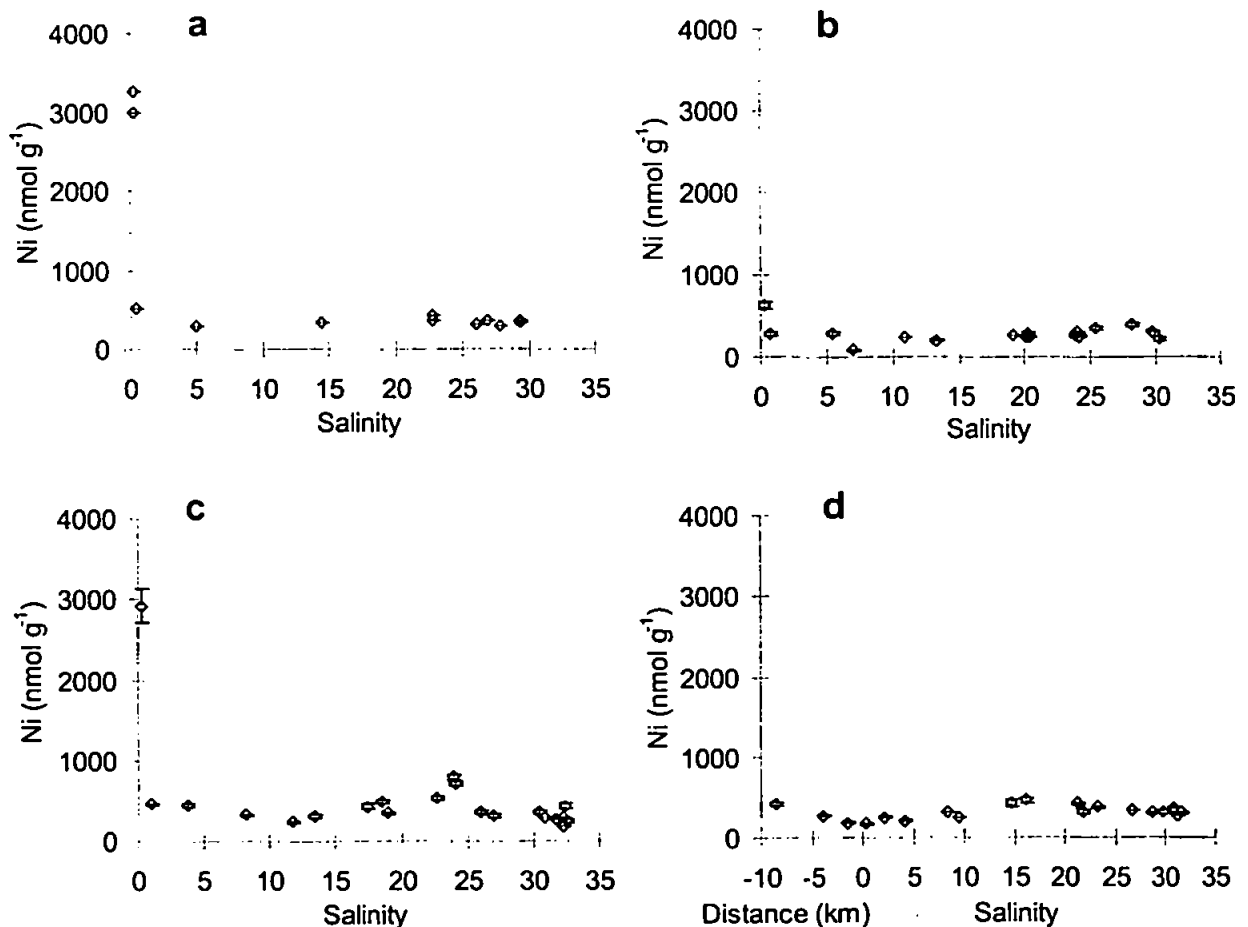


Figure 3.27. Particulate Ni (available to 1 M HCl) in the Mersey Estuary in (a) December '97, (b) March '98, (c) June '98, and (d) October '98.

Particulate Ni correlates well with both particulate Fe and loss on ignition (Table 3.11), suggesting that the metal may be bound to the organic and/or Fe oxy-hydroxides coatings on the particles. No statistically significant relationship was found for Ni and Mn. Association of Ni with Fe in estuarine SPM has been reported for the Mersey and Humber estuaries by Comber et al. (1995), and for the Humber mouth and plume by Sands (1997).

Particulate Fe and LOI are shown in Figures 3.28 and 3.29. The decrease in the LOI (from 40% in the river to 10-15% in the estuary) suggests that fluvial particles, rich in organic carbon, are diluted with particles advected from the outer estuary, which are relatively depleted in organic carbon. It appears, therefore, that the decrease in particulate trace metal concentration is due to the dilution of fine river borne particles by coarser and denser marine particulates entering the estuary from Liverpool Bay (Turner, 1999).

**Table 3.10.** Ranges in concentrations of particulate Ni (nmol g<sup>-1</sup>) in the Mersey Estuary and coastal zone.

Study area	Ni <sub>particulate</sub>	Extraction technique	Reference
Estuary	170-530	1 M HCl	This study
Estuary	850-2600	Not reported	Campbell et al. (1988)
Estuary	500-850	HCl-HNO <sub>3</sub>	Comber et al. (1995)
Outer Estuary	320-940	Conc. HNO <sub>3</sub>	Laslett (1995)
Irish Sea	200-650	Conc. HNO <sub>3</sub>	Laslett (1995)

**Table 3.11.** Values of r<sup>2</sup> for statistically significant (P<0.05) correlation between particulate Ni, Fe and loss on ignition (LOI) in the Mersey Estuary (numbers in brackets represent the number of paired observations).

	December '97 (n=12)	March '98 (n=18)	June '98 (n=21)	October '98 (n=19)
Ni/Fe	0.99	0.75	0.94	- <sup>a</sup>
Ni/LOI	0.96			

<sup>a</sup>The non significant correlation between particulate Ni and Fe is due to the presence of two outliers; the correlation becomes statistically significant (r<sup>2</sup>=0.26, p<0.05) if a non-parametric method (Spearman's rank correlation) is used for the statistical analysis.



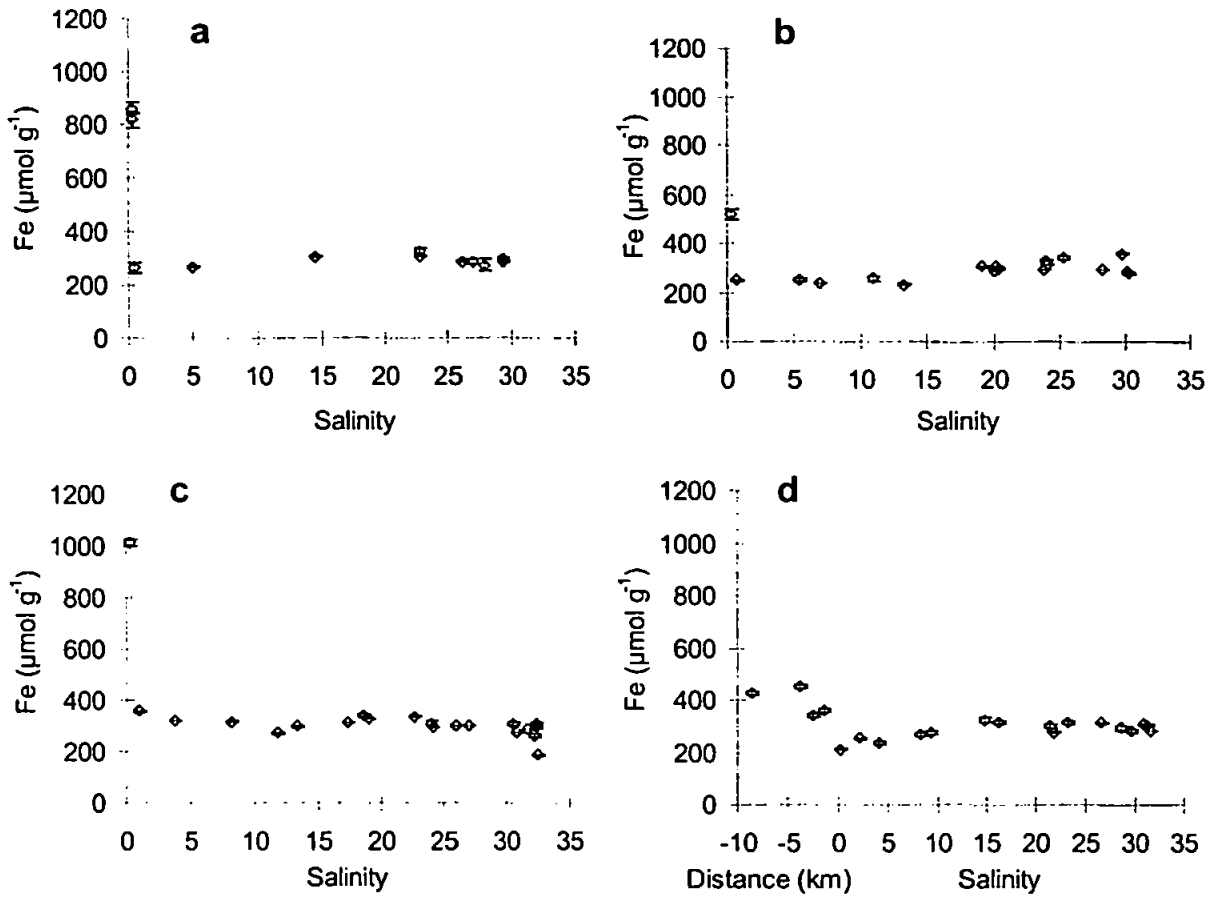


Figure 3.28. Particulate Fe (available to 1 M HCl) in the Mersey Estuary in (a) December '97, (b) March '98, (c) June '98, and (d) October '98.

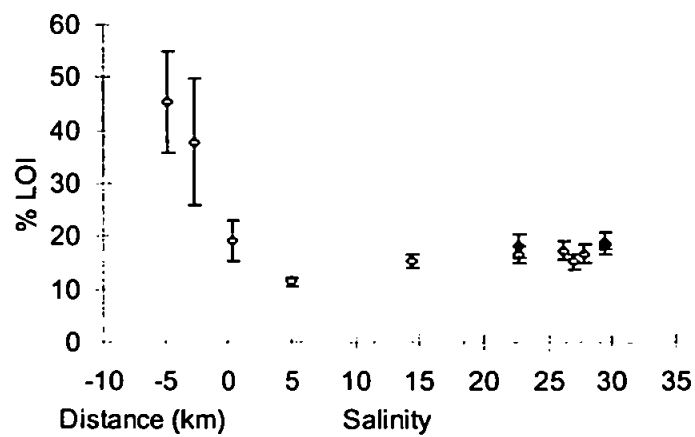
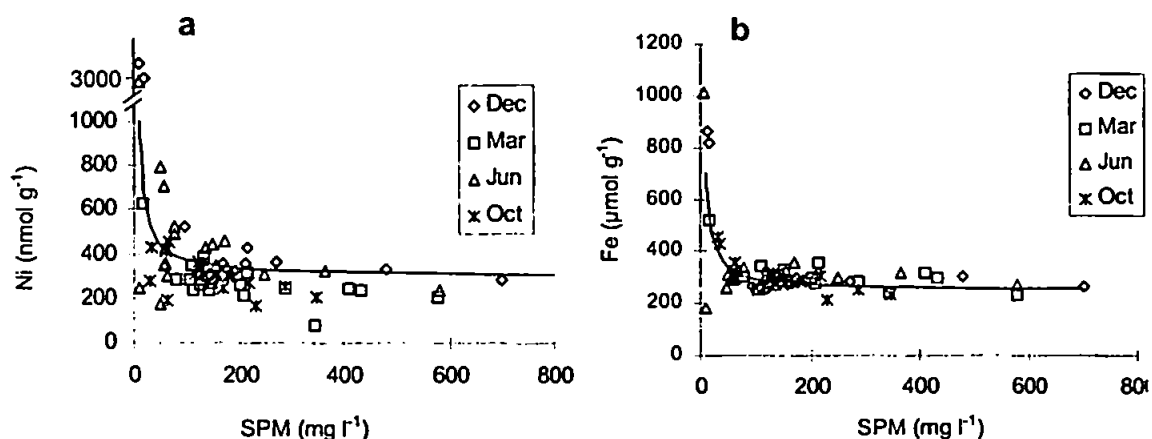


Figure 3.29. Loss on ignition for the December '97 survey on the Mersey Estuary.

Moreover, the relatively constant concentration of particulate trace metals, together with the LOI data for December '97, and the SSA data by Millward et al. (1990) suggests a particle source of uniform chemical composition, such as resuspended bed sediments, and indicates that the lower 40 km of the estuary are well mixed in terms of the suspended particulate matter, due to the tidally-induced transport and re-distribution of particulate material throughout the estuary (Kraepiel et al., 1997). As a consequence, particulate trace metals distribution patterns do not reflect the original input sources, or particle-water interactions, but rather the long-term mixing of riverine and marine particles (Turner, 1999).

Plots of particulate Ni and Fe concentrations versus SPM (Figure 3.30) indicate that the highest concentrations occur in the less turbid waters of the Mersey River and Estuary. According to Duinker (1983), in tidally dominated environments the SPM is composed of two main particle populations: (i) a low-density fraction, which is permanently in suspension and dominates at low SPM concentrations, and (ii) a high-density fraction, temporarily in suspension, which dominates the particle population at high SPM loads, and is derived from resuspension of bottom sediments. The variation of a



**Figure 3.30.** (a) Particulate Ni, and (b) particulate Fe (both as available to 1 M HCl) versus SPM in the Mersey Estuary. Curves represent the predicted concentrations according to Equation 3.1.

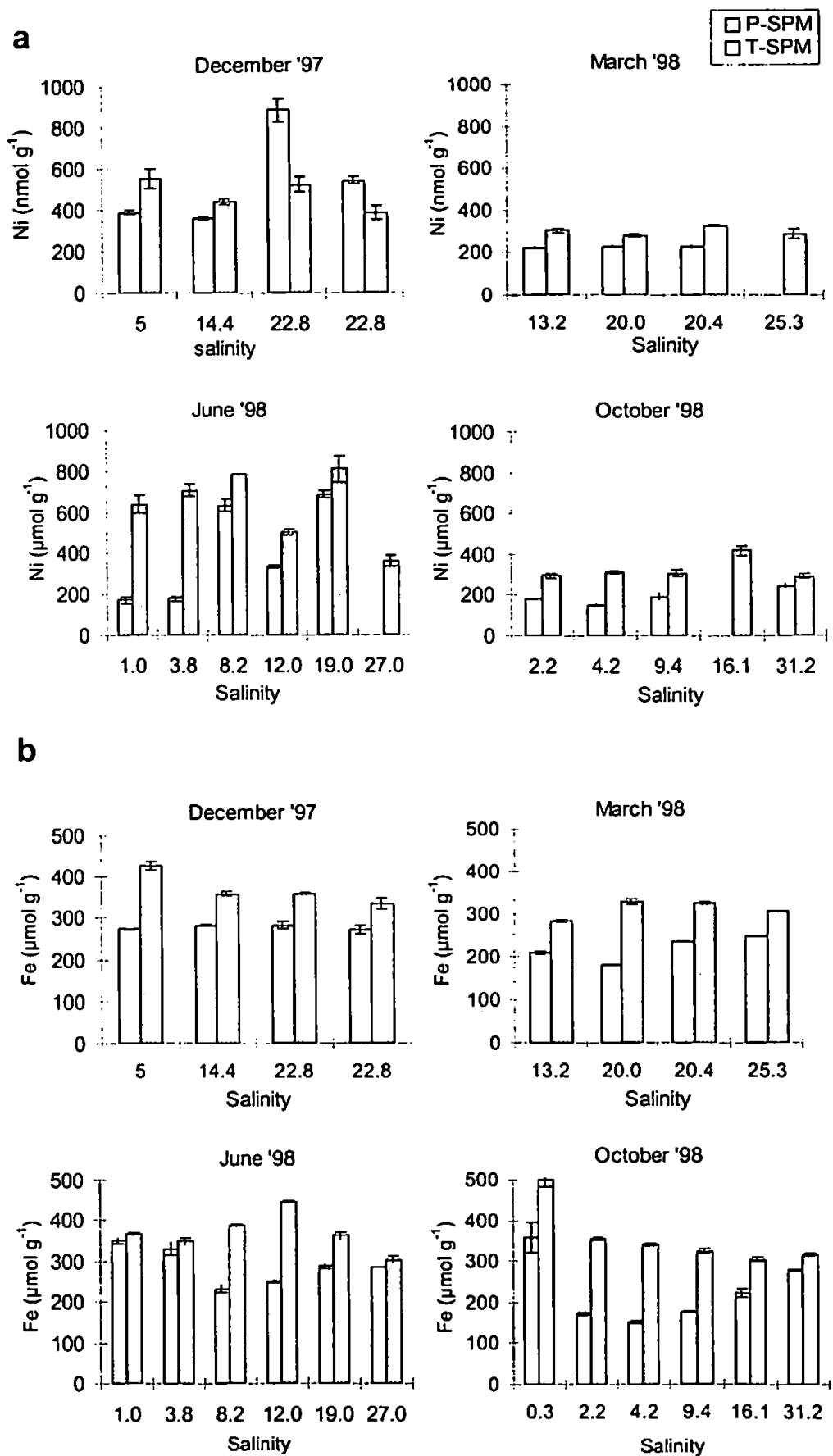
metal concentration with SPM concentration is the result of differences in the relative contributions of smaller and/or low density particles, and larger and/or denser particles (Nolting et al., 1990). Sands (1997) observed a preferential association of Ni and Fe with the denser, temporarily suspended fraction in the Humber coastal zone, whilst higher concentrations of Ni and Fe occurred in the finer SPM fractions of the Tamar Estuary (Liu et al., 1998) and the Dover Straight (Ni only: James et al., 1993). In the Mersey Estuary, both Ni and Fe concentrations are higher at low SPM loads, and their preferential association with the permanently suspended matter in the Mersey Estuary can be seen in the results of settling experiments (Figure 3.31). On the basis of the assumptions of the Duinker model, it is possible to derive a predictive equation which describes the variation in concentration of particulate trace metal with concentration of SPM as a function of the relative proportions of riverine and marine particles. For particulate Ni ( $[Ni_P]$ ) the relationship is as follows:

$$[Ni_P] = \frac{SPM_R[Ni_P]_R + SPM_M[Ni_P]_M}{SPM} \quad (3.1)$$

with:

$$SPM = SPM_R + SPM_M \quad (3.2)$$

where  $SPM_R$  is the observed riverine SPM concentration of  $[Ni_P]_R$  concentration;  $SPM_M$  is the varying marine SPM concentration of  $[Ni_P]_M$  concentration; and SPM is the observed estuarine particulate matter concentration. The values used for the model are average end-member concentrations from this study ( $SPM_R = 10 \text{ mg l}^{-1}$ ;  $[Ni_P]_R = 1000 \text{ nmol g}^{-1}$ ;  $[Ni_P]_M = 300 \text{ nmol g}^{-1}$ ;  $[Fe_P]_R = 700 \text{ } \mu\text{g g}^{-1}$ ;  $[Fe_P]_M = 250 \text{ } \mu\text{g g}^{-1}$ ). The model is in good agreement with the observations for both Ni and Fe (Figure 3.30), and suggests that the mixing of riverine particles rich in trace metals with estuarine bed sediments, relatively depleted in trace metals, and of likely marine origin, can explain the sharp gradients observed in the low salinity region of the Mersey Estuary.



**Figure 3.31.** Variations in (a) particulate Ni and (b) particulate Fe concentrations (as available to 1 M HCl) in density-separated fractions of Mersey SPM for samples collected at different salinities. P-SPM = Permanently suspended matter (shaded); T-SPM = Temporarily suspended matter (unshaded). A settling time of 30 minutes was decided on an operational basis.

### 3.3.6 PARTICLE-WATER INTERACTIONS OF NI THE MERSEY ESTUARY

Conditional distribution coefficients for the stable isotopes (field  $K_d$ s) have been calculated from the ratio between particulate and dissolved trace metal data according to Equation 1.10, and those for Ni are plotted in Figure 3.32. It should be noted that these distribution coefficients have been calculated using particulate trace metals concentrations available to 1 M HCl, which overestimates the fraction of trace metal available for exchange reactions as it partially releases metals bound to the carbonate and crystalline iron oxides fraction of the particle matrix (Chao, 1984; Whitworth et al., 1999). Therefore the  $K_d$  value represents an empirical description of the particle-water distribution, without any implication of equilibrium between the two phases (Burton et al., 1993).

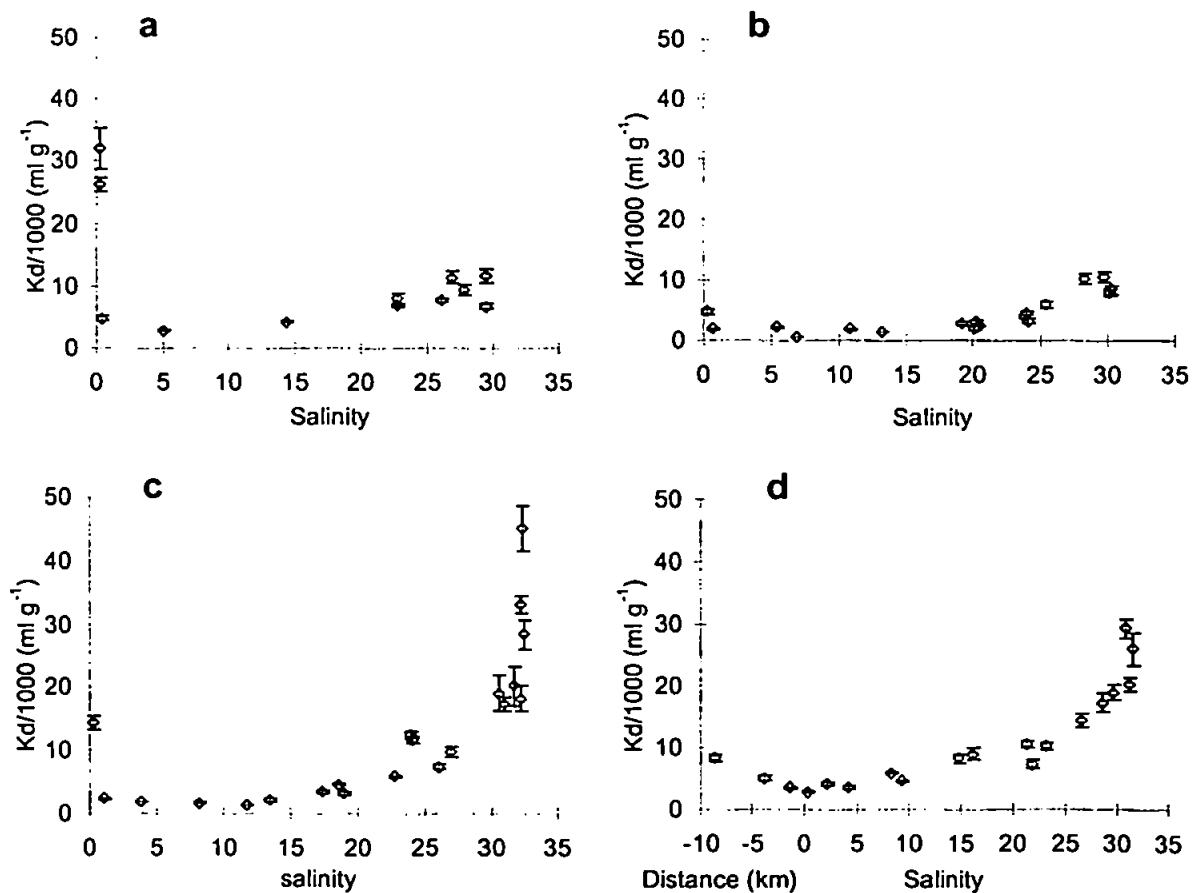


Figure 3.32. Field distribution coefficients for Ni in the Mersey Estuary in (a) December '97, (b) March '98, (c) June '98, and (d) October '98.

The field distribution coefficients obtained for Ni in this study compare well with those reported in the literature (Table 3.12), even though different particle digests were used. The variation encountered in this study is, however, nearly two orders of magnitude broader than that of other studies, reflecting the large range in dissolved and particulate Ni concentrations encountered in the Mersey Estuary.

**Table 3.12.** Comparison of field  $K_d$ s for Ni from a variety of estuaries and coastal waters.

Location	Particulate metal extraction	$\log K_d$ (ml g <sup>-1</sup> )	Reference
Mersey Estuary	1 M HCl	2.8-4.7	This study
Humber Estuary	1 M HCl	4.3-4.6	Sands (1997)
Weser Estuary	25% CH <sub>3</sub> COOH/ 0.05 M NH <sub>2</sub> OH HCl	3.7	Turner et al. (1992b)
Weser Estuary	conc. HNO <sub>3</sub>	4.3	Turner et al. (1992b)
Scheldt Estuary	conc. HNO <sub>3</sub>	3.5-4.2	Paucot and Wollast (1997)
Seine Estuary	HCl, HNO <sub>3</sub> , HF	4.2-4.4	Chiffolleau et al. (1994)
British coastal waters	conc. HNO <sub>3</sub>	4.0-4.5	Balls (1989)

For this study, the mean values of the field distribution coefficients for all trace metals are shown in Table 3.13. The magnitude of the field  $K_d$ s of all metals generally follows the sequence:

$$\text{Pb} > \text{Cu} > \text{Co} > \text{Zn} > \text{Cd} \sim \text{Ni}$$

which is similar to the trends observed for other estuaries (Turner et al., 1992b, Balls, 1989; Chiffolleau et al., 1994; see also Table 1.8). Lead ( $\log K_d = 4.8-5.4$ ) shows the highest particle affinity among all the metals, whilst Ni shows the lowest particle affinity ( $\log K_d = 3.5-3.9$ ). The three latter metals in the sequence above (Zn, Cd, Ni) are well known to be extensively complexed in the dissolved phase in estuarine waters. The affinity of Cd for chloride is well documented (Comans and van Dijk, 1988), and Ni and Zn have been shown to be complexed to a high extent by strong ligands (van den Berg et al., 1987; van den Berg et al., 1991; Donat et al., 1994; this study), which may lower their affinity for the particulate phase, decreasing their retention in the estuarine environment.

**Table 3.13.** Comparison of mean field  $K_{ds}$  (log values) for trace metals in the Mersey Estuary.

	Ni	Co	Zn	Cu	Pb	Cd
December '97	3.9 ± 0.3	4.3 ± 0.5	4.5 ± 0.2	3.9 ± 0.2	5.4 ± 0.3	3.9 ± 0.7
March '98	3.5 ± 0.3	4.3 ± 0.5	4.0 ± 0.1	4.4 ± 0.1	4.8 ± 0.6	3.9 ± 0.3
June '98	3.9 ± 0.5	4.3 ± 0.6	4.0 ± 0.1	4.7 ± 0.2	5.3 ± 0.3	4.1 ± 0.3
October '98	3.9 ± 0.3	4.3 ± 0.4	3.7 ± 0.2	4.5 ± 0.2	5.4 ± 0.1	3.8 ± 0.6

### 3.4. A comparison of Ni behaviour and reactivity in the Tamar, Tweed and Mersey Estuaries

Thus far, it is clear that the behaviour of total dissolved Ni is widely different for the three estuaries, showing removal followed by addition in the Tamar, largely conservative behaviour in the Tweed, and addition in the Mersey Estuary.

The composite behaviour of Ni in the Tamar Estuary can be attributed to flocculation of colloidal Ni at the freshwater/seawater interface, followed by desorption from seaward-advected particles upon an increase in salinity (Morris, 1986; this study).

Total dissolved Ni behaviour in the Tweed Estuary has been shown to be largely conservative, a factor attributed to the combination of short estuarine flushing time and low SPM concentrations, which would both hinder the promulgation of heterogeneous chemical reactions (Morris, 1990). The large variations in riverine end-member concentrations of total dissolved Ni have been attributed to variations in river flow. A significant positive correlation between total dissolved Ni concentration and river flow (Figure 3.7) suggests that the increase in dissolved Ni concentration is probably due to filterable (0.45 µm) particulate soil material, being washed into the estuary during heavy rain and stormflow events (Robson and Neal, 1997; Neal et al., 1997). Dissolved Ni concentration increases at the onset of the salinity gradient during the winter Tweed survey. There are several possible explanations for this effect. Sedimentary inputs seem unlikely as the Tweed has a gravel bed, and desorption from seaward-advected sediments

is equally improbable due to the very low suspended particle load. Although anthropogenic inputs may be an explanation, the observed peak may result from the similar timescales of estuarine flushing time and variations in the riverine dissolved Ni input (Cifuentes et al., 1990).

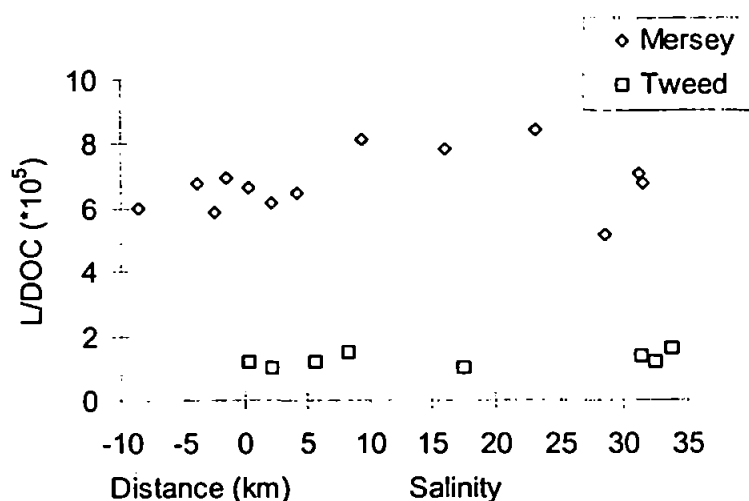
In the Mersey, large variations occur in the riverine total dissolved Ni concentration, which can be due to variations in river flow and anthropogenic inputs. Increased river flows result in the decrease of riverine Ni concentrations, as a result of dilution of Ni point-sources (Figure 3.16). The behaviour of total dissolved Ni in the Mersey Estuary varies between conservative and non-conservative (addition). There are a number of explanations for the addition showed by total dissolved Ni in the Mersey Estuary. The first possibility is anthropogenic inputs, due to the industrialised/populated nature of the river and estuarine banks. A second explanation is geochemical sources, i.e. pore-water infusion from disturbed bed sediments and desorption from seaward-advected SPM. Benthic infusion is based on the accumulation of dissolved Ni in the pore waters of the estuarine bed, which may occur during neap tides, when lower tidal energies (compared to springs) cause smaller bed sediment resuspension (Morris et al., 1982a). Pore waters would then be injected into the overlying water column during tidal remobilization of bed sediments at spring tides (Laslett and Balls, 1995). The possibility of desorption from seaward-advected sediments will be tested in Section 4.3.4. A further, alternative explanation for the addition of Ni in the Mersey Estuary may be the variation of the riverine end-member Ni concentration under the effect of the river flow, with timescales similar to or smaller than the estuarine flushing time, leading to non-linear mixing curves (Cifuentes et al., 1990).

A better insight into the behaviour of Ni can be obtained when comparing the different chemical species and their relationship with bulk estuarine properties. In the Tamar Estuary, the fraction of labile Ni sharply increases from 10 to 60% from freshwater to seawater, whilst in the Tweed the labile Ni fraction does not show any particular trend



and is scattered between 30 and 70% for all the seasons. The behaviour in the Mersey is different again, with the fraction of labile Ni being relatively constant between 30 and 50% in all seasons. Whilst the apparent lack of equilibrium between species in the Tweed Estuary can probably be associated with the very short flushing time of the estuary (and probably with analytical uncertainties due to the low concentrations), it seems that both in the Tamar and Mersey Estuaries equilibrium is established. This can be seen in the re-equilibration between the labile and non-labile species in the Tamar Estuary in the region of high salinity (where the total dissolved Ni is diluted conservatively), and in the fairly constant values of the labile fraction in the Mersey at all salinities. The change in speciation in the Tamar Estuary is likely caused by the increase in salinity (i.e. dissociation of the Ni-ligand complex occurs as a result of competition by Ca and Mg). The same effect is not observed in the Mersey, where the non-labile Ni concentration is determined by the concentration of Ni-complexing ligands (Section 3.3.3). Unfortunately no Ni-complexing capacity data are available for the Tamar Estuary, but the difference in the behaviour of the two Ni fractions may be due to the different nature (and possibly concentrations) of the Ni-complexing ligands in the two estuaries. The data suggest that the composition and concentration of the estuarine dissolved (truly dissolved and colloidal) organic matter may affect the speciation of dissolved Ni in estuaries, which may in turn affect Ni water-particle interactions. An indication of this can be seen when plotting the ratio of Ni complexing ligands over DOC versus salinity for the Tweed and Mersey Estuaries (Figure 3.33). Although from a molecular point of view no meaning can be attributed to this ratio, and it should only be seen as a bulk estuarine property, the higher values obtained for the ratio in the Mersey possibly indicate that a higher proportion of the DOC in the Mersey is able to bind Ni compared to the Tweed (assuming that the molecular weight of the ligands are similar in the two estuaries). The values of the conditional stability constants are however of the same order of magnitude ( $\log K' = 19.0 \pm 0.4$  for the Tweed and  $18.7 \pm 0.5$  for the Mersey), suggesting similar binding properties of the ligands for the two estuaries.

From all the above considerations, it appears that complexation by natural ligands is fundamental in determining the speciation and particle-water interactions of Ni, as already suggested by Turner et al (1998) for Ni in the Beaulieu Estuary. Although the physico-chemical nature of these ligands is unknown (truly dissolved organic or colloidal organic/inorganic), their effect on Ni sorptive behaviour in estuarine waters can be studied empirically in laboratory experiments: this issue will be the subject of the following chapter.



**Figure 3.33.** The ratio of Ni-complexing ligands (derived by complexing capacity titrations) to the total DOC in the Tweed and Mersey Estuaries.

## CHAPTER 4

### PROCESS-ORIENTATED STUDIES

In order to achieve a better understanding of the factors affecting Ni particle-water interactions, process-orientated studies were carried out using the radiotracer  $^{63}\text{Ni}$  with water and particle samples originating from the Tamar, Tweed, Mersey and Beaulieu estuaries. Radiolabelled Ni has been previously used to monitor the particle-water interactions of Ni in estuarine and coastal waters (Barbeau and Wollast, 1994; Sands, 1997; Turner et al., 1998). However, some of the experiments reported here (salinity gradient and kinetics of uptake: Sections 4.2 and 4.3, respectively) were designed specifically to examine the effect of dissolved Ni complexation by natural ligands on its sorptive behaviour, and in this respect are novel. The experiments described in Section 4.4 were carried out to assess the partitioning of Ni in unmodified samples in *in-situ* or in quasi *in-situ* conditions (Tweed and Mersey Estuaries, respectively).

Throughout this chapter, the term *sorption* will be used to indicate the overall uptake of  $^{63}\text{Ni}$ , i.e. its removal from solution to the solid phase, whilst the term *adsorption* will be used to indicate the metal complexation at the particle surface (Honeyman and Santschi, 1988). All the error bars in the graphs represent one standard deviation of three replicates, unless otherwise specified.

#### 4.1. Laboratory studies

In the two following sections the results are shown of an investigation into the effect of  $^{63}\text{Ni}$  complexation with dissolved ligands on its sorptive behaviour.

Nickel is known to be a metal with slow complexation kinetics with natural ligands (Morel et al., 1991; Price and Morel, 1991; Mandal et al., 1999). This effect was tested in all experiments by allowing  $^{63}\text{Ni}$  to equilibrate with the filterable ligands for 0, 24 and 120 hours prior to the start of the incubation experiments. A period of five days was selected

for all sorption experiments, as uptake by natural particles using  $^{137}\text{Cs}$ ,  $^{109}\text{Cd}$ , and  $^{65}\text{Zn}$  (Turner et al., 1992a; Turner et al., 1993) and  $^{63}\text{Ni}$  (Sands, 1997) have shown that this is generally a suitable period for trace metals to achieve quasi-equilibrium conditions between the dissolved and particulate phases. A salinity gradient experiment (Section 4.3) was designed to study the competition between Ni-complexing ligands, natural particles and inorganic seawater ions in the Tamar, Tweed and Mersey Estuaries. The kinetic of uptake experiments focussed on freshwater samples, and were designed to try to identify the timescales for Ni uptake onto in presence and absence of dissolved organic matter (DOM). In addition to samples from the above mentioned estuaries, the kinetic experiments were also carried out with samples from the Beaulieu Estuary, which is characterised by high concentrations of natural humic materials (Turner et al., 1998). Additional experiments were also carried out after the removal of DOM by UV-irradiation of the water samples, and after addition of a synthetic humic acid to UV-treated Tamar river water.

The characteristics of the water and sediment samples used for the experiments are shown in Tables 4.1 and 4.2. Riverine pH values are comparable for the Tamar, Tweed and Mersey, although they are lower in the Beaulieu river due to the presence of humic materials (Environment Agency, 1998). High humic material concentrations are responsible for the high DOC concentrations in the Beaulieu (Turner et al., 1998), with intermediate values occurring in the Tweed and Mersey Estuaries. Although the DOC concentrations are similar in the latter two estuaries, the nature of the dissolved carbon is likely to be rather different. Natural DOC of humic origin may predominate in the Tweed, whereas anthropogenic DOC (domestic/industrial) is likely to be more significant in the Mersey. The lowest DOC concentration occurs in the Tamar Estuary. The UV-irradiation process is partially effective in destroying organic matter, reducing the DOC concentrations to a lower, common value of about  $0.5 \text{ mg l}^{-1}$  in the Tamar, Tweed and Beaulieu Estuaries, and to  $0.8 \text{ mg l}^{-1}$  in the Mersey. The residual DOC is probably due to

the presence of high molecular weight, refractory humic materials, and in the Mersey Estuary it may also be due to the anthropogenic nature of the DOC.

The sediment extractant 0.05 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25% v/v  $\text{CH}_3\text{COOH}$  was chosen as it is known to remove primarily Fe and Mn oxides coatings (Millward et al., 1990; Turner et al., 1994), which are the principal inorganic sorbent phases in aquatic sediments. The Tamar and Mersey Estuaries suspended particles are characterised by similar concentrations of particulate Fe which are twice as high as in the Tweed Estuary. The Mn, Al, Ca and % organic carbon in the Mersey particles are higher than in the other estuaries. Specific surface area is highest for particles from the Tamar Estuary.

**Table 4.1.** Characteristics of the water samples used for the radiotracer experiments

Estuary	Freshwater (REM)					Seawater (MEM)		
	Salinity	pH	pH, UV <sup>a</sup>	DOC, (mg l <sup>-1</sup> )	DOC, UV <sup>b</sup> (mg l <sup>-1</sup> )	Salinity	pH	DOC (mg l <sup>-1</sup> )
Tamar	<0.3	7.70	7.80	2.4 ± 0.1	0.5 ± 0.1	35.0	8.2	1.4 ± 0.1
Tweed	<0.3	7.70	7.60	5.8 ± 0.1		30.0	8.0	1.6 ± 0.1
	<0.3 <sup>c</sup>	7.60 <sup>c</sup>	7.60 <sup>c</sup>	4.5 ± 0.1 <sup>c</sup>	0.5 ± 0.1 <sup>c</sup>			
Mersey	<0.3	7.30	7.70	7.1 ± 0.2	0.8 ± 0.2	24.2	7.8	3.0 ± 0.2
Beaulieu	<0.3	6.35	6.45	18.4 ± 0.2	0.5 ± 0.1			2.3 ± 0.1

<sup>a</sup> pH of the UV-irradiated sample; <sup>b</sup> DOC concentration of the UV-irradiated sample; <sup>c</sup> Sample used for the kinetic experiment.

**Table 4.2.** Characteristics of the sieved sediment samples used for the radiotracer experiments

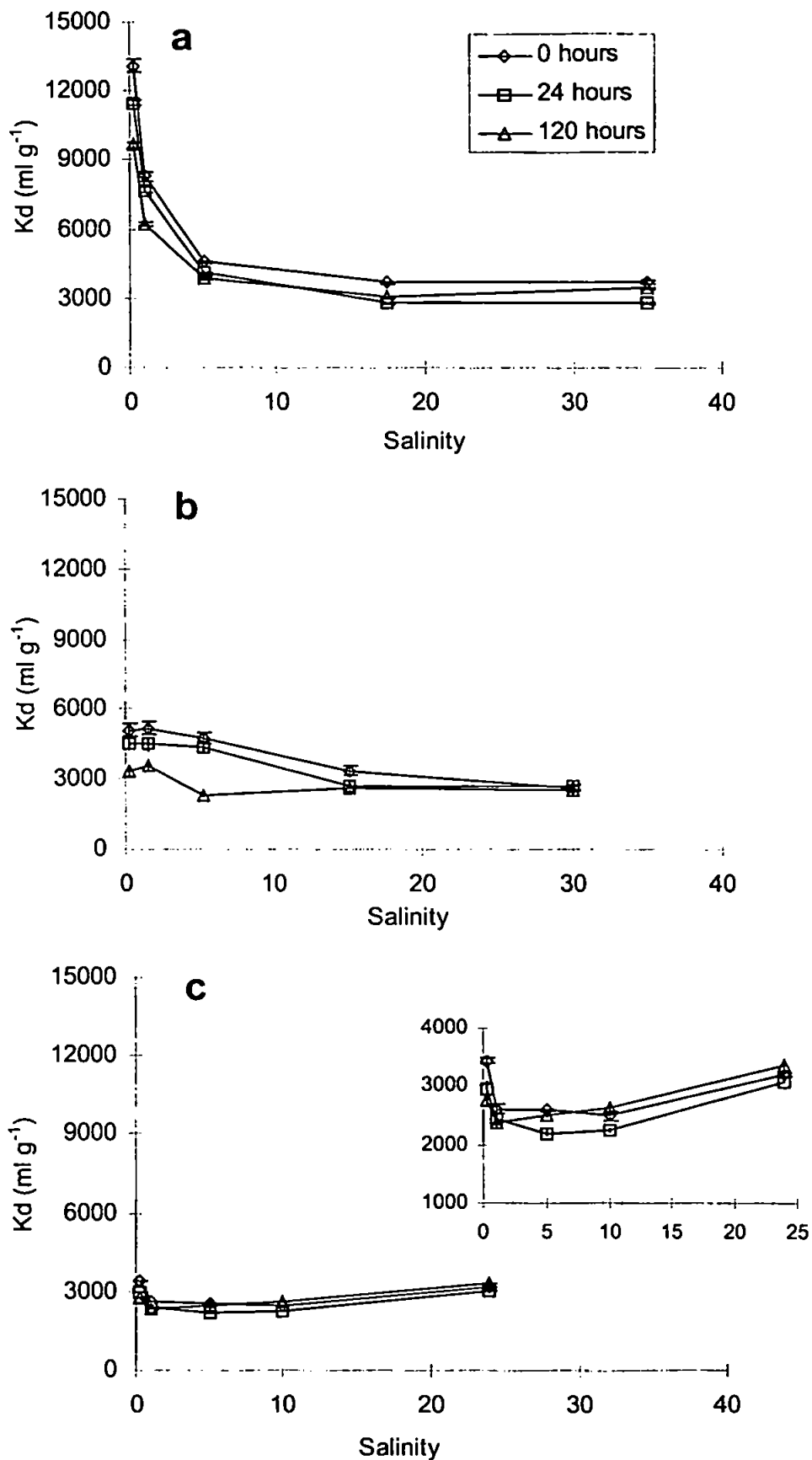
SPM, < 63 µm, 200 mg l <sup>-1</sup>	Fe (µmol g <sup>-1</sup> ) <sup>a</sup>	Mn (µmol g <sup>-1</sup> ) <sup>a</sup>	Al (µmol g <sup>-1</sup> ) <sup>a</sup>	Ca (µmol g <sup>-1</sup> ) <sup>a</sup>	% Organic Carbon	SSA (m <sup>2</sup> g <sup>-1</sup> )
Tamar	166 ± 1	12.9 ± 0.1	68 ± 1	48.7 ± 0.2	3.4 <sup>c</sup>	12.8 ± 0.3
Tweed <sup>b</sup>	87 ± 1	12.7 ± 0.1	62 ± 1	130 ± 1	1.2 <sup>c</sup>	10.3 ± 0.4
Mersey	161 ± 2	17.8 ± 0.1	97 ± 1	317 ± 3	9.1 <sup>c</sup>	9.8 ± 0.4
Beaulieu <sup>c</sup>	656 <sup>c,d</sup>	5.1 <sup>c,d</sup>	1250 <sup>c,d</sup>		6.9 <sup>c</sup>	6.9 <sup>c</sup>
PACS-1	177 ± 3	1.19 ± 0.02	87 ± 1	86.0 ± 0.5		
PACS-1 (certified)	435 ± 7	8.6 ± 0.2	1200 ± 20	520 ± 25		
Kaolinite						15.9 ± 0.3
Kaolinite (certified)						15.9 ± 0.8

<sup>a</sup> Available to 0.05 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25% v/v  $\text{CH}_3\text{COOH}$ ; <sup>b</sup> Sediment sample used for the kinetic of uptake experiment. <sup>c</sup> All Beaulieu data from S. Le Roux (University of Plymouth). <sup>d</sup> Total digest using HF/HCl/HNO<sub>3</sub>. <sup>e</sup> Data from P. Sammes (Marine Biological Association).

## 4.2. Salinity gradient

The uptake of  $^{63}\text{Ni}$  under simulated estuarine conditions was studied as a function of salinity and different pre-equilibration times of  $^{63}\text{Ni}$  with filterable ligands. The results of the salinity gradient experiments are shown in Figure 4.1 for the Tamar, Tweed and Mersey Estuaries. The magnitude and salinity-dependence of the  $K_{ds}$  are different for the three estuaries.

In the Tamar Estuary (Figure 4.1a) the  $K_{ds}$  decrease with increasing salinity, from  $9.6\text{-}13.1 \times 10^3 \text{ ml g}^{-1}$  in freshwater to  $2.8\text{-}3.7 \times 10^3 \text{ ml g}^{-1}$  in seawater, and this decrease occurs for all the three pre-equilibration times. The decrease in  $K_{ds}$  probably results from increased competition for the particle adsorption sites by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and complexation of Ni by  $\text{Cl}^-$  (Tables 1.3 and 1.4; Paalman et al, 1994; Liu, 1996). The  $K_d$ -salinity trend suggests that the adsorbing species is the free  $\text{Ni}^{2+}$ . For the freshwater samples ( $S=0.3$ ),  $K_{ds}$  decrease with increasing pre-equilibration time from  $13 \times 10^3$  to  $9.7 \times 10^3 \text{ ml g}^{-1}$ , due to slow complexation kinetics of Ni with riverine dissolved ligands (Mandal et al., 1999). The decrease of  $K_{ds}$  with increasing pre-equilibration time suggests that the freshwater ligands increase Ni stability in the dissolved phase and prevent its sorption onto particles (Gerringa, 1990; Turner et al., 1998). This effect disappears for higher salinities, and for seawater the  $K_{ds}$  are largely the same. Probably the ligands responsible for the observed complexation of Ni in freshwater flocculate in the low salinity region, and/or Ni dissociates from the ligands with increasing salinity due to cation competition and/or anion complexation. This effect was hypothesised for explaining the decrease of the ACSV-non labile fraction of Ni in the Tamar Estuary (Section 3.1.2), although it is not known whether the ligands which prevent Ni sorption are the same as those detected by voltammetry. Alternatively, the ligands which complex Ni in seawater may be of marine origin and therefore may behave differently from those observed in freshwater.



**Figure 4.1.** Five-day  $K_d$ s as a function of salinity in the (a) Tamar, (b) Tweed, and (c) Mersey estuaries. The times in the box represent the pre-equilibration time of  $^{63}\text{Ni}$  with filterable ligands prior to the addition of particles ( $200 \text{ mg l}^{-1}$ ). The inset in graph c is a close-up which better shows the trends of the  $K_d$ s with increasing salinity.

The trend of decreasing  $K_{ds}$  with increasing salinity is evident also in the Tweed Estuary (Figure 4.1b). However, the freshwater  $K_d$  values in the Tweed are nearly half than those of the Tamar ( $3.3 \times 10^3$ - $5.1 \times 10^3$  ml g<sup>-1</sup>). This may result from the higher DOC concentrations of the Tweed (Table 4.1), but also from the lower Fe and particulate organic carbon content of the sorbent phase in the Tweed compared to the Tamar (Table 4.2). Similar to the Tamar Estuary, the effect of varying the pre-equilibration time of Ni with filterable ligands is also evident at low salinities in the Tweed Estuary. At higher salinities the  $K_{ds}$  are the same for different pre-equilibration times, an effect probably due to the high concentrations of competing cations ( $Ca^{2+}$  and  $Mg^{2+}$ ) for the ligand binding sites.

Freshwater and low-salinity  $K_{ds}$  are 3 times lower in the Mersey (Figure 4.1c) than in the Tamar Estuary, and vary little with salinity. The effect of pre-equilibration is not statistically significant throughout the whole salinity range. Along the salinity gradient,  $K_{ds}$  initially decrease, but then, in contrast to observations in the Tamar and Tweed Estuaries, they increase with increasing salinity. Thus, Ni affinity for the particulate phase increases, despite the increase in salinity, with a trend resembling that observed for some hydrophobic organic micropollutants in estuarine waters, such as polycyclic aromatic hydrocarbons (Brunk et al., 1997; Rawling et al., 1998). The decrease of the aqueous solubility of hydrophobic organic compounds with increasing salinity ("salting-out" effect) is due to the modification of the water structure caused by electrolytes, which results in the reduction of the volume of water available for the compound dissolution (Means, 1995). Moreover, it has been suggested that in natural waters, an increase in salinity may cause conformational changes in the particulate organic matter, which would increase its "solvent" properties compared to the dissolved phase (Means, 1995). If the Ni-complexing ligands in the Mersey Estuary have a hydrophobic nature, then Ni will behave like its "host phase", and its sorption to particulate matter will tend to increase with increasing salinity. Indeed, for the 120-hours experiment (i.e. that where Ni has had the longest equilibration time with ligands), there is a significant positive correlation between  $K_{ds}$  and salinity



( $r^2=0.98$ ;  $P<0.05$ ;  $n=4$ ) if the freshwater  $K_d$  is not taken into account. These observations suggest that the adsorbing species (or one of the adsorbing species) in the Mersey Estuary may be a Ni-organic complex. Alternatively, assuming that the adsorbing species is  $Ni^{2+}$  throughout the whole salinity gradient, the observed increase in  $K_d$ s with increasing salinity may be due to the decrease in concentration of Ni-complexing ligands (Section 3.3.3), as hypothesised for Fe in the Dee Estuary (Turner and Millward, 1994).

#### 4.3. Kinetic experiments

Studies carried out on trace metal uptake by natural systems have shown that the kinetics of uptake can be slow, with overall uptake reaction half-lives often of the order of days or weeks (Li et al., 1984b; Jannasch et al., 1988). Therefore a kinetic approach is of fundamental importance when studying water-particle interactions of trace metals in environments with high water turnover rates (such as the low salinity region of estuaries), as the extent of sorption/desorption will depend on the interplay between water-particle reaction rates and water residence times (Morris, 1990; Millward et al., 1992).

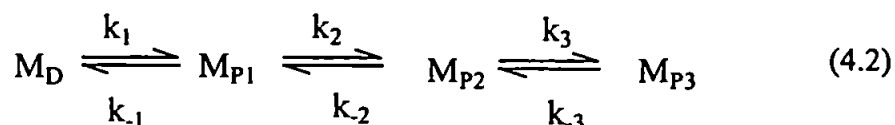
In Section 4.2 it was shown that the equilibration of  $^{63}Ni$  with filterable freshwater ligands decreases its removal onto suspended matter, and that the complexation kinetics of  $^{63}Ni$  are slow, occurring over a time scale of one to at least five days. This effect, due to the introduction of  $^{63}Ni$  in solution as  $NiCl_2$ , is important for two reasons. First, complexation of Ni with filterable ligands should be allowed prior to kinetic experiments in order to simulate realistic freshwater/estuarine conditions where Ni complexation occurs extensively (Nimmo, 1987; van den Berg et al., 1991; Turner et al., 1998). Second, competition between complexation and uptake may play a major role in determining the fate of trace metals which are discharged as inorganic ions into a natural system, for example through acid mine drainage or industrial discharges, as the time-dependent, sorptive behaviour of Ni will be affected by the water transit time between its point of discharge and a high turbidity zone. Therefore, all the uptake kinetic experiments

described in this Section have been carried out after 0, 24, and 120 hours pre-equilibration of  $^{63}\text{Ni}$  with filterable ligands, and also after removal of dissolved organic matter through UV-irradiation.

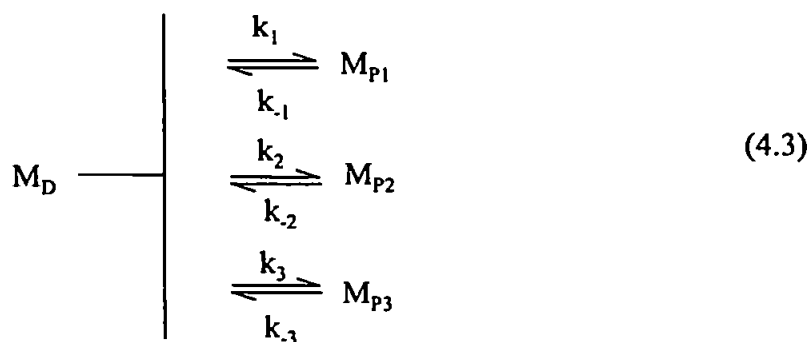
Models for describing the time-dependent uptake of trace metals onto particles have been developed by Nyffeler et al. (1984) and Jannasch et al. (1988), and will be described here only briefly. The simplest kinetic model assumes that there is only one type of sorption site and that the sorptive reaction is fully reversible and follows a first-order kinetic:



In reaction 4.1,  $M_D$  and  $M_P$  represent the dissolved and sorbed metal, respectively, and  $k_1$  and  $k_{-1}$  are the forward and backward first-order rate constants. However, often an initial fast uptake (occurring in timescales of minutes to hours) is observed, followed by a slower uptake occurring over longer timescales (e.g. Jannasch et al., 1988). Two reaction mechanisms have been hypothesised. The first involves an initial, rapid and reversible sorption onto the particle surface, which is followed by the migration to stronger sites within the particle matrix (sometimes referred to as “tunnelling” into porous solids, Millward, 1995), through a sequence of increasingly slower consecutive reversible first-order reactions:



In reaction 4.2,  $M_{P1}$ ,  $M_{P2}$  and  $M_{P3}$  represent the metal held to the particle binding sites with increasing strength, and  $k_i$  and  $k_{-i}$  ( $i=1,2,3$ ) represent the forward and backward rate constants for the  $i^{\text{th}}$  reaction. An alternative reaction mechanism assumes the overall uptake to occur onto surface sites of different binding strength through parallel reversible first-order reactions; in this model the surface is assumed to be non-porous:



Although the models described by mechanisms 4.2 and 4.3 cannot be distinguished through experimental curve fitting (Jannasch et al., 1988), the two mechanisms have different implications for metal availability and exchangeability, as in mechanism 4.2 the metal has the potential to be irreversibly held into the porous particle microstructure, whilst in mechanism 4.3 the adsorbed metal is in contact with the bulk solution. Therefore in the latter case desorption does not have the complication of migration through the micropores of the particles.

In this study a kinetic analysis of the sorption profiles will be carried out in order to model the uptake of Ni onto suspended particles in the Tamar, Tweed, Mersey and Beaulieu Estuaries.

#### 4.3.1. <sup>63</sup>Ni UPTAKE PROFILES

The time-dependent sorption of Ni onto estuarine particles is shown in Figures 4.2 to 4.6 at varying pre-equilibration times of Ni with filterable freshwater ligands, and upon UV-irradiation of the riverine end member water samples for removal of dissolved organic matter. For ease of reading, the experiments: 0-24-120 hours pre-equilibration and UV-irradiated will be simply termed 0-hours, 24-hours, 120-hours and UV, respectively.

##### 4.3.1.1. Tamar Estuary

For all of the Tamar Estuary profiles (Figure 4.2a), the uptake of Ni is rapid in the first 8 hours, followed by a slower uptake occurring over the following 110 hours. The extent of Ni uptake increases in the order 120-, 24-, 0-hour and UV experiments, with final, 5-day  $K_d$ s varying between  $8.8 \times 10^3$  and  $14 \times 10^3$  ml g<sup>-1</sup> for the different pre-

equilibration times, and with a 5-day  $K_d$  of  $2.3 \times 10^4 \text{ ml g}^{-1}$  for the UV experiment. An analysis of the sorption profiles for the 0-, 24- and 120-hour experiments suggests that the introduction of the radiotracer prior to that of the SPM significantly affects the uptake profile, and suggests that the lack of pre-equilibration leads to an overestimation of the final  $K_d$  by up to 60%.

The removal of dissolved organic matter (UV experiment) results in a two-fold increase in the 5-day  $K_d$  value. Conversely, the addition of Aldrich synthetic humic acids (Figure 4.2b), leading to a DOC concentration of  $8.3 \text{ mg l}^{-1}$ , results in a decrease of the 5-day  $K_d$ s to values of  $4.0 \times 10^3$ ,  $4.9 \times 10^3$  and  $6.9 \times 10^3 \text{ ml g}^{-1}$  for the 120-, 24- and 0-hour experiments, respectively (Figure 4.2b): these values are roughly half of those obtained in the samples with natural DOC (Figure 4.2a). These observations suggest that dissolved organic matter strongly complexes Ni and prevents its sorption onto particles also in a low-DOC riverine/estuarine system such as the Tamar Estuary. The results of the stable Ni kinetic experiment (Figure 4.3) show a decrease of labile Ni from 20 to 14 nM, but a rapid,

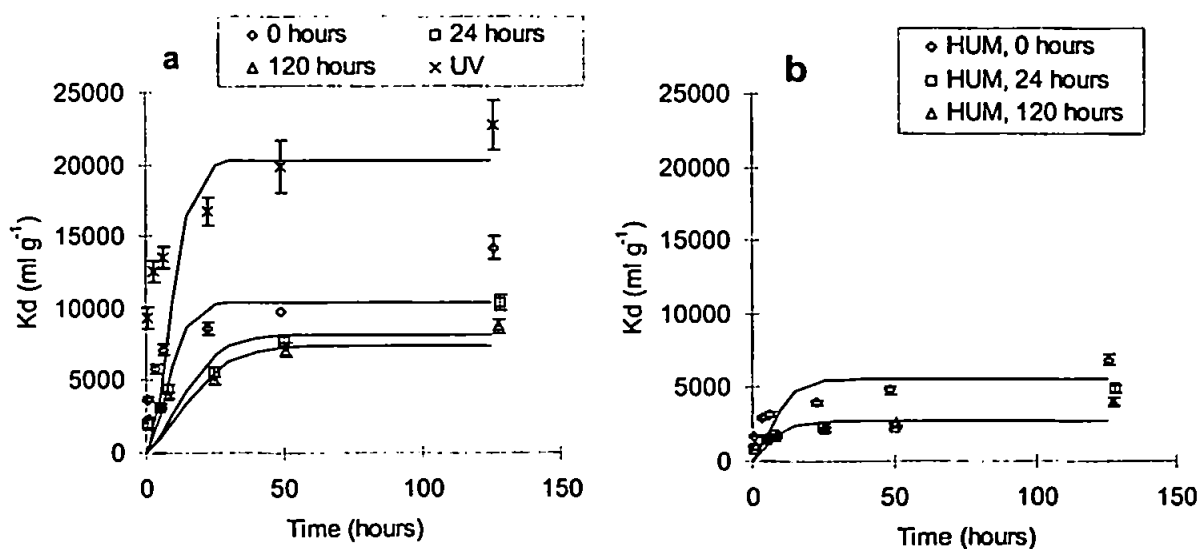
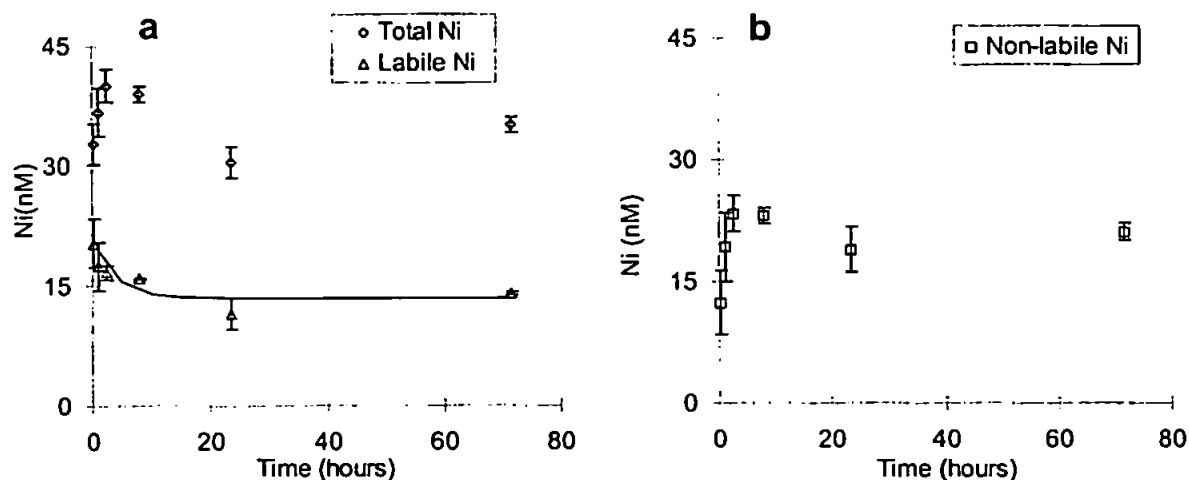


Figure 4.2. Distribution coefficients for the time-dependent uptake of  $^{63}\text{Ni}$  onto Tamar particles. (a): river water at different pre-equilibration times ( $\text{DOC} = 2.4 \pm 0.1 \text{ mg l}^{-1}$ ), and UV-irradiated riverwater ( $\text{DOC} = 0.5 \pm 0.1 \text{ mg l}^{-1}$ ). (b): Tamar UV-irradiated riverwater with addition of  $12.5 \text{ mg l}^{-1}$  synthetic humic acid ( $\text{DOC} = 8.3 \pm 0.1 \text{ mg l}^{-1}$ ) at different pre-equilibration times. The solid lines represent the predicted  $K_d$  values on the basis of the kinetic analysis.

initial increase in non-labile Ni from 12 to 23 nM, followed by a decrease to 21 nM. This suggests that whilst the free  $\text{Ni}^{2+}$  is the adsorbing species, non-labile Ni is initially desorbed from the particles as a result of re-equilibration of organic matter between particulate and dissolved phase. This effect is not observed when monitoring the radiolabelled Ni, as the initial particulate  $^{63}\text{Ni}$  concentration is zero.



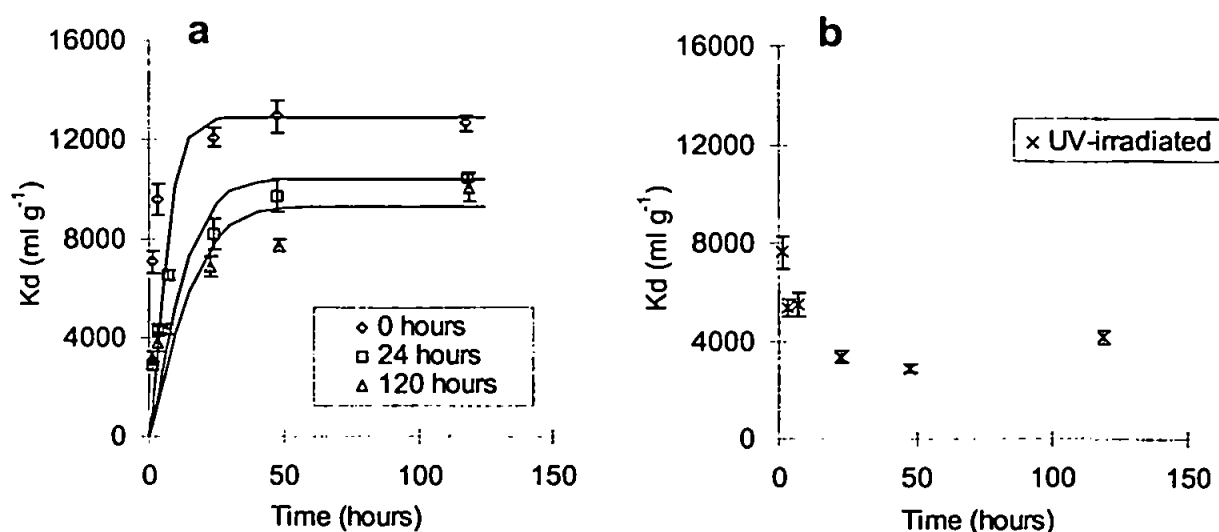
**Figure 4.3.** (a) Dissolved total and ACSV labile Ni and (b) ACSV non-labile Ni as a function of time for the mixing of Tamar riverwater and particles. The solid line represents the predicted labile Ni values on the basis of the kinetic analysis

#### 4.3.1.2. Tweed Estuary

For the Tweed Estuary the 0-, 24- and 120-hour experiments follow the same trend as for the Tamar samples, with a fast uptake in the first 24 hours followed by a slower uptake in the following 4 days (Figure 4.4a). Final, 5-day  $K_d$ s vary from  $10 \times 10^3 \text{ ml g}^{-1}$  for the 24- and 120-hour experiments to  $13 \times 10^3 \text{ ml g}^{-1}$  for the 0-hour experiment. As for the Tamar, the effect of pre-equilibration of Ni with filterable ligands results in a decrease in the 5-day  $K_d$ s of around 30%. The uptake profile of the UV experiment follows a different trend to that observed for the Tamar, with a fast initial uptake with a timescale of  $\sim 1$  hour, followed by release to solution (Figure 4.4b). This profile suggests that initially  $\text{Ni}^{2+}$  is adsorbed at the particle surface, and then is released in the form of a Ni-ligand complex to

solution, due to re-equilibration of organic matter between the particulate and dissolved phase following the UV-removal of dissolved organic matter from solution, as observed for the ACSV-non labile Ni in the Tamar Estuary. The  $K_d$  values of the UV experiment are somewhat anomalous when compared to those from the other UV experiments (Figures 4.2, 4.5, 4.6), as in the Tweed UV sample no increase in  $K_d$ s upon UV irradiation is observed. This, together with the fast initial uptake followed by a decrease in  $K_d$ , suggests that organic matter is being released from the particles to the organic-free solution, and a Ni-organic complex is desorbing as well.

The 5-day  $K_d$  values reported for the Tweed samples are significantly different from those reported for the freshwater samples in the salinity gradient experiment (Section 4.2). This could be due to the fact that the sediment samples used for the two experiments were collected at different locations and therefore have different origin and characteristics (Figure 2.2), with riverine sediments collected for the uptake kinetic experiment (site S2) and sediments from the outer estuary collected for the salinity gradient experiment (site S1).



**Figure 4.4.** Distribution coefficients for the time-dependent uptake of  $^{63}\text{Ni}$  onto Tweed particles. (a): River water at different pre-equilibration times ( $\text{DOC} = 4.5 \pm 0.1 \text{ mg l}^{-1}$ ). (b): UV-irradiated river water ( $\text{DOC} = 0.5 \pm 0.1 \text{ mg l}^{-1}$ ). The solid lines represent the predicted  $K_d$  values on the basis of the kinetic analysis.

#### 4.3.1.3. Mersey Estuary

Kinetic profiles in the Mersey Estuaries are shown in Figure 4.5. Distribution coefficients after 5 days vary between  $3.0 \times 10^3$  and  $3.6 \times 10^3 \text{ ml g}^{-1}$ , with the lowest value observed for the 120-hour experiment and the highest for the 0-hours experiment. Although the difference between the lowest and highest  $K_d$  values is statistically significant, it is much smaller than those observed for the Tamar and Tweed Estuaries, where differences up to 60 % were observed between 0- and 120-hour pre-equilibration. The time-dependent profile of the 0-hour experiment is however different from those observed in the 24- and 120-hour experiments. Whilst the latter show a rapid uptake in the first 8 hours followed by slower uptake in the following 4 days, the 0-hour experiment indicates a very rapid initial uptake (with a timescale of 5 hours) to a  $K_d$  value of  $4.1 \times 10^3 \text{ ml g}^{-1}$ , followed by a slow decline to  $3.6 \times 10^3 \text{ ml g}^{-1}$  in the next 5 days. The same trend can be observed for the UV experiment (Figure 4.5b), with  $K_d$ s varying between  $43 \times 10^3$  (after 8 hours) and  $27 \times 10^3 \text{ ml g}^{-1}$  (after 5 days).

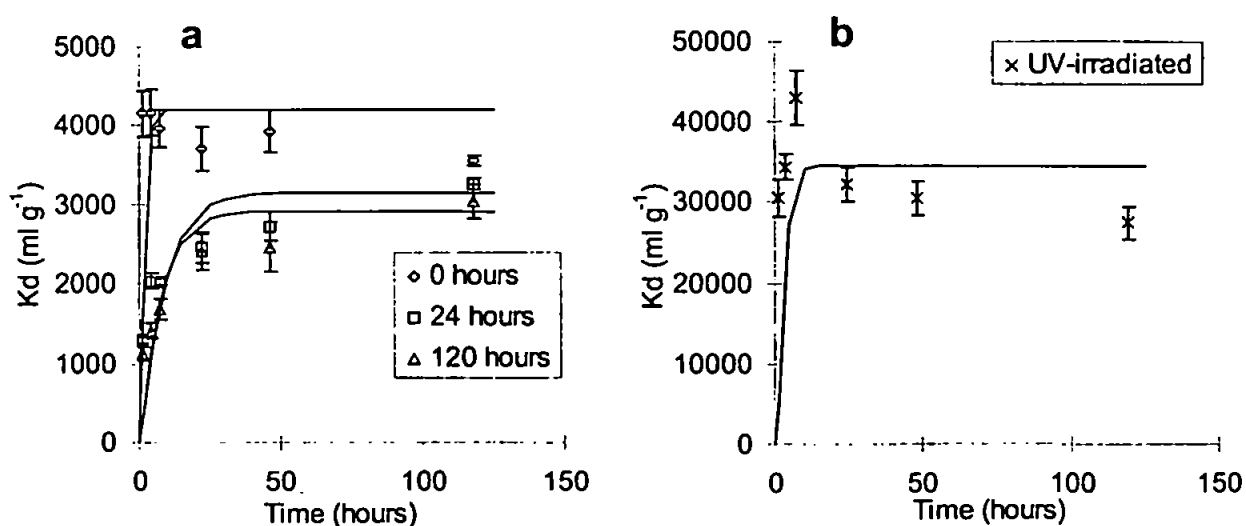


Figure 4.5. Distribution coefficients for the time-dependent uptake of  $^{63}\text{Ni}$  onto Mersey particles. (a): River water at different pre-equilibration times ( $\text{DOC} = 7.1 \pm 0.2 \text{ mg l}^{-1}$ ). (b): UV-irradiated riverwater ( $\text{DOC} = 0.8 \pm 0.2 \text{ mg l}^{-1}$ ). Note the different Y-scales. The solid lines represent the predicted  $K_d$  values on the basis of the kinetic analysis.

As observed for the Tweed UV experiment (Figure 4.4b) and for the stable Ni Tamar experiment (Figure 4.3), this trend suggests the involvement of at least two Ni species in the sorption/desorption process: the free  $\text{Ni}^{2+}$  as adsorbing species, and a Ni-ligand complex which slowly desorbs from the particles, as a consequence of re-equilibration of organic matter between the particulate and dissolved phases. The removal of dissolved organic matter (DOM) results in a 10-fold increase in the  $K_{ds}$  (Figure 4.5b). This clearly indicates that Ni complexation by riverine DOM prevents its adsorption onto Mersey SPM.

#### 4.3.1.4. Beaulieu Estuary

The time-dependent Ni sorption profiles for the Beaulieu Estuary are shown in Fig. 4.6. The 5-day  $K_{ds}$  for the 0-hour and 24-hour experiments are generally lower than those from the other estuaries ( $3.8 \times 10^3$  and  $1.7 \times 10^3 \text{ ml g}^{-1}$  for 0 and 24 hours), which is probably due to the higher concentrations of DOC in the Beaulieu (Table 4.1). The slope of the profiles for the 0- and 24-hour experiments suggest that after 5 days equilibrium conditions have not yet been achieved, which may be due to one or more of the following: (i) slow equilibration between complexed and sorbed Ni, (ii) slow migration of Ni to

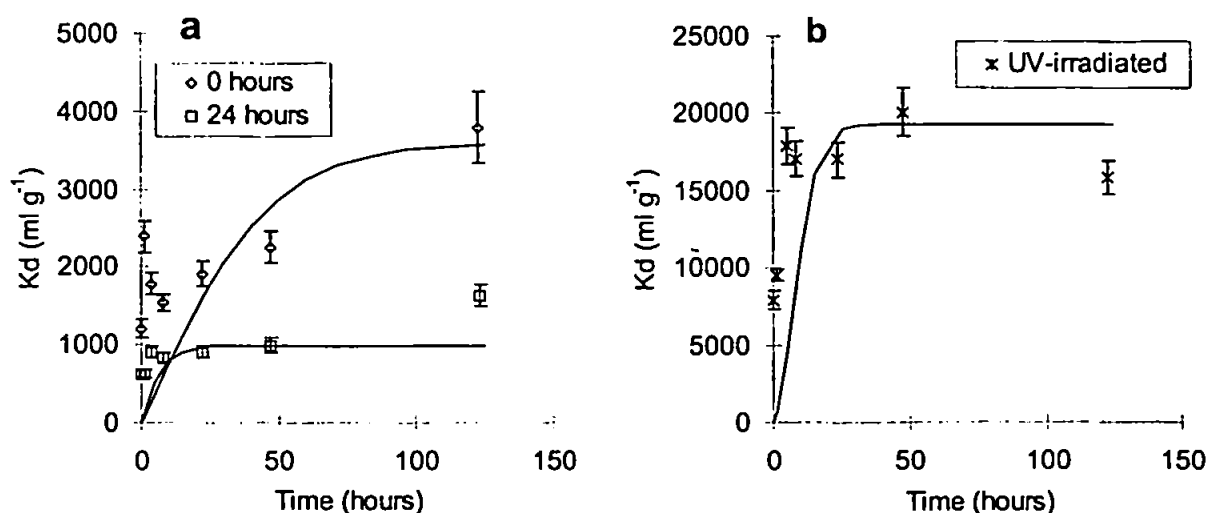


Figure 4.6. Distribution coefficients for the time-dependent uptake of  $^{63}\text{Ni}$  onto Beaulieu particles. (a): River water at different pre-equilibration times ( $\text{DOC} = 18.4 \pm 0.2 \text{ mg l}^{-1}$ ). (b): UV-irradiated riverwater ( $\text{DOC} = 0.5 \pm 0.1 \text{ mg l}^{-1}$ ). Note the different Y-scales. The solid lines represent the predicted  $K_d$  values on the basis of the kinetic analysis.



binding sites within the particle matrix. The sorptive profile for the 0-hour experiment can be clearly separated into three stages: (i) a fast initial uptake of free Ni<sup>2+</sup> (with timescale ~ 1.2 hours), (ii) desorption, probably of a Ni-ligand complex (1.2-8 hours), (iii) Ni<sup>2+</sup> and/or Ni-ligand complex uptake onto particles. In the latter stage, Ni<sup>2+</sup> is most likely the adsorbing species, as the uptake in absence of dissolved organic matter is much higher than in its presence, with a final K<sub>d</sub> value of 16 x 10<sup>3</sup> ml g<sup>-1</sup> (Figure 4.6b). Removal of dissolved organic matter (UV experiment) results in significantly greater uptake of Ni onto particles, as observed for the Tamar and Mersey Estuaries.

#### 4.3.2. KINETIC ANALYSIS OF <sup>63</sup>Ni UPTAKE PROFILES

Although in this study the uptake of <sup>63</sup>Ni exhibits fast and slow components (Figures 4.2-4.6), the number of experimental points for each curve is too small to allow a careful multi-step modelling. Therefore a relatively simple model was chosen which allows the reproduction of the general form of the uptake curves, and the uptake of <sup>63</sup>Ni was investigated through application of a reversible, first-order kinetic model developed after Jannasch et al. (1988) and Millward et al. (1992). For reaction 4.1, the rate of disappearance of M<sub>D</sub> is given by:

$$\frac{-d[M_D]}{dt} = k_1[M_D] - k_{-1}[M_P] \quad (4.4)$$

To solve this equation, it is useful to incorporate two other equations. The first (Eq. 4.5) is the stoichiometry of reaction 4.1, and is based on the assumption that at time t = 0, M<sub>P</sub> = 0:

$$[M_D]_0 = [M_D]_e + [M_P]_e = [M_D]_t + [M_P]_t \quad (4.5)$$

where [M<sub>D</sub>]<sub>0</sub> is the dissolved metal concentration at time t = 0; [M<sub>D</sub>]<sub>e</sub> and [M<sub>P</sub>]<sub>e</sub> are the dissolved and particulate metal concentrations at quasi-equilibrium (after 5 days), and [M<sub>D</sub>]<sub>t</sub> and [M<sub>P</sub>]<sub>t</sub> are the dissolved and particulate metal concentrations at the generic time t. The second equation (Eq. 4.6) defines the thermodynamic equilibrium condition, obtained by setting d[M<sub>D</sub>]/dt = 0:

$$K = \frac{k_1}{k_{-1}} = \frac{[M_p]_e}{[M_D]_e} \quad (4.6)$$

Incorporating Eq. 4.6 in Eq. 4.5 leads to:

$$[M_p]_t = [M_D]_e \frac{k_{-1} + k_1}{k_{-1}} - [M_D]_t \quad (4.7)$$

and, substituting Eq. 4.7 in Eq. 4.4 and rearranging, the following is obtained:

$$-\frac{d[M_D]}{dt} = (k_1 + k_{-1})\{[M_D]_t - [M_D]_e\} \quad (4.8)$$

Integration of Eq. 4.8 between  $t = 0$  and  $t = t$  and between  $[M_D]_0$  and  $[M_D]_t$  gives:

$$\ln \left\{ \frac{[M_D]_t - [M_D]_e}{[M_D]_0 - [M_D]_e} \right\} = -(k_1 + k_{-1})t \quad (4.9)$$

From equations 4.5 and 4.6,  $k_{-1}$  can be expressed as function of  $k_1$ :

$$k_{-1} = k_1 \frac{[M_D]_e}{[M_D]_0 - [M_D]_e} \quad (4.10)$$

and therefore:

$$k_1 + k_{-1} = k_1 \left( 1 + \frac{[M_D]_e}{[M_D]_0 - [M_D]_e} \right) = k_1 \frac{[M_D]_0}{[M_D]_0 - [M_D]_e} \quad (4.11)$$

substitution of Eq. 4.11 in Eq. 4.9 allows the integrated form of the rate equation to be derived in terms of  $k_1$  only:

$$\ln \left\{ \frac{[M_D]_t - [M_D]_e}{[M_D]_0 - [M_D]_e} \right\} = -k_1 t \left\{ \frac{[M_D]_0}{[M_D]_0 - [M_D]_e} \right\} \quad (4.12)$$

$$k_1 t = \left\{ \frac{[M_D]_0 - [M_D]_e}{[M_D]_0} \right\} \ln \left\{ \frac{[M_D]_0 - [M_D]_e}{[M_D]_t - [M_D]_e} \right\} \quad (4.13)$$

Here  $[MD]_0$  and  $[MD]_t$  are the % dissolved  $^{63}\text{Ni}$  activity prior to addition of particles (i.e.  $[MD]_0 = 100\%$ ) and at time  $t$ , respectively; the dissolved metal concentration at equilibrium,  $[MD]_e$ , is assumed to be represented by the final measured dissolved  $^{63}\text{Ni}$

percentage activity (i.e. measured after 5 days). A plot of the right hand side of Eq. 4.13 versus  $t$  yields a straight line of slope  $k_1$  for a first order reversible reaction.

Values of  $k_1$  can be calculated from Equation 4.10. Once  $k_1$  is known, it is possible to use Eq. 4.13 to calculate a model value for  $[M_D]_t$ , and therefore for  $K_d$ :

$$K_d^t = \frac{100 - [M_D]_t}{[M_D]_t} \frac{1000v}{w} \quad (4.14)$$

where  $v$  and  $w$  represent the volume (ml) and SPM weight (mg) of the sample, respectively. The model curves in Figures 4.2-4.6 were obtained by plotting the right hand side of Eq. 4.14 versus time.

The rate at which the system reaches a new equilibrium state may be described by the system response time  $\tau^{\text{resp}}$ , defined as the reciprocal of the rate constant in Eq. 4.9:

$$\tau^{\text{resp}} = (k_1 + k_{-1})^{-1} \quad (4.15)$$

$\tau^{\text{resp}}$  represents the time required for the system to achieve 63% or  $1 - (1/e)$  of the new equilibrium (Honeyman and Santschi, 1988). The values of  $k_1$ ,  $k_{-1}$  and  $\tau^{\text{resp}}$  obtained in this study are shown in Table 4.3, together with literature values for the Tamar Estuary (Liu et al., 1998).

Complexation of dissolved Ni by organic or colloidal ligands not only affects the overall extent of Ni sorption (Figures 4.2-4.6), but also the progression of sorptive reactions, as can be seen from a comparison of the  $\tau^{\text{resp}}$  for the different pre-equilibration times for different estuaries (Table 4.3). The  $\tau^{\text{resp}}$  are smaller for the UV samples, and their magnitude increases with increasing the extent of  $^{63}\text{Ni}$  complexation with the natural ligands. The  $\tau^{\text{resp}}$  of the 0-hour experiments are generally half (or less than half) the values than those for the 24- and 120-hour experiments, suggesting competition between dissolved ligands and suspended particles for  $^{63}\text{Ni}$  complexation.

The chemical response times in Table 4.3 can be compared with the physical

turnover times for the corresponding estuaries. Morris (1990) suggested that when the ratio of reaction half life to flushing time is higher than 10, then the slow reaction kinetics will limit the progression of chemical reactions. For comparable values of  $\tau^{\text{resp}}$  and flushing time, there will be enough time for (heterogeneous) chemical reactions to approach equilibrium, and non-conservative behaviour may be observed under appropriate physical conditions (e.g. high SPM concentrations).

**Table 4.3.** A comparison of rate constants ( $k_1$ ,  $k_{-1}$ ) and response times ( $\tau^{\text{resp}}$ ) for Ni derived from laboratory experiments. All experiments were carried out with freshwater samples. Tamar P-SPM and T-SPM are reported from Liu et al. (1998).

Study site	Sample type	$k_1$ ( $\text{h}^{-1}$ )	$k_{-1}$ ( $\text{h}^{-1}$ )	$\tau^{\text{resp}}$ (h)
<b>Tamar</b>				
	UV	0.24	0.02	3.8
	0-hours	0.20	0.03	4.4
	24-hours	0.11	0.02	7.5
	120-hours	0.09	0.02	8.9
	Labile Ni <sup>a</sup>	0.10	0.17	3.7
	P-SPM <sup>a,b</sup>	0.03	0.04	14
	T-SPM <sup>a,c</sup>	0.03	0.04	13
<b>Tweed</b>				
	0-hours	0.18	0.08	3.9
	24-hours	0.09	0.05	7.4
	120-hours	0.07	0.04	8.8
<b>Mersey</b>				
	UV	0.5	0.11	1.6
	0-hours	0.3	0.4	1.4
	24-hours	0.05	0.09	7.3
	120-hours	0.04	0.11	6.7
<b>Beaulieu</b>				
	UV	0.22	0.03	4.0
	0-hours	0.05	0.04	11
	24-hours	0.04	0.1	6.8

<sup>a</sup>Stable Ni experiment; <sup>b</sup>Permanently suspended matter; <sup>c</sup>Temporarily suspended matter.

The flushing time for the water in the low salinity, turbidity maximum zone (TMZ) of the Tamar Estuary is strongly dependent on the river flow, and has been estimated at 5 hours for typical summer river flows of  $1.8 \text{ m}^3 \text{ s}^{-1}$  (Uncles et al., 1983), and to less than one hour for winter river flows ( $> 50 \text{ m}^3 \text{ s}^{-1}$ , Liu et al., 1998). Therefore, at low flow conditions, the comparable values of flushing time and  $\tau^{\text{resp}}$ , coupled with high SPM concentrations

and high specific surface areas of TMZ particles (Millward et al., 1990) lead to favourable conditions for Ni removal. Indeed, Ni removal is a persistent feature in this highly reactive part of the estuary (e.g. Morris et al., 1986; van den Berg et al., 1991). The  $\tau^{\text{resp}}$  values obtained in this study are lower than those reported by Liu et al. (1998) for density-separated SPM samples from the Tamar Estuary. The difference can probably be attributed to different experimental conditions used in the experiments by Liu et al. (1998) such as the use of stable Ni at  $\text{mg l}^{-1}$  levels.

In the Tweed Estuary, although the  $\tau^{\text{resp}}$  and flushing time (0.5-1 day: Uncles and Stephens, 1996) are comparable, the SPM concentrations are low ( $<1\text{-}20 \text{ mg l}^{-1}$ ) throughout the estuary, and hinder the possibility for non-conservative behaviour. It is possible to show that conservative behaviour of Ni is likely to occur in the Tweed Estuary with the following considerations. The percentage of dissolved Ni can be expressed as a function of turbidity using the following equation (Duursma and Carrol, 1996):

$$\% \text{ Dissolved Ni} = \frac{100}{1 + (K_d \times \text{SPM} \times 10^{-6})} \quad (4.16)$$

Assuming a freshwater  $K_d$  value of  $7000 \text{ ml g}^{-1}$ , and an SPM concentration of  $5 \text{ mg l}^{-1}$ , the percentage of dissolved Ni is 96.6%. If the turbidity changes to  $10 \text{ mg l}^{-1}$ , the percentage of dissolved Ni would be 93.5%. Thus, a 3% decrease of the dissolved Ni concentration is predicted, which is within the analytical uncertainties of the voltammetric method. Indeed, no Ni removal has been observed to occur in the Tweed Estuary (This study; A.D. Tappin, CCMS, pers. comm.).

In the upper Mersey Estuary, the combination of high SPM concentrations and the lower values of reaction  $\tau^{\text{resp}}$  compared to the upper estuary flushing time (typically 48 hours: Jones, 1978) suggests that there is a potential for sorptive reactions to take place for Ni. However, no Ni removal has been observed (this study; Campbell et al., 1988; Comber et al, 1995), which can be attributed to a combination of factors, among which: the

uniformity of specific surface areas throughout the estuary (Millward et al., 1990), and the presence of strong Ni-complexing ligands (this study). A comparison of the distribution coefficients from the Tamar, Tweed and Mersey Estuaries also shows that the Mersey exhibits the lowest  $K_{ds}$  (Figures 4.1 and 4.5a). It has been shown in Section 3.3.3 that strong natural ligands complex Ni (possibly specifically) throughout the whole Mersey salinity gradient; it is suggested that these ligands are responsible for maintaining Ni in solution and completely shift its interaction with particles.

#### 4.3.3. MERSEY ESTUARY: DESORPTION EXPERIMENTS

In Section 3.3.2, it was observed that Ni shows positive deviations from conservative behaviour in the Mersey Estuary. Therefore desorption experiments were designed in order to examine the extent of sorption reversibility, to understand if there is a potential for Ni release from particles under realistic estuarine conditions, and to quantify the rates of Ni desorption reactions (Hegeman et al., 1992; Liu et al., 1998).

The desorption experiments were carried out on particles after 5-day incubation in riverwater (Section 4.3.1). Desorption experiments have been often carried out by filtering the incubated particles and resuspending them in filtered seawater or estuarine water of intermediate salinity (Hegeman et al., 1992; Liu et al., 1998). However, this method does not simulate realistically the natural estuarine conditions, where mixing of freshwater with riverwater is a continuous process occurring between water masses of similar salinity (Bale and Morris, 1981). In this study, the 5-day incubated freshwater samples were not filtered. Instead, their salinity was increased by additions of triple-strength artificial seawater either to final salinity values ( $S=1, 2, 5$ , batch experiment), or through 3 incremental steps (continuous experiment) to achieve a final salinity of 5. This experiment did not encompass the whole salinity gradient, because at salinity higher than 5 the percentage variation in volume (due to the salinity spikes) would have been  $>5\%$ . This would have caused a significant dilution of particles, which would probably lead to variations in

sorptive behaviour of Ni (caused by the particle concentration effect: Turner, 1996).

The results of the two experiments are shown in Figure 4.7, and are expressed in terms of percentage of  $^{63}\text{Ni}$  in solution. The initial 5-day incubation (adsorption phase) in freshwater can be seen on the left-side of the graphs, where the percentage dissolved Ni decreases from 100% to 80% before the salinity is increased. Both graphs show that removal of Ni from solution continues also after the increase in salinity. For the three batch experiments (Figure 4.7a), the extent of Ni uptake decreases with increasing salinity, an effect probably due to competition by Ca and Mg for the surface active sites (Li et al., 1984a; Millward et al., 1992). A small increase in dissolved Ni (from 79 to 83%) is observed when the freshwater is spiked to salinity=5 (batch experiment), which is followed

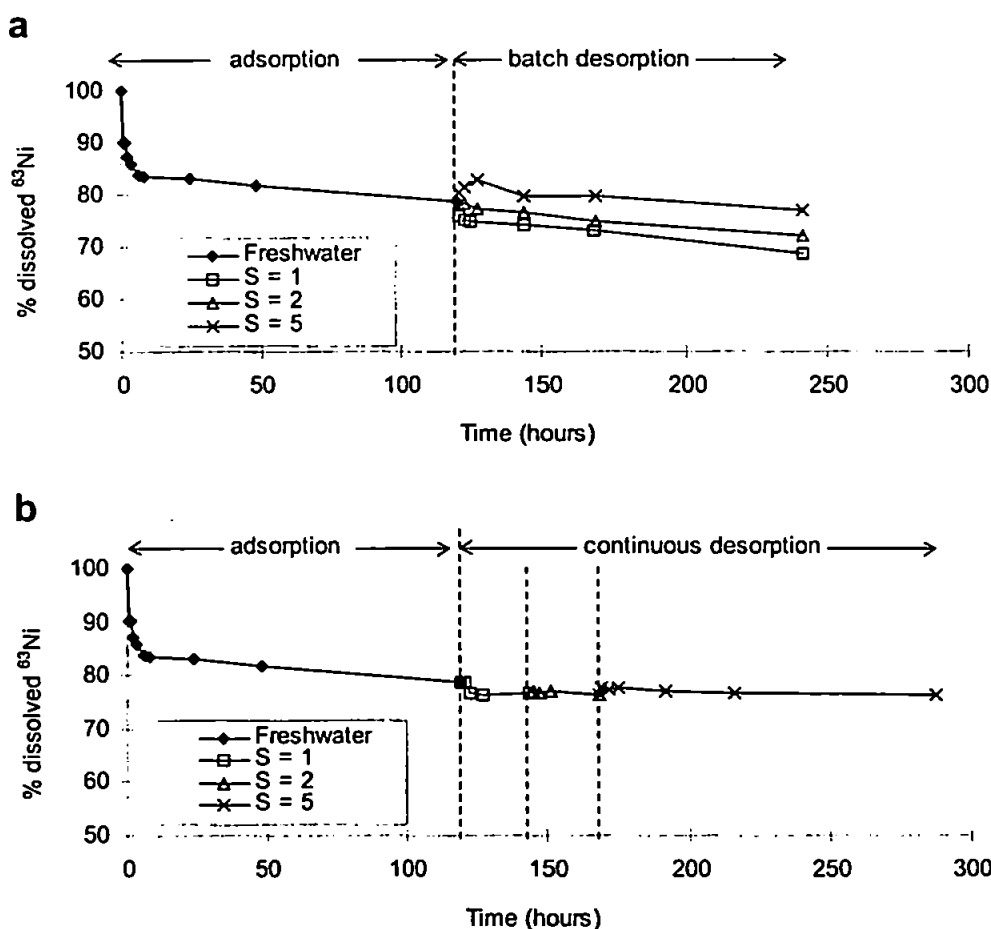


Figure 4.7. The fraction of  $^{63}\text{Ni}$  in solution as a function of time, upon an increase in salinity. Incubation in freshwater occurs for the first 120 hours ("adsorption"), and is followed by the salinity spikes. In (a), the salinity of 3 different samples is increased, respectively, to 1, 2, and 5. In (b) the salinity of the same sample is gradually increased to 5. The dotted lines represent the time of the salinity spikes. The solid lines represent eye-fitted curves. The errors in all the plots are below 2%, and have been omitted for clarity.

by a decrease in % dissolved Ni to a value of  $76.8 \pm 0.2$ . This trend is probably due to the instantaneous desorption of weakly bound Ni due to competition by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , superimposed on (or offset by) the ongoing slow sorption of Ni. The final value ( $76.8 \pm 0.2$ ) obtained in this experiment is remarkably similar to that obtained in the continuous experiment ( $76.4 \pm 0.4$ , Figure 4.7b). This observation suggests that both batch and continuous additions lead to similar results in the salinity range 0-5.

Desorption of Ni is generally not observed in the salinity range sampled in these experiments ( $S=0.3-5$ ). Results in Figure 4.7 rather show that Ni sorption continues also upon an increase in salinity. However, the absence of desorption may be simply caused by the fact that not all the salinity gradient was encompassed. In Section 4.4.2.1 it will be shown that seawater leaches of incubated Mersey SPM lead to desorption of  $^{63}\text{Ni}$ . This effect will be discussed in the context of the different experimental setups.

#### 4.4. Incubations with unfiltered samples

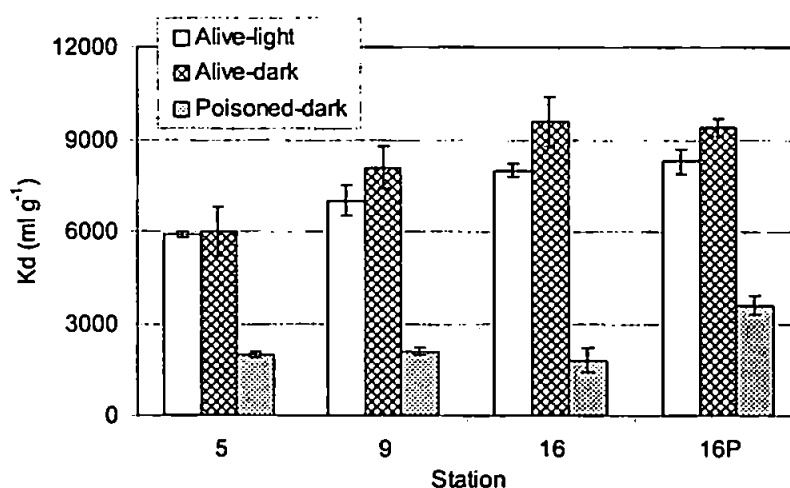
##### 4.4.1. TWEED ESTUARY: *IN-SITU* RADIOCHEMICAL EXPERIMENTS

The Tweed Estuary is characterised by relatively high nutrient concentrations and low turbidity (Balls, 1994), which result in high levels of primary production (Clayton, 1997). Therefore, *in-situ* incubations using  $^{63}\text{Ni}$  were conducted during the June '97 survey in order to assess the significance of phytoplankton uptake on Ni particle-water interactions. The methodology used for the *in-situ* incubations using  $^{63}\text{Ni}$  was adapted from Sands (1997), who performed similar experiments in the Humber Estuary. An incubation period of 24 hours was used as it simulates the flushing time of the estuary, and also provides an indication of the uptake over a complete diurnal cycle. Moreover, incubation times of 24 hours were used by Barbeau and Wollast (1994) and Sands (1997) in similar experiments with  $^{63}\text{Ni}$ , which allows a direct comparison of the results.

The results of the *in-situ* experiments are plotted in Figure 4.8, and shown in Table 4.4 together with the corresponding hydrographic parameters and Ni concentrations. All



the incubations show significantly higher  $K_d$  values for the non-poisoned samples ( $\sim 5.9$ - $9.6 \times 10^3 \text{ ml g}^{-1}$ ) than for the poisoned ones ( $1.8$ - $3.6 \times 10^3 \text{ ml g}^{-1}$ ), suggesting that Ni uptake is enhanced by biological activity. The latter could be due to the presence of phytoplankton, as evidence of autotrophic activity was found when monitoring parallel samples (Shaw et al., 1998). Moreover, no significant differences between “alive” incubations in the light and in the dark suggests that the light-activated, photosynthetic activity plays a minor role in the biologically-mediated Ni uptake, at least within the



**Figure 4.8.** Comparison of  $^{63}\text{Ni}$  uptake at selected stations under different incubation conditions during the June '97 survey on the Tweed Estuary.

**Table 4.4.** Nickel  $K_{ds}$  determined in the *in-situ* incubations during the June '97 survey on the Tweed Estuary. The incubation conditions and the concentrations of total and ACSV-labile Ni are also shown.

Conditions	Station 5	Station 9	Station 16	Station 16 (pre-equilibration)
$K_{ds}$				
Light	$5900 \pm 100$	$7000 \pm 500$	$8000 \pm 200$	$8300 \pm 400$
Dark	$6000 \pm 800$	$8100 \pm 700$	$9600 \pm 800$	$9400 \pm 300$
Poisoned	$2000 \pm 100$	$2100 \pm 100$	$1800 \pm 400$	$3600 \pm 300$
Salinity	17.6	3.9	0.2	0.2
PH	8.1	8.0	8.1	8.1
Temperature ( $^{\circ}\text{C}$ )	12.2	13.5	15.5	15.5
SPM ( $\text{mg l}^{-1}$ )	3.5	3.7	2.8	2.8
Chl-a ( $\mu\text{g l}^{-1}$ ) <sup>a</sup>	0.42 (@ 03:38 GMT) 0.76 (@ 09:49 GMT)	0.51	0.77	0.77
$\text{Ni}_{\text{Total}}$ (nM)	$5.4 \pm 0.2$	$6.5 \pm 0.2$	$10.5 \pm 0.5$	$10.5 \pm 0.5$
$\text{Ni}_{\text{Labile}}$ (nM)	$3.0 \pm 0.3$	$3.4 \pm 0.2$	$3.28 \pm 0.02$	$3.28 \pm 0.02$

<sup>a</sup>Data courtesy of Dr. P.Shaw (University of Southampton).

timescales of the experiment. It should be noted that the decrease in  $K_{ds}$  following  $HgCl_2$  addition may be due to an experimental artefact, as Hg could outcompete Ni for the organic binding sites on the particle surfaces, because of its high concentration (500  $\mu M$ , compared to nM levels of Ni) and higher stability of its complexes with organic ligands (up to 5 orders of magnitude higher than the correspondent Ni complexes: Martell and Smith, 1974).

The results from this study are compared with literature results (carried out using the same protocol and incubation time) in Table 4.5. The values obtained for uptake in the light compare well with the value of 6300  $ml\ g^{-1}$  reported by Barbeau and Wollast (1994) during a phytoplankton bloom off the Belgian coast. In contrast, Sands (1997) reported  $K_d$  values for the Humber coastal zone which are nearly one order of magnitude lower than those in this study. The lower values obtained by Sands (1997) may be due to the lower biologically-mediated uptake.

Although the  $K_{ds}$  are very high for the non-poisoned samples, the percentage of Ni uptake onto particles never exceeds 2.5%, due to the low SPM concentrations which characterize the Tweed Estuary. This factor, together with the rapid flushing time of the estuary, suggest that biologically-mediated uptake of Ni does not lead to measurable dissolved Ni removal in the Tweed Estuary: indeed, the behaviour of dissolved Ni during the June '97 survey is largely conservative.

**Table 4.5.** A comparison of  $^{63}Ni$   $K_{ds}$  ( $ml\ g^{-1}$ ) determined in the Tweed *in situ* experiments with those in the literature. For all experiments an incubation time of 24 hours was used.

Location	Salinity	Light	Dark	Poisoned	Reference
Tweed Estuary (June '97)	0.2-17.6	6000-8300	6100-8500	1600-2700	This study
Humber Coastal zone (Spring '95)	> 30	480-720	410-610	330-500	Sands (1997)
Humber Coastal zone (Summer '95)	> 30	1300-2200	760-1400	560-980	Sands (1997)
Scheldt Estuary (May '92)	5	1260 <sup>a</sup>			Barbeau and Wollast (1994)
Belgian coastal zone (May '92)	>30	6300 <sup>a</sup>			Barbeau and Wollast (1994)

<sup>a</sup>These values have been obtained in laboratory conditions and not *in-situ*.

#### 4.4.2. MERSEY ESTUARY: LABORATORY INCUBATIONS

The sorptive behaviour of Ni in the Mersey Estuary was investigated further by undertaking five-day uptake experiments with unfiltered samples using  $^{63}\text{Ni}$ . The fundamental difference between these experiments and those in Section 4.2.2 is that in this case the particle composition and concentration is that of the native water samples. Moreover, the use of five-day  $K_d$ s allows direct comparison with studies on Ni partitioning carried out on the Humber coastal zone (Sands, 1997). Time-dependent uptake experiments carried out with Mersey samples in this study (Section 4.3) suggest that a period of 5 days approximates quasi-equilibrium conditions, and therefore are also suitable for studying the uptake of trace metals in an estuarine system with a long flushing time such as the Mersey.

The results of incubations with unfiltered samples are shown in Figures 4.9-4.11. In March and June '98, Ni exhibits an increase in  $K_d$  with increasing salinity, with values for the non-poisoned samples ranging from  $200 \text{ ml g}^{-1}$  at low salinity to around  $1400 \text{ ml g}^{-1}$  in both seasons. In October '98, the highest  $K_d$  value occurs in the freshwater sample:  $K_d$  values drop sharply below the weir and then gradually increases to a seawater value of  $1600 \text{ ml g}^{-1}$ . The effect of a biologically mediated uptake of  $^{63}\text{Ni}$  is evident only for the October '98 samples (Figure 4.11b), although it does not enhance significantly the percentage of Ni taken up by the particulate phase (Figure 4.11.c). The 5-day  $K_d$ s obtained from this study compare well with those for the Humber coastal zone (Sands, 1997), which were obtained using the same protocol and the same incubation time (Table 4.6).

**Table 4.6.** A comparison of 5-day  $^{63}\text{Ni}$   $K_d$ s ( $\text{ml g}^{-1}$ ) determined in the Mersey Estuary with those from literature using the same protocol.

Location	Salinity	Incubation time (h)	$K_d$ ( $\text{ml g}^{-1}$ )	Reference
Mersey Estuary	1-30	120	200-1400	This study
Humber coastal zone	> 30	120	290-1300	Sands (1997)

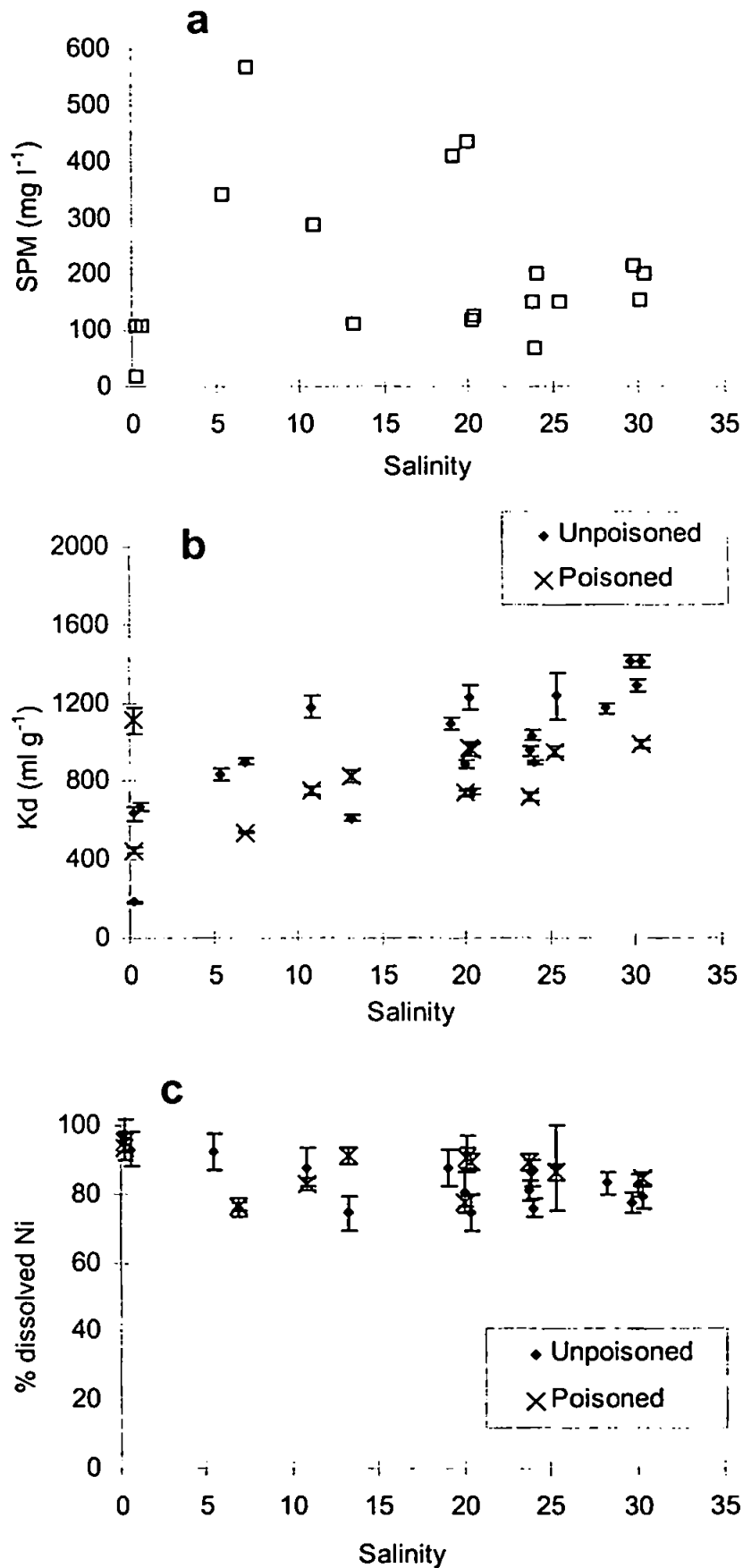


Figure 4.9. (a) SPM, (b) 5-day  $K_d$ s, and (c) percentage of dissolved Ni (Equation 4.16), as a function of the distance from weir for the March '98 survey on the Mersey Estuary. The error bars in the  $K_d$ s represent the analytical errors, rather than the environmental variability, as the samples were not incubated in replicates.

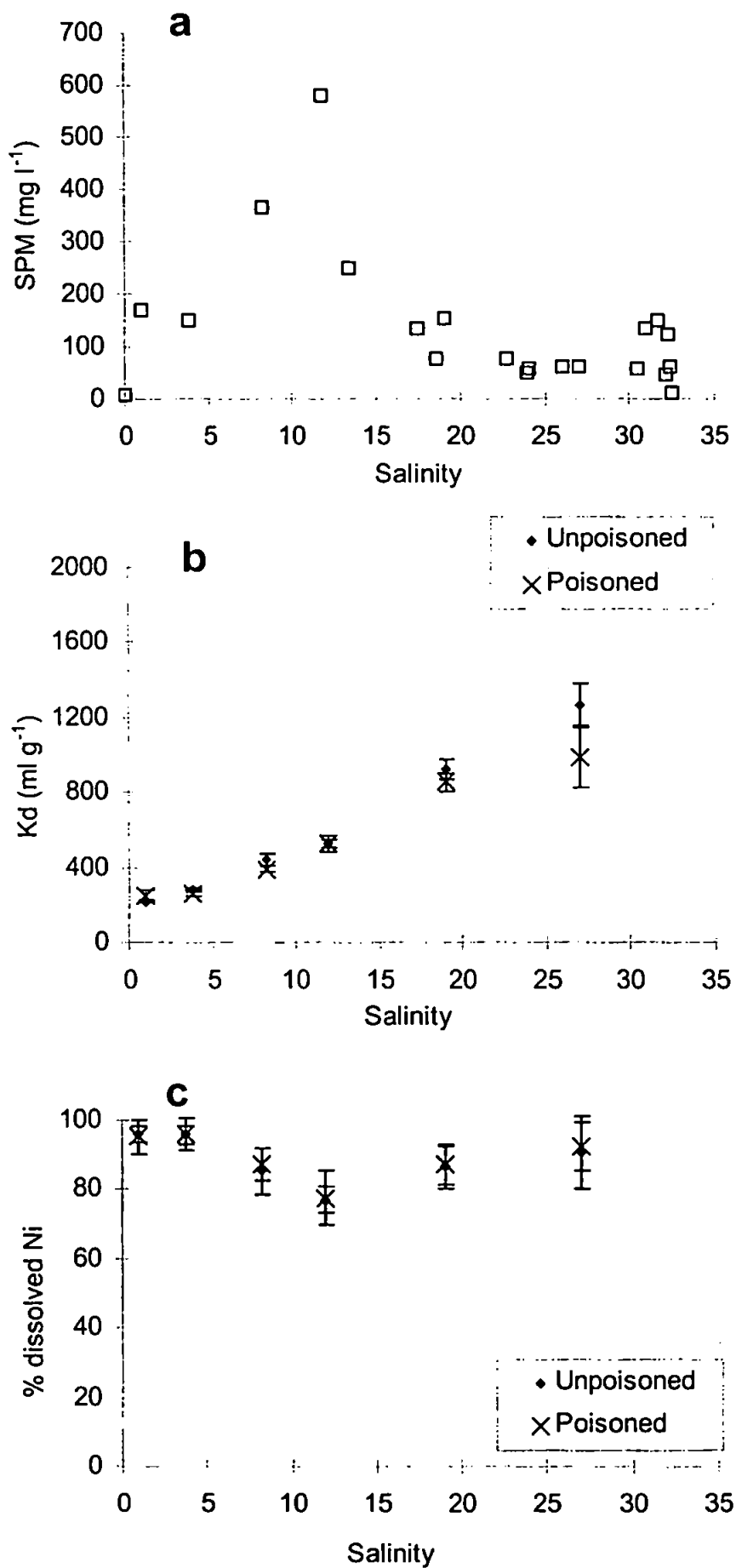


Figure 4.10. (a) SPM, (b) 5-day  $K_d$ s, and (c) percentage of dissolved Ni (Equation 4.16), as a function of the distance from weir for the June '98 survey on the Mersey Estuary.

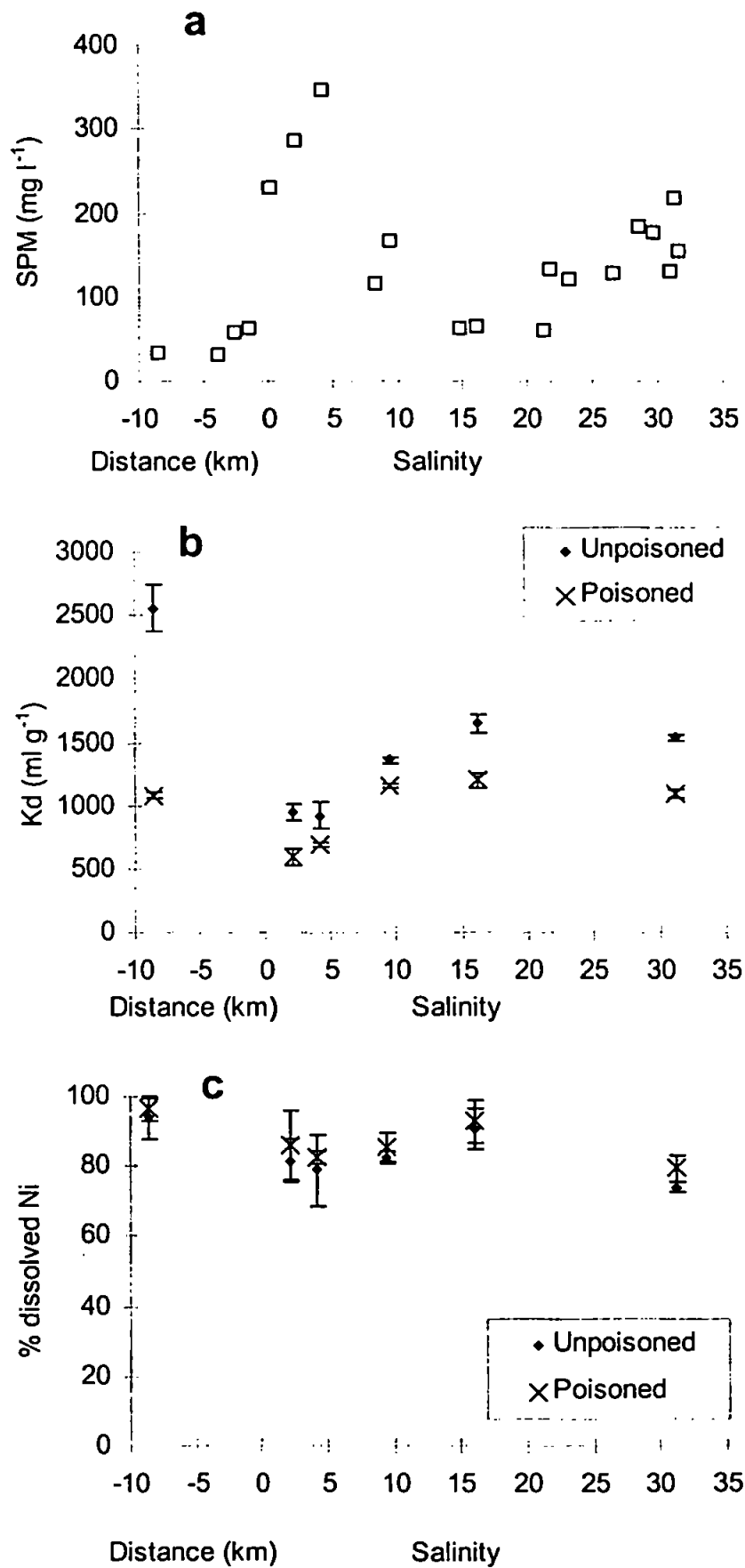


Figure 4.11. (a) SPM, (b) 5-day  $K_d$ s, and (c) percentage of dissolved Ni (Equation 4.16), as a function of the distance from weir for the October '98 survey on the Mersey Estuary.

A statistically significant positive relationship exists between  $K_{ds}$  and salinity for the unpoisoned March samples ( $r^2=0.60$ ;  $P<0.05$ ;  $n=19$ ), and for the unpoisoned and poisoned June samples ( $r^2=0.99$  and  $0.97$ , respectively;  $P<0.05$ ;  $n=6$ ). The increase of  $K_d$  with increasing salinity (also observed in the salinity gradient experiment, Section 4.2) is in contrast with model studies (Bourg, 1987) and experimental results for Ni and other trace metals, where a decrease of  $K_d$  was observed with increasing salinity. This effect was attributed to formation of trace metal-chloride complexes and competition for the adsorption sites by dissolved  $Mg^{2+}$  and  $Ca^{2+}$  (Li et al., 1984a; Turner and Millward, 1994; Turner, 1996). However it should be noted that the Mersey Estuary is characterised by high DOC concentrations, which may be paramount in affecting Ni partitioning. The same effect reported in this study has been shown for Ni in the Scheldt Estuary (Barbeau and Wollast, 1994; Paucot and Wollast, 1997), Fe in the Dee Estuary (Turner and Millward, 1994) and for Cu in the Mersey Estuary (Comber et al., 1995). The latter was attributed to the presence of Cu-complexing organic ligands, whose concentration would decrease with increasing salinity, making Cu more available for adsorption. There is a good inverse correlation between DOC and  $K_{ds}$  for June ( $r^2=0.99$ ,  $P<0.05$ ,  $n=6$ ) and for March ( $r^2=0.64$ ,  $P<0.05$ ,  $n=19$ ), which suggests that organic ligands (whether truly dissolved or colloidal) may play a major role in preventing Ni adsorption onto particles, but no significant correlation exists between DOC and  $K_{ds}$  or between Ni-complexing ligands and  $K_{ds}$  in October '98. Indeed, Ni occurs strongly complexed in the Mersey Estuary, with percentages of non-labile Ni in the range 50-70%. As discussed in Section 4.2, an alternative explanation for the observed increase of  $K_{ds}$  with increasing salinity is based on the assumption that the adsorbing species is a Ni-organic complex, which is salted-out at high salinity.

The percentage of dissolved  $^{63}\text{Ni}$  (Figures 4.9-4.11c) is calculated according to Equation 4.16. The fraction of dissolved Ni is generally  $> 70\%$  even at relatively high SPM loads, suggesting a low particle affinity for Ni, compared, for example, to Hg.

Incubations carried out with  $^{203}\text{Hg}$  on the same Mersey samples using the same protocol showed that the percentage of dissolved Hg was 0.1-40% (S. Watts, pers. comm.). Moreover, the results in Figure 4.9-4.11c suggest that around 10% of dissolved  $^{63}\text{Ni}$  is removed in the high turbidity region. However removal of stable Ni is not observed in the TMZ (Figure 3.15). This discrepancy could be due to the analytical and environmental variability in the dissolved Ni determinations, which probably would not allow the detection of Ni removal. Moreover, the increase of  $K_{ds}$  with increasing salinity indicates that Ni sorptive tendency is higher at high salinity (as also discussed in Section 4.2). It is possible to calculate the fractional removal of Ni that would result solely from the increase in  $K_{ds}$ , using the following equations, and assuming that the SPM behaves conservatively and that there are no external sinks or sources of Ni (Turner et al., 1993):

$$D_{\text{REM}} + P_{\text{REM}} \times \text{SPM} = D_{\text{MEM}} + P_{\text{MEM}} \times \text{SPM} \quad (4.17)$$

where  $D_{\text{REM}}$  and  $D_{\text{MEM}}$  are the dissolved Ni concentration in the riverine and marine end members, respectively,  $P_{\text{REM}}$  and  $P_{\text{MEM}}$  are the adsorbed Ni concentration on the particles in the riverine and marine end members, respectively, and SPM is the concentration of the seaward fluxing particles. By substituting Equation 1.1 for  $P_{\text{REM}}$  and  $P_{\text{MEM}}$  in Equation 4.17, the following is obtained:

$$\frac{D_{\text{MEM}}}{D_{\text{REM}}} = \frac{1 + (K_{d\text{REM}} \times \text{SPM} \times 10^{-6})}{1 + (K_{d\text{MEM}} \times \text{SPM} \times 10^{-6})} \quad (4.18)$$

where  $K_{d\text{REM}}$  and  $K_{d\text{MEM}}$  are the Ni  $K_{ds}$  for the riverine and marine end-members, respectively, and the factor  $10^{-6}$  accounts for the dimensions. By using the June '98 values of the end-member  $K_{ds}$  (200 and 1250  $\text{ml g}^{-1}$  for low and high salinity, respectively), the decrease in Ni concentration in seawater relative to freshwater due to adsorption would vary between 1 and 10% (ratio in equation 4.18 equal to 0.90 and 0.99, respectively), for SPM varying between 10 and 100  $\text{mg l}^{-1}$ . Such a low decrease in Ni concentrations would therefore not be detected from the analyses of total dissolved Ni or particulate Ni

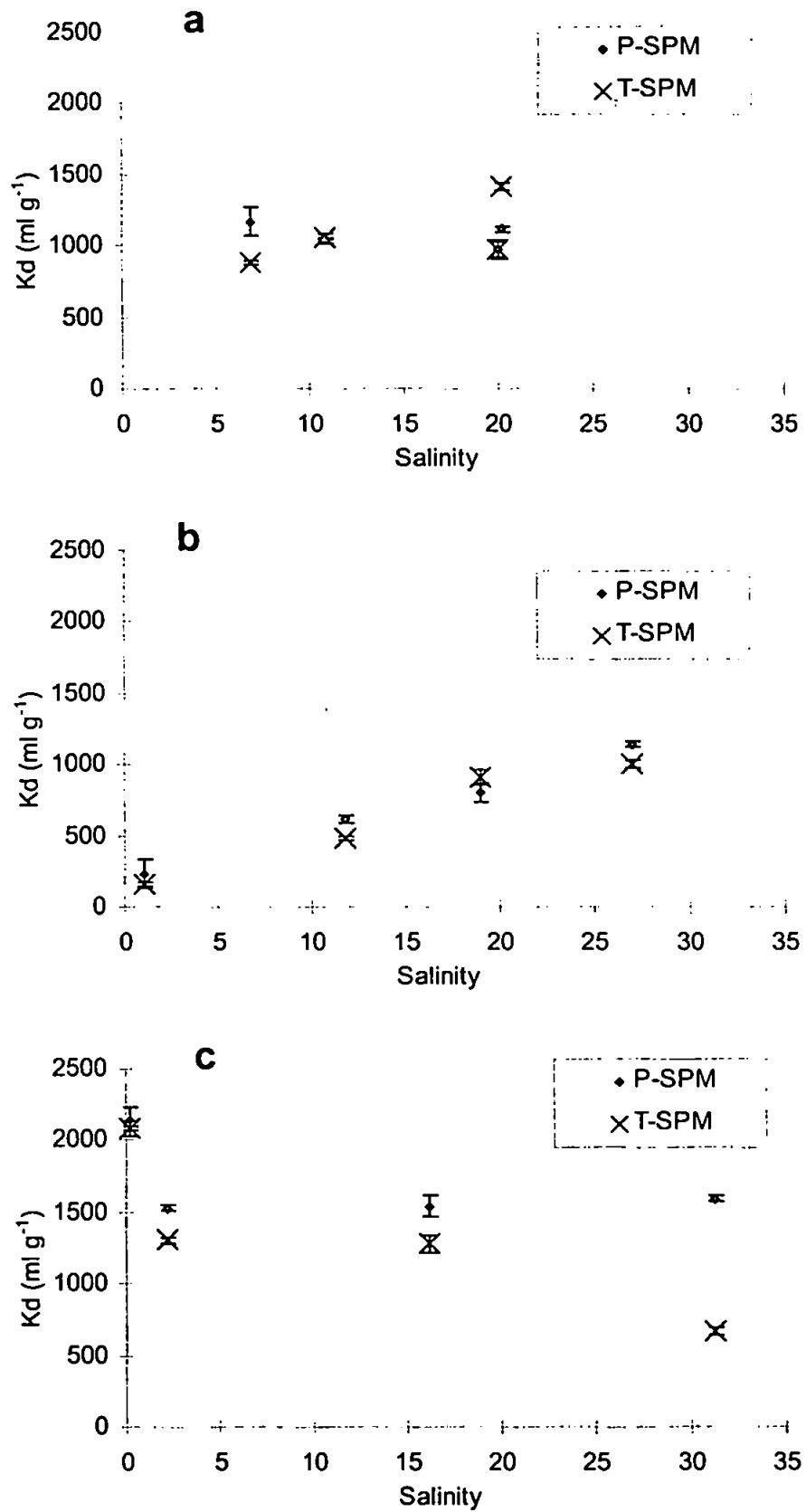


distributions owing to environmental and analytical variability in dissolved and particulate Ni concentrations (Figures 3.15 and 3.27, respectively).

The radiotracer  $K_d$ s obtained in this study are between one and two orders of magnitude lower than those obtained from the stable Ni field data (Section 3.3.6). The difference arises because the particulate Ni obtained in the radiotracer method is that which is in (quasi-) equilibrium with dissolved Ni, whilst particulate Ni extracted with 1 M HCl comprises, in addition to exchangeable Ni, also Ni more strongly bound to sites in the particle matrix, such as carbonates and crystalline Fe oxides (Chao, 1984; Turner et al., 1992b; Whitworth et al., 1999).

In Section 3.3.5 it was shown that higher concentrations of particulate Ni (available to 1 M HCl) occur in the finer, permanently suspended fraction of the Mersey SPM (P-SPM), and the lowest occurred generally in the temporarily suspended matter (T-SPM). However, as discussed above, a comparison of  $K_d$ s from stable and radiolabelled Ni suggests that the fraction of Ni which is potentially available for exchange reactions (and therefore can be released from the particles) is smaller than that leached by 1 M HCl. Therefore 5-day incubations with  $^{63}\text{Ni}$  were also carried out on density-separated fractions in order to assess the relative affinity of Ni for the two fractions and their potential for exchange. Separation of P-SPM and T-SPM was carried out by S. Watts (University of Plymouth). A settling time of 30 minutes was chosen because it is considered to be representative of the time available for particle settling around slack water (Turner et al., 1994).

The results of the 5-day incubations of  $^{63}\text{Ni}$  with P-SPM and T-SPM are shown in Figure 4.12. For March and June '98, there is no significant difference in the  $K_d$  values for the two settled fractions, nor is there with the "whole SPM" samples (Figures 4.9 and 4.10). However, higher  $K_d$ s occur for the P-SPM compared to the T-SPM in October '98 in the outer estuary. The results generally indicate that the P-SPM and T-SPM have similar



**Figure 4.12.** Distribution coefficients ( $K_{ds}$ ) for permanently (P-SPM) and temporarily suspended matter (T-SPM) for (a) March '98, (b) June '98, and (c) October '98 surveys.

Ni sorptive capacity throughout the estuary, in contrast with the determinations of particulate (stable) Ni concentrations for the two fractions (Figure 3.31). The difference probably lies in the operational nature of the definition of particulate Ni for the two methods. Whilst the differences between the two settled fractions in Figure 3.31 indicates a compositional effect, for the radiotracer experiments the difference is based on the reactivity of the particle surface, and indicates a sorptive capacity effect. Thus, the composition of the two settled fractions is different (Figure 3.31), but the sorptive behaviour is similar (Figure 4.12).

#### 4.4.2.1. Sequential leaches on $^{63}\text{Ni}$ -incubated particles

Sequential leaches were carried out on the 5-days incubated SPM in order to assess the reversibility of  $^{63}\text{Ni}$  sorption. Seawater was chosen as a digest because it provides a realistic estimate of the fraction of Ni undergoing desorption under natural conditions as a result of exchange reactions with seawater cations (Santschi et al., 1984). The results (Figure 4.13) show that between 8 and 40 % of sorbed Ni is held in the exchangeable form (as recovered by seawater), and there is generally no difference between the exchangeable Ni in poisoned and non-poisoned samples. The remaining 60-92% of particulate  $^{63}\text{Ni}$  is recovered by 0.1 M HCl. This result indicates that the sorption of Ni onto Mersey SPM is only partially reversible: after an incubation time of only 5 days, a considerable fraction (60-92%) of Ni has migrated to stronger binding sites (possibly within the particle matrix) from which it is not easily remobilised by seawater cations. The results agree with the finding of Sands (1997) who observed that the exchangeable fraction of  $^{63}\text{Ni}$  (as recovered by 1 M  $\text{CH}_3\text{COONa}$ ) in Humber Estuary SPM varied from 40 to 10 % after 1 and 5 days, respectively. The extent of Ni sorption reversibility as determined by seawater is also comparable with that of Mn, Zn and Cs (~ 40% for all the 3 metals, Turner et al, 1992a). In contrast, literature data show that nearly 100 % of Cd, is leached by seawater, suggesting complete reversibility (Comans and van Dijk, 1988; Turner et al., 1992a).

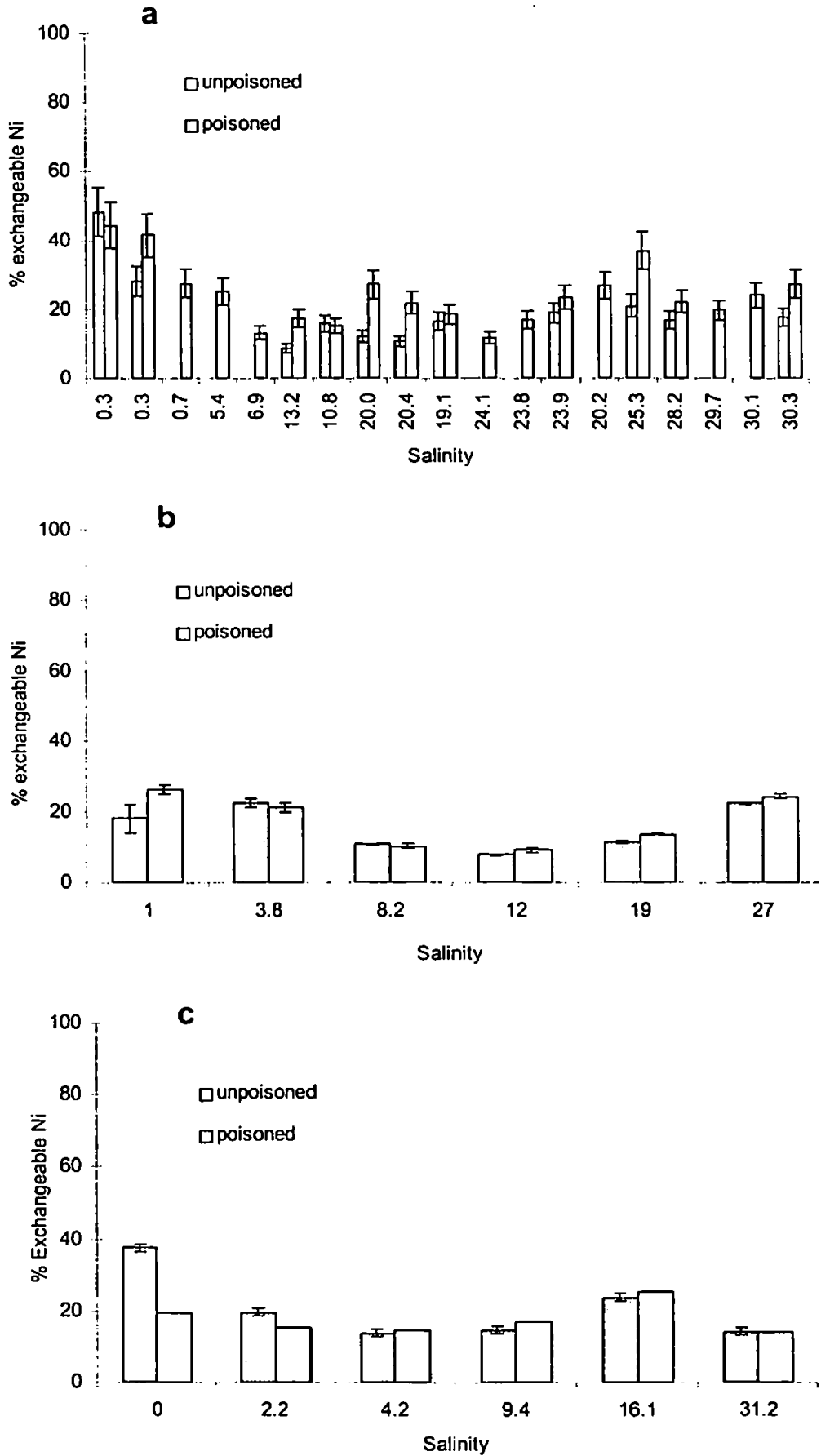
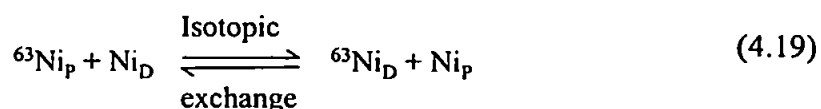


Figure 4.13. Percentage of exchangeable Ni (as extracted by seawater) for (a) March '98, (b) June '98, and (c) October '98.

The results obtained from the sequential leach experiments seem in contrast with those from the desorption experiments (Section 4.3.3), which show no evidence for  $^{63}\text{Ni}$  desorption in the salinity range 0.3-5. The reason for this contrasting behaviour is that in the desorption experiments salinity only increased to a value of 5, whilst in the seawater leaches the particles are in contact with seawater at  $S \sim 30$ . In the latter case, competition by seawater cations will therefore be more effective than at lower salinity. However, not all of the  $^{63}\text{Ni}$  removed by the seawater leach has desorbed as a consequence of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  competition and/or  $\text{Cl}^-$  complexation. In this experiment, the incubated particles are filtered and resuspended in seawater, where the initial concentration of  $^{63}\text{Ni}$  is = 0. Therefore, the  $^{63}\text{Ni}$  in the particles will be released into solution not only as a result of competition with seawater cations and anion complexation, but also as consequence of isotopic exchange due to equilibration with dissolved stable Ni:



In contrast, in the experiment in Section 4.3.3,  $^{63}\text{Ni}$  is always in (pseudo-) equilibrium between particles and solution, even after each salinity spike: despite the limited salinity range which is encompassed, this approach is highly representative of real environmental conditions.

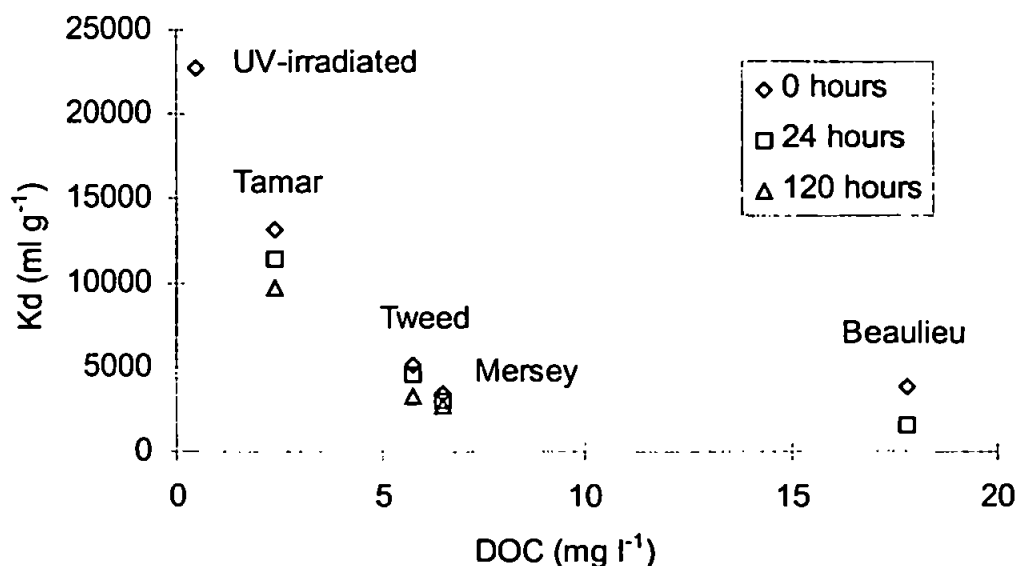
#### 4.5. Comparison of the sorptive behaviour of Ni in the estuaries under study

There are two major conclusions that can be drawn from the salinity gradient and uptake kinetics experiments. The first concerns the nature of the Ni species that undergo sorption; the second concerns the effect of DOM on Ni sorptive behaviour.

For the Tamar and Tweed Estuaries, the decrease of  $K_{ds}$  with increasing salinity (due to competition by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  for the sorption sites and Ni complexation by  $\text{Cl}^-$ ) suggests that throughout the estuaries the sorbing species is fundamentally  $\text{Ni}^{2+}$ . On the other hand, in the Mersey Estuary the  $K_{ds}$  generally tend to increase (the same trends are

observed for the incubations with unfiltered samples, Section 4.4.2), suggesting that a Ni-ligand complex species is “salted-out” and tends to adsorb with increasing salinity. Alternatively, Ni may be kept in solution by strong binding ligands (truly dissolved organic or colloidal organic/inorganic), as shown by the 10-fold increase in the freshwater  $K_d$  values resulting from the removal of dissolved organic matter (Figure 4.5): the increase in  $K_d$ s would then reflect the decrease of ligand concentration (Turner and Millward, 1994; Comber et al., 1995).

The salinity gradient and uptake kinetics experiments have also shown that the  $K_d$ s in freshwater are higher for the Tamar than the Tweed and Mersey: this trend is opposite to that followed by the freshwater DOC concentration in the three estuaries (Table 4.1). A plot of the freshwater  $K_d$ s versus DOC for the different estuaries (Figure 4.14) shows a clear inverse dependency of  $K_d$ s on DOC concentration, suggesting that complexation by natural ligands plays an important role in preventing Ni sorption onto particles, regardless of the nature of the DOC. Moreover, although the nature of the Ni-complexing ligand is not known (truly dissolved organic or colloidal organic/inorganic), from the observations



**Figure 4.14.** Freshwater  $K_d$ s for the Tamar, Tweed, Mersey and Beaulieu Estuaries as a function of the riverine DOC concentration, at different pre-equilibration times of  $^{63}\text{Ni}$  with freshwater ligands. Values for the UV-irradiated Tamar sample are shown as well. Errors are omitted for clarity.

in Section 4.3 carried out with UV-irradiation of water samples and upon addition of synthetic humic acids, it is suggested that at least a fraction of the ligands that keep Ni in solution has an organic, or mixed colloidal organic/inorganic nature (Powell et al., 1996).

For the freshwater/low salinity regions of the Tamar and Tweed (and probably also the Mersey) Estuaries, the results in Sections 4.2 and 4.3 also suggest that the complexation kinetics of Ni by freshwater ligands is slow (Mandal et al., 1999), and the extent of Ni sorption depends on the competition for Ni complexation between the dissolved ligands (colloidal or truly dissolved) and the particles, as shown by the differences in  $K_{ds}$  with changing pre-equilibration time:



where L is a dissolved ligand, S is a particle surface site and charges are omitted for simplicity. These results also suggest that slow complexation kinetics of Ni has important implications on the extent of Ni uptake, as this is affected by the amount of Ni complexation occurring during the water transit between its point discharge and a high turbidity zone.

The effect of slow complexation kinetics on Ni sorption is not seen at higher salinities and in seawater, where the  $K_{ds}$  are largely the same for different pre-equilibration times. This is probably because Ni is outcompeted from binding to both dissolved ligands and particles by the much higher concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , and this effect can be clearly seen in the decrease of the ACSV non-labile Ni fraction in the October '96 Tamar Estuary axial transect (Section 3.1.2).

Results from the uptake kinetics experiments further suggest that there is a big difference in the pathway to (pseudo-) equilibrium between samples where Ni is equilibrated with the dissolved ligands and samples where it is not. This is clear in the

Mersey and Beaulieu 0-hour experiments, where a rapid initial uptake of free Ni is followed by a slower release of a Ni-ligand complex from the particle surface to solution:



Monitoring of the dissolved total and ACSV-labile (stable) Ni in a kinetic experiment using Tamar samples suggests that the release of complexed Ni occurs (although not detected through the monitoring of  $^{63}\text{Ni}$ ), probably as a consequence of re-equilibration of organic matter between the particulate and dissolved phases (Section 4.3.1).

The results of the kinetic analyses of the uptake profiles indicate the importance of a kinetic approach to the study of heterogeneous chemical reactions in highly dynamic estuaries. The response time for Ni sorption onto estuarine particles (i.e. the time necessary to achieve 63% of sorptive equilibrium) is of the order of a few hours (3-8) for all the estuaries under study. These values are of the same order of magnitude or lower than the flushing time of the low salinity region of the Tamar (~5 hours) and Mersey Estuaries (~48 hours) under low flow or base-flow conditions, suggesting a potential for heterogeneous chemical reactions to take place under appropriate conditions (e.g. high turbidity, high specific surface areas, Millward et al., 1990). Removal of dissolved Ni is often observed in the low salinity region of the Tamar Estuary (Morris, 1986; Morris et al., 1986; Nimmo, 1987; van den Berg et al., 1991). Field data (Section 3.3.2) show that no removal of dissolved Ni is observed in the turbidity maximum zone of the Mersey Estuary, probably because of a combination of factors, such as uniform specific surface areas (Millward et al., 1990) of the SPM, and high degree of Ni complexation by dissolved natural ligands. Rather, positive deviations from conservative behaviour are often observed. Such trends



cannot be accounted for by the radiotracer experiments illustrated in this chapter, which also suggest that Ni sorptive tendency increases with increasing salinity, with  $K_{ds}$  exhibiting a significant positive correlation with salinity in March and June '98. The results also indicate that ~10% of Ni is removed in the high turbidity region of the Mersey Estuary (Figure 4.9-4.11c). However, it has been shown that any removal of Ni in the estuary would be too small to be detected by voltammetry due to the analytical and environmental variability in the dissolved (stable) Ni concentration. The results from the desorption experiment further suggest that the only increase in salinity does not lead to any significant Ni desorption in the salinity range 0-5. However it is possible that at higher salinity competition by seawater cations becomes more effective, leading to Ni desorption. Seawater leaches carried out on incubated SPM showed that 8- ~40% of sorbed  $^{63}\text{Ni}$  is potentially removed by seawater: this is probably an upper estimate of the percentage of desorbable Ni, as an unknown fraction of Ni is released by seawater upon isotopic exchange, rather than competition by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and/or complexation of Ni by  $\text{Cl}^-$ . The desorption experiments also showed that sorption of Ni still takes place up to salinity 5 and over a several day period (up to 12 days). This behaviour however may be due to the slow migration of Ni to binding sites within the particle matrix that still occurs despite the increase in salinity. The latter effect is confirmed by the sequential leaches carried out on incubated SPM, which show that up to ~60% of sorbed  $^{63}\text{Ni}$  is not held in an exchangeable form, suggesting a two stage sorptive process (Jannasch et al., 1988; Garnier et al., 1997; Liu et al., 1998).

*In-situ* incubations were only carried out in the Tweed Estuary. The results from this study suggest that although biological activity significantly enhances the uptake of Ni, with  $K_{ds}$  increasing by a factor of between 3 and 5, the overall effect on Ni removal from the water column is not significant (<2.5 % dissolved Ni removal), because of a combination of the low SPM concentrations (<20 mg l<sup>-1</sup>) and fast flushing times (0.5-1 day).

## CHAPTER 5

### MODELLING Ni SPECIATION IN THE TWEED AND MERSEY ESTUARIES

The aim of this chapter is to estimate the equilibrium distributions of Ni species in the Mersey and Tweed Estuaries, under a variety of environmental conditions, on the basis of the information derived in Chapters 3 and 4. The reader is referred to Section 1.2 for a theoretical introduction to equilibrium speciation modelling. The calculations presented here are based on the assumption that the systems under study are at equilibrium, i.e. complexation and adsorption reactions are fully reversible and reach equilibrium quickly compared to the estuarine flushing time (Turner, 1995; Tipping et al., 1998). Although this is most likely true for the Mersey Estuary (flushing time 20-50 days), the very short flushing time of the Tweed Estuary (0.5-1 days) suggests that the equilibrium assumption may not strictly apply (Sections 3.2.2 and 4.3.2), and therefore the speciation calculations may not reflect the actual distributions occurring in the system.

The information on the interaction of Ni with natural ligands (L) derived in Chapter 3 is initially used here to model the speciation of dissolved Ni in the Tweed and Mersey Estuaries. The calculations are initially carried out at pH 8.3 and at 25 °C (Section 5.2.1), as (i) the complexing capacity titrations were conducted at pH 8.3 and ambient temperature (~ 20 °C) and (ii) the majority of the available thermodynamic data are for 25 °C. The assumptions made on the pH and temperature dependence of the NiL conditional stability constants ( $K'_{NiL}$ ) will be explained in Section 5.2.2, and then calculations will be presented for dissolved Ni speciation at the pH and temperature of the original samples. Finally, some of the information on the particle-water interactions of Ni derived in Chapter 4 will be used in the speciation calculations in order to include adsorbed Ni in the model for the Mersey Estuary (Section 5.2.3).

## 5.1. Speciation calculations

The majority of the speciation calculations will be carried out with the aid of the speciation software Mineql+ (Version 3.01a) (Schecher and McAvoy, 1992). This program performs chemical equilibrium calculations using the Debye-Hückel equation for ionic strength corrections of the stability constants (Section 1.2.1) and the standard enthalpy change of reactions for temperature correction of the stability constants. The thermodynamic stability constants for inorganic Ni complexes used in this study (Table 5.1) are taken from Baes and Mesmer (1976) and Turner et al. (1981); those for all the other inorganic species are from the Mineql+ built-in thermodynamic database. The riverine concentrations of the major ions used for the calculations (Table 5.2) are average annual values for the River Tweed (Neal et al., 1997), and those for the 23<sup>rd</sup> October 1998 for the River Mersey (Jones, EA-North West, pers. comm.). Concentration of major seawater ions (S=35) are those from Dyrssen and Wedborg (1980) (Table 1.2). Concentrations for intermediate salinities are calculated assuming conservative behaviour of the major ions and of alkalinity. The Ni speciation calculations are performed using the data from the September '98 survey on the Tweed Estuary (Table 3.4) and from the October '98 survey on the Mersey Estuary. For the latter estuary, the concentrations are those after correction for wall adsorption (Table 3.8).

**Table 5.1.** Thermodynamic data for inorganic Ni complexes used in the speciation model. For hydrolytic species  $\log \beta^\circ$  is the overall thermodynamic stability constant for the reaction:  $\text{Ni}^{2+} + n\text{H}_2\text{O} \rightleftharpoons \text{Ni}(\text{OH})_n^{(2-n)+} + n\text{H}^+$ . For all other species  $\log \beta^\circ$  is the overall thermodynamic stability constant for the reaction:  $\text{Ni}^{2+} + n\text{X}^{-m} \rightleftharpoons \text{NiX}^{(2-nm)+}$ .

Species	$\log \beta^\circ$ (@ 25 °C)	$\Delta H$ (kcal mol <sup>-1</sup> )
NiOH <sup>+</sup>	-9.86 <sup>a</sup>	11.9 <sup>c</sup>
Ni(OH) <sub>2aq</sub>	-19 <sup>a</sup>	23.2 <sup>d</sup>
Ni(OH) <sub>3</sub> <sup>-</sup>	-30 <sup>a</sup>	32.9 <sup>d</sup>
NiCl <sup>+</sup>	0.72 <sup>b</sup>	0.5 <sup>c</sup>
NiCO <sub>3 aq</sub>	5.37 <sup>b</sup>	3 <sup>c</sup>
NiSO <sub>4aq</sub>	2.29 <sup>b</sup>	1.5 <sup>f</sup>
Ni(SO <sub>4</sub> ) <sub>2</sub> <sup>2-</sup>	3.20 <sup>b</sup>	2 <sup>g</sup>

<sup>a</sup> Baes and Mesmer (1976); <sup>b</sup> Turner et al. (1981); <sup>c</sup> from Mineql+ built-in database; <sup>d</sup> estimated as shown in Byrne et al. (1988); <sup>e</sup> assumed identical to the value from Byrne et al. (1988) for 2 M ionic strength; <sup>f</sup> assumed identical to the estimated value by Byrne et al. (1988) for seawater; <sup>g</sup> from Smith and Martell (1976); <sup>h</sup> assumed similar to Cd and Pb complexation (after Byrne et al., 1988).

**Table 5.2.** Riverine major ion concentrations (mM) and carbonate alkalinity used for the speciation calculations. All the Tweed data are from Neal et al. (1997), Mersey data are from the EA (P. Jones, pers. comm.)

Element	River Tweed	River Mersey
Na <sup>+</sup>	0.33	0.10
K <sup>+</sup>	0.033	0.14
Mg <sup>2+</sup>	0.21	0.22
Ca <sup>2+</sup>	0.44	0.82
Cl <sup>-</sup>	0.38	0.78
SO <sub>4</sub> <sup>2-</sup>	0.10	0.41
Alk. (meq l <sup>-1</sup> )	0.055	1.16

In the following discussion, L indicates those complexing ligands whose concentration and complex stability with Ni ( $K'_{NiL}$ ) are determined upon ligand competition with DMG. It should be noted that the physico-chemical nature of these ligands is not known and therefore they may occur as truly dissolved organic or colloidal organic/inorganic ligands.

The speciation calculations which follow are based on the assumption that in the original sample, total dissolved Ni ( $C_{Ni}$ ) is distributed between inorganic species ( $Ni'$ ) and  $NiL$  (Donat et al., 1994):

$$C_{Ni} = [Ni'] + [NiL] \quad (5.1)$$

where

$$[Ni'] = [Ni^{2+}] \alpha_{Ni'} \quad (5.2)$$

In Equation 5.2,  $\alpha_{Ni'}$  is the  $\alpha$ -coefficient for the inorganic complexation of Ni (Ringboom and Still, 1972):

$$\alpha_{Ni'} = 1 + \sum_{ij} \beta_{ij} [X_j]^i \quad (5.3)$$

where  $\beta_{ij}$  is the overall stoichiometric stability constant for the formation of the  $i^{\text{th}}$  order complex between Ni and the  $j^{\text{th}}$  inorganic ligand X ( $X = Cl^-, OH^-, SO_4^{2-}, \dots$ ).

It should be noted that other ligands weaker than L are likely to be present in natural waters, which are not detected by the technique adopted in this study. Therefore the Ni' concentration calculated in this study is probably an upper estimate of the "effective" inorganic Ni concentration (Donat et al, 1994).

In order to determine the role of the ligand L on the speciation of dissolved Ni, the inorganic Ni complexation and therefore the value of  $\alpha_{Ni'}$  must be first assessed. For each sample, the inorganic speciation is initially calculated with the aid of Mineql+. Once the value of  $\alpha_{Ni'}$  is known, the concentrations of  $[Ni^{2+}]$ ,  $[Ni']$ , and  $[NiL]$  are determined using the calculations shown in Appendix 2. Finally, Mineql+ is used to re-calculate the inorganic speciation of Ni'<sup>§</sup>. The speciation calculations reported here are carried out assuming that the dissolved phase is in equilibrium with the atmospheric CO<sub>2</sub> (Tipping et al., 1998). This is plausible because it is most likely that natural waters, being in contact with the atmosphere, are near equilibrium with the atmospheric CO<sub>2</sub>.

## 5.2. Nickel speciation in the Tweed and Mersey Estuaries

### 5.2.1. CALCULATIONS AT pH 8.3 AND T = 25°C

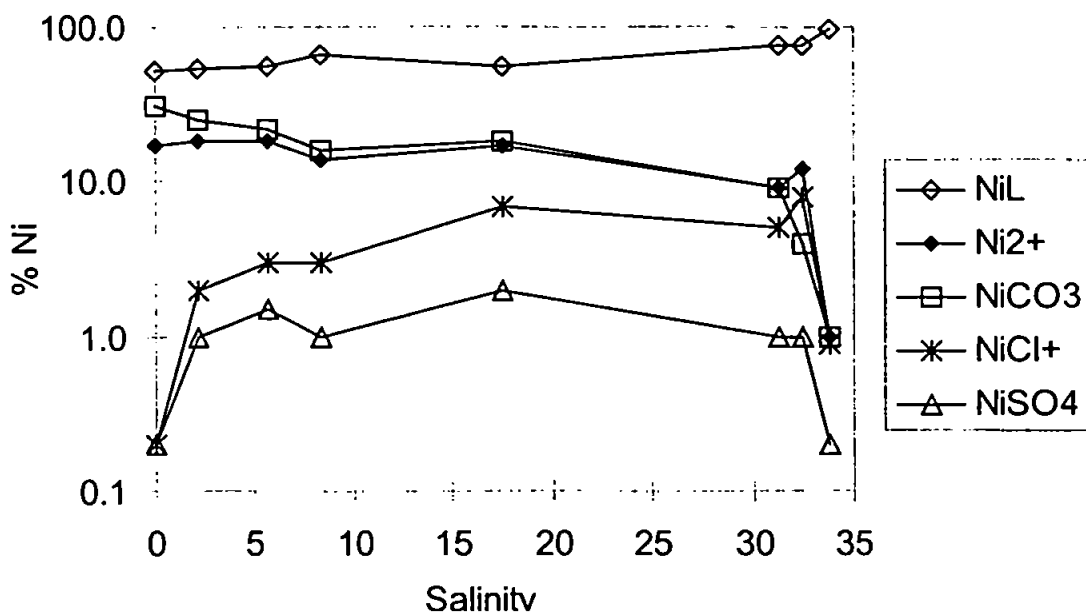
The speciation calculations are initially carried out at pH 8.3 and 25 °C. The pH value of 8.3 is used for the initial calculations because the complexing capacity titrations were carried out at this pH, and therefore the calculated  $K'_{NiL}$  are strictly valid only at this pH. The possible effects of pH variations is discussed in Section 5.2.2. The results from the speciation calculations are shown in Figures 5.1 and 5.2 for dissolved Ni in the Tweed and Mersey Estuaries.

In the Tweed Estuary (Figure 5.1) generally between 50 and 76% of total dissolved Ni ( $C_{Ni}$ ) occurs as NiL. Inorganic Ni is primarily distributed between NiCO<sub>3</sub> and Ni<sup>2+</sup>; the

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<sup>§</sup> The values of  $C_L$  and  $\log K'_{NiL}$  can be introduced directly in Mineql+ , which shortens the time of the analyses. However, the program always uses the stability constants at ionic strength = 0 as a starting point for the calculations, whilst the  $\log K'_{NiL}$  values correspond to a well-defined ionic strength. Therefore an empirical correction is made to the input value of  $K'_{NiL}$  so that the equilibrium ratio  $[NiL] / ([Ni^{2+}] [L'])$  is equal to the experimentally determined  $K'_{NiL}$  value.

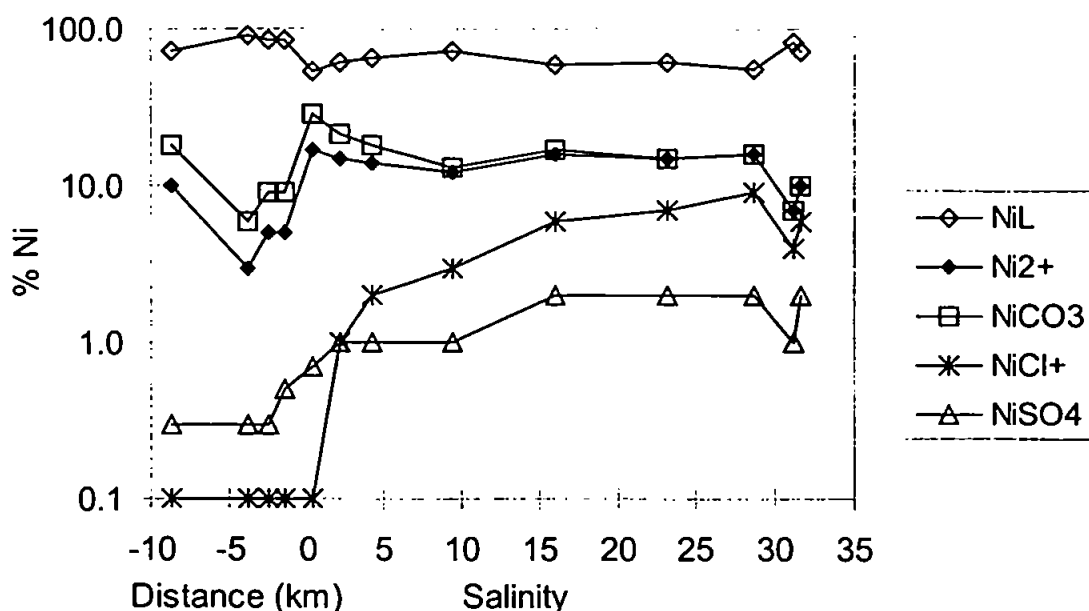
latter constitutes up to ~ 18% of  $C_{Ni}$ . The fraction of  $NiCl^+$  increases from <1% to 8% with increasing salinity, whilst  $NiSO_4$  is always below 2% of  $C_{Ni}$ . The concentration of  $Ni^{2+}$  decreases towards seawater from 1.3 nM to < 1 nM. In the sample with the highest salinity, 97% of  $C_{Ni}$  occurs as  $NiL$ , and therefore only 3% of Ni is distributed among the inorganic species.



**Figure 5.1.** The speciation of dissolved Ni (as percentage of total dissolved Ni) in the Tweed Estuary at pH 8.3 and 25 °C.

Similarly, in the Mersey Estuary (Figure 5.2), Ni speciation is dominated by  $NiL$ , with percentages varying between 53 and 91% of  $C_{Ni}$ . The highest fractions of  $NiL$  generally occur in riverwater (71-91%), due to the high concentrations (relatively to total dissolved Ni) of the Ni-binding ligands. In the freshwater region, inorganic Ni is distributed between  $Ni^{2+}$  and  $NiCO_3$ ; the increase in  $NiL$  from 70% (the most landward point) to 91% results in the decrease of  $Ni^{2+}$  and  $NiCO_3$  from 10 and 18% to 3 and 9%, respectively. At the onset of the salinity gradient, the fraction of  $NiL$  drops to 50%, reflecting the decrease in ligand concentration (Figure 3.19). Perhaps the colloidal fraction of Ni-binding ligands flocculates in the very low salinity region, however this is difficult to

assess with certainty, because of the scatter of the data in the low-salinity ligand distributions and the uncertainties deriving from freezing artefacts (Figure 3,19; Table 3.8). In the mid-estuarine region, complexation by  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  increases with increasing salinity, whilst NiL is relatively constant between 50 and 60%, and then rises to 70-80% at salinity  $>30$ . This reflects the increase in ligand concentration relatively to the total dissolved Ni concentration (as for the Tweed Estuary). Free  $\text{Ni}^{2+}$  varies between 1 and 10 nM, the highest values occurring in the mid-estuarine region.



**Figure 5.2.** The speciation of dissolved Ni (as percentage of total dissolved Ni) in the Mersey Estuary at pH 8.3 and 25 °C.

### 5.2.2. DISSOLVED Ni SPECIATION AT NATURAL pH AND TEMPERATURE

Although the speciation calculations shown in Section 5.2.1 were carried out at pH 8.3 and 25 °C, the pH and temperature of the original samples are different from these values, and a number of assumptions have to be made in order to model the data using the appropriate pH and T values.

The complexing capacity titrations were carried out at pH 8.3, however the pH of the estuarine samples varied between 7.2 and 7.9 in the Mersey Estuary, and between 7.9 and 8.3 in the Tweed Estuary. There is likely to be a pH dependence of the  $K'_{\text{NiL}}$  (Gledhill

and van den Berg, 1994; Achterberg et al., 1997), which is a function of the acidity constants ( $K_{a,L}$ ) of the functional groups coordinating Ni. The  $K_{a,L}$  for the ligand L are, however, not known. Moreover, in this study the Ni-binding ligands L are saturated by the ambient Ni concentrations: proton competition may then result directly in a decrease of the concentration of NiL complexes (i.e. the ligands would not be saturated with Ni), the extent of such decrease depending on  $K_{a,L}$ . Owing to the high stability of the NiL complexes, however, proton competition will be effective only for  $pK_a$  values comparable or greater than the  $\log K'_{NiL}$  (i.e. for  $pK_{a,L}$  values equal to or higher than  $\sim 16$  at  $pH > 7$ ). Literature data show that the  $pK_{a,s}$  for natural humic and fulvic acids are in the range 3-9 (Muller, 1996a). Assuming similar acidity constants for the functional groups of the ligands binding Ni in the Tweed and Mersey Estuaries, then proton competition with Ni for binding L would not be significant. For this model, it is therefore assumed that variations in pH do not affect the NiL equilibrium (Coale and Bruland, 1990).

It is also likely that temperature affects the equilibrium between Ni and L, however the standard enthalpy changes for this reaction are not known. For comparison, it is possible to use the standard enthalpy changes for Ni complexes with EDTA and salicylic acid ( $-7.6$  and  $+1.8$  Kcal mol<sup>-1</sup>, respectively; Martell and Smith, 1977) in order to estimate the potential effect of temperature on the NiL complex formation. At 10 °C, the  $\log K'_{NiL}$  would only vary of  $+0.1$  and  $-0.02$  log units, (respectively), however this variation is insignificant compared to the magnitude of the errors in the  $\log K'_{NiL}$  estimation.

Figure 5.3 and 5.4 show the speciation of Ni in the Tweed and Mersey Estuaries at the ambient pH and temperature, as calculated on the basis of the assumptions outlined above. Compared to the results at pH 8.3 and 25 °C, these results show that the % NiL has not varied. However, the inorganic Ni speciation has been shifted towards lower percentages of NiCO<sub>3</sub> (< 15% in both estuaries) and higher percentages of Ni<sup>2+</sup> and NiCl<sup>+</sup>, whilst NiSO<sub>4</sub> is the species contributing the smallest percentage (2-3%). The free Ni concentrations in this case range between 0.06 and 2.7 nM in the Tweed Estuary, and



between 1.3 and 22 nM in the Mersey Estuary.

The calculated  $\alpha$ -coefficients for NiL ( $\log \alpha_{\text{NiL}} = 9.6-11.2$ ) are several orders of magnitude higher than the  $\alpha$ -coefficients for inorganic Ni complexation ( $\log \alpha_{\text{Ni}} = 0.15-0.34$  in the Tweed, and 0.02-0.28 in the Mersey), which result in the much higher stability of NiL compared to the inorganic Ni complexes. As a consequence, the speciation of

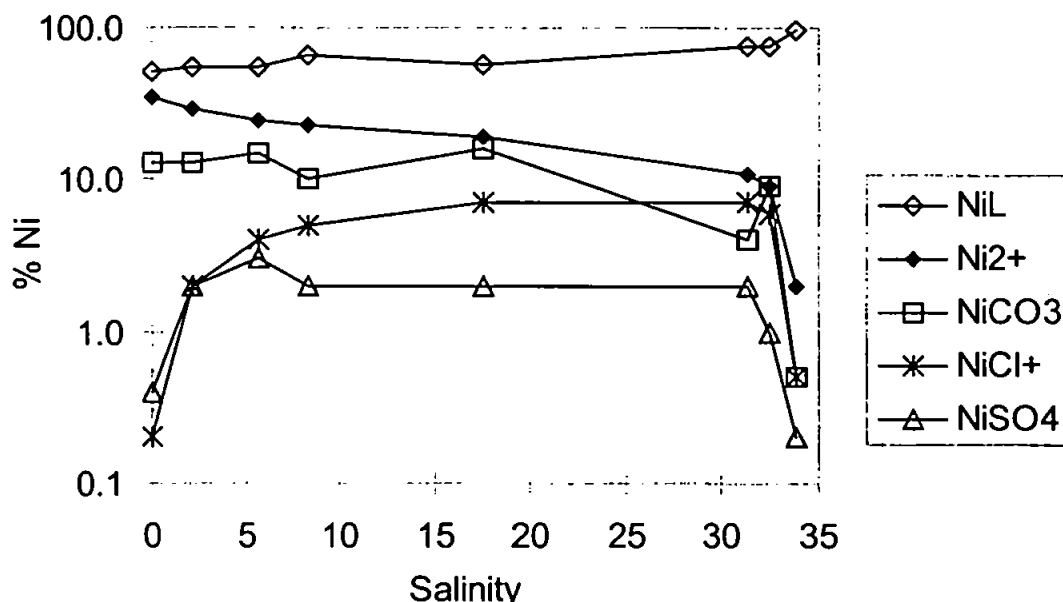


Figure 5.3. The speciation of dissolved Ni (as percentage of total dissolved Ni) in the Tweed Estuary at pH and temperature of the original samples.

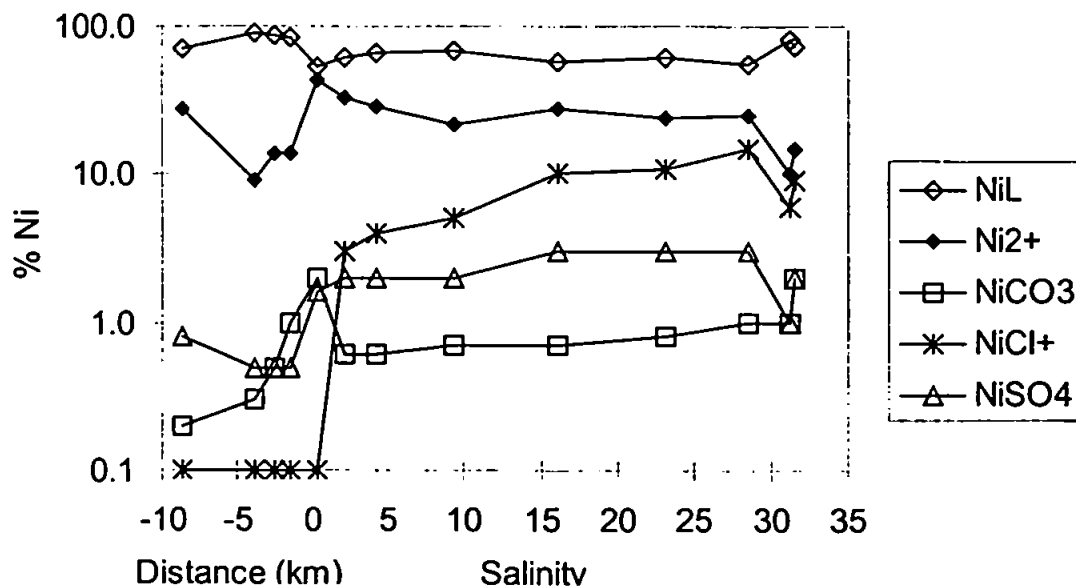


Figure 5.4. The speciation of dissolved Ni (as percentage of total dissolved Ni) in the Mersey Estuary at pH and temperature of the original samples.

dissolved Ni in the Tweed and Mersey Estuaries is determined primarily by the concentration of the ligands L, which bind Ni strongly and perhaps specifically (van den Berg and Nimmo, 1987). The speciation of the remaining fraction of dissolved Ni (Ni') depends primarily on the pH of the system. Tipping et al. (1998) simulated the effect of increasing alkalinity (and thus pH) on the speciation of trace metals in the Humber Estuary. The authors showed that with increasing pH from 6.5 to 8.5 (and at constant  $p\text{CO}_2$ ), the fraction of free Ni decreased by a factor of ~5 due to the increased complexation of Ni with carbonate. In the Tweed Estuary, where the natural pH of the samples varies between 7.9 and 8.3,  $\text{Ni}^{2+}$  is the primary inorganic species (45-70% of Ni'), and  $\text{NiCO}_3$  constitutes 15-30% of Ni'. In the Mersey Estuary, where the natural pH of the samples varies between 7.2 and 7.9, the percentage of  $\text{NiCO}_3$  is never above 7% of Ni'. The free metal ion constitutes between 50 and 95% of Ni', and in freshwater it is the only significant inorganic species. In both estuaries, the percentages of chloride and sulphate species increase with increasing salinity, and constitute up to 30% and 7% of Ni', respectively.

An important result from the speciation calculations is that in both the Tweed and Mersey Estuaries the ligands are saturated by the ambient Ni concentration, as observed also by Nimmo (1987), van den Berg and Nimmo (1987) and Donat et al. (1994) for coastal and oceanic waters.

### 5.2.3. NICKEL SPECIATION (INCLUDING ADSORBED SPECIES) IN THE MERSEY ESTUARY

In this section, the results from the incubations with  $^{63}\text{Ni}$  carried out in the Mersey Estuary are incorporated in Mineql+ for calculating the speciation of Ni including the adsorbed species. Only the incubations carried out on the unfiltered samples will be taken into account here (Section 4.4), as in this case the experimental (incubation) conditions are those most similar to the environmental ones. The calculations are carried out only for the Mersey Estuary, as the same identical samples were characterised for both ligand (L)

concentrations and distribution coefficients (Section 4.4.2).

Distribution coefficients are used here to determine conditional stability constants describing the interaction of Ni with surface sites of Mersey Estuary particles under equilibrium conditions. The approach used here is entirely empirical, because no studies were carried out to determine the parameters describing Ni adsorption onto Mersey estuarine particles (i.e. the determination of the concentration of surface sites available for adsorption and of the apparent constants for Ni binding onto Mersey particulate matter: see for example Mouvet and Bourg, 1983). The model only considers the particulate Ni in equilibrium with the dissolved phase (i.e. whose concentration is related to that of total dissolved Ni by the radiotracer  $K_d$ ), i.e. adsorbed Ni.

The fundamental hypothesis of the model is that the adsorbing species is  $\text{Ni}^{2+}$ . This is based on the results in Section 4.3.1 and Figure 4.5, which show that the  $K_d$  for the uptake of  $^{63}\text{Ni}$  onto estuarine particles increases by a factor of 10 when dissolved organic matter is removed by UV-irradiation.

The surface sites for adsorption/desorption reactions are here treated as conventional ligands (Mouvet and Bourg, 1983; Tipping et al., 1998), and the reaction between  $\text{Ni}^{2+}$  and the particle surface:



is represented by a conditional (apparent) stability constant:

$$K'_{\text{NiS}} = [\text{Ni-S}^{(2-n)+}] / [\text{Ni}^{2+}] [\text{S}^{n-}] \quad (5.5)$$

Proton competition is not included in the reaction of  $\text{Ni}^{2+}$  with the particle surface because the pH dependence of Ni adsorption onto Mersey particles is not known and the incubations were carried out at fixed pH. However, results from other adsorption studies show that proton competition with Ni is unlikely to occur at pH values corresponding to those of the Mersey samples (Bryce et al., 1994; Coughlin and Stone, 1995). The

alternative use of a reaction such as:



had to be excluded because its stoichiometry cannot be accounted for in Mineql+.

The conditional stability constant defined by Equation 5.5 is entirely conditional upon the pH and medium composition. In the model, the  $K'_{\text{NiS}}$  is used as an adjustable parameter in order to reproduce the observed  $K_d$  values.

In order to include Equation 5.5 in Mineql+, the concentration of the surface sorption sites must be known. Here the value of  $1.3 \times 10^{-3} \text{ mol g}^{-1}$  (taken from the estimate for Meuse River SPM by Mouvet and Bourg, 1983) was used as a fixed parameter in the model. The  $K_d$  and concentration of SPM are used to calculate the concentration of particulate Ni in equilibrium with the observed (measured) dissolved Ni:

$$[\text{Ni}]_P = [\text{Ni}]_D \times K_d \times \text{SPM} \times 10^{-6} \quad (5.7)$$

where  $[\text{Ni}]_D$  is the total dissolved Ni concentration. The concentration of  $[\text{Ni}]_P$  is then added to  $[\text{Ni}]_D$  to obtain the total “reactive” Ni concentration ( $\text{Ni}_R$ ), which is used as input in Mineql+. The next step is to run Mineql+ at variable values of  $K'_{\text{NiS}}$ , until the calculated adsorbed fraction of Ni becomes equal to the observed value. The calculations are run at 20°C, which is the temperature at which the radiotracer incubations were carried out. The values of  $K'_{\text{NiS}}$  which allow to reproduce the measured Ni partitioning are shown in Table 5.3.

**Table 5.3.** Values of  $\log K'_{\text{NiS}}$  used to calculate the equilibrium distribution of “reactive” Ni in the Mersey Estuary.

Salinity	$\log K'_{\text{NiS}}$
<0.3	4.10
2.2	4.00
4.2	4.02
9.4	4.73
16.1	4.81
31.2	5.28

The results from the model are shown in Figure 5.5a. Between 50 and 70 % of  $Ni_R$  is present as  $NiL$ , whilst the remaining 30-50% is present mainly as free or adsorbed Ni. The fundamental inorganic species is  $Ni^{2+}$ , with concentrations ranging between 1.3 and 16 nM. Concentrations of chloride and sulphate species increase with increasing salinity, but are always below 10% of  $Ni_R$ ; complexation by carbonate is negligible throughout the estuary ( $\leq 1\%$ ). Adsorbed Ni constitutes up to 26% of  $Ni_R$ , and its distribution mirrors that of the SPM (Figure 5.5b). The percentage adsorbed Ni increases from 6 to 19% in the low salinity region and corresponds to the increase in SPM due to the presence of the turbidity

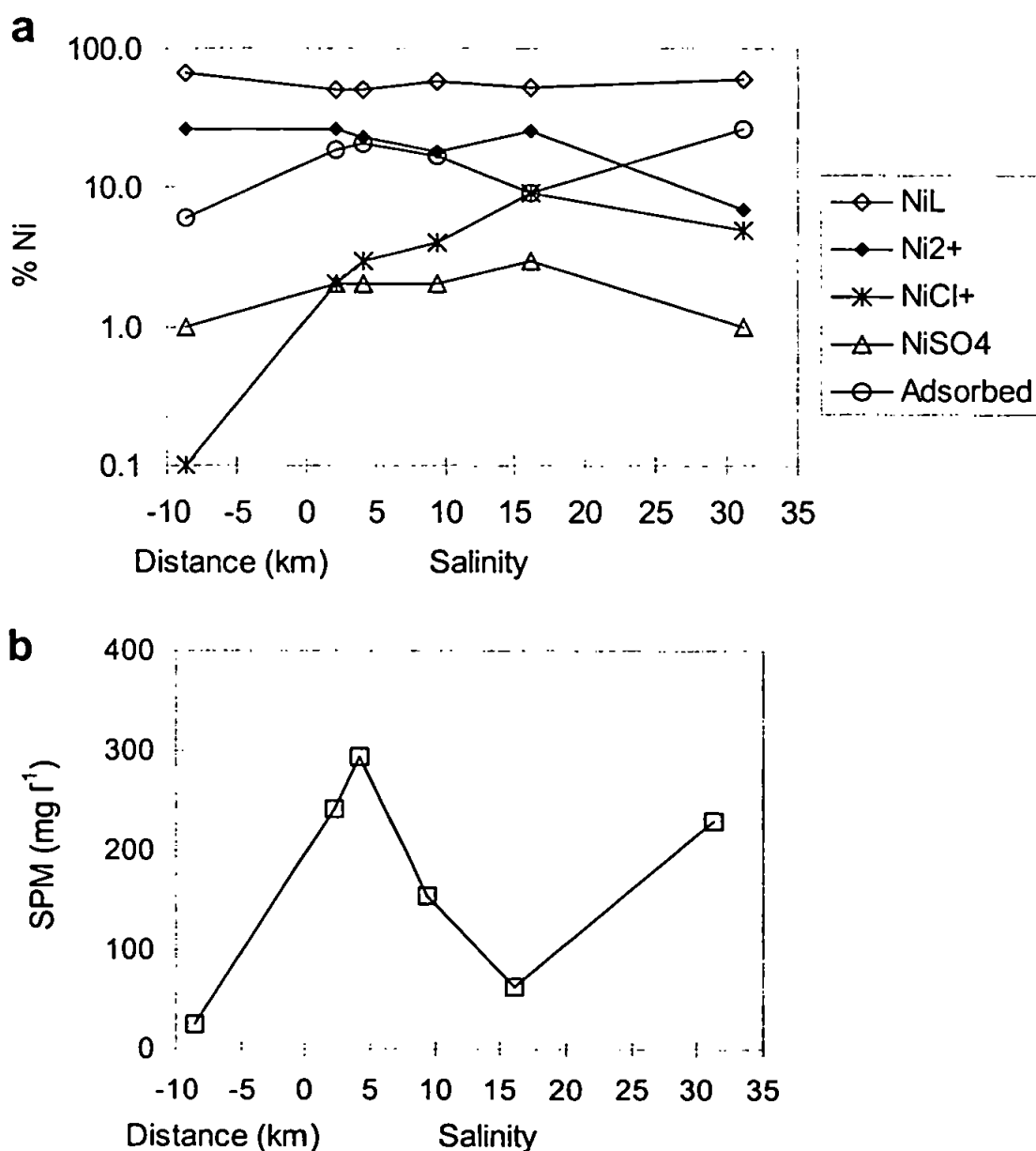


Figure 5.5. (a) The speciation of “reactive” Ni in the Mersey Estuary (as percentage of “reactive” Ni) at natural pH and 20°C; (b) the SPM concentration.

maximum (despite the decrease in  $K_d$  from 2560 to 920 ml g<sup>-1</sup>). The increase in adsorbed Ni concentration suggests that a decrease in total dissolved Ni should occur around the turbidity maximum. However, no decrease in the observed total dissolved Ni concentration is measured in the Mersey low salinity region: this is probably due to the scatter of the data, which does not allow the detection of a possible removal of dissolved Ni in the high turbidity area.

The equilibrium concentrations of dissolved Ni species in the presence of adsorbed Ni are the same (within 1-2%) as those calculated in the absence of particulate matter at pH and temperature corresponding to those of the natural samples. The concentration of Ni bound to L equals the concentration of the ligand itself, i.e. the ligands are still saturated by ambient Ni concentrations in the presence of particulate matter. This result is to be expected because the  $K'_{NiS}$  values are much smaller than the values of  $K'_{NiL}$ , and therefore the particles cannot compete with the dissolved ligands, L, for Ni complexation (i.e. complexation by L prevents Ni from adsorbing onto the particles, as also observed in Chapter 4). Moreover, the sum of all inorganic Ni dissolved species (Ni') equals the measured labile Ni concentration (Table 5.3), which suggests that the determination of labile Ni and total dissolved Ni alone are sufficient for determining the fraction of total dissolved Ni bound to the strong ligand L (Nimmo et al., 1989).

#### 5.2.4. A CRITICAL EVALUATION OF NI SPECIATION RESULTS

There are a number of fundamental limitations of the speciation model adopted in this study. Firstly, the complexing capacity titrations have been carried out at pH and temperature rather different from the ambient values. As a consequence, a number of assumptions had to be made concerning the dependency of  $K'_{NiL}$  upon pH and temperature. Although these assumptions and therefore the resulting calculations are believed to be reasonable estimates of the Ni-L interaction, clearly more accurate determinations would be obtained at the pH and temperature of the original samples (Gledhill and van den Berg,

1994). Secondly, the detection window used for the voltammetric determinations only allows the detection of complexes with very high stability. No information is obtained on concentration and strength of complexes with lower stability, which are likely to occur in natural waters, but are detected as labile complexes.

Nickel speciation in the Tweed and Mersey Estuaries was evaluated through the application of the chemical equilibrium software Mineql+. The calculations were carried out assuming that the systems under study were at equilibrium, although this may not be strictly true for natural systems, where kinetic factors may limit the extent of heterogeneous and metal-ligand exchange reactions (Hering and Morel, 1989; Wood et al., 1995). This may especially apply for Ni, which is among the metals with the slowest ligand-exchange reactions (Morel et al., 1991; Mandal et al., 1999; this work, Section 4.3.1). The results, therefore, may not reflect the effective Ni distributions in the estuaries under study; however they give a general indication of the possible speciation scenarios. Moreover, the modelling has identified some of the factors governing Ni speciation in the Tweed and Mersey Estuaries; it is possible that these results may be generalised to a variety of estuarine environments. These factors are:

- pH, which is fundamental in determining Ni inorganic speciation. At constant major ion concentrations, Ni complexation by carbonate increases at the expense of  $\text{Ni}^{2+}$  when the pH increases.
- The concentration of strong binding ligands detected by voltammetry. These ligands, characterised by  $\log K'_{\text{NiL}} > 17$ , are fully saturated by the ambient Ni concentrations. Due to the strength of the ligands, the NiL complexes are inert and do not dissociate easily.

The majority of Ni speciation models reported so far in the literature only consider the inorganic Ni complexes (e.g. Byrne et al., 1988), or complexation by humic acids (Mantoura et al., 1978; Turner et al., 1981; Bourg, 1983; Mouvet and Bourg, 1983;

Tipping et al., 1998). The latter has usually been calculated not to exceed 10% in freshwater and ~1% in seawater (Table 5.4), the only exception being a value of ~ 40% calculated by Tipping et a. (1998) at pH 8.

**Table 5.4.** A comparison of calculated dissolved Ni species with results from the literature.

	pH	Freshwater			Seawater		
		% NiL	% Ni'	% Ni <sup>2+</sup>	% NiL	% Ni'	% Ni <sup>2+</sup>
This study	7.5	50-85	15-50	15-40			
Mantoura et al. (1978)	7.5	1	99	50			
Tipping et al. (1998)	7.5	6	94	16			
This study	8.1				50-80	20-50	10-20
Mantoura et al. (1978)	8.1				<0.1	>99.9	30
Turner et al. (1981)	8.2				< 0.1	>99.9	47
Donat et al. (1994)	8.1				50	50	28
Tipping et al. (1998)	8.0				1	99	34

Tipping et al. (1998) suggested that considering natural humics as the only organic ligands is most appropriate for unpolluted waters. However, results obtained in this and previous voltammetric studies (Nimmo, 1987; van den Berg and Nimmo, 1987; Nimmo et al., 1989; Donat et al., 1994; Achterberg et al., 1997; Turner et al., 1998) show that a high fraction (~20-80%) of Ni occurs as complexes with high stability ( $\log K'_{NiL} > 17$ ) in natural waters. These complexes have been detected in unpolluted waters (e.g. the Tweed and Tamar Estuaries [this study], the North-East Atlantic Ocean [Nimmo, 1987]) as well as in more polluted waters (the Mersey Estuary [this study], San Francisco Bay Estuary [Donat et al., 1994]), and all have remarkably similar conditional stability constants for Ni binding, suggesting that these ligands are ubiquitous in natural waters. The speciation calculations from voltammetric studies therefore suggest that Ni complexation by strong natural ligands is more important than previously believed. This has often a considerable effect on the fraction of inorganic Ni (Ni') estimated through the voltammetric and pure modelling approaches. Moreover, it is likely that other complexes, which are detected as labile in ACSV (e.g. Ni-humic complexes, with  $\log K' \sim 5.3$ : Mouvet and Bourg, 1983),



exist in natural waters. This may render the actual fraction of Ni' even lower than it is currently estimated, and may have important consequences for Ni bioavailability, especially in those oceanic areas where Ni is required for urea assimilation (Price and Morel, 1991).

## CHAPTER 6

### CONCLUSIONS AND FUTURE WORK

Although Ni is a bioactive element which undergoes biological cycling in oceans (Morel et al., 1991), it is generally believed to have a weak reactivity in estuaries (Morris, 1986; Chiffoleau et al., 1994; Campbell et al., 1988; Turner et al., 1998). The low water-particle reactivity of Ni in estuaries has been attributed to its low affinity for the particulate phase (owing to complexation by strong natural ligands in the dissolved phase: Turner et al., 1998), or to its preferential association with the refractory phase in the particulate matter (Campbell et al., 1988; Comber et al., 1995). Thus, this study was carried out in order to (i) identify the major factors (common and contrasting) affecting the distributions, speciation and particle-water interactions of Ni, and (ii) assess the effect of complexation by dissolved natural ligands on Ni sorptive behaviour in estuaries. To a large extent, these aims have been achieved.

Three estuaries with contrasting hydrodynamics, contamination levels, and physical and geochemical characteristics were selected for this study: the Tamar (characterised by low dissolved organic carbon concentrations, a metal mining history and a pronounced turbidity maximum), the Tweed (relatively pristine, with a short flushing time and low turbidity), and the Mersey (affected by industrial and domestic pollution, with a long flushing time and high turbidity).

#### 6.1. Summary of results

Nickel reactivity, distributions and speciation in the Tamar, Tweed and Mersey Estuaries were investigated using adsorptive cathodic stripping voltammetry (ACSV) and a radiotracer method based on the partitioning of  $^{63}\text{Ni}$ . A total of eight axial transects were carried out, during which master variables were monitored and samples were collected for the ACSV analysis of total and labile Ni. In the Tweed and Mersey Estuaries, samples

were also collected for the determination of natural Ni-complexing ligands. Process-orientated studies were carried out to investigate the partitioning of  $^{63}\text{Ni}$  as function of salinity, extent of Ni complexation by natural ligands and time. Information gathered in the field and process-orientated studies was used to model Ni speciation in the Tweed and Mersey Estuaries; in the latter estuary, the model also included the adsorbed species. Schematic diagrams of the processes believed to regulate Ni speciation and reactivity in the Tamar, Tweed and Mersey Estuaries are shown in Figures 6.1-6.3 for each estuary.

### 6.1.1. TAMAR

A relatively high particle reactivity was observed in the Tamar Estuary (Figure 6.1), with removal of total dissolved Ni in the low salinity region, followed by addition and then conservative dilution. The removal of total dissolved Ni was attributed to removal of non-labile Ni, as labile Ni sharply increased in the low salinity region and did not show evidence of removal in the turbidity maximum zone. Non-labile Ni could be removed by either (i) adsorption onto SPM, or (ii) flocculation. Laboratory experiments showed that

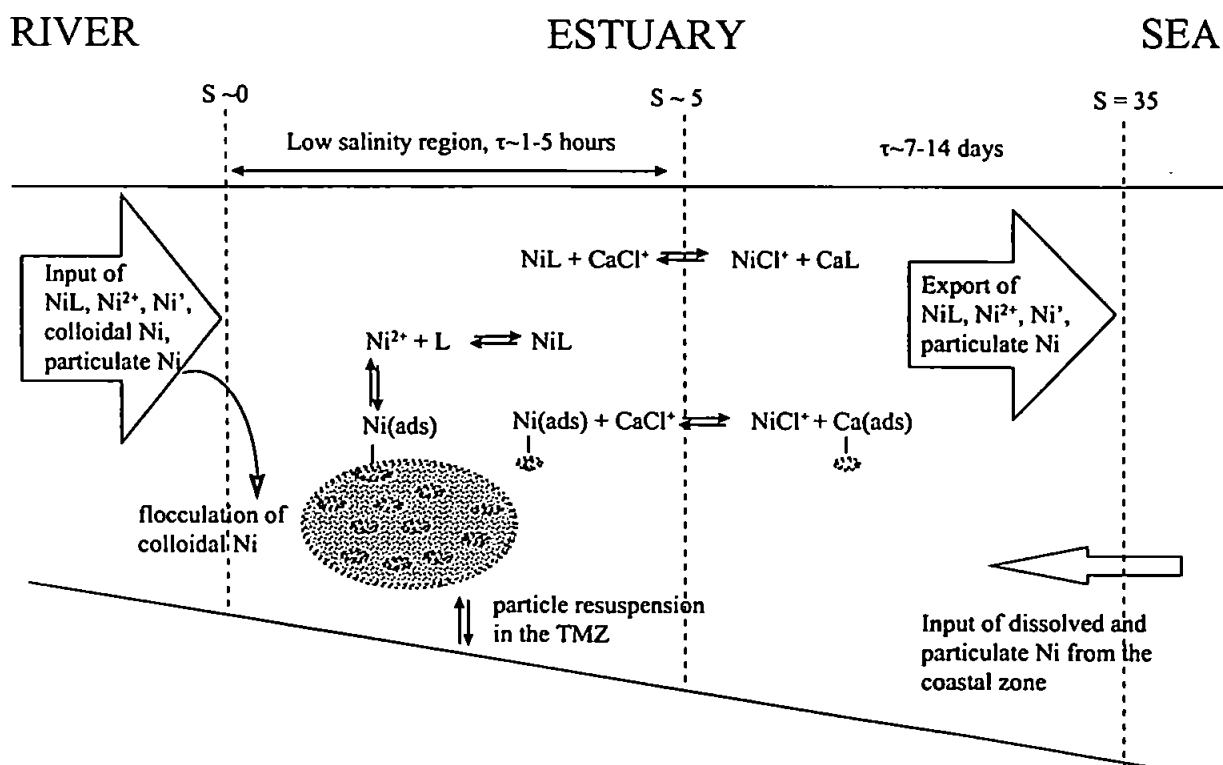


Figure 6.1. Schematic diagram showing the processes believed to affect Ni speciation and reactivity in the Tamar Estuary.  $\tau$  represents the flushing time.

complexation by natural ligands prevented Ni sorption onto Tamar SPM (Section 4.3.1), and therefore it is believed that the observed total dissolved Ni removal in the low salinity region during the October '96 survey was probably due to flocculation of part of the non-labile Ni fraction. At higher salinity, Ni undergoes desorption from seaward-advected particles (S=1-4), followed by a re-equilibration between ACSV labile and non-labile Ni in the less reactive mid-outer estuary.

### 6.1.2. TWEED

The largely conservative behaviour of Ni observed in the Tweed Estuary (Figure 6.2) was attributed to the combination of short flushing time and low suspended particulate loads, which prevent Ni sorption from being a significant process affecting the overall Ni reactivity (Morris, 1990). The speciation of Ni in the Tweed Estuary was found to be dominated by a class of strong complexing ligands ( $\log K'_{NiL} = 19.0 \pm 0.4$ ), which were saturated by the ambient Ni concentrations throughout the estuary during the September

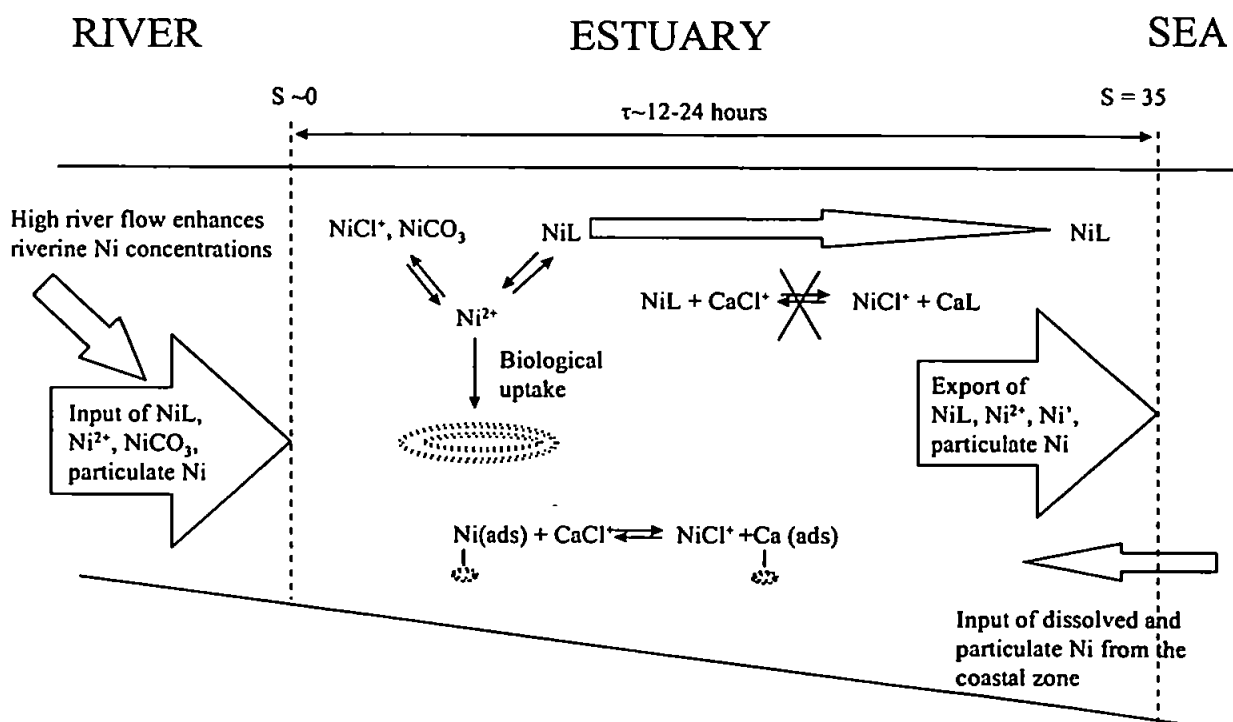


Figure 6.2. Schematic diagram showing the processes believed to affect Ni speciation and reactivity in the Tweed Estuary.  $\tau$  represents the flushing time.

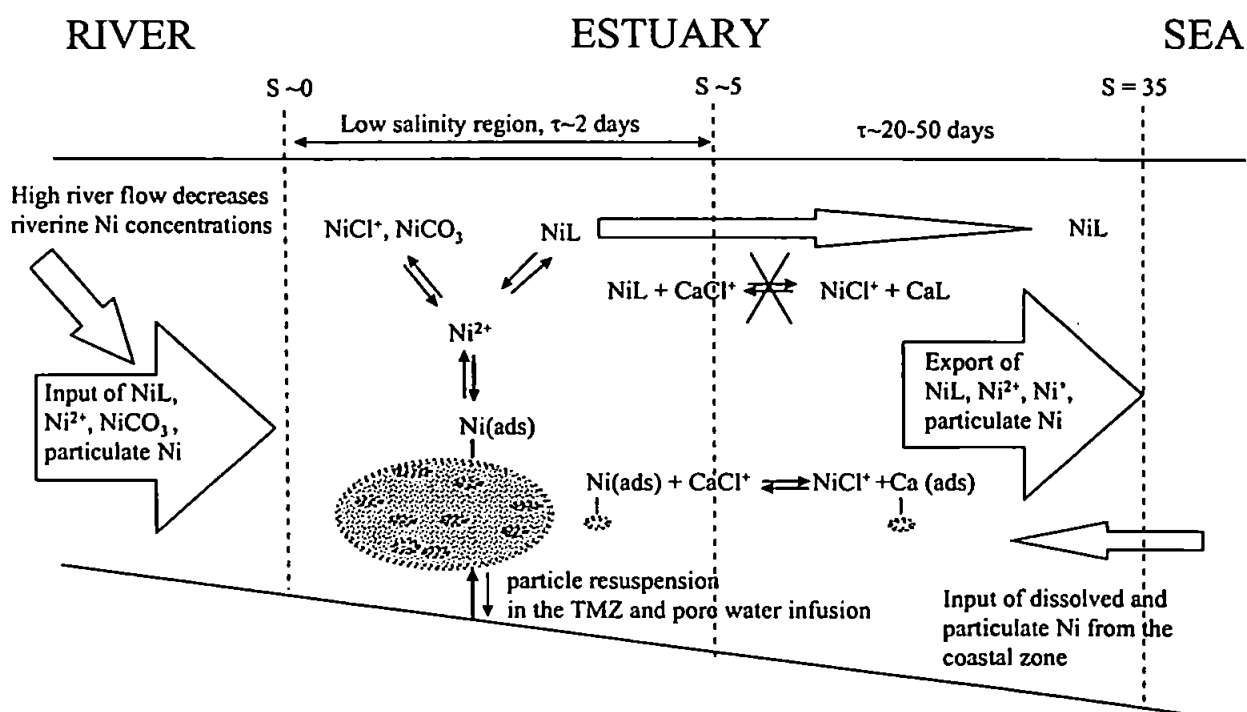
'98 survey. This suggests that the increase in concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  with increasing salinity does not affect the Ni-L equilibrium, i.e. the ligands show high specificity towards Ni. Nickel speciation in the Tweed Estuary was modelled with the aid of the equilibrium software Mineql+ (Schecher and McAvoy, 1992). The results showed that between 50 and 75% of Ni was bound to these strong ligands. The remaining inorganic Ni was distributed primarily between  $\text{Ni}^{2+}$  and  $\text{NiCO}_3$ . Complexation by chloride and sulphate increased with increasing salinity, but never exceeded 10% of total dissolved Ni.

Radiotracer experiments showed that Ni complexation by natural ligands prevented its sorption onto Tweed estuarine SPM. The vast majority of "reactive" Ni (i.e. that available for exchange reactions within the dissolved phase and between the dissolved and particulate phases) in the Tweed Estuary was transported in the dissolved phase (~98%), due to the very low SPM concentrations in the estuary. *In-situ* incubations using  $^{63}\text{Ni}$  showed that biological activity significantly enhanced Ni uptake onto particulate matter, but the overall effect on Ni removal from the dissolved phase was not significant because of the low SPM concentrations in the estuary.

The concentration of riverine total dissolved Ni was found to be positively correlated with the Tweed river flow, probably due to an increase in colloidal material derived from soil erosion during rainfall events (Figure 3.7). Hydrological trends show that the ratio of winter to summer runoff has considerably increased over the last 40 years in the Tweed catchment, suggesting that climate change could cause an increase in the magnitude and frequency of flooding during winter (Fox and Johnson, 1997). This may have significant consequences on the fluxes of Ni (and possibly other metals) to the North Sea, as the Tweed constitutes the second most important freshwater input (after the Humber) to the North Sea (Robson and Neal, 1997).

### 6.1.3. MERSEY

In the Mersey Estuary (Figure 6.3), Ni often showed positive deviations from conservative behaviour, with either localised inputs, or broad mid-estuarine maxima, both in the total dissolved Ni and its ACSV species. Nickel addition was attributed to either anthropogenic or geochemical inputs. The field studies and laboratory experiments carried out during this study helped to explain part of the variability observed in Ni distributions. Between 50 and 70% of total dissolved Ni was observed to be bound to a class of very strong ligands ( $\log K'_{NiL} = 18.7 \pm 0.5$ ), which were saturated by the ambient Ni concentrations throughout the salinity gradient. As for the Tweed Estuary, saturation of the ligands with Ni suggests that the ligands are highly specific towards Ni. In addition, it was observed that the concentration of these ligands was equal (within analytical errors) to that of the ACSV non labile Ni, which suggests that measurement of this fraction gives an indirect estimate of the concentration of the ligands themselves. Thus, the mixing behaviour of ACSV non-labile Ni simply reflects that of the corresponding Ni-complexing



**Figure 6.3.** Schematic diagram showing the processes believed to affect Ni speciation and reactivity in the Mersey Estuary.  $\tau$  represents the flushing time.

ligands. On the other hand, the mid-estuarine addition of labile Ni was not fully explained by the desorption experiments with  $^{63}\text{Ni}$ , and there is only indirect evidence of Ni desorption from the seawater leaches experiments (which are, however, not representative of realistic estuarine conditions). Labile Ni addition may therefore be due to desorption from contaminated sediments and/or anthropogenic inputs.

The speciation of Ni, with and without taking into account the adsorbed species, was calculated for the Mersey Estuary October '98 transect with the aid of Mineql+. The analysis of the dissolved Ni speciation model (for which more data points are available, allowing better resolution), shows that the fraction of NiL drops from 70-90% (of total dissolved Ni) in freshwater to ~50% at the fresh-seawater interface, suggesting that the colloidal fraction of NiL flocculates. This effect is however difficult to assess with certainty because of the analytical and environmental uncertainties in L determination and distribution (Section 3.3.3).

The results of speciation calculations including the adsorbed species showed that, for the October '98 transect, between 50 and 70% of total "reactive" Ni (i.e. total dissolved and adsorbed Ni) was present as NiL throughout the estuary. The remaining 30-50% of Ni was present mainly as free  $\text{Ni}^{2+}$  or adsorbed Ni. The latter constituted up to 26% of total "reactive" Ni. Complexation by chloride increased with increasing salinity up to ~10%, whilst  $\text{NiSO}_4$  always occurred at percentages below 3%.

#### 6.1.4. PROCESS-ORIENTATED STUDIES

The process-orientated studies have shown that dissolved natural ligands play a major role in preventing Ni sorption onto particulate matter. The studies also helped to identify  $\text{Ni}^{2+}$  as the fundamental adsorbing species. This conclusion was supported by three separate sets of observations: (i) Ni uptake onto estuarine SPM generally increased significantly when the natural complexing ligands were removed by UV-irradiation; (ii) the longer  $^{63}\text{Ni}$  was allowed to complex with natural ligands (prior to addition of SPM), the

smaller was the uptake onto particles (this effect being highest in freshwater); (iii) generally the  $K_d$ s decreased along a salinity gradient, due to competition by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and Ni complexation by  $\text{Cl}^-$ . In the Mersey Estuary, however, the  $K_d$ s generally increased with increasing salinity, possibly because of salting-out effects or decrease in Ni-complexing ligands concentration. The latter hypothesis is supported by the increase in Ni sorption upon UV-removal of freshwater ligands, and also by the clear inverse relationship between  $K_d$ s and dissolved organic carbon (DOC) for most seasons (Figure 4.14).

The fundamental result of the process-orientated studies was that removal of organic matter from solution generally enhanced Ni uptake onto estuarine particulate matter. Although the nature of the Ni-complexing ligands in the estuaries under study is not known (truly dissolved organic or colloidal organic/inorganic), these experiments have shown that at least a fraction of these ligands has an organic, or mixed colloidal organic/inorganic nature. Thus, complexation by natural ligands plays an important role in preventing Ni sorption, and this finding may at least partly explain the low reactivity exhibited by Ni in a variety of estuaries (Table 1.6).

The process-orientated studies also showed that generally the longer  $^{63}\text{Ni}$  was allowed to equilibrate with natural freshwater ligands, the smaller was the extent of Ni sorption onto particulate matter (e.g. Figure 4.2). This effect, due to the slow complexation kinetics of Ni by dissolved ligands (Mandal et al., 1999), has important implications in natural systems, as the extent of Ni uptake is affected by the amount of Ni complexation occurring during the water transit between its point discharge and a high turbidity zone.

The uptake of  $^{63}\text{Ni}$  onto suspended particulate matter was investigated through the application of a first-order kinetic model. Reaction rate constants were estimated, from which the reaction response times were calculated ( $\tau^{\text{resp}}$ , i.e. the time to achieve 63% of the equilibrium). Complexation of Ni by natural ligands was observed to affect not only the overall extent of Ni sorption, but also the progression of the sorptive reactions, as the



magnitude of  $\tau^{\text{resp}}$  increased with increasing the extent of Ni complexation by dissolved ligands. This result suggested competition between dissolved ligands and suspended particulate matter for Ni complexation. Furthermore, the comparable magnitudes of the response time and the flushing time of the estuaries under study suggested that in all estuaries removal may be potentially observed. Indeed, Ni removal is a persistent feature in the Tamar Estuary. Removal is not observed in the Tweed and Mersey Estuaries, because of the low SPM concentrations in the Tweed, and probably because of the high dissolved phase Ni complexation in the Mersey Estuary.

The speciation and particle-water interactions of Ni have been investigated in three estuaries with contrasting hydrodynamic and physico-chemical characteristics. Through the coupling of field and process-orientated studies, this study suggests that a combination of hydrodynamic, physical and chemical factors such as river flow, estuarine flushing time, nature, concentration and reaction kinetic of natural Ni-complexing ligands, suspended particulate matter (SPM) concentration, all contribute to the modification of the physico-chemical speciation and reactivity of Ni in estuaries. This study has shown that Ni has generally a low particle reactivity, and that natural ligands play an important role in maintaining Ni in solution and preventing its reaction at the particle surface.

## 6.2. Suggestion for future work

An improvement on the voltammetric technique adopted in this study would be the use of automated systems for the in-situ determinations of total dissolved Ni concentration and speciation, which (i) would allow a better spatial and temporal resolution of Ni distributions, and (ii) would prevent artefacts deriving from sample storage (Achterberg and van den Berg, 1996; Whitworth et al., 1998).

The voltammetric method which was adopted in this study only allowed the detection of very strong Ni-complexing ligands whose  $\alpha$ -coefficients lay within a well-defined analytical detection window centred on the  $\alpha$ -coefficient for Ni(DMG)<sub>2</sub>. However,

a range of Ni-complexing ligands of different strength and concentrations are likely to occur in natural waters, which probably may be detected by working at different detection windows (Donat et al., 1994). One way of achieving this would be, for example, through the identification of suitable Ni-complexing ligands for voltammetric studies at detection windows different from that of Ni(DMG)<sub>2</sub>.

The main factor which could not be assessed in this study concerns the chemical and physical nature of the Ni-complexing ligands which are detected through voltammetric studies. Further investigations are necessary to characterise Ni-complexing ligands in terms of chemical composition and size-range distribution. Nickel-complexing ligands may be isolated from natural waters through the use of immobilized metal affinity chromatography, and some functional groups (such as amines and carbohydrates) may be identified through chemical and spectral analysis (e.g. Midorikawa and Tanoue 1996; Gordon et al., 1996). Voltammetric speciation studies may be used in conjunction with size-fractionation techniques (such as ultrafiltration: Muller 1996b) to identify the physical nature (i.e. truly dissolved and/or colloidal), the concentration and the conditional stability constants for Ni binding of each size-separated fraction.

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## APPENDIX 1

### INSTRUMENTATION USED FOR MONITORING ESTUARINE MASTER VARIABLES

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<i>Tamar, October '96; Tweed, September '98; all Mersey surveys</i>	
Conductivity	WPA CM 35 Conductivity meter
Temperature and Salinity	MC5 T-S bridge, National Institute of Oceanography
pH	Hanna pHOX 52E pH meter
Dissolved oxygen	YSI-58 Dissolved oxygen meter

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<i>Tweed, November '96 and June '97</i>	
All master variables	YSI-6000 multi- analyser (LOIS-PML)

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## APPENDIX 2

### THEORETICAL ASPECTS ON THE DETERMINATION OF THE INTERACTION OF Ni(II) WITH NATURAL LIGANDS

The method adopted in this study for the determination of Ni speciation in estuarine waters is based on the work of Nimmo (1987) and van den Berg and Nimmo (1987), who determined the interaction of dissolved Ni with natural ligands in seawater. The theoretical basis of the determination of ligand concentration and the stability constants of its metal complexes have been extensively described by Ruzic (1982), Zhang et al., (1990), and Gledhill and van den Berg (1994), and will be summarised here briefly.

A2.1. The voltammetric determination of ligand concentration and conditional stability constants for the interaction with Ni.

The following discussion is based on the assumption of a 1:1 complex, NiL, between Ni and a natural ligand L (which actually represents a class of ligands with the same or similar binding strength).

The determination of the interaction of Ni with natural ligands is based on the titration of a water sample with incremental amounts of Ni. Therefore, increasing amounts of Ni are added to a number of aliquots (usually 10-12) of a water sample containing identical amounts of added ligand (0.2 mM DMG in this study). After equilibration of Ni between the natural ligands and DMG, the total concentration of dissolved Ni in each titration aliquot is given by:

$$C_{\text{Ni}} = [\text{Ni}'] + [\text{Ni}(\text{DMG})_2] + [\text{NiL}] \quad (\text{A1})$$

where  $[\text{Ni}']$  is the sum of the concentrations of free  $\text{Ni}^{2+}$  and all inorganic species,  $[\text{Ni}(\text{DMG})_2]$  is the concentration of Ni complexed by DMG, and  $[\text{NiL}]$  is the concentration

of Ni complexed by the natural ligand L. For each titration aliquot, the following equations also apply:

$$C_L = [L'] + [NiL] \quad (A2)$$

$$K'_{NiL} = [NiL]/([Ni^{2+}][L']) \quad (A3)$$

where  $C_L$  is the total ligand concentration (i.e. the complexing capacity),  $L'$  is the concentration of ligand not complexed by Ni (comprising free L and its complexes with  $H^+$  and with major and minor water cations),  $NiL$  is the concentration of Ni complexed by L, and  $K'_{NiL}$  is the conditional stability constant for the complex  $NiL$ , which is conditional upon the pH and salinity of the water sample. By substituting  $[L']$  from Equation A3 in Equation A2, and then multiplying each side of (2) by  $[Ni^{2+}]/([NiL]C_L)$ , the following equation is obtained (Ruzic, 1982):

$$[Ni^{2+}]/[NiL] = [Ni^{2+}]/C_L + 1/(K'_{NiL} C_L) \quad (A4)$$

If only one single class of ligands complexes Ni, then a plot of  $[Ni^{2+}]/[NiL]$  versus  $[Ni^{2+}]$  is linear, and values for  $C_L$  and  $K'_{NiL}$  can be obtained from the slope and Y-axis intercept with a linear least-squares regression. A curved plot is obtained in the presence of more than one class of complexing ligands. For every aliquot of the titration, the labile Ni concentration is given by:

$$[Ni_{lab}] = [Ni'] + [Ni(DMG)_2] \quad (A5)$$

The reduction current,  $i_p$ , measured in the voltammetric scan, is proportional to the amount of labile Ni:

$$i_p = S [Ni_{lab}] \quad (A6)$$

where  $S$  is the sensitivity (nA/nM), which is calibrated by standard Ni additions to the sample. Alternatively,  $S$  is calculated from the slope of the titration curve ( $[Ni_{lab}]$  versus

$C_{Ni}$ ) at high Ni concentrations, where the ligands are saturated and any addition of Ni contributes entirely to the labile Ni concentration. The definition of labile Ni in Equation A5 includes  $Ni'$  because the added Ni re-equilibrates between  $Ni'$  and  $[Ni(DMG)_2]$ . The concentration of  $Ni^{2+}$  is related to that of labile Ni by:

$$[Ni_{lab}] = [Ni^{2+}] \alpha' \quad (A7)$$

where  $\alpha'$  is the overall  $\alpha$ -coefficient of  $Ni^{2+}$  excluding the complexation by L (Ringbom and Still, 1972):

$$\alpha' = \alpha_{Ni'} + \alpha_{Ni(DMG)_2} \quad (A8)$$

In Equation A8,  $\alpha_{Ni'}$  is the  $\alpha$ -coefficient for the inorganic side reactions of Ni:

$$\alpha_{Ni'} = 1 + \sum_j (\beta'_{NiX_j} [X]^j) \quad (A9)$$

where  $\beta'_{NiX_j}$  is the overall conditional stability constant for the formation of the j-th complex with the ligand X (=  $OH^-$ ,  $Cl^-$ , etc.).  $\alpha_{Ni(DMG)_2}$  is the  $\alpha$ -coefficient for the complexation of Ni by DMG:

$$\alpha_{Ni(DMG)_2} = \beta'_{Ni(DMG)_2} [DMG']^2 \quad (A10)$$

where  $\beta'_{Ni(DMG)_2}$  is the conditional stability constant for the complex  $[Ni(DMG)_2]$ , and  $[DMG']$  is the concentration of DMG not complexed by  $Ni^{2+}$ , which is approximately equal to the total DMG concentration,  $C_{DMG}$  ( $C_{DMG} = 0.2\text{mM} \gg [Ni(DMG)_2]$ ). At the DMG concentrations used in the titrations, the concentration of the 1:1 complex ( $NiDMG$ ) is negligible compared to the concentration of  $Ni(DMG)_2$  (van den Berg and Nimmo, 1987). The values of  $\beta'_{Ni(DMG)_2}$  used in this study were calculated by van den Berg and Nimmo (1987) and are shown in Table A2.1. For  $[DMG] = 0.2\text{ mM}$ ,  $\log \alpha_{Ni(DMG)_2} = 9.8 - 0.1$  in the salinity range 2-35 (van den Berg and Nimmo, 1987), thus  $\alpha_{Ni(DMG)_2} \gg \alpha_{Ni'}$ .

**Table A2.1.** Values of  $\beta'_{\text{Ni(DMG)}_2}$  used in the titration calculations (from van den Berg and Nimmo, 1987).

Salinity	$\log \beta'_{\text{Ni(DMG)}_2}$
32.5	$17.2 \pm 0.1$
24	$17.45 \pm 0.06$
12	$17.6 \pm 0.2$
2	$17.5 \pm 0.1$

It is more convenient to express Equation A4 in terms of labile Ni rather than  $\text{Ni}^{2+}$ , because the labile Ni concentration is measured directly (Equation A6). Therefore substitution of  $[\text{Ni}^{2+}]$  in Equation A4 by using Equation A7 gives:

$$[\text{Ni}_{\text{lab}}]/[\text{NiL}] = [\text{Ni}_{\text{lab}}]/C_L + \alpha' / (K'_{\text{NiL}} C_L) \quad (\text{A11})$$

For each aliquot of the titration,  $[\text{NiL}]$  can be calculated from the mass balance:

$$[\text{NiL}] = C_{\text{Ni}} - [\text{Ni}_{\text{lab}}] \quad (\text{A12})$$

The total Ni concentration,  $C_{\text{Ni}}$ , is that present in the initial sample plus that added during the titration (which is a known amount). The total Ni concentration in the initial sample is determined by ACSV upon UV-irradiation of the sample.

In order to calculate values for  $C_L$  and  $K'_{\text{NiL}}$ , the quantity  $[\text{Ni}_{\text{lab}}]/[\text{NiL}]$  is plotted versus  $[\text{Ni}_{\text{lab}}]$ . A linear least-square regression of the linearized plot gives then the values of  $1/C_L$  (slope) and  $\alpha' / (K'_{\text{NiL}} C_L)$  (Y-intercept).

## A2.2. The calculation of Ni speciation in natural water samples

The total Ni concentration in the original water sample (in absence of DMG) is given by:

$$C_{\text{Ni}} = [\text{Ni}'] + [\text{NiL}] \quad (\text{A13})$$

where  $[Ni']$  represents the sum of all Ni inorganic complexes. Equation A13 can be written as:

$$C_{Ni} = [Ni^{2+}] (\alpha_{Ni'} + \alpha_{NiL}) \quad (A14)$$

where  $\alpha_{Ni'}$  is the  $\alpha$ -coefficient for Ni-inorganic side reactions (Equation A9), and  $\alpha_{NiL}$  is the  $\alpha$ -coefficient for the complex formation of  $Ni^{2+}$  with L:

$$\alpha_{NiL} = K'_{NiL} [L'] \quad (A15)$$

The concentration of  $Ni^{2+}$  can be calculated by combining Equations A14 and A15:

$$[Ni^{2+}] = C_{Ni} / (\alpha_{Ni'} + K'_{NiL} [L']) \quad (A16)$$

In Equation A16, the only unknowns are  $[L']$  and  $[Ni^{2+}]$  in the natural water sample; an expression for  $[L']$  can be derived by combining Equations A2 and A3:

$$[L'] = C_L / (1 + [Ni^{2+}] K'_{NiL}) \quad (A17)$$

Equation A16 can be therefore solved for  $[Ni^{2+}]$  by substitution of  $[L']$  from Equation A17.

The resulting expression is a second-order equation where  $[Ni^{2+}]$  is the only unknown:

$$(\alpha_{Ni'} K'_{NiL}) [Ni^{2+}]^2 + (\alpha_{Ni'} + K'_{NiL} C_L - K'_{NiL} C_{Ni}) [Ni^{2+}] - C_{Ni} = 0 \quad (A18)$$

Once  $[Ni^{2+}]$  is known, it is possible to calculate  $[Ni']$  from the following equation:

$$[Ni'] = [Ni^{2+}] \alpha_{Ni'} \quad (A19)$$

The concentration of  $[NiL]$  can be therefore calculated from Equation A13, and  $[L']$  can be then calculated from Equation A3.

## APPENDIX 3

### CHARACTERIZATION OF PARTICLES USED FOR THE RADIOTRACER EXPERIMENTS

Prior to physico-chemical characterization, the wet-sieved particles (< 63  $\mu\text{m}$ ) were frozen and subsequently freeze-dried for 48 hours. The particles were then stored in a dessiccator until further analyses.

#### A3.1. Specific surface area analysis

Specific surface area was determined by a BET  $\text{N}_2$  adsorption method using a Micromeritics Gemini 2360 surface area analyzer (Millward et al., 1990). Kaolinite, supplied by Micromeritics, was used as reference material: although this material is not a certified standard reference material, it was repeatedly analysed within the supplier's laboratories using different instruments and different operators. The results of analyses of the reference material carried out for this study ( $15.9 \pm 0.3 \text{ m}^2\text{g}^{-1}$ ) well compare with the certified value ( $15.9 \pm 0.8 \text{ m}^2\text{g}^{-1}$ ).

#### A3.2. Particulate organic carbon analysis

Particulate organic carbon was determined by Ms. P. Sammes (Marine Biological association), using a Carlo Erba NA1500 Series 2 N/C/S Autoanalyser.

#### A3.3. Particulate trace metals analysis

About 100 mg of the freeze-dried particles were accurately weighed and transferred to a PTFE beaker: they were extracted for 16 hours at room temperature in 10 ml of a solution of 0.05 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25 % v/v  $\text{CH}_3\text{COOH}$  (both BDH AristaR) at pH 3. The mixture was filtered (acid-washed, cellulose acetate Sartorius 0.45  $\mu\text{m}$  pore size filters) and the filtrate was made up to 25 ml using the  $\text{NH}_2\text{OH}\cdot\text{HCl}$  /  $\text{CH}_3\text{COOH}$  solution. This digest is believed to selectively remove Fe and Mn surface coatings and associated trace



metals (Tessier et al., 1979), and has been widely used in our laboratories (Millward et al. 1990; Turner et al., 1994, Liu et al., 1998).

Certified reference material (marine sediment PACS-1) was digested and analysed along with the particle samples to evaluate the recovery of the digestion method. Operational blanks were carried out using exactly the same procedures as for the samples, but in absence of the particles.

Particulate Fe, Mn, Al and Ca were determined by flame atomic adsorption spectrometry in the two sets of digests. The instruments used were a Varian SpectrAA 400 Plus (for Fe, Mn and Ca), and a GBC 902 (for Al) spectrophotometers. Manipulation of samples and reagents was carried out under a class-100 laminar flow hood. Standard solutions of Fe, Mn, Al, Ca and Mg were prepared by dilution of atomic absorption (Spectrosol, BDH) stock solutions. The standards were made up in 0.05 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  / 25 % v/v  $\text{CH}_3\text{COOH}$ . For each metal, a calibration curve was made using four standards; five analyses of each standard were carried out and a calibration curve passing from zero was built using the mean absorbance of the standards. Samples were analysed in duplicate. For each sample, five determinations were made and the reagent blank and standards analysed again at the end of each analysis to check for any drifts in absorbance. Samples for Mg analyses were diluted 100 times prior to the determinations in order for their concentration to fall within the calibration range. The instrumental conditions for the analyses are shown in Table A3.1.

Blanks, detection limits and calibration ranges are shown in Table A3.2. The instrumental detection limit was calculated as three times the standard deviation of five determinations of the blanks. Recoveries for the analysis of the PACS-1 materials are shown in Table A3.3.

**Table A3.1.** Instrumental conditions used for the determination of particulate trace metals.

Parameter/condition	Fe	Mn	Al	Ca
Flame type	Air/C <sub>2</sub> H <sub>2</sub>	Air/C <sub>2</sub> H <sub>2</sub>	N <sub>2</sub> O C <sub>2</sub> H <sub>2</sub>	Air/C <sub>2</sub> H <sub>2</sub>
Wavelength (nm)	372	279.5	285.2	422.7
Slit width (nm)	0.2	0.2	0.5	0.5
Beam	Single	Single	Single	Single
Replicates	5	5	5	5

**Table A3.2.** Blanks, detection limits and standards for particulate trace metal determinations in 0.05 M NH<sub>2</sub>OH.HCl / 25 % v/v CH<sub>3</sub>COOH.

Parameter	Fe	Mn	Al	Ca
Detection limit (μmol/l)	2	0.2	6.1	1.2
Operational blank (μmol/l)	n.d. <sup>a</sup>	n.d. <sup>a</sup>	n.d. <sup>a</sup>	n.d. <sup>a</sup>
Calibration range (μmol/l)	0-1450	0-75	0-450	0-250

<sup>a</sup> below the detection limit.

**Table A3.3.** Recoveries for the PACS-1 material.

	Fe	Mn	Al	Ca
Analysed (μmol/g) <sup>a</sup>	178 ± 2	1.19 ± 0.1	86.4 ± 0.7	86.2 ± 0.6
Certified (μmol/g)	435 ± 7	8.6 ± 0.2	1200 ± 22	521 ± 22
Recovery (%)	40.8	13.9	7.2	16.5

<sup>a</sup> The error represents the spread of two determinations.

## APPENDIX 4

### MASTER VARIABLES AND DISSOLVED TRACE METAL CONCENTRATIONS FROM FIELD STUDIES

Throughout the following tables, the station numbers correspond to those shown in the maps of the estuaries (Figures 2.1, 2.2, 2.3). Moreover, the following abbreviations are used throughout the table headings:

D	Distance from tidal limit (km)
C	Conductivity (mS)
S	Salinity
T	Temperature (°C)
DO <sub>2</sub>	Dissolved oxygen (% saturation)
SPM	Suspended particulate matter (mg l <sup>-1</sup> )
DOC	Dissolved organic carbon (mg C l <sup>-1</sup> )
LOI	Loss on ignition (% weight)
Chl-a	Chlorophyll-a (µg l <sup>-1</sup> )
Ni <sub>T</sub>	Total dissolved Ni (nM)
Ni <sub>lab</sub>	ACSV-labile dissolved Ni (nM)
Co <sub>T</sub>	Total dissolved Co (nM)
Zn <sub>T</sub>	Total dissolved Zn (nM)
Cu <sub>T</sub>	Total dissolved Cu (nM)
Cd <sub>T</sub>	Total dissolved Cd (nM)
Pb <sub>T</sub>	Total dissolved Pb (nM)

**Table A4.1.** Tamar Estuary, 14 October '96. Master variables and dissolved Ni.

Sample	Time (h:min)	Station	D (km)	C (mS)	S	T (°C)	pH	DO <sub>2</sub> (% sat.)	SPM (mg l <sup>-1</sup> )	Ni <sub>T</sub> (nM)	Ni <sub>lab</sub> (nM)
TA1	12:13	1	0.50	0.12	0.1	13.0	8.0	97.5	285 ± 10	46 ± 2	5.9 ± 0.5
TA2	12:30	2	0.80	0.12	0.1	13.0	7.8	97.8	330 ± 20	42 ± 2	4.4 ± 0.2
TA3	14:00	3	9.40	0.8	0.64	13.4	7.8	72.3	1580 ± 45	40.2 ± 0.9	5.3 ± 0.9
TA4	14:30	4	13.15	1.2	1.0	13.4	7.7	74.5	1070 ± 30	36 ± 1	8.5 ± 0.4
TA5	14:50	5	13.55	1.7	1.6	13.5	7.7	75	450 ± 20	40 ± 2	14.7 ± 0.8
TA6	15:00	6	14.65	4.0	3.6	13.6	7.5	78.2	180 ± 15	43 ± 2	19 ± 1.8
TA7	15:12	7	14.90	10	5.75	13.6	7.6	82.2	130 ± 20	43 ± 1	21 ± 2
TA8	15:20	8	15.65	24	10.5	13.8	7.5	81.2	170 ± 15	39.8 ± 0.4	22.4 ± 0.4
TA9	15:35	9	17.15	36	17.4	13.8	7.6	81	80 ± 8	36.0 ± 0.9	25 ± 2
TA10	16:00	10	19.65	42	26.4	14.2	7.5	83.3	53 ± 5	31 ± 1	19.7 ± 0.5



**Table A4.2. Tweed Estuary master variables (continued)**

Sample	Date	Time (h:min)	Station	D (km)	C (mS)	S	T (°C)	pH	DO <sub>2</sub> (% sat.)	SPM (mg l <sup>-1</sup> )
TW20-A1	22-Sep-98	12:25		13.2	40.5	33.8	13.6	8.10	86.2	
TW20-A2	"	12:44		13.1	39.0	32.5	12.8	8.09	92.8	
TW20-A3	"	13:00	3	13.0	22.0	18.3	12.8	8.10	90.5	
TW20-A4	"	13:10		12.5	22.0	18.3	13.4	8.20	68.8	
TW20-A5	"	14:45	15	5.3	0.26	0.2	14.5	8.00	79.5	
TW20-A6	"	14:50	14	6.0	0.26	0.2	14.4	7.97	80.6	
TW20-A7	"	15:00	13	6.7	0.26	0.2	14.4	8.15	80.1	
TW20-A8	"	15:10	12	7.7	0.30	0.3	14.3	8.54	80.9	
TW20-A9	"	15:20	11	7.8	0.42	0.4	14.3	8.48	78.8	
TW20-A10	"	15:30	10	8.5	2.60	2.2	14.6	8.14	77.1	
TW20-A11	"	15:40	9	8.7	6.80	5.7	14.8	8.20	74.3	
TW20-A12	"	16:00		8.8	7.50	6.3	14.6	8.18	70.3	
TW20-A13	"	16:20		8.9	7.60	6.3	14.6	8.03	76.6	
TW20-A14	"	16:50	8	9.2	21.0	17.5	14.3	8.31	76.1	
TW20-A15	"	16:55	7	9.6	10.0	8.3	14.1	7.91	68.8	
TW20-A16	"	17:10		10.6	23.0	19.2	13.8	8.13	71.4	
TW20-A17	"	17:20	5	11.1	37.5	31.3	13.3	8.10	74.5	
TW20-A18	"	17:30	4	12.0	40.5	33.8	13.0	8.08	74.0	
TW20-A19	"	09:10	20	2.6	0.2	0.2	13.9	7.66	77.0	

**Table A4.2.** Tweed Estuary master variables (continued)

Sample	DOC (mg C l <sup>-1</sup> )	Chl-a (µg l <sup>-1</sup> )
TW4-A3	3.1 ± 0.2	0.76
TW4-A4		0.24
TW4-A5	4.3 ± 0.1	0.29
TW4-A6	5.26 ± 0.03	0.48
TW4-A7	5.3 ± 0.1	0.10
TW4-A8	5.5 ± 0.3	0.38
TW4-A9	5.3 ± 0.1	0.24
TW4-A10	5.5 ± 0.3	0.33
TW4-A11		0.31
TW4-A12		0.19
TW4-A13		0.38
TW4-A14	5.59 ± 0.05	0.29
TW4-A15		0.26
TW4-A16		0.33
TW4-A17	4.76 ± 0.07	0.52
TW4-A18		0.29
TW4-A19	5 ± 0.1	0.31
TW4-A20	5.8 ± 0.3	0.36
TW4-P	4.55 ± 0.15	
TW11-A4	2.5 ± 1	0.76
TW11-A6	1.4 ± 0.2	0.57
TW11-A8	2.1 ± 0.2	0.53
TW11-A10	2.3 ± 0.4	0.14
TW11-A12	3.1 ± 0.1	0.12
TW11-A14	2.8 ± 0.2	0.31
TW11-A16	2.9 ± 0.4	0.53
TW11-A18	3.1 ± 0.1	0.45
TW11-A20	3.1 ± 0.1	0.15
TW20-A1	2.1 ± 0.2	
TW20-A2	2.1 ± 0.2	
TW20-A3	2.5 ± 0.2	
TW20-A4	3.5 ± 0.2	
TW20-A5	3.9 ± 0.2	
TW20-A6	4.4 ± 0.3	
TW20-A7	4.1 ± 0.1	
TW20-A8	4.1 ± 0.2	
TW20-A9	4.2 ± 0.1	
TW20-A10	4.4 ± 0.3	
TW20-A11	4.2 ± 0.3	
TW20-A12	3.9 ± 0.2	
TW20-A13	4 ± 0.3	
TW20-A14	3.6 ± 0.1	
TW20-A15	2.9 ± 0.1	
TW20-A16	3.9 ± 0.2	
TW20-A17	2.4 ± 0.3	
TW20-A18	2.8 ± 0.1	

**Table A4.3.** Tweed Estuary dissolved Ni.

Sample	Ni <sub>T</sub> (nM)	Ni <sub>lab</sub> (nM)
TW4-A3	16.0 ± 0.2	
TW4-A4	16.2 ± 0.4	6.9 ± 0.7
TW4-A5	16.5 ± 0.1	10.3 ± 0.9
TW4-A6	16.0 ± 1.4	6.0 ± 0.35
TW4-A7	17.4 ± 1.0	8.5 ± 1.3
TW4-A8	15.6 ± 0.2	9.5 ± 2.0
TW4-A9	12.6 ± 0.8	7.3 ± 0.2
TW4-A10	13.2 ± 0.8	
TW4-A11	14.1 ± 2.0	
TW4-A12	18.4 ± 1.7	
TW4-A15	15.8 ± 1.2	5.2 ± 0.8
TW4-A16	12.7 ± 0.4	
TW4-A20	12.5 ± 0.8	7.1 ± 0.2
TW4-P	13.8 ± 0.2	6.6 ± 0.05
TW4-T21	8.1 ± 0.1	
TW4-T22	12.7 ± 1.0	
TW4-T23	9.7 ± 0.4	
TW4-T24	18.1 ± 1.5	
TW4-T25	14.1 ± 1.4	
TW4-T26	11.0 ± 0.9	
TW4-T27	21.7 ± 0.5	
TW4-T28	33.5 ± 0.5	
A20/TW11	6.8 ± 0.1	4.6 ± 0.4
A18/TW11	8.2 ± 0.2	3.1 ± 0.2
A16/TW11	7.4 ± 0.4	3.2 ± 0.2
A14/TW11	7.4 ± 0.2	2.1 ± 0.2
A12/TW11	6.3 ± 0.6	2.6 ± 0.2
A10/TW11	7.0 ± 0.5	2.8 ± 0.2
A8/TW11		2.0 ± 0.1
A6/TW11	4.5 ± 0.2	2.7 ± 0.1
A4/TW11	4.2 ± 0.3	2.2 ± 0.1
MEM3/TW11	4.0 ± 0.1	
MEM4/TW11	4.2 ± 0.6	2.2 ± 0.1
MEM6/TW11	4.3 ± 0.3	2.5 ± 0.1
REM3/TW11	7.3 ± 0.1	
REM4/TW11	6.8 ± 0.4	4.6 ± 0.1
REM6/TW11	7.9 ± 0.1	4.8 ± 0.1
TW20-A1	2.9 ± 0.1	1.6 ± 0.1
TW20-A2	2.7 ± 0.1	1.45 ± 0.08
TW20-A3	4.0 ± 0.1	2.0 ± 0.2
TW20-A4	4.32 ± 0.1	3.11 ± 0.01
TW20-A5	7.8 ± 0.3	5.2 ± 0.6
TW20-A6	6.5 ± 0.2	4.3 ± 0.2
TW20-A7	6.2 ± 0.1	3.4 ± 0.5
TW20-A8	7.7 ± 0.1	2.8 ± 0.1
TW20-A9	6.9 ± 0.3	4.4 ± 0.3
TW20-A10	6.9 ± 0.1	3.6 ± 0.1
TW20-A11	7.30 ± 0.01	3.5 ± 0.2
TW20-A12	7.2 ± 0.1	2.9 ± 0.2
TW20-A13	6.2 ± 0.2	3.6 ± 0.2
TW20-A14	5.37 ± 0.09	3.4 ± 0.3
TW20-A15	5.45 ± 0.07	3.6 ± 0.1
TW20-A16	4.3 ± 0.1	1.5 ± 0.1
TW20-A17	3.7 ± 0.2	1.45 ± 0.01
TW20-A18	4.07 ± 0.09	2.6 ± 0.3





**Table A4.4. Mersey Estuary master variables (continued)**

Sample	Date	Time (h:min)	Station	D (km)	S	T (°C)	pH	DO <sub>2</sub> (% sat.)	SPM (mg l <sup>-1</sup> )
M4-HW1	24-Jun-98		S1	-0.1*	0.3	17.3	7.03	53.3	9 ± 1
M4-HW2	25-Jun-98		S1	-0.1*	0.3	17.5	7.03	54.7	6 ± 1
M5-4	20-Oct-98	09:50	4	55.1	31.2	11.1	7.88	92.0	218 ± 38
M5-5	"	10:03	5	50.0	30.9	10.9	7.91	90.0	131 ± 2
M5-6	"	10:16	6	46.2	31.6	10.9	7.92	92.0	154 ± 6
M5-7	"	10:27	7	42.4	29.7	10.9	7.84	89.0	178 ± 0
M5-8	"	10:37	8	39.3	28.6	11.0	7.68	86.0	185 ± 1
M5-9	"	10:46	9	36.0	26.6	10.9	7.66	83.0	129 ± 2
M5-10	"	10:57	10	32.6	23.2	10.9	7.61	77.0	122 ± 28
M5-11	"	11:36	11	30.1	21.3	10.8	7.60	76.0	61 ± 1
M5-12	"	11:43	12	26.4	21.8	10.8	7.57	76.0	133 ± 1
M5-13	"	11:51	13	25.0	14.8	10.3	7.50	78.0	63 ± 8
M5-14	"	01:57	14	20.6	16.1	10.4	7.54	77.0	66 ± 2
M5-15	"	12:06	15	17.5	8.3	10.0	7.52	77.0	116 ± 25
M5-16	"	12:14	16	15.4	9.4	10.0	7.56	77.0	168 ± 12
M5-17	"	12:23	17	12.8	4.2	10.0	7.51	77.0	347 ± 18
M5-18	"	12:30	18	11.1	2.2	10.2	7.39	77.0	287 ± 6
M5-19	"	12:41	19	8.6	0.3	10.5	7.57	83.0	230 ± 7
M5-20	"	12:52	20	7.2	0.3	10.5	7.44	85.0	63 ± 11
M5-21	"	12:59	21	6.1	0.3	10.8	7.50	87.0	57 ± 1
M5-22	"	13:04	22	4.8	0.2	10.5	7.39	87.0	31 ± 1
M5-HW	"	17:00	S1	-0.1*	0.2		7.2		34 ± 2

\*Freshwater sample collected 100 m above the weir

**Table A4.4. Mersey Estuary master variables (continued)**

Sample	DOC (mg C l <sup>-1</sup> )	Chl-a (µg l <sup>-1</sup> )	LOI (%)
M2-5		7.14*	18.7 ± 0.2
M2-6			18.1 ± 0.0
M2-7		9.28*	16.8 ± 0.2
M2-8			15.2 ± 0.1
M2-9		5.61*	17.3 ± 0.2
M2-10			18.2 ± 0.3
M2-11			16.6 ± 0.2
M2-16		8.39*	15.3 ± 0.1
M2-19		48.2*	11.4 ± 0.1
M2-22			19.0 ± 0.8
M2-23			37.8 ± 3.8
M2-HW			45.5 ± 2.0
M3-5	2.7 ± 0.4	11.2	
M3-6	2.7 ± 0.2		
M3-7	2.8 ± 0.2	14.6	
M3-8			
M3-9	3.2 ± 0.1	12.9	
M3-10	3.7 ± 0.2		
M3-11	4.9 ± 0.3		
M3-12	4.4 ± 0.2		
M3-13	4.1 ± 0.3		
M3-14	4.0 ± 0.2		
M3-15	4.9 ± 0.5		
M3-16	4.7 ± 0.2	19.0	
M3-17	5.8 ± 0.1		
M3-18	7.1 ± 0.2		
M3-19	6.6 ± 0.1	20.9	
M3-20	7.6 ± 0.3		
M3-21	7.9 ± 0.1		
M3-22	9.0 ± 0.3		
M3-HW1	10.6 ± 0.2		
M3-HW2	11.3 ± 0.2		
M4-3	1.0 ± 0.1		
M4-4	1.5 ± 0.1		
M4-5	1.7 ± 0.3	9.2	
M4-6	1.5 ± 0.3		
M4-7	1.8 ± 0.1	11.4	
M4-8	1.8 ± 0.2		
M4-9	2.3 ± 0.3	16.8	
M4-10	2.8 ± 0.3		
M4-11	2.9 ± 0.3		
M4-12	3.3 ± 0.3		
M4-13	3.4 ± 0.3		
M4-14	3.6 ± 0.2		
M4-15	4.8 ± 0.3		
M4-16	4.4 ± 0.2	19.5	
M4-17	5.1 ± 0.3		
M4-18	5.9 ± 0.2		
M4-19	6.7 ± 0.3	44.6	
M4-20	7.3 ± 0.2		
M4-21	8.1 ± 0.2		
M4-22	8.6 ± 0.2		

\* The chlorophyll-a data are from the 15-Dec-97 EA survey.

**Table A4.4. Mersey Estuary master variables (continued)**

Sample	DOC (mg C l <sup>-1</sup> )	Chl-a (µg l <sup>-1</sup> )
M4-HW1	9.7 ± 0.1	
M4-HW2	9.3 ± 0.2	
M5-4	1.9 ± 0.3	
M5-5	2.1 ± 0.1	15
M5-6	1.5 ± 0.2	
M5-7	2.3 ± 0.2	13.9
M5-8	2.3 ± 0.1	
M5-9	3.0 ± 0.1	10.2
M5-10	3.1 ± 0.2	
M5-11	4.0 ± 0.1	
M5-12	4.0 ± 0.3	
M5-13	4.9 ± 0.3	
M5-14	4.9 ± 0.2	
M5-15	6.5 ± 0.3	
M5-16	6.0 ± 0.3	15.2
M5-17	7.6 ± 0.3	
M5-18	7.6 ± 0.3	
M5-19	8.1 ± 0.2	8.57
M5-20	8.1 ± 0.2	
M5-21	8.4 ± 0.3	
M5-22	8.8 ± 0.3	
M5-HW	9.2 ± 0.3	

**Table A4.5. Mersey Estuary dissolved trace metals**

Sample	Ni <sub>T</sub> (nM)	Ni <sub>lab</sub> (nM)	Co <sub>T</sub> (nM)	Zn <sub>T</sub> (nM)	Cu <sub>T</sub> (nM)
M2-5	29 ± 2	8.5 ± 0.9	1.5 ± 0.1	116 ± 2	40 ± 1
M2-6	53 ± 1	31.1 ± 0.9	3.4 ± 0.1	127 ± 6	32 ± 2
M2-7	31 ± 2	12 ± 1	2.2 ± 0.1	142 ± 14	31 ± 4
M2-8	32 ± 1	13.7 ± 0.1	2.8 ± 0.1	148 ± 5	42 ± 1
M2-9	42 ± 1	13.9 ± 0.9	4 ± 0.1	487 ± 26	55 ± 4
M2-10	63 ± 1	24.8 ± 1.5	6.7 ± 0.1	207 ± 6	62 ± 2
M2-11	45 ± 3	23 ± 1	5.3 ± 0.4	232 ± 11	50 ± 4
M2-16	79 ± 3	40.5 ± 0.3	17.8 ± 0.4	220 ± 6	38 ± 3
M2-19	102 ± 3	38 ± 3	35 ± 0.4	175 ± 12	38 ± 3
M2-22	109 ± 1	34.0 ± 0.1	26 ± 0.5	167 ± 6	64 ± 3
M2-23	114 ± 3	33.1 ± 0.6	23.6 ± 1.5	169 ± 4	65 ± 3
M2-HW	102 ± 3	49.2 ± 0.3	19 ± 0.4	147 ± 2	68 ± 1
M3-5	26 ± 1	9.75 ± 0.6	1.9 ± 0.1	158 ± 1	28 ± 2
M3-6	30 ± 2	11.3 ± 0.4	2.8 ± 0.4	196 ± 2	30 ± 1
M3-7	30 ± 2	11.3 ± 0.8	2.3 ± 0.2	179 ± 6	27 ± 1.0
M3-9	38 ± 2	19 ± 3	3.2 ± 0.2	262 ± 11	34.0 ± 0.9
M3-10	57 ± 5	20.5 ± 0.7	4.5 ± 0.2	291 ± 3	33 ± 3
M3-11	88 ± 8	68.3 ± 14.5	11 ± 1	278 ± 22	40 ± 3
M3-12	65 ± 2	21 ± 3	5 ± 0.3	270 ± 26	41 ± 1
M3-13	67 ± 4	25 ± 3	5.6 ± 0.4	252 ± 11	39 ± 1
M3-14	75 ± 12	30.3 ± 0.4	8.1 ± 2	257 ± 10	42 ± 3
M3-15	92 ± 12	41 ± 3	15 ± 3	273 ± 14	47 ± 3
M3-16	103 ± 4	42 ± 4	14 ± 0.7	262 ± 8	47 ± 0.7
M3-17	122 ± 11	44 ± 2	14 ± 2	307 ± 1	63.8 ± 0.1
M3-18	127 ± 6	44 ± 1	21 ± 3	260 ± 35	51 ± 1.5
M3-19	136 ± 4	51 ± 2	27 ± 3	225 ± 3	39 ± 0.5
M3-20	137 ± 13	59.2 ± 0.2	36 ± 1	211 ± 4	49 ± 3
M3-21	134 ± 5	58 ± 2	30.5 ± 0.5	248 ± 3	50.0 ± 0.3
M3-22	146 ± 3	59.4 ± 0.4	37 ± 0.2	176 ± 6	65.3 ± 0.1
M3-HW1	131 ± 10	56.9 ± 0.9	26 ± 3	313 ± 2	89 ± 0.8
M3-HW2	138 ± 5	53.0 ± 0.8	30 ± 4	249 ± 6	94 ± 0.1
M4-3	8.6 ± 0.1	4.3 ± 0.3	0.8 ± 0.11	49 ± 1	24 ± 0.07
M4-4	8.6 ± 0.1	4.53 ± 0.01	0.8 ± 0.06	108 ± 4	23 ± 0.07
M4-5	9.6 ± 1.1	5.1 ± 0.2	0.9 ± 0.09	55 ± 3	25 ± 1
M4-6	9.5 ± 0.1	4.9 ± 0.3	0.9 ± 0.03	43 ± 3	24 ± 0.4
M4-7	13 ± 2	5.8 ± 0.7	1.0 ± 0.2	114 ± 8	26 ± 2
M4-8	16.4 ± 0.9	5.3 ± 0.6	1.5 ± 0.1	72 ± 2	27 ± 2
M4-9	18 ± 3	6.4 ± 0.3	1.74 ± 0.09	79 ± 1	29 ± 1
M4-10	31 ± 1	13.7 ± 0.2	2.4 ± 0.3	133 ± 2	39 ± 1
M4-11	48.0 ± 0.4	19.9 ± 0.3	3.2 ± 0.2	141 ± 9	39 ± 1
M4-12	60.1 ± 0.8	22.0 ± 0.4	4.1 ± 0.1	192 ± 6	45 ± 0.5
M4-13	64.0 ± 0.9	24.9 ± 0.8	5.6 ± 0.3	186 ± 10	36 ± 1
M4-14	90 ± 1	30.3 ± 0.3	6.1 ± 0.1	221 ± 6	42 ± 2
M4-15	103 ± 4	39 ± 3	14 ± 1.2	241 ± 23	42 ± 3
M4-16	109 ± 9	34.6 ± 0.5	12 ± 0.7	252 ± 7	52 ± 3
M4-17	118 ± 2	47.3 ± 0.1	17 ± 0.3	267 ± 17	52 ± 0.1
M4-18	146 ± 12	53 ± 5	22 ± 1.1	314 ± 14	57 ± 0.4
M4-19	168 ± 1	53 ± 3	31 ± 1.3	240 ± 28	44 ± 2
M4-20	184 ± 4	59 ± 5	34 ± 0.5	274 ± 26	53 ± 1
M4-21	228 ± 6	65 ± 1	41 ± 1.4	222 ± 6	59 ± 1

**Table A4.5. Mersey Estuary dissolved trace metals (continued)**

Sample	Ni <sub>T</sub> (nM)	Ni <sub>lab</sub> (nM)	Co <sub>T</sub> (nM)	Zn <sub>T</sub> (nM)	Cu <sub>T</sub> (nM)
M4-22	196 ± 3	57 ± 2	34 ± 1	212 ± 8	70 ± 1
M4-HW1	203 ± 5	55 ± 8	16 ± 0.1	249 ± 3	55 ± 2
M4-HW2	174 ± 3	68 ± 2	24 ± 0.7	258 ± 10	45 ± 2
M5-4	13.4 ± 0.4	5.7 ± 0.2	1.5 ± 0.1	129 ± 6	37 ± 0.3
M5-5	12.4 ± 0.6	5.7 ± 0.2	1.0 ± 0.1	214 ± 2	38 ± 2
M5-6	12 ± 1	5.5 ± 0.2	0.8 ± 0.02	130 ± 4	33 ± 2
M5-7	15.9 ± 0.2	7.9 ± 0.0	1.54 ± 0.04	193 ± 12	45 ± 0.1
M5-8	17 ± 2	8 ± 1	1.56 ± 0.06	240 ± 2	54 ± 3
M5-9	23 ± 2	14 ± 3	2.5 ± 0.2	250 ± 9	66 ± 2
M5-10	36 ± 1	18.2 ± 0.9	3.1 ± 0.05	258 ± 2	69 ± 2
M5-11	39 ± 1	18.9 ± 0.5	3.6 ± 0.1	237 ± 12	64 ± 0.8
M5-12	42 ± 2	18.3 ± 0.2	3.9 ± 0.2	254 ± 22	81 ± 0.8
M5-13	50.6 ± 0.6	20.7 ± 0.4	6.7 ± 0.4	227 ± 7	65 ± 3
M5-14	51 ± 4	21 ± 1	6.2 ± 0.2	260 ± 4	64 ± 0.6
M5-15	52 ± 2	38 ± 1	14 ± 0.3	191 ± 3	63 ± 3
M5-16	54 ± 2	24 ± 1	11 ± 1	223 ± 11	68 ± 3
M5-17	58 ± 3	25.3 ± 0.7	17 ± 0.4	239 ± 3	73 ± 2
M5-18	60 ± 1	25.1 ± 0.6	17 ± 0.4	221 ± 3	81 ± 0.1
M5-19	59 ± 1	19.9 ± 0.5	12 ± 0.8	187 ± 6	86 ± 2
M5-20	54 ± 2	18.0 ± 0.4	8.9 ± 0.1	243 ± 10	81 ± 5
M5-21	48 ± 1	17 ± 1	8.6 ± 0.3	261 ± 13	72 ± 2
M5-22	54 ± 3	19.3 ± 0.6	8.7 ± 0.1	215 ± 4	75 ± 1
M5-HW	51 ± 2	16.2 ± 0.6	6.9 ± 0.05	194 ± 9	85 ± 3

**Table A4.5. Mersey Estuary dissolved trace metals (continued)**

Sample	Cd <sub>T</sub> (nM)	Pb <sub>T</sub> (nM)
M2-5	0.69 ± 0.1	1.11 ± 0.08
M2-6	0.71 ± 0.1	1.25 ± 0.2
M2-7	0.54 ± 0.1	1.15 ± 0.3
M2-8	0.58 ± 0.05	2.33 ± 0.04
M2-9	1.8 ± 0.2	2.95 ± 0.3
M2-10	1.7 ± 0.1	3.15 ± 0.5
M2-11	1.42 ± 0.3	2.75 ± 0.6
M2-16	4.3 ± 0.7	4.25 ± 0.5
M2-19	0.26 ± 0.06	3.93 ± 0.07
M2-22	0.66 ± 0.17	2.05 ± 0.4
M2-23	0.4 ± 0.09	1.43 ± 0.05
M2-HW	0.38 ± 0.03	2.14 ± 0.01
M3-5	0.8 ± 0.05	1.0 ± 0.05
M3-6	0.9 ± 0.06	1.8 ± 0.2
M3-7	0.62 ± 0.05	0.9 ± 0.3
M3-9	0.68 ± 0.06	1.6 ± 0.1
M3-10	1.4 ± 0.2	2.7 ± 0.3
M3-11	0.9 ± 0.2	2.8 ± 0.2
M3-12	0.83 ± 0.08	3.0 ± 0.1
M3-13	1.13 ± 0.01	3.0 ± 0.1
M3-14	2.23 ± 0.05	3.0 ± 0.1
M3-15	1.7 ± 0.18	4.4 ± 1
M3-16	2.0 ± 0.08	3.7 ± 0.3
M3-17	2.09 ± 0.06	4.1 ± 0.1
M3-18	3.7 ± 0.2	5.3 ± 0.5
M3-19	1.0 ± 0.05	4.6 ± 0.1
M3-20	1.17 ± 0.01	5.6 ± 0.9
M3-21	0.94 ± 0.06	4 ± 0.4
M3-22	0.41 ± 0.06	2.3 ± 0.6
M3-HW1	1.34 ± 0.03	2.2 ± 0.1
M3-HW2	0.75 ± 0.04	2.66 ± 0.01
M4-3	0.36 ± 0.07	0.31 ± 0.01
M4-4	1.5 ± 0.1	0.42 ± 0.06
M4-5	0.29 ± 0.08	0.63 ± 0.09
M4-6	0.35 ± 0.03	0.65 ± 0.02
M4-7	0.95 ± 0.04	1.0 ± 0.1
M4-8	0.8 ± 0.1	1.1 ± 0.2
M4-9	0.51 ± 0.05	0.91 ± 0.02
M4-10	0.69 ± 0.05	1.6 ± 0.3
M4-11	1.0 ± 0.1	1.6 ± 0.1
M4-12	1.0 ± 0.1	1.7 ± 0.1
M4-13	0.77 ± 0.03	1.19 ± 0.06
M4-14	1.07 ± 0.01	2.0 ± 0.1
M4-15	0.65 ± 0.08	2.94 ± 0.06
M4-16	0.96 ± 0.03	3.02 ± 0.04
M4-17	0.60 ± 0.04	3.3 ± 0.1
M4-18	1.4 ± 0.1	3.86 ± 0.06
M4-19	0.87 ± 0.01	4.9 ± 0.3
M4-20	0.9 ± 0.1	6.0 ± 0.3
M4-21	0.6 ± 0.1	4.0 ± 0.2
M4-22	0.43 ± 0.04	3.1 ± 0.3
M4-HW1	0.50 ± 0.09	2.4 ± 0.2
M4-HW2	0.48 ± 0.08	2.37 ± 0.1

**Table A4.5. Mersey Estuary dissolved trace metals (continued)**

Sample	Cd <sub>T</sub> (nM)	Pb <sub>T</sub> (nM)
M5-4	1.5 ± 0.2	2.5 ± 0.2
M5-5	1.5 ± 0.1	1.50 ± 0.04
M5-6	1.3 ± 0.1	2.0 ± 0.1
M5-7	1.5 ± 0.1	1.9 ± 0.1
M5-8	1.54 ± 0.02	1.3 ± 0.1
M5-9	1.58 ± 0.08	2.08 ± 0.02
M5-10	1.38 ± 0.09	2.8 ± 0.1
M5-11	1.44 ± 0.03	3.0 ± 0.1
M5-12	1.62 ± 0.05	2.7 ± 0.1
M5-13	1.0 ± 0.2	3.28 ± 0.02
M5-14	1.33 ± 0.05	3.73 ± 0.07
M5-15	0.72 ± 0.05	2.87 ± 0.05
M5-16	0.8 ± 0.1	3.9 ± 0.2
M5-17	0.53 ± 0.01	3.59 ± 0.05
M5-18	0.53 ± 0.03	2.70 ± 0.08
M5-19	0.44 ± 0.02	3.7 ± 0.1
M5-20	0.50 ± 0.02	3.9 ± 0.1
M5-21	0.55 ± 0.03	4.3 ± 0.1
M5-22	0.5 ± 0.1	2.89 ± 0.01
M5-HW	0.48 ± 0.02	2.9 ± 0.2

## APPENDIX 5

### LABORATORY DATA FROM PROCESS-ORIENTATED STUDIES

**Table A5.1. Salinity gradient**

Tamar Estuary			
Salinity	Pre-equilibration time		
	0 hours	24 hours	120 hours
	$K_d$ (ml g <sup>-1</sup> )	$K_d$ (ml g <sup>-1</sup> )	$K_d$ (ml g <sup>-1</sup> )
0.3	13100 ± 300	11500 ± 150	9650 ± 120
1	8290 ± 220	7690 ± 130	6190 ± 80
5	4570 ± 70	4090 ± 60	3890 ± 85
17.5	3700 ± 50	2790 ± 40	3030 ± 50
35	3700 ± 60	2790 ± 70	3440 ± 50

Tweed Estuary			
Salinity	Pre-equilibration time		
	0 hours	24 hours	120 hours
	$K_d$ (ml g <sup>-1</sup> )	$K_d$ (ml g <sup>-1</sup> )	$K_d$ (ml g <sup>-1</sup> )
0.3	5120 ± 260	4530 ± 270	3340 ± 200
1.5	5180 ± 260	4490 ± 270	3600 ± 220
5.3	4800 ± 240	4350 ± 260	2340 ± 140
15.15	3370 ± 170	2740 ± 160	2590 ± 160
30	2640 ± 130	2670 ± 160	2570 ± 150

Mersey Estuary			
Salinity	Pre-equilibration time		
	0 hours	24 hours	120 hours
	$K_d$ (ml g <sup>-1</sup> )	$K_d$ (ml g <sup>-1</sup> )	$K_d$ (ml g <sup>-1</sup> )
0.3	3430 ± 50	2960 ± 110	2760 ± 80
1	2610 ± 70	2440 ± 170	2360 ± 80
5	2590 ± 20	2190 ± 40	2510 ± 50
10	2500 ± 80	2240 ± 40	2630 ± 80
24	3190 ± 30	3070 ± 10	3360 ± 100



Table A5.2. Uptake kinetics

## Tamar riverwater

0 hours		Pre-equilibration time 24 hours		120 hours		UV-irradiated	
Time (h)	Kd (ml g <sup>-1</sup> )	Time (h)	Kd (ml g <sup>-1</sup> )	Time (h)	Kd (ml g <sup>-1</sup> )	Time (h)	Kd (ml g <sup>-1</sup> )
0.4	3700 ± 190	0.3	2000 ± 350	1	2350 ± 130	0.3	9400 ± 700
3.2	5820 ± 300	4.9	3150 ± 160	5.15	3260 ± 170	3.0	12500 ± 800
6.4	8580 ± 420	8.0	4420 ± 250	8.2	3990 ± 220	6.3	13500 ± 800
22.6	8580 ± 440	24.5	5630 ± 320	24.8	5030 ± 280	22.6	16800 ± 1000
48.5	9800 ± 300	50.0	7710 ± 440	50.3	7130 ± 450	48.5	19800 ± 1800
126	14200 ± 800	128	10410 ± 560	127.6	8780 ± 470	126	22700 ± 1700

## Tamar riverwater + humic acids

0 hours		Pre-equilibration time 24 hours		120 hours	
Time (h)	Kd (ml g <sup>-1</sup> )	Time (h)	Kd (ml g <sup>-1</sup> )	Time (h)	Kd (ml g <sup>-1</sup> )
0.4	1710 ± 80	0.4	820 ± 50	1.1	1100 ± 80
3.5	2950 ± 140	5.0	1470 ± 80	5.3	1530 ± 110
6.4	3160 ± 150	8.1	1820 ± 100	8.3	1680 ± 120
22.7	3970 ± 170	24.6	2350 ± 130	25.2	2190 ± 150
48.5	4780 ± 240	50.2	2330 ± 140	50.4	2590 ± 170
126.1	6870 ± 380	128.0	4890 ± 270	127.7	4040 ± 250

## Tamar stable Ni

Time (h)	Ni <sub>T</sub> (nM)	Time (h)	Ni <sub>lab</sub> (nM)
0.3	32.7 ± 2.5	0.3	20.3 ± 3
1.0	36.7 ± 3	1.0	17.5 ± 3
2.5	40 ± 2	2.5	16.7 ± 0.9
7.8	39 ± 1	7.8	15.9 ± 0.1
23.5	30.4 ± 2	23.5	11.5 ± 2
71.6	35 ± 1	71.6	14 ± 0.2

## Tweed riverwater

0 hours		Pre-equilibration time 24 hours		120 hours		UV-irradiated	
Time (h)	Kd (ml g <sup>-1</sup> )	Time (h)	Kd (ml g <sup>-1</sup> )	Time (h)	Kd (ml g <sup>-1</sup> )	Time (h)	Kd (ml g <sup>-1</sup> )
1.0	7090 ± 450	1	2870 ± 170	1.0	3150 ± 270	1.0	7620 ± 670
3.0	9590 ± 650	3	4370 ± 140	3.5	3770 ± 320	3.5	5340 ± 350
24.0	12090 ± 380	7	6550 ± 190	6.7	4320 ± 200	6.8	5490 ± 490
47.2	12930 ± 630	24.0	8210 ± 650	22.8	6890 ± 430	22.9	3370 ± 240
117.9	12670 ± 300	47.3	9750 ± 640	47.6	7750 ± 250	47.7	2860 ± 180
		118	10500 ± 100	119.2	10090 ± 560	119.2	4150 ± 190

**Table A5.2. Uptake kinetics (continued)****Mersey riverwater**

0 hours		Pre-equilibration time 24 hours		120 hours		UV-irradiated	
Time (h)	Kd (ml g <sup>-1</sup> )	Time (h)	Kd (ml g <sup>-1</sup> )	Time (h)	Kd (ml g <sup>-1</sup> )	Time (h)	Kd (ml g <sup>-1</sup> )
1.1	4150 ± 280	1.1	1290 ± 40	1.1	1120 ± 90	1.0	30600 ± 2400
4.6	4170 ± 290	4.0	2040 ± 90	3.3	1410 ± 100	3.3	34400 ± 1500
7.3	3960 ± 240	7.2	2030 ± 50	7.0	1680 ± 130	7.2	43000 ± 3400
22.1	3700 ± 290	22.1	2450 ± 190	24.0	2140 ± 230	24.3	32200 ± 2100
46.1	3930 ± 270	46.1	2720 ± 190	48.0	2460 ± 310	48.3	30500 ± 2100
118.2	3560 ± 70	118.2	3260 ± 80	119.2	3040 ± 220	119.1	27500 ± 2000

**Beaulieu Riverwater**

0 hours		Pre-equilibration time 24 hours		UV-irradiated	
Time (h)	Kd (ml g <sup>-1</sup> )	Time (h)	Kd (ml g <sup>-1</sup> )	Time (h)	Kd (ml g <sup>-1</sup> )
0.1	1200 ± 120	0.2	630 ± 50	0.1	7910 ± 560
1.2	2385 ± 210	1.2	630 ± 60	1.3	9510 ± 360
4.0	1780 ± 140	4.0	910 ± 80	5.1	17900 ± 1200
8.0	1530 ± 110	8.1	840 ± 70	8.1	17100 ± 1100
22.5	1900 ± 160	22.5	910 ± 80	23.3	17000 ± 1200
47.4	2240 ± 200	47.4	990 ± 90	47.2	20100 ± 1600
123.0	3790 ± 160	123.1	1630 ± 140	123.0	15900 ± 1100

**Table A5.3. Mersey Estuary desorption experiments**

**Separate additions**

Time (h)	% dissolved Ni	Salinity
0	100 ± 2	0.3
0.5	90 ± 1	0.3
1	90.2 ± 0.4	0.3
2	87.3 ± 0.8	0.3
3	85.8 ± 0.4	0.3
6	83.8 ± 0.9	0.3
8	83.3 ± 0.4	0.3
24	83 ± 2	0.3
48	81.7 ± 0.5	0.3
120	79 ± 1	0.3
121.0	76 ± 1	1.0
122.9	75.3 ± 0.5	1.0
124.7	74.7 ± 0.9	1.0
144.0	74 ± 1	1.0
167.8	73.0 ± 0.5	1.0
241.8	68.6 ± 0.5	1.0

Time (h)	% dissolved Ni	Salinity
0	100 ± 2	0.3
0.5	90 ± 1	0.3
1	90.2 ± 0.4	0.3
2	87.3 ± 0.8	0.3
3	85.8 ± 0.4	0.3
6	83.8 ± 0.9	0.3
8	83.3 ± 0.4	0.3
24	83 ± 2	0.3
48	81.7 ± 0.5	0.3
120	79 ± 1	0.3
120.9	78.4 ± 0.3	2.0
122.8	78.2 ± 0.4	2.0
127.4	77.3 ± 0.2	2.0
144.0	76.6 ± 0.9	2.0
168.9	75.0 ± 0.5	2.0
241.8	72.0 ± 0.7	2.0

Time (h)	% dissolved Ni	Salinity
0	100 ± 2	0.3
0.5	90 ± 1	0.3
1	90.2 ± 0.4	0.3
2	87.3 ± 0.8	0.3
3	85.8 ± 0.4	0.3
6	83.8 ± 0.9	0.3
8	83.3 ± 0.4	0.3
24	83 ± 2	0.3
48	81.7 ± 0.5	0.3
120	79 ± 1	0.3
120.9	80.5 ± 0.9	5.0
122.6	81.3 ± 0.3	5.0
127.3	82.7 ± 1.0	5.0
144.1	79.6 ± 1.0	5.0
169.0	79.7 ± 0.3	5.0
241.9	76.8 ± 0.2	5.0

**Continuous addition**

Time (h)	% dissolved Ni	Salinity
0	100 ± 2	0.3
0.5	90 ± 1	0.3
1	90.2 ± 0.4	0.3
2	87.3 ± 0.8	0.3
3	85.8 ± 0.4	0.3
6	83.8 ± 0.9	0.3
8	83.3 ± 0.4	0.3
24	83 ± 2	0.3
48	81.7 ± 0.5	0.3
120	78.8 ± 0.9	1.0
121.0	78.8 ± 0.7	1.0
122.8	76.7 ± 0.4	1.0
127.5	76.3 ± 0.3	1.0
144.2	76.8 ± 0.2	2.0
145.1	77.1 ± 0.3	2.0
147.4	76.7 ± 0.7	2.0
151.3	77.2 ± 0.1	2.0
168.2	76 ± 1	5.0
169.1	77.8 ± 0.4	5.0
171.9	77.4 ± 0.4	5.0
175.1	77.7 ± 0.4	5.0
191.5	76.9 ± 0.8	5.0
216.0	76.8 ± 0.7	5.0
287.6	76.4 ± 0.4	5.0

**Table A5.4. Tweed Estuary, in-situ incubations, June 1997**

Station	Sample	Kd (ml g <sup>-1</sup> )	Conditions
5	5	5900 ± 100	Alive-light
9	9	7000 ± 500	Alive-light
16	16	8000 ± 200	Alive-light
16	16P	8300 ± 400	Alive-light
5	5	6000 ± 800	Alive-dark
9	9	8100 ± 700	Alive-dark
16	16	9600 ± 800	Alive-dark
16	16P	9400 ± 300	Alive-dark
5	5	2000 ± 100	Poisoned-dark
9	9	2100 ± 100	Poisoned-dark
16	16	1800 ± 400	Poisoned-dark
16	16P	3600 ± 300	Poisoned-dark

**Table A5.5. Mersey Estuary, incubations with unfiltered samples**

Sample	Unpoisoned Kd (ml g <sup>-1</sup> )	% Exchangeable Ni	Poisoned Kd (ml g <sup>-1</sup> )	% Exchangeable Ni	P-SPM* Kd (ml g <sup>-1</sup> )	T-SPM** Kd (ml g <sup>-1</sup> )
M3-5	1410 ± 30	27 ± 4	990 ± 20	18 ± 3		
M3-6	1290 ± 30	24 ± 4				
M3-7	1410 ± 30	20 ± 3				
M3-9	1170 ± 30	22 ± 3	950 ± 25	17 ± 3		
M3-10	1230 ± 120	37 ± 6	970 ± 30	21 ± 3	1120 ± 50	1420 ± 60
M3-11	1230 ± 60	27 ± 4				
M3-12	1030 ± 30	23 ± 3	720 ± 20	19 ± 3		
M3-13	960 ± 20	17 ± 3				
M3-14	900 ± 10	12 ± 2				
M3-15	1090 ± 30	18 ± 3	960 ± 30	17 ± 2		
M3-16	750 ± 15	22 ± 3	740 ± 10	11 ± 2	980 ± 30	980 ± 10
M3-17	890 ± 20	27 ± 4	750 ± 20	12 ± 2	1040 ± 70	1060 ± 50
M3-18	1180 ± 60	15 ± 2	830 ± 30	16 ± 2		
M3-19	610 ± 15	17 ± 3	540 ± 10	8 ± 1	1170 ± 30	880 ± 20
M3-20	900 ± 10	13 ± 2				
M3-21	830 ± 30	25 ± 4				
M3-22	670 ± 20	27 ± 4	450 ± 15	28 ± 4		
M3-HW1	180 ± 6	41 ± 6				
M3-HW2	635 ± 35	44 ± 7	1110 ± 70	48 ± 7		
M4-10	1270 ± 110	24.2 ± 0.7	980 ± 160	22.2 ± 0.3	1140 ± 20	1000 ± 93
M4-16	920 ± 60	13.7 ± 0.3	850 ± 50	11.3 ± 0.5	810 ± 60	910 ± 150
M4-19	530 ± 20	9.1 ± 0.5	520 ± 40	7.9 ± 0.1	620 ± 100	480 ± 40
M4-20	440 ± 30	10.3 ± 0.7	390 ± 20	10.8 ± 0.2		
M4-21	280 ± 4	21 ± 1	260 ± 10	22 ± 1		
M4-22	217 ± 5	26 ± 1	250 ± 30	18 ± 4	230 ± 10	160 ± 2
M5-4	1540 ± 20	14 ± 1	1090 ± 30	14.3 ± 0.7	1600 ± 190	670 ± 50
M5-14	1650 ± 70	25.2 ± 0.2	1200 ± 60	23.8 ± 0.7	1550 ± 80	1280 ± 150
M5-16	1360 ± 20	17 ± 1	1150 ± 20	14.6 ± 0.8		
M5-17	920 ± 100	14.6 ± 0.6	690 ± 10	13.9 ± 0.4		
M5-18	940 ± 60	15 ± 2	590 ± 60	19.6 ± 0.3	1530 ± 50	1300 ± 100
M5-HW	2560 ± 180	19.6 ± 0.8	1080 ± 20	37.7 ± 0.8	2140 ± 350	2080 ± 270

\*P-SPM=Permanently suspended particulate matter; \*\*T-SPM=Temporarily suspended particulate matter.

## APPENDIX 6

### SPECIATION MODELLING DATA

**Table A6.1.** Equilibrium distributions of Ni complexes (as percentage of total dissolved Ni) and free Ni<sup>2+</sup> concentrations in the Tweed Estuary at pH 8.3 and 25 °C.

Salinity	% NiL	% Ni <sup>2+</sup>	% NiCO <sub>3</sub>	% NiCl <sup>+</sup>	% NiSO <sub>4</sub>	[Ni <sup>2+</sup> ] (nM)
0.3	51	17	31	*	*	1.3
2.2	54	18	25	2	1	1.2
5.7	55	18	22	3	2	1.2
8.3	66	14	16	3	1	0.8
17.5	56	17	18	7	2	0.9
31.3	76	9	9	5	1	0.3
32.5	52	17	17	11	3	0.4
33.8	97	1	1	1	*	0.03

\* = Species contributing for less than 1%.

**Table A6.2.** Equilibrium distributions of Ni complexes (as percentage of total dissolved Ni) and free Ni<sup>2+</sup> concentrations in the Mersey Estuary at pH 8.3 and 25 °C.

Salinity	% NiL	% Ni <sup>2+</sup>	% NiCO <sub>3</sub>	% NiCl <sup>+</sup>	% NiSO <sub>4</sub>	[Ni <sup>2+</sup> ] (nM)
0.2	71	10	18	*	*	4.5
0.2	91	3	6	*	*	1.3
0.3	85	5	9	*	*	1.9
0.3	85	5	9	*	*	2.3
0.3	53	17	29	*	*	8.1
2.2	61	15	21	1	1	8.3
4.2	65	14	18	2	1	7.7
9.4	71	12	13	3	1	6.5
16.1	59	16	17	6	2	9.9
23.2	61	15	15	7	2	5.7
28.6	55	16	16	9	2	3.1
31.6	72	10	10	6	2	1.3
31.2	82	7	7	4	*	1.0

\* = Species contributing for less than 1%.

**Table A6.3.** Equilibrium distributions of Ni complexes (as percentage of total dissolved Ni) and free Ni<sup>2+</sup> concentrations in the Tweed Estuary at pH and temperature of the natural samples.

Salinity	pH	T (°C)	% NiL	% Ni <sup>2+</sup>	% NiCO <sub>3</sub>	% NiCl <sup>+</sup>	% NiSO <sub>4</sub>	[Ni <sup>2+</sup> ] (nM)
0.3	8.0	14.5	51	35	13	*	*	2.7
2.2	8.1	14.6	54	29	13	2	2	1.7
5.7	8.2	14.8	55	24	15	4	3	1.7
8.3	7.9	14.1	66	23	4	5	2	1.3
17.5	8.3	14.3	56	19	16	7	2	1.0
31.3	8.1	13.3	76	11	4	7	2	0.4
32.5	8.1	12.8	52	22	7	15	3	0.6
33.8	8.1	13.6	97	2	1	*	*	0.06

<sup>a</sup>Values are expressed as percentage of total dissolved Ni. \* = Species contributing for less than 1%.

**Table A6.4.** Equilibrium distributions of Ni complexes (as percentage of total dissolved Ni) and free Ni<sup>2+</sup> concentrations in the Mersey Estuary at pH and temperature of the natural samples.

Salinity	pH	T (°C)	% NiL	% Ni <sup>2+</sup>	% NiCO <sub>3</sub>	% NiCl <sup>+</sup>	% NiSO <sub>4</sub>	[Ni <sup>2+</sup> ] (nM)
0.2	7.2	10.5	71	28	1	*	*	12.4
0.2	7.4	10.5	91	9	*	*	*	3.8
0.3	7.5	10.8	86	14	*	*	*	5.6
0.3	7.4	10.5	85	14	*	*	*	6.6
0.3	7.6	10.5	53	43	2	*	2	22
2.2	7.4	10.2	61	33	*	3	2	16
4.2	7.5	10.0	65	29	*	4	2	14
9.4	7.6	10.0	69	22	*	5	2	9.6
16.1	7.5	10.4	58	28	*	10	3	14
23.2	7.6	10.9	61	24	*	11	3	8.5
28.6	7.7	11.0	55	25	1	15	3	4.4
31.2	7.9	11.1	82	10	1	6	1	1.3
31.6	7.9	10.9	72	15	2	9	2	1.78

\* = Species contributing for less than 1%.

**Table A6.5.** Equilibrium distributions of “reactive” Ni (as percentage of total “reactive” Ni) in the Mersey Estuary at natural pH and 20 °C.

Salinity	% NiL	% Ni <sup>2+</sup>	% NiCO <sub>3</sub>	% NiCl <sup>+</sup>	% NiSO <sub>4</sub>	% adsorbed Ni
0.2	67	26	*	*	1	6
2.2	50	27	*	2	2	19
4.2	49	25	*	3	2	21
9.4	58	18	*	4	2	17
16.1	53	25	*	9	3	9
31.2	60	7	*	5	1	26

<sup>a</sup>Values are expressed as percentage of total “reactive” Ni. \* = Species contributing for less than 1%.