DISSOLVED AND PARTICULATE TRACE METALS IN THE FORTH AND TAY ESTUARIES

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Abstract

The estuarine biogeochemistries of Cd, Cu, Mn, Ni, Pb and Zn have been examined. Two adjacent, contrasting estuaries were selected to assess the effects of riverine discharge, hydrodynamic régime and particulate phase composition. Sampling throughout an annual cycle enabled seasonal differences in primary productivity and meteorological conditions to be included. Simultaneous nutrient determinations and fresh water flow measurements were used to assist in the interpretation of metal data.

Dissolved Mn profiles in both estuaries are dominated by benthic inputs, a consequence of the reduction of Mn in sub-oxic sediments. Highest benthic fluxes occur in summer, and coincide with dissolved oxygen minima in the upper Forth. High wintertime fluxes are caused by the injection of porewater following sediment resuspension. Dissolved Ni and Zn are remobilised with Mn during summer in the Forth. Dissolved Cd concentrations in both estuaries increase with salinity as a result of chloro-complexation. Both Cd and Cu are remobilised during the breakdown of particulate material. Only about 5% of the Pb is in the dissolved phase.

Suspended particulate trace element contents do not vary much within each estuary. The Ca contents, however, increase with distance seaward, since the coastal zone acts as a source of $CaCO_3$ to the estuaries. Non-detrital Mn contents increase in the outer Forth during summer, a consequence of precipitative Mn oxidation. The behaviours of Ni and Zn mimic that of Mn, as they are scavenged from the dissolved phase by newly formed particulate Mn oxides. Particulate Mn contents are higher in summer than in winter, and higher in the well-oxygenated

Tay than in the Forth. This is attributed to faster Mn oxidation rates at higher temperatures and dissolved oxygen concentrations. Suspended particulate Cd contents in both estuaries are highest in summer due to the binding of Cd to phytoplankton cells. Partition coefficients in the Forth and Tay follow the order Pb > Mn, Zn > Ni > Cu > Cd.

Flux estimates indicate that the Forth and Tay discharge approximately equal amounts of dissolved Cd, Cu, Ni, Pb and Zn to the North Sea. The Forth, however, discharges about ten times as much dissolved Mn as the Tay. The particulate discharges from the Tay are greater than those from the Forth by factors of 4 for Cd, 7 for Cu, 8 for Ni and Pb, 10 for Zn and 19 for Mn. The Tay is the greater source of these metals to the North Sea. This reflects the larger catchment area of the estuary. The combined metal discharges from the Forth and Tay are approximately 2, 90, 2000, 60, 100 and 350 ta^{-1} for Cd, Cu, Mn, Ni, Pb and Zn respectively.

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CHAPTER 1: INTRODUCTION

1.1: Trace metal cycling in oceanic environments

Nearly all the dissolved and particulate material entering the oceans is derived from the weathering of continental rock. Less than an estimated 2% comes from marine erosion or hydrothermal activity (*eg* Raiswell *et al* 1980). Oceanic concentrations of dissolved trace metals are lower than would be predicted from the solubility products of their source minerals, thus indicating that efficient removal processes are operating in the water column (Honeyman *et al* 1988, Turekian 1977).

Particulate matter scavenging is the main mechanism for the removal of metals from the oceans (Li 1981, Schindler 1975, Whitfield and Turner 1987). The mean oceanic residence time (MORT) of an element therefore depends on its particle-reactivity (*eg* Li 1991, Santschi 1984). Metals can be divided into three categories according to their behaviour in the oceans, namely "conservative", "recycled" or "scavenged" (Bruland 1983, Li 1991). Table 1.1 summarises the speciation, residence times and distribution of some metals in the oceans.

1.1.1: Conservative elements

"Conservative" or "accumulated" elements are those with low particle-reactivity. They have residence times greater than 10^5 years, *ie* 100 times longer than the mean oceanic mixing time. Their relative proportions therefore remain constant in sea water. Elements in this category have ions with small electrostatic charges and include Na, K, Rb, Cs, Mg, F, Cl, Br and U. Although some of these elements are involved in biological cycles (*eg* Na, K, Mg, Cl), their concentrations are too high for this to have a noticeable effect. The distributions of these elements are purely the results of physical mixing processes (Bruland 1983).

Table 1.1. The speciation, residence times and distributions of some elements in the oceans.

Element	Probable main species present (Bruland 1983; Li 1991)	MORT (years) (Tait 1980)	Type of oceanic distribution
Na	Na^+	3×10^8	Conservative
K	K^+	1×10^7	Conservative
Rb	Rb^+	3×10^5	Conservative
Mg	Mg^{2+}	5×10^7	Conservative
U	$UO_2(CO_3)_2^{2-}$; $UO_2(CO_3)_3^{4-}$	5×10^5	Conservative
Si	$H_4SiO_4^0$	8×10^3	Nutrient
Ni	Ni^{2+} ; $NiCO_3^0$; $NiCl^+$	2×10^4	Nutrient
Cu	$CuCO_3^0$; $CuOH^+$; Cu^{2+} ; Cu-organic	5×10^4	Nutrient/scavenged/ coastal enrichment
Cd	$CdCl_2^0$	5×10^5	Nutrient
Zn	$ZnOH^+$; Zn^{2+} ; $ZnCO_3^0$; $ZnCl^+$	2×10^5	Nutrient
Fe	$FeOH^+$; $Fe(OH)_3^0(s)$	1×10^2	Scavenged/ surface depletion/ depletion at depth
Mn	Mn^{2+} ; $MnCl^+$	1×10^3	Scavenged/ surface enrichment/ depletion at depth
Hg	$HgCl_4^{2-}$	4×10^4	Scavenged/ coastal enrichment
Pb	$PbCO_3^0$; $Pb(CO_3)^{2-}$; $PbCl^+$	2×10^3	Scavenged/ surface enrichment/ coastal enrichment/ depletion at depth

1.1.2: Recycled elements

"Recycled" elements have residence times between 10^3 and 10^5 years. They have nutrient-type distributions in the oceans, *ie* their dissolved concentrations in surface waters are much lower than their concentrations at depth. This is because they are incorporated into biogenic particles in the surface waters and remobilised as these decompose in the deep ocean (Noriki *et al* 1985). The recycled elements include N, Si, P, Ca, Fe, Ni, Cu, Cd and Zn (Bruland 1983). Some metals (*eg* Cu, Ni, Mn and Cd) appear to be incorporated in constant "Redfield-like" ratios in phytoplankton (Bruland *et al* 1991); their particulate metal/phosphorus ratios remain relatively constant despite large differences in the surrounding dissolved metal/phosphorus ratios (Collier and Edmond 1984). Generally these elements have low particle-reactivity and are found mainly in the dissolved phase in sea water (Baeyens *et al* 1987, Balls 1985, Brügmann 1986a, Kremling and Petersen 1978, Vuceta and Morgan 1978). The behaviours of some of the recycled elements are discussed below.

1.1.2.1: Nickel and zinc

Removal of nickel and zinc from the water column occurs when concentrations of surface ligands increase (Vuceta and Morgan 1978). Zinc is removed mainly by the formation and precipitation of colloids, though organic chelation, hydrous sorption or ion-exchange processes may also occur (Onishi *et al* 1980). Unlike Cd, Cu, Ni and Mn, particulate zinc shows no relationship with phosphorus in phytoplankton, and little zinc is regenerated with phosphorus in leaching experiments. Only about 5% of biogenic particulate nickel is recycled in the surface oceans; the rest is regenerated at depth (Collier and Edmond 1984).

1.1.2.2: Cadmium

Cadmium is incorporated into biogenic particulate organic matter (POM) much more readily than non-biogenic particles (Noriki *et al* 1985). Although cadmium is recycled with phosphorus, a portion of the particulate cadmium is preferentially regenerated in sinking particles, and particulate Cd/P ratios become smaller with increasing depth (Collier and Edmond 1984).

1.1.2.3: Copper

The oceanic distribution of copper is midway between the nutrient (recycled) and the lead/manganese (scavenged) types (Bruland 1983). Its surface depletion is caused by the scavenging of biogenic particulate matter and this is the major carrier of copper from surface waters to the deep oceans. There is a strong correlation, therefore, between copper removal rates and the biological productivity within an area (Noriki *et al* 1985). Unlike Cd, Ni and Mn, however, the association of copper with POM is so strong that it is not remobilised with phosphorus. Instead, total copper concentrations in deep oceans continue to increase with depth and copper is only regenerated near the sediment-water interface (Collier and Edmond 1984). Nearshore waters generally have higher concentrations of copper than oceanic waters, due to sedimentary processes and the influence of riverine and anthropogenic inputs (Balls 1985). Surface water concentrations tend to vary with dissolved manganese rather than ^{210}Pb, indicating a riverine rather than an atmospheric source of copper (Bruland 1983).

1.1.3: Scavenged elements

"Scavenged" elements have residence times which are similar to or shorter than the mean oceanic mixing time. They are very particle-reactive and mostly occur in the particulate phases in the water column (Baeyens *et al* 1987, Balls 1985, Brügmann 1986a, Elbaz-Poulichet *et al* 1984). These elements have very low sea water concentrations compared with their crustal abundance and, in contrast with the recycled elements, often have profiles showing enrichment in surface waters, due to atmospheric or ocean margin input. Some examples are given below.

1.1.3.1: Iron and manganese

Iron and manganese are removed from the water column by "oxidative" scavenging (*ie* removal in oxic waters, as in the case of ferromanganese nodule formation, Bruland 1983). They are redox-reactive elements and are relatively mobile in marine environments. Their hydroxides act as efficient scavengers of other metals (Glasby 1984) and, being ubiquitous, they affect the geochemical cycling of many elements in the marine environment (Balls 1986, Duinker *et al* 1979a, Olsen *et al* 1982, Onishi *et al* 1980, Whitfield and Turner 1987). The thermodynamically stable states of iron and manganese in oxygenated sea water are the insoluble Fe (III) and Mn (IV) ions. In reducing conditions, the soluble Fe (II) and Mn (II) ions are produced. The conversion of Fe (II) to Fe (III) occurs quickly in oxygenated sea water. The rate of manganese oxidation is much slower, however, and the unstable Mn (II) ion may persist for some time in sea water (Hem 1963). The adsorption of Mn (II) is partly autocatalytic, since manganese oxides in particulate coatings act as oxidising agents for the ions (Glasby 1984). ~~For example,~~ Adsorption of Zn, Cd and Ba by red clays is greatly enhanced by cation exchange with the Mn of the MnO_2 particulate coatings (Li *et al* 1984). Both riverine input (Bruland 1983) and hydrothermal activity (*eg* Collier and Edmond 1984, Glasby 1984) are important sources of manganese in the oceanic environment.

1.1.3.2: Lead and mercury

Lead and mercury are removed by "hydrolytic" scavenging (*ie* surface adsorption). Their concentrations are dominated by the presence of suspended particles and tend to be higher in turbid coastal environments than in oceanic waters (Bruland 1983). Lead is enriched in surface waters due to a significant atmospheric input for this element (Whitfield and Turner 1987).

1.2: Importance of coastal waters in global geochemical cycles

A knowledge of trace metal inputs, concentrations and movements at ocean boundaries is a prerequisite for understanding their geochemistries in marine environments (Portmann 1986). Dissolved and particulate materials enter the oceans from a number of sources (Table 1.2), but riverine transport accounts for more than 80% of the total (Raiswell *et al* 1980).

Table 1.2. Estimated fluxes of dissolved and particulate material into the oceans. (Raiswell *et al* 1980)

	Dissolved x10^{14}gyr^{-1}	Particulate x10^{14}gyr^{-1}	Total x10^{14}gyr^{-1}	Per cent
CONTINENTAL SOURCES				
Rivers	39.0	183.0	222.0	81.9
Ice	<7.0	20.0	27.0	10.0
Subsurface waters	4.7	4.8	9.5	3.5
Atmosphere	2.5	6.0	8.5	3.1
SUB-MARINE SOURCES				
Marine erosion		2.5	2.5	0.9
Hydrothermal		1.5	1.5	0.6
Total	53.2	217.8	271.0	100.0

Efficient removal processes trap much of the riverine-derived particulate material in estuaries or nearshore waters.

Dissolved nutrients often stimulate the development of phytoplankton blooms at estuary mouths. The blooms remove some trace metals from the water column, along with the nutrients, preventing them from reaching offshore waters (Church 1986, Olsen *et al* 1982).

Trace metals are rapidly adsorbed onto particulate material as they enter coastal environments. In turbid rivers like the Mississippi, Amazon and Yukon, for example, more ~~the~~ than 90% of the metals are associated with suspended solids (Gibbs 1977, Trefry *et al* 1985, 1986). Coastal zone processes then prevent these suspended particles and their contaminants from reaching offshore waters (Martin and Whitfield 1983, Olsen *et al* 1982).

In macrotidal estuaries (tidal ranges greater than 4m), sediments are transported upstream by strong flood currents (Dyer 1986). Suspended particles in the Gironde estuary, for example, have residence times ranging from two months to two years. More than 90% of this eventually settles within or immediately adjacent to the estuary (Elbaz-Poulichet *et al* 1984).

In mesotidal areas (2-4m tidal range), suspended solids become trapped by the gravitational circulation pattern of partially-mixed estuaries. The net movement of the lower salinity surface water is seaward, while the flow of the underlying water is landward. Settling particles in the outer reaches of the estuary are therefore transported upstream again with the bottom water currents (Dyer 1986, Martin and Whitfield 1983, Olsen *et al* 1982).

Strong decreases in environmental energy cause rapid sediment deposition as rivers enter microtidal areas (0.5-1m tidal range). Most of the suspended matter and heavy metals carried by the Adige River, for example, are deposited at its mouth in the Adriatic Sea (Juračić *et al* 1987). Similarly, artificial radionuclides discharged into the Rhône River are deposited only a few kilometres into the Mediterranean (Martin and Thomas 1990). The vast Mississippi delta system acts as a "giant filter" for most of the riverine sediment, all the lead and much of the cadmium and manganese, preventing them from entering the gulf of Mexico (Trefry *et al* 1986).

Yeats *et al* (1978) examined the sensitivity of coastal waters to increased anthropogenic discharges entering the St Lawrence River. Metals are removed from the system by particulate scavenging/settling as the river passes the Great Lakes. Consequently inputs of Mn, Ni, Cd, Cu and Zn would have to be increased by 38%, 81%, 130%, 150% and 170% respectively before changes in coastal water concentrations would be detectable.

Despite such removal processes, the elemental composition of deep sea clays is influenced, over very long time-scales, by riverine inputs (except for Mn, Cu, and Co) (Martin and Whitfield 1983). Since the deep ocean-surface ocean mixing time is about 10^3 years and trace element residence times are of the order of 10^3-10^5 years (Bruland 1983, Whitfield and Turner 1987, Yeats and Bewers 1983), it will take considerable periods of time before local anthropogenic inputs equilibrate with the rest of the oceans. Coastal environments which already receive much of the naturally-added material are therefore subject to further stress by the addition of anthropogenic contaminants. If they are to be protected for their present uses (recreation, tourism, fishing and industrial exploitation, and as a natural ecosystem), then adequate management strategies must be found.

Only when contaminant fates are known can areas subject to the greatest impact be targeted for monitoring, and effective management decisions be made. Trace element budgets have therefore been calculated for a number of coastal areas including the Baltic Sea (Brügmann 1986b, Cd, Co, Cu, Fe, Hg, Ni, Pb, Zn), Narragansett Bay (Santschi *et al* 1984, Pb, Cu; Graham *et al* 1976, Mn), San Francisco Bay (Kuwabara *et al* 1989, Cu, Cd; Eaton 1979b, Cu, Fe, Ni, Zn), Delaware Bay (Church 1986, Fe, Mn, Co, Zn, Ni, Cu, Cd), Mediterranean Sea (Ruiz-Pino *et al* 1991, Zn) and Abu-kir Bay, Egypt (Abdel-Moati 1991, Pb). Since particulate matter is so important in contaminant cycling, separate dissolved and particulate metal budgets are necessary to indicate where the greatest impacts will be. Budgets calculated for the Puget Sound, for example (Paulson *et al* 1989c), indicate that there is no net transfer of copper or zinc between the dissolved and particulate phases. Reducing solid copper or zinc inputs, therefore, is likely to reduce the sediment concentrations but have little effect on the water column and *vice versa*. Lead, however, is scavenged by the suspended particles, so a reduced lead input in either phase would be likely to reduce lead concentrations in the bottom sediments.

1.3: Particle-water interactions in natural environments

As has been described in the previous section, the solid-solution partitioning of metals controls their movements and fates within estuaries (Elbaz-Poulichet *et al* 1984, Morris 1986, Morris *et al* 1982, 1986, Mouchel 1986, Uncles *et al* 1987, 1988), coastal waters (Balls 1989, Olsen *et al* 1982, Pentreath 1987) and oceans (Li 1981, Santschi 1984). The main processes are shown in Figure 1.1.

The overall partitioning behaviour of metals can be described by partition coefficients (K_d). These are ratios of the concentration of the metal in the solid phase Cp (μgg^{-1}) to that in solution Cw (μgkg^{-1}): K_d = Cp x 1,000/Cw. The coefficients summarise a number of solid-solution interactions, including precipitation, co-precipitation, adsorption, diffusion within the particulate structures, inclusion in mineral lattices and inorganic and organic complexation (Bourg 1986).

Although operationally defined, partition coefficients have been useful in describing the relative particle-reactivity of metals. Laboratory and field experiments have shown that, within a particular set of conditions, the trend of decreasing partition coefficients amongst metals occurs in the order Pb, Hg > Cu, Zn, Ni > Cd (Baeyens *et al* 1987, Balls 1988, 1989). Partition coefficients in coastal environments typically fall within the range 10^5 - 10^7 for lead, 10^4 - 10^6 for mercury, 10^4 - 10^5 for copper, nickel and zinc, and 10^3 - 10^5 for cadmium.

The variation in particle reactivity observed between the elements has been attributed to a number of thermodynamic parameters. The log K_ds of 51 elements in manganese nodules, for example, correlate well with the logs of their crystal lattice energies (Green and Chave 1988). Since lattice energies

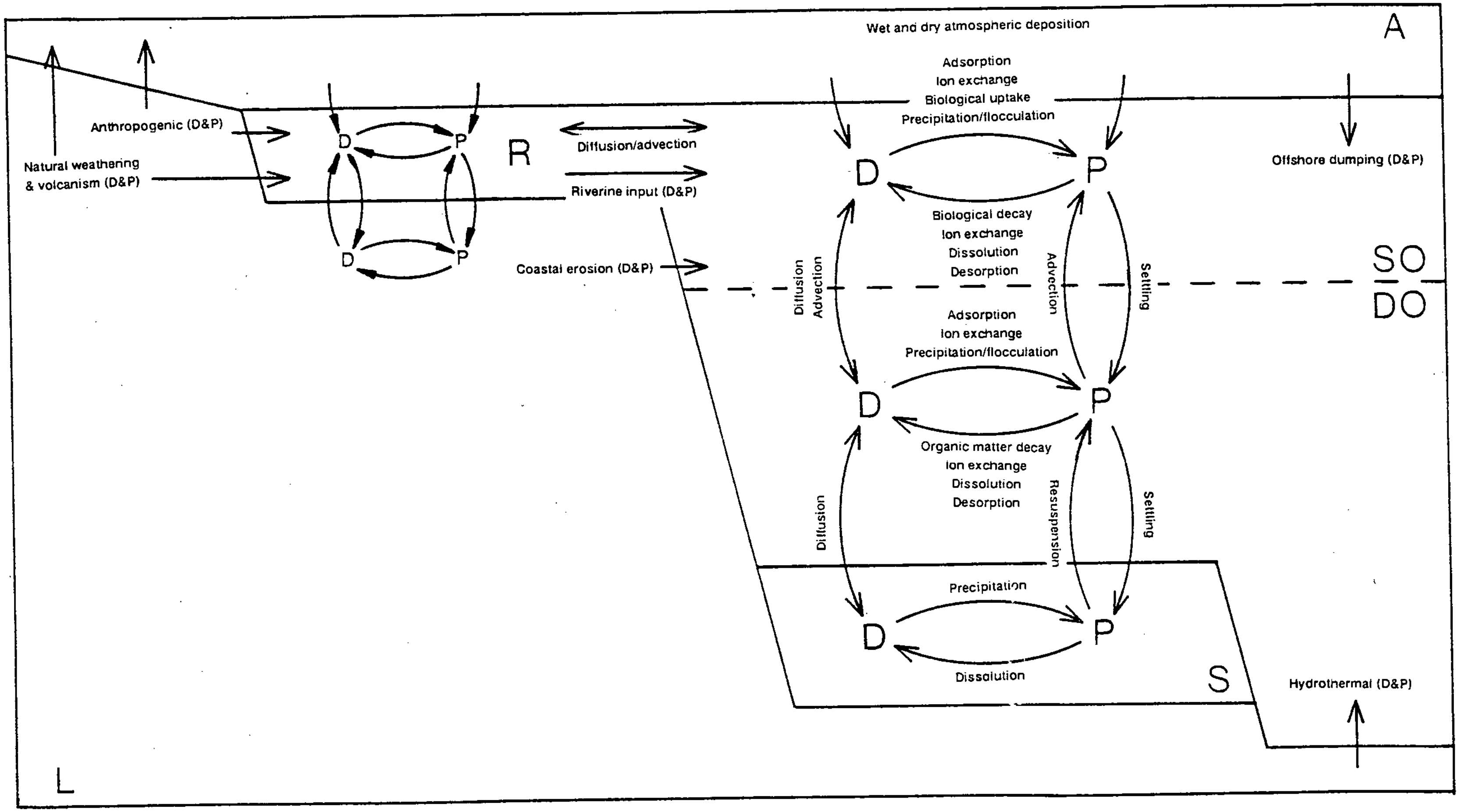

Figure 1.1. Particle-water interactions in marine environments

D = Dissolved, P = Particulate, L = Land, R = Rivers, A = Atmosphere, S.O. = Surface Ocean, D.O. = Deep Ocean, S = Oceanic Sediments.

are a measure of the total interaction between an ion and its environment, this possible relationship would explain:

(i) why metal enrichments in particulate phases correlate with ionic charge and with the reciprocal of the ionic radius (Whitfield and Turner 1983);

(ii) why the more easily-polarisable (softer) metal, for atoms of similar charge and radius, is enriched in the solid phase. (Lattice energies indicate that the bond between the softer metal and its oxide would be stronger and more stable than the bond between the harder metal and its oxide.)

Other parameters that have been linked with partition coefficients include ionisation energies, ionic potentials, hydrolysis constants, solubility products and electronegativities. Since these parameters are all linked with one another (as discussed by Li 1991), it has been proposed that metal electron binding energies be used to explain the partitioning behaviour of the elements between dissolved and particulate phases in the marine environments (Li 1991).

1.3.1: Factors affecting partition coefficients

Partition coefficients depend on many environmental variables, and it is difficult to determine what measured values actually represent. Great care must therefore be taken when applying them to environmental or experimental conditions other than those for which they were determined (Balls 1988, 1989, Bourg 1987, Cremers and Maes 1986). Some of the factors affecting partition coefficients are discussed below.

1.3.1.1: Redox potential

Redox potential affects the partitioning behaviour of metals in different ways (Cremers and Maes 1986, Piro *et al* 1975). The coefficients of Fe and Mn decrease in anoxic conditions, since their oxidation states change from the insoluble Fe(III) and Mn(IV) forms to the soluble Fe(II) and Mn(II) forms. Conversely the partition coefficients of Zn, Sr, Cu, Cd, Pb, Co and Pu increase in reducing conditions (Duursma and Eisma 1973, Sholkovitz 1983). Nickel and mercury appear not to be affected by redox potential (Brügmann 1988). Duursma and Bewers (1986) question the importance of redox potentials, however, since partition coefficients only vary by about one order of magnitude between completely oxic and anoxic conditions.

1.3.1.2: pH

Lower pHs usually favour desorption of metals from particles. Removal of dissolved iron in the mixing zone of the Bang Pakong estuary, Thailand, for example, is attributed to its lower solubility at the greater pHs of sea water (Windom *et al* 1988). In laboratory experiments, all three forms of zinc present at pH 8 - ionic (dissolved), particulate and complexed - are rapidly converted to the ionic (dissolved) form as the pH is lowered. At pH 2, therefore, all the zinc present is in the dissolved phase (Piro *et al* 1975). The partitioning behaviours of ^{57}Co and ^{106}Ru are most affected by pH in the range observed in natural environments (Schell and Sibley 1982), and the partition coefficient of Cm is strongly pH-dependent, with a peak value occurring between pH 5-6 (Alberts *et al* 1986).

1.3.1.3: Complexation

Since soluble ligands "compete" with surface ligands during the partitioning of metals, their behaviour depends on, and will change, the compositions of both aqueous and particulate phases (Bourg 1986, Li *et al* 1984, Schell and Sibley 1982). The chemistry of the aqueous phase changes considerably during estuarine mixing. The increasing ionic strength (salinity) often causes desorption of metals from particles (Di Toro *et al* 1986, Nikodic and Pieri 1986). For some elements, this may be due to the increase in dissolved ligands which form strong soluble complexes with trace metals. For example, chloride ions form strong soluble complexes with cadmium (Elbaz-Poulichet *et al* 1987) and mercury (de Groot *et al* 1976). Desorption may also be caused by the increased competition between the trace elements and the major "salt" elements for the particulate ligands (Elbaz-Poulichet *et al* 1987). For example, calcium competes with cadmium for adsorption sites on illite (Comans 1987). The resulting changes in partition coefficients are most pronounced in areas of low salinity and are not apparent at salinities greater than 30 °/₀₀ (Balls 1989, Valenta *et al* 1986).

Different chemical species of the same element may have different partition coefficients (Balls 1988, 1989, Kershaw *et al* 1986, Olsen *et al* 1982, Pentreath 1987, Piro *et al* 1975, Sholkovitz 1983). Plutonium, for example, is strongly adsorbed by particulate material in the reduced (III) or (IV) forms, but remains in solution in the oxidised (V) or (VI) forms (Olsen *et al* 1982). This is the converse behaviour to that of iron and manganese mentioned above. In radiotracer experiments Piro *et al* (1975) found that ionic zinc added to sea water did not equilibrate with the complexed forms present even after a year. Since speciation is important in partitioning behaviour, the chemical forms of an element left in solution will depend on the partition coefficients of each species, their relative concentrations and the numbers of possible adsorbing sites. If there are few adsorption sites, then the most preferentially adsorbed species will be removed, leaving an enrichment of the other species behind in the sea water (Wangersky 1986). As adsorption proceeds there is a decreasing tendency for metals to adsorb onto surfaces, since the surface ligands of high affinity are used up first, leaving only the less favourable ligands free (Xue *et al* 1988).

Dissolved complexing ligands like phosphate, bicarbonate and those associated with organic matter affect the partitioning behaviour of metals in sea water (Sholkovitz 1983, Valenta *et al* 1986, Vuceta and Morgan 1978). In the Scheldt estuary, for example, the concentrations of dissolved zinc and copper are controlled by interactions with dissolved organic ligands (van den Berg *et al* 1987). The effects of complexing ligands on partitioning behaviour depend on the specific ligand and the metal involved (Schell and Sibley 1982).

Particulate organic matter (POM), including algae, phytoplankton, biological debris and biologically coated surfaces, is especially important in controlling the concentrations, residence times, distributions and fates of trace metals in marine environments. This is because it forms a significant fraction of the suspended solids present in aquatic systems and contains many functional groups with high affinities for trace metals (Dawson and Duursma 1974, Fisher 1986, Hamilton 1986, Santschi 1984, Schell and Sibley 1982, Sigg 1985, Wangersky 1986, Whitfield and Turner 1987, Xue *et al* 1988). Living phytoplankton cells have similar metal binding capacities to non-living particulate organic matter and (for radioisotopes at least) partition coefficients on sterilised sediment are similar to those on natural sediment (Duursma and Bosch 1970). The chemical surface properties of the particles therefore appear to be more important than biological or metabolic processes (Fisher *et al* 1984, Wangersky 1986). Microbial processes are, however, very important in causing the oxidation and precipitation of manganese at the surfaces of suspended particles (Sunda and Huntsman 1987). Other metals may be scavenged during this process (Section 1.1.3.1).

The relative affinities of metals for biogenic particles are different from those for pure mineral phases. Cadmium has the highest affinity for POM, followed by Pb, Ni, Cu, then Co, while Mn, Fe and Al are least likely to be incorporated into POM (Noriki *et al* 1985). Particulate cadmium concentrations, for example, were raised considerably by the presence of particulate organic matter in the Scheldt estuary (Valenta *et al* 1986) and the Saguenay Fjord (Cossa and Poulet 1978).

The effect of primary productivity varies with species composition and the stage of the population growth. Quickly growing populations tend to have lower metal concentrations due to a "diluting effect" of the rapid cell turnover rate. Conversely, metals tend to accumulate in cells with slow turnover rates. Different species have different effects on metal partitioning. Dinoflagellates, for example, have been observed to take up more Cu per unit of algal biomass than other algae (Knauer and Martin 1973, Martin and Knauer 1973).

The mineralogy, structure and elemental composition of the solid phase affects partition coefficients (Baeyens *et al* 1987, Kremling and Petersen 1978, Li 1981, Li *et al* 1984, Sholkovitz 1983). Particulate metal concentrations often increase with increasing clay mineral content, and the partition coefficient of nickel can vary by two orders of magnitude for different solid phases in the same environment (Nevissi 1986). Many metals correlate well with several different mineral types, though some of these correlations may not be the results of causal relationships (Duursma and Bewers 1986). Particle size is important in influencing trace metal partition coefficients (Sholkovitz 1983). Particles of small diameter (usually the clay minerals) tend to have higher concentrations than larger particles (Duursma and Eisma 1973). This could be due to the negative charges associated with the aluminosilicate structure of the clay minerals (*eg* montmorillonite), or to the larger specific surface area of small particles

(Berner 1976). Alternatively, there may be kinetic reasons for this variation: the lower residence times of large particles may prevent them from equilibrating with the dissolved phases, while smaller particles have more time to adsorb contaminants (Balls 1989). Differences in solid phase mineralogy, chemical composition or grain size may partly account for the variation of partition coefficients between different areas (Duursma and Bewers 1986). There is evidence that unfilterable colloidal material (> 10,000 amu) is important in partitioning reactions. If truly dissolved metals become associated with colloidal material before being removed onto larger particles, then removal rates will be faster for metals with high colloidal concentrations (Honeyman and Santschi 1989). The fraction of colloidal thorium present in the dissolved phase is higher than the fraction of colloidal aluminium, for example. This may explain why thorium has a lower oceanic residence time than aluminium (Moran and Moore 1989). Further evidence for the involvement of colloidal material in metal partitioning reactions comes from the apparent dependence of partition coefficients on suspended particulate matter loadings as discussed below.

1.3.1.4: Suspended particulate matter loadings

Partition coefficients have been found to be dependent on suspended particulate matter loadings both in laboratory experiments (*eg* Di Toro *et al* 1986, Duursma and Bewers 1986, Duursma and Bosch 1970, O'Connor and Connolly 1980) and in the field (*eg* Bacon and Anderson 1982, Balls 1988, Cremers and Maes 1986). In most cases, and especially for particle-reactive elements, partition coefficients increase with decreasing suspended solid loadings (Balls 1989, Nevissi 1986). Theoretical calculations, however, predict that partition coefficients should not vary by more than a factor of ten over a wide range of suspended sediment loadings (Duursma and Hoede 1967) and, even though their partition coefficients are not low, Mn, Zn, Cs and Co do not follow the inverse relationship (Duursma and Bosch 1970, Hamilton 1986, Schell and Sibley 1982). Alberts *et al* (1986) suggested that the negative regression of the log K_d against log particle concentrations was an artefact caused by the theoretical constraints of the K_d expression, while Duursma and Bosch (1970) attributed it to the methodology used. Gschwend and Wu (1985) suggested that the partition coefficients of polychlorinated biphenyls would become constant if non-filterable material were taken into account. Using cross-flow filtration, Moran and Moore (1989) found that 10-15% of oceanic "dissolved" carbon, aluminium and thorium were associated with colloidal material, but that the fraction for thorium rose to 50% in coastal waters. Experimental and field results as well as a mathematical model were used to compare "true" K_ds (taking into account colloidal matter) with "apparent" K_ds, and to investigate the relationship of "apparent" K_ds with concentrations of particulate matter. Partition coefficients were found not to be affected by particulate concentration in the range 0.01 to $1 mgl^{-1}$, but decreased with greater particulate loadings. It was concluded that the particle-concentration effect was important for riverine, estuarine and coastal environments with high SPM loadings but insignificant for most of the global ocean. Other workers have attributed the negative regression to particle-particle interactions (*eg* Bacon and Anderson 1982). Di Toro *et al* (1986) used dilution and resuspension experiments to test this hypothesis. They demonstrated that particle-particle interactions, not colloidal material, caused the apparent changes in partition coefficients. They modelled the adsorption of Ni and Co onto montmorillonite and quartz assuming that an additional desorption reaction occurred resulting from particle-particle interaction and their model agreed with the experimental results.

1.4: The behaviour of trace elements in estuarine environments

Estuaries are zones where "sea water is substantially diluted with fresh water entering from land drainage" (Burton 1976). Since the composition of river water differs significantly from that of sea water, estuarine mixing zones are characterised by strong gradients of ionic strength (salinity), pH and redox potential (Burton 1978, Liss 1976). Partially-mixed tidally-dominated estuaries often have a turbidity maximum zone in the low salinity region, and sometimes a productivity maximum zone at the mouth of the estuary (Church 1986). These variations may cause chemical interactions between dissolved constituents and particulate matter.

Assuming a single riverine source, the behaviour of a species within an estuary can be described as conservative or non-conservative (*eg* Liss 1976). Conservative behaviour occurs when there is no (detectable) exchange between dissolved and particulate phases, *ie* when the overriding factor governing dissolved concentrations of the element is the physical mixing of the riverine water with the sea water. In this case, the observed concentration at any point along the estuary is dependent on the end-member concentrations and the extent of dilution of river water with sea water at that point. In practice, since the major dissolved "salt" elements in sea water have residence times much greater than those of estuarine waters or sediments, salinity is often used as a conservative index, and trace elements are classed as conservative if their concentrations vary linearly with salinity. If concentrations are greater in the river water than in sea water, then the concentration/salinity plot will have a negative slope. If the converse is true, then the plot will have a positive slope. Non-conservative species have concentration profiles which deviate from the theoretical dilution line joining the two end-member concentrations. Profiles showing a positive deviation from the theoretical dilution line indicate that the species is being added to the system, while profiles with negative deviations show that the species is being removed (Figure 1.2). Primary sources of metals to estuaries include natural weathering or anthropogenic additions (atmospheric or riverine sources), and secondary sources include diagenetic remobilisation from bottom sediments (*eg* redox cycling) or desorption from suspended particles. Primary sinks include sedimentation, or advection out of the estuarine basin to coastal waters (Church 1986). Other sinks would include uptake by phytoplankton, or adsorption onto particles.

Dissolved trace metal profiles in estuaries may be the results of two or more opposing processes. Dissolved manganese, for example, may be added to the water column by diffusion from bottom sediments and be simultaneously removed from solution by oxidation and adsorption onto suspended particulate matter (Graham *et al* 1976). Some profiles show that metals are removed from one part of the estuary but added to another part, *eg* manganese in the Rhine (Duinker *et al* 1979a), Scheldt (Duinker *et al* 1982c) and Yaquina estuaries (Callaway *et al* 1988). Sometimes it is difficult to determine whether profiles are a result of addition in one part of an estuary or removal in another (*eg* nickel in the Humber, Barnett *et al* 1989).

For positive or negative deviations from a conservative mixing line to be detectable, rates of "addition" or "removal" of a constituent must be fast compared with the net water flow through the system. Even when rates of reaction are fast, water dynamics may prevent the dissolved constituents from reaching equilibrium, *ie* the observed deviation from the mixing line may be partly dependent on riverine flow. To fully interpret mixing curves, therefore, it is necessary to compare the water residence time with the rates of reaction involving the constituent. The flushing time of water through an estuary (or

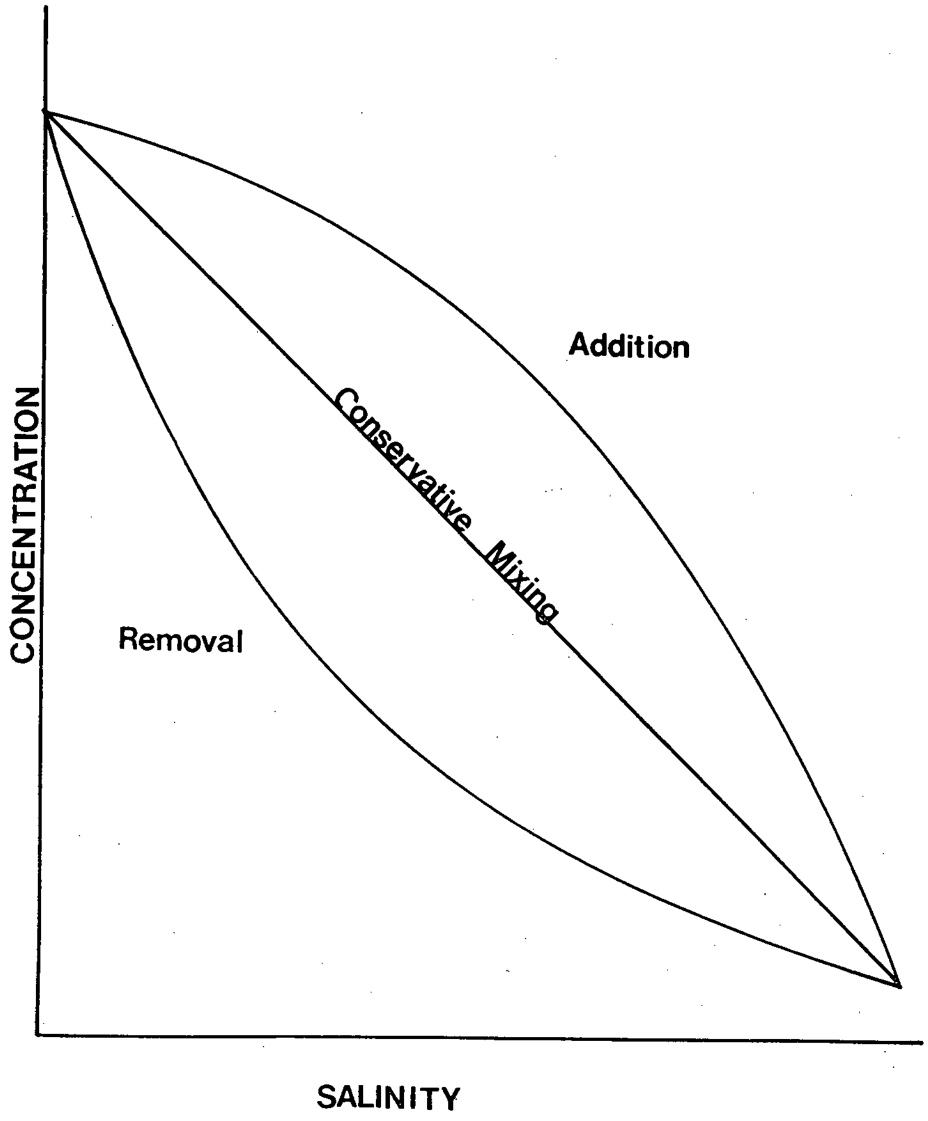

Figure 1.2. Conservative and non-conservative behaviour in estuarine mixing zones.

part of an estuary) can be calculated from a knowledge of the volume and salinity of the estuarine water and the fresh water flow rate. Since fresh water flows are dependent on rainfall variations, turnover times within a single system will vary throughout the year (Morris 1990). Positive deviations from the conservative mixing line are smaller in high flow conditions than low flow conditions, for example, in the Mae Klong estuary (Cd, Cu, Pb and Zn, Hung~~e~~spreugs *et al* 1990) and in the Yaquina estuary (Mn, Callaway *et al* 1988). Similarly, removal of zinc from the Clyde was much more pronounced in low flow than in spate conditions (Mackay and Leatherland 1976).

Varying riverine end-member concentrations may result in non-linear mixing curves even for conservative elements. The magnitude of this effect, and the resulting shape of the mixing curve, is dependent on the rate of change of the end-member concentration compared with the flushing time of the estuary. It is therefore necessary to know whether end-member concentrations are stable, and the time scales over which any variation occurs (Loder and Reichard 1981). Both the short-term effects of changing riverine concentrations and flow rates are usually dampened out in lower parts of estuaries because of the larger water volume and longer residence times (Callaway *et al* 1988).

The behaviour of dissolved metals in various estuaries is summarised in Table 1.3. One of the immediate conclusions from inspection of the literature in this way is that there is no universal pattern of behaviour for all estuaries. Metal behaviour is complex and different combinations of processes dominate in each estuary. Some of the processes which cause the observed behaviours are given below.

Table 1.3. Trace metal behaviour in various estuaries

Behaviour	Metal	Estuary
Conservative Increase	Cd	Gota [12]
	U	Tamar [38] ; Clyde [38]
Conservative Decrease	Cd	Humber [4]
	Co	St Lawrence [5]
	Cu	Severn [2] ; outer Forth [3] ; Gota [12] ; St Lawrence [5]
	Fe	Elliott Bay [34]
	Mn	Beaulieu [26,30] ;Elliott Bay [34]
	Ni	Severn [2,31] ; Gota [12] ; Scheldt [19] ; St Lawrence [5]
	Pb	Elliott Bay [34]
	Zn	Severn [2] ; Beaulieu [26] ; Gota [12]
Addition	As	Severn [2]
	Cd	Severn [2,31] ; Ems [20] ; Gironde, Rhône [22] ; Scheldt [19] ; Elbe [23] ; St Lawrence [5] ; Elliott Bay [33] ; Geum [7] ; Huanghe [22] ; Yangtze [22] ; Mae Klong [27]
	Cr	Severn [2]
	Cu	Humber [4] ; Ems [20] ; Weser [17] ; Elliott Bay [33,34] ; San Francisco Bay [21] ; Geum [7] ; Mae Klong [27]
	Fe	Humber [4] ; Weser [17]
	Hg	Forth [13] ; Krka [29]
	Mn	Tamar [28] ; Tees [37] ; Scheldt [16,19] ; Rhine [16] ; St Lawrence [5] ; Narragansett Bay [24] ; Peconic River [39] ; Yaquina [8] ; Mae Klong [27]
	Ni	Mersey [9] ; Elliott Bay [33] ; San Francisco Bay [21] ; Geum [7]
	Pb	Elliott Bay [33] ; Geum [7] ; Mae Klong [27]
	Zn	Mersey [9] ; Severn [31] ; Tees [37] ; Humber [4] ; Ems [20] ; Weser [17] ; Scheldt [19] ; St Lawrence [5] ; Fraser [25] ; Mae Klong [27] ; Elliott Bay [33,34] ; San Francisco Bay [21]
Removal	Cd	Weser [17] ; Rhine [14]
	Co	Delaware Bay [10]
	Cu	Water of Luce [36] ; Tamar [32] ; Elbe [18] ; Rhine [14,15] ; Amazon [6] ; Nile [1]
	Fe	Beaulieu [26,30] ; Water of Luce [36] ; Elbe [18] ; Weser [17] ; Gota [12] ; St Lawrence [5,42] ; Peconic [39] ; Delaware Bay [10] ; Geum [7] ; Bang Pakong [27,41]
	Mn	Severn [31] ; Water of Luce [36] ; Elbe [18] ; Weser [17] ; St Lawrence [11] ; Delaware Bay [10] ; Geum [7]
	Ni	Humber [4] ; Tamar [32] ; Water of Luce [36]
	Pb	Puget Sound [35] ; Savannah [40] ; Nile [1] ; Bang Pakong [41]
	U	Forth [38]
	Zn	Tamar [32] ; Elbe [18] ; Rhine [14]

References

1	Abdel-Moati (1990)
2	Apte *et al* (1990)
3	Balls and Topping (1987)
4	Barnett *et al* (1989)
5	Bewers and Yeats (1979)
6	Boyle *et al* (1982)
7	Byrd *et al* (1990)
8	Callaway *et al* (1988)
9	Campbell *et al* (1988)
10	Church (1986)
11	Cossa *et al* (1988)
12	Danielsson *et al* (1983)
13	Davies (1980)
14	Duinker and Nolting (1977)
15	Duinker and Nolting (1978)
16	Duinker *et al* (1979a)
17	Duinker *et al* (1982a)
18	Duinker *et al* (1982b)
19	Duinker *et al* (1982c)
20	Duinker *et al* (1985)
21	Eaton (1979b)
22	Elbaz-Poulichet *et al* (1987)
23	Förstner *et al* (1990)
24	Graham *et al* (1976)
25	Grieve and Fletcher (1977)
26	Holliday and Liss (1976)
27	Hungspreugs *et al* (1990)
28	Knox *et al* (1981)
29	Mikac *et al* (1989)
30	Moore *et al* (1979)
31	Morris (1984)
32	Morris (1986)
33	Paulson *et al* (1989a)
34	Paulson *et al* (1989b)
35	Paulson *et al* (1989c)
36	Sholkovitz (1978)
37	Taylor (1982)
38	Toole *et al* (1987)
39	Wilke and Dayal (1982)
40	Windom *et al* (1985)
41	Windom *et al* (1988)
42	Yeats (1988)

1.4.1: Conservative behaviour

Conservative behaviour occurs when river water or sea water sources dominate the metal concentrations, (or there are no changes in concentrations throughout the estuary) and removal or addition processes within an estuarine mixing zone are undetectable. Trace metal concentrations are usually higher in river water than in sea water (*eg* because of anthropogenic additions and bedrock weathering), so profiles with inverse relationships with salinity are more usual than profiles which increase with salinity. Copper, zinc and nickel concentrations in the Severn estuary, for example, decrease with increasing salinity (Apte *et al* 1990). Geochemically unreactive constituents, like lithium, uranium, molybdenum and fluorine, have long oceanic residence times and therefore have higher concentrations in sea water than in river water (Burton 1976). Since sea water is the major source of these elements, their concentrations increase with salinity, *eg* uranium in the Tamar and Clyde estuaries (Toole *et al* 1987).

1.4.2: Addition

Point sources, which can arise from anthropogenic or natural (*eg* riverine) discharges, give sharp mid-estuarine maxima, with ~~conservative~~ mixing upstream and downstream of the source. Such behaviour has been observed for Zn in the Scheldt, where the input was tentatively attributed to release from the decay of freshwater phytoplankton as it entered brackish waters (Duinker *et al* 1982c).

Non-point sources usually show wide peaks over large salinity ranges. These are caused by release from bottom sediments, suspended sediments, biological material, or by multiple "point" sources. The rate of addition can be calculated from the area between the metal salinity profile curve and the line for conservative mixing (*ie* the "excess" concentration) multiplied by the river flow (Windom *et al* 1991). Fluxes from bottom sediments can be calculated from the "excess" concentration multiplied by the estuary volume, divided by the bottom area and the residence time (Callaway *et al* 1988).

Manganese has a benthic source which results in a broad mid-estuarine peak in many, but not all, estuaries. This has been observed in the St Lawrence (Bewers and Yeats 1979), Geum (Byrd *et al* 1990), Tamar (Knox *et al* 1981) and Newport estuaries (Evans *et al* 1977). The manganese enrichment in the Peconic river estuary was 200% above its predicted concentration (Wilke and Dayal 1982). Because of its benthic source, bottom water concentrations exceed surface water concentrations in Narrangansett Bay (Graham *et al* 1976), St Lawrence estuary (Bewers and Yeats 1979) and the upper part of the Yaquina estuary (Callaway *et al* 1988).

In some estuaries, *eg* the Geum and the Tamar, dissolved manganese has been found to correlate with ammonia in the water column. Though ammonia and reduced manganese are involved in quite different chemical reactions, they are both thermodynamically stable in anoxic sediments. Their similar estuarine profiles are therefore caused by physical processes, *eg* sediment resuspension and/or diffusion of interstitial water into the water column (Byrd *et al* 1990, Knox *et al* 1981). A mathematical formulation of this release has been tested statistically against field measurements of water and interstitial concentrations. The results are positive and calculated benthic fluxes are consistent with measured water column concentrations (Knox *et al* 1981). Other estimations of benthic fluxes are summarised in Table 1.4.

Manganese remobilisation is dependent on redox potential (Duinker *et al* 1979a, 1982c, Wollast *et al* 1979) and benthic fluxes are enhanced in the warmer summer months, when biological activity is increased and oxygen concentrations are generally lower (Dehairs *et al* 1989). Manganese fluxes in water temperatures of 20°C, for example, are an order of magnitude higher than fluxes in temperatures of 5°C (Elderfield *et al* 1981).

Table 1.4. Estimated benthic manganese fluxes.

Study area	Flux ($\mu gcm^{-2}d^{-1}$)	Method of estimation	Reference
Yaquina estuary	0.8-2.0	Calculated	Callaway *et al* 1988
Peconic River	5	Calculated	Wilke and Dayal 1982
Mississippi Delta	1-8	Calculated	Trefry *et al* 1986
Scheldt estuary	1	Calculated	Duinker *et al* 1979a
Tamar estuary	5.3-53	Calculated	Knox *et al* 1981
Tamar estuary	38-92	Sediment cores	Knox *et al* 1981
Long Island Sound	<0-20	Sediment cores	Aller and Benniger 1981
Narragansett Bay	1-3	Bottom chambers	Graham *et al* 1976
Narragansett Bay	2.7-3.5	Bottom chambers	Elderfield *et al* 1981
Chesapeake Bay	0.2-2.2	Microcosm experiments	Hunt 1983
Chesapeake Bay	<1.7-38.5	Core experiments	Eaton 1979a
Newport River	5-13	Core experiments	Evans *et al* 1977
Belgian Coast	2-61	Interstitial profiles	Dehairs *et al* 1989
Calico Creek	0.7	Interstitial profiles	Sanders 1978
Guatemala Basin	0.021-0.22	Interstitial profiles	Sawlan and Murray 1983
Mexican Cont. Shelf	0.017-0.47	Interstitial profiles	Sawlan and Murray 1983

Dissolved manganese maxima are not always coincident with peak suspended loads in estuaries (Callaway *et al* 1988), suggesting that sediment resuspension is not necessarily the dominant mechanism causing manganese fluxes across the sediment water interface. During periods of low river flow for example, manganese removal occurs at the turbidity maximum in the freshwater portion of the Tamar, while addition occurs in the saline portion of the estuary. Neither peak is well defined during periods of high river flow (Knox *et al* 1981). In the turbidity maximum, however, Mn concentrations increase from neap to spring tides as maximum tidal currents increase (Morris *et al* 1982). The long residence time and high suspended solids loading of the Scheldt estuary give rise to pronounced microbial activity and an oxygen sag. Here, also the resulting peak in dissolved manganese is coincident with the turbidity maximum (Duinker *et al* 1982c).

Remobilisation processes in sub-oxic sediments can result in increased interstitial water concentrations of other metals (Duinker *et al* 1982a). The sediments may therefore act as a source of these metals. If their release is caused directly by the remobilisation of manganese, the dissolved concentrations of the trace elements will covary with the dissolved manganese concentrations. This is the case for zinc and cadmium in the St Lawrence estuary (Bewers and Yeats 1979) and zinc, copper and lead in the Geum estuary. Alternatively, metals may be released by sediment resuspension and would then covary with the suspended solids loadings. This is the case for nickel in the Geum estuary (Byrd *et al* 1990). Similarly, cadmium, copper, iron, manganese and zinc concentrations in the bottom waters of the Weser estuary are elevated during peak flows of the flood tide, when strong currents cause a large amount of sediment resuspension (Duinker *et al* 1982a).

Ion exchange processes may cause desorption of heavy metals from suspended particles as they mix with water of increasing ionic strength (salinity). For example, particulate manganese undergoes exchange reactions with sea water cations like Ca, Mg and Na in the Peconic River estuary. The increase in dissolved manganese concentrations is reflected by a corresponding decrease in particulate concentrations (Wilke and Dayal 1982). Similar processes have been observed by Graham *et al* (1976) in Narragansett Bay.

Dissolved chloride ions, which are more abundant in sea water than river water, form highly stable soluble complexes with cadmium and cause dissolved cadmium concentrations to increase with salinity. Such chloro-complexation has been observed in the Gironde, Rhône, Huanghe and Changjiang river estuaries, though the increases in dissolved cadmium concentrations do not always occur at the same salinities. It is thought that the desorption of cadmium, which depends on a number of variables, occurs first and is followed by the formation of the chloro-complexes which prevent its readsorption onto particles (Elbaz-Poulichet *et al* 1987). This has been tested by adsorption and desorption experiments using sediment from the Rhine (Comans and van Dijk 1988). The experiments confirm that Cd adsorption is reversible and the adsorption equilibrium moves progressively towards the dissolved phase with increasing salinity. Desorption is rapid for the first two days, but complete equilibrium is only reached after two weeks. The experimental results suggested that the concentration of free Cd^{2+} drives the desorption reactions. When the free Cd^{2+} ions are removed by complexation with chloride ions, further desorption of particulate cadmium occurs.

Concentrations of many trace metals in estuarine and sea water are influenced by phytoplankton uptake (Collier and Edmond 1984, Sunda 1989). Conversely, the bacterial degradation of organic matter re-releases these metals. During experimental degradation of organic matter, nickel and copper are released in association with dissolved organic matter, while cadmium forms chloro-complexes. Any lead released does not enter the dissolved phase, but immediately precipitates as a salt or oxide (Gerringa 1990). The effects of degradation of biological material have been observed in estuaries. For example, zinc has been found to correlate with nitrate concentrations in the Bang Pakong estuary of Thailand, where broad maxima in concentrations of Zn, Cd and Co coincide with nitrate and phosphate maxima. Since nutrient increases are due to the breakdown of organic detritus by microbial activity, it would appear that increased Zn and, perhaps, Co and Cd are also the result of this process (Windom *et al* 1988). Church (1986) observed similar relationships between cadmium and phosphate in the Delaware estuary and reached similar conclusions.

1.4.3: Removal

Mechanisms of removal in estuaries include scavenging by suspended particles and hydroxide coatings, flocculation of colloidal material, pH increases and biological uptake. Rates of removal can be calculated by determining the difference between the actual concentration at zero salinity and that of the intercept of a projected line from the metal-salinity plot and multiplying this difference by the fresh water flow (Windom *et al* 1991).

The removal of trace metals by particulate scavenging is especially important in the low-salinity high-turbidity zones of turbid estuaries, *eg* the Tamar (Cu, Ni, Zn; Morris *et al* 1986), Geum, Korea (Mn; Byrd *et al* 1990), Forth (U; Toole *et al* 1987), Elbe (Cd, Cu, Fe, Mn, Zn; Duinker *et al* 1982b), and Rhine (Cd, Cu, Fe, Zn; Duinker and Nolting 1978). Removal in the Rhine accounts for 40% of the cadmium, 50% of the copper and 30% of the zinc at a salinity of 20 °/₀₀ (Duinker and Nolting 1977). Discharges of particulate matter may have similar effects. For example, manganese is removed from the surface waters of the Saguenay Fjord by adsorption onto particulate organic matter discharged by the Saguenay River. Here, the depth and degree of stratification of the fjord prevent the flux of dissolved manganese from the bottom sediments from reaching the surface waters (Bewers and Yeats 1979).

A large proportion of "dissolved" riverine iron (*eg* 90% in the Beaulieu) is associated with colloidal organic matter. As river water mixes with estuarine water, these colloids become unstable and aggregate, causing an increase in particle size ~~break down and release the iron. The iron then flocculates and forms insoluble hydrous oxides~~ (Moore *et al* 1979). This behaviour can be reproduced experimentally. For example, when filtered river water (Water of Luce, Scotland) is mixed with filtered sea water, 95% of the riverine iron is removed by flocculation between salinities of 0-18 ‰ (Sholkovitz 1978). This non-conservative removal of iron is common in the low salinity zones of many estuaries, including the Peconic estuary, New York (Wilke and Dayal 1982), Geum estuary, Korea (Byrd *et al* 1990) and Beaulieu estuary, UK (Holliday and Liss 1976, Moore *et al* 1979).

The scavenging ability of iron and manganese hydrous oxides is well known (*eg* Gibbs 1973, Jenne 1968). Coprecipitation of metals with iron hydroxide is important in the Tees (Taylor 1982), Geum (Co, Zn; Byrd *et al* 1990), Gota (Pb; Danielsson *et al* 1983) and San Francisco Bay estuaries (Cu; Eaton 1979b). In the Water of Luce experiments, removal accounted for 40% of the Cu and Ni and 10% of the Co, but only 5% of the Cd (Sholkovitz 1978). The importance of scavenging by the Fe-Mn hydrous oxide coatings of particles can be determined directly by leaching with 1M hydroxylamine-hydrochloride/acetic acid solution (Tessier *et al* 1979), or indirectly by correlating trace metal concentrations with manganese or iron concentrations. Such removal has been shown for zinc in the Fraser River estuary (Grieve and Fletcher 1977) and for lead and copper in Puget Sound and Elliott Bay (Paulson *et al* 1989b). Precipitation of the oxide phases, and the associated metal removal, appears to be more pronounced in periods of low river flow (Eaton 1979b, Paulson *et al* 1989b).

The mechanism of iron removal in tropical estuaries may be quite different from that in temperate estuaries. Concentrations of dissolved organic carbon in the Bang Pakong estuary, Thailand, for example, are too low to account for the colloidal release of dissolved iron. Instead, removal is attributed to the lower solubility of iron at the increasing pHs encountered in estuarine water (Windom *et al* 1988).

Although phytoplankton decomposition may cause measurable additions of trace metals to estuarine waters (*eg* Church 1986, Windom *et al* 1988), biological uptake has been observed less frequently and seems to be cited more tentatively. Copper removal in the low salinity, high turbidity zone of the San Francisco Bay estuary in July, for example, was partly attributed to biological uptake, since phytoplankton accounted for 30% of the suspended particulate matter in this zone (Eaton 1979b). Biological removal has also been observed in the Amazon (Cu; Boyle *et al* 1982) and Nile estuaries (Cu, Pb; Abdel-Moati 1990). Windom *et al* (1991) studied relationships between nutrients and trace metals in estuaries. Metal and nitrogen removal were both observed in the Medway estuary, though the metal/nutrient ratios were too high to be explained by biological uptake alone. They therefore concluded that processes other than biological uptake are more important in controlling trace metal removal from estuaries.

Where estuaries are too turbid for phytoplankton growth, nutrients travel through the estuary to the less turbid outer reaches where phytoplankton blooms may develop. Metal removal in this "productivity maximum" may be more easily attributed to biological activity, since this is away from the zone of flocculation/precipitation of iron and from the turbidity maximum, both of which may cause removal of trace metals from the dissolved phase. A productivity maximum, thriving on nutrients leaving the highly turbid Severn estuary, has been observed in the Bristol Channel. Here, seasonal changes in nutrient concentrations and in suspended particulate composition have been attributed to primary productivity (Morris 1984). Trace elements (including Zn, Ni, Cu, and Cd) are recycled in the productivity maximum zone of the outer Delaware estuary. The behaviour of the trace elements (*eg* Fe, Cd) and nutrients (*eg* PO_4) appear biogeochemically linked. During periods of peak production at the higher salinities, cadmium and phosphate were correlated with molar ratios very similar to those found in the open Pacific ($3.50 \pm 0.4 \times 10^4$). This implies that the biological processes controlling cadmium and phosphorus recycling in estuarine waters are similar to those in open ocean waters (Church 1986).

1.5: Sampling and analytical considerations

The quality of trace metal data from marine environments has improved greatly during the last twenty years. Few data sets were reliable before the early 1980's (Windom *et al* 1985), as was reflected by the high level of disagreement between experienced marine laboratories during intercomparison exercises (Bewers and Windom 1982, Hume 1974). Since then, problems of sample contamination during collection, handling and analysis have been recognised and controlled. These factors have led to orders of magnitude decreases in accepted values for dissolved metal concentrations in sea water (Berman and Yeats 1985, Bruland *et al* 1979, Bruland 1983, Johnson *et al* 1987, Patterson and Settle 1976).

some metals (not all)

1.5.1: Sample collection

The importance of using clean materials for sea water samplers was recognised in the 1970's, when many of the early samplers were shown to give contaminated dissolved metal results. Such samplers included glass bottles (Duinker *et al* 1979a) and "Niskin" bottles with internal closures (Segar and Berberian 1974). Currently the best oceanic samplers for trace metals are those which (i) are made of, and deployed with, relatively inert materials like teflon, polythene and kevlar, (ii) avoid contamination from the metal rich surface layers and (iii) are deployed away from the research vessel. Uncontaminated deep water samples can be collected using teflon coated Go-Flo bottles, deployed on a kevlar wire and triggered with teflon coated messengers (Brügmann *et al* 1985). These bottles avoid contamination from the ship and from surface waters by remaining closed until they reach depths of a few metres. Surface water samples have been collected successfully using a peristaltic pump with plastic tubing (*eg* Balls and

Topping 1987) and a teflon bellows pump with FEP tubing (*eg* Harper 1987). In the first case, the sample tubing was pushed away from the research vessel with a bamboo pole, and in the second, by suspending it from a surface buoy deployed away from the vessel. The sample tubing of each system can be thoroughly cleaned before use and flushed with sea water on site before samples are taken.

1.5.2: Sample treatment

Dissolved and particulate metal fractions are operationally defined and partly depend on the separation procedures used, for example speed of centrifugation or filter type. Filters which become clogged retain smaller particles, while centrifuged samples may not include smaller, less dense particles (Duinker *et al* 1979b). Conversely, Comba and Kaiser (1990) reported that filtration resulted in lower total particulate concentrations than centrifugation and attributed this to particle flocculation or disaggregation caused by the sheer stress involved in centrifugation. Various methods of suspended sediment concentration have been compared, including batch centrifugation, settling centrifugation, sample evaporation by heating or freeze-drying, pressure filtration and backflush filtration (*ie* filtering using a peristaltic pump until the filter clogs, then back-filtering to resuspend the sediment and analysing the suspension). Batch centrifugation and pressure filtration were preferred because of their reproducibility, relative speed and comparative ease of contamination-free handling (Horowitz 1988).

Pressure filtration of the sample directly from the receiving apparatus (*eg* Go-Flo bottle) is "on-line" filtration, while "off-line" filtration refers to samples which have been collected, transferred to bottles and then filtered at a later stage. Both filtration procedures are capable of yielding uncontaminated trace metal samples, but on-line filtration involves less sample handling. If filtration is slow, however, samplers may be prevented from being redeployed immediately and suspended particulate matter loadings may be more difficult to evaluate because of particle settling (Calvert and McCartney 1979). Off-line systems avoid these problems and enable whole samples to be filtered (Bewers *et al* 1985).

The performances of different membranes for dissolved and particulate trace metal analyses vary greatly (see Table 1.5). Cellulose nitrate filters give suspended loadings five times higher than Nuclepore polycarbonate or Dubna polyethylene-terephthalate membranes for suspended solids loadings ranging from 0.5 to 4 mgl^{-1} (Brzezinska-Paudyn *et al* 1985, Danielsson 1982, Tambiyev and Demina 1982). Nuclepore membranes are much cleaner than other membranes with respect to trace metals and can be further cleaned with high purity acids. They are also preferred for gravimetric analysis, since they have well defined pore sizes which give precise cut-off points. Polycarbonate membranes do not retain water and are therefore easy to dry for re-weighing after sample collection. They

Table 1.5 Comparison of various filters for gravimetric and trace metal analysis

Filter	Pore size (μm)	SPM	Blanks	Reference
Nuclepore polycarbonate	0.4	OK	OK	1,3
Millipore cellulose acetate/nitrate	0.45	High	High	1,2,3
Mytishchi nitrocellulose	0.7	High	High	3
Dubna polyethylene-terephthalate	0.5	OK	OK	3
Glass fibre	0.45	High		1

References:

1 Brzezinska-Paudyn *et al* (1985)
2 Danielsson (1982)
3 Tambiyev and Demina (1982)

are less brittle than Millipore filters and can be handled without undue risk of damage. They clog at relatively low loadings, however, and this may limit the amount of material that can be collected (Yeats and Brügmann 1990).

1.5.3: Sample analysis

Methods of avoiding errors during trace metal analysis have been described in detail by Tölg (1972) and Moody and Beary (1982). Potential errors arise from reactions occurring at the interfaces of reagent or sample solutions with container walls and are most noticeable for dilute solutions. Teflon, polypropylene and polythene materials are least prone to such reactions and adsorption is less likely in acidic solutions because hydrogen ions have high affinities for surface sites. Adsorption/desorption reactions can be further reduced by equilibrating the surfaces with aliquots of the solution to be stored before use. However, Muller *et al* (1991) reported that the adsorptive properties of FEP separating funnels changed after more than 200 hours of use in the dithiocarbamate-freon extraction technique. These changes caused trace metal extraction recoveries to fall considerably and were attributed to the presence of adsorption sites involving the "aged" FEP surfaces and the dithiocarbamate complexing agents. No materials are completely inert, therefore, and reagents and samples should be stored for as short a time as possible.

Reagent blank values should be less than 10% of analyte concentrations. The quality of some manufactured reagents is sufficient for trace analytical work, but others need to be cleaned or made up in the laboratory. Reagents can be purified by a number of methods, including ion-exchange chromatography, electrochemistry, sub-boiling distillation, isothermal distillation, low temperature sublimation, solvent extraction, direct synthesis and gas, liquid and column chromatography (Mitchell 1982).

1.5.4: Instrumental techniques

Few instrumental techniques give detection limits low enough for analysis of trace metals in sea water. The methods currently used include atomic absorption spectrometry, inductively coupled plasma mass spectrometry and electrochemistry. These are compared in Table 1.6 and are discussed below.

Table 1.6 Comparison of analytical instruments for analysis of trace metals in sea water samples. (Mainly from Nürnberg 1984, Sturgeon 1990).

	GFAAS	ICP-MS	Voltammetry
Elements analysed	45	75	> 13
Multi-element capability	No	Yes	Limited
<u>Detection limits (ppb):</u>			
Cd	0.01	0.07	0.0015 (MFE)
Cu	0.05	0.03	0.05 (MFE)
Mn	0.05	0.04	
Ni	0.5	0.03	0.02 (HMDE)
Pb	0.3	0.05	0.0015 (MFE)
Zn	0.005	0.08	0.5 (HMDE)
<u>Sample preparation:</u>			
Separation from matrix	Yes	Yes	No
Preconcentration	Yes	Yes	Electrochemical
Other treatment	None	None	UV-irradiation
Speciation application	No	No	Yes
Isotope ratios	No	Yes	No
Sample throughput/h	20-30	1000-2000	20-30
Dynamic range	10^2-10^3	10^4-10^6	10^4-10^6
Interferences	Moderate	Moderate	Few
Ship-board analysis	No	No	Yes
Relative cost	Intermediate	Very high	Low

GFAAS = graphite furnace atomic absorption spectrometry
ICP-MS = inductively coupled plasma mass spectrometry
MFE = mercury film electrode
HMDE = hanging mercury-drop electrode

1.5.4.1: Atomic absorption spectrometry

Atomic absorption spectrometry has become the most commonly used method for trace element analysis of environmental materials. It involves the absorption of light of a specific wavelength by ~~thermally excited atoms of the analyte element~~ analyte atoms in the ground state,. The amount of light absorbed is proportional to the number of analyte atoms present. Samples are atomised by aspiration into a flame, or heating in a graphite furnace. Flame atomic absorption spectrometry (FAAS) is quicker and cheaper than graphite furnace techniques (GFAAS), though the increased sensitivity of GFAAS is required for trace analysis of natural waters (Aston 1985). Some authors have determined metals in coastal waters by direct injection into a GFAAS, using carefully optimised furnace conditions to control background effects (*eg* Campbell and Ottaway 1977). The presence of sea salts, however, decreases instrumental sensitivities so much that even for waters containing high dissolved metal concentrations, direct injection is limited to a small number of elements. It is normally necessary to preconcentrate trace metals from sea water and to remove the interfering salt elements (Sturgeon *et al* 1980).

Methods of analyte preconcentration include chelation with immobilised ligands (separation column), chelation/solvent extraction and coprecipitation. These enable simultaneous separation of a number of trace elements for subsequent analysis (Sturgeon and Berman 1988).

Solvent extraction procedures usually involve the complexation of heavy metals with dithiocarbamate (or similar agents) into an organic phase and may include a back extraction step into dilute acid. Back extraction into acid increases the stability of the extract and gives a second step for concentration of the heavy metals. Dithiocarbamate complexing agents remove heavy metals from sea water samples without removing the group I and II elements. This eliminates interference problems during subsequent analysis by GFAAS (Sturgeon *et al* 1980).

Chelating resins enable larger sample volumes to be used than solvent extraction methods, so larger concentration factors can be achieved. Group I and II elements are stripped from the column along with the trace elements, unless they are removed with ammonium acetate buffer at pH 5.2 before the heavy metals are eluted with acid. Sturgeon *et al* (1980) compared both solvent extraction and ion exchange preconcentration methods and found that they gave comparable results for GFAAS analysis.

A method of on-line separation and preconcentration for analysis by GFAAS has recently been described. This involves modification of the autosampler tubing to allow insertion of a microcolumn containing ammonium pyrrolidinedithiocarbamate as a complexing agent. After concentration on the column, the samples are eluted with acetonitrile into the furnace tube (Porta *et al* 1991).

Volatile hydrides (*eg* As, Bi, Ge, Te, Sb, Se, Sn, and Pb) can be preconcentrated *in situ* during furnace analysis. They are generated conventionally and transported to a preheated graphite tube (<800 °C), where they decompose and are deposited on the tube wall. The sample is atomised and the signal recorded in the usual way. The detection limits are lowered using this technique because of the preconcentration step involved (Sturgeon and Berman 1988).

Reductive precipitation is capable of separating and concentrating 15 elements of environmental interest, including elements which form volatile hydrides (Sturgeon and Berman 1988). The method involves the precipitation of trace elements with Fe and Pd carriers, reducing the precipitates with $NaBO_4$ and redissolving the filtered precipitate with a small volume of aqua regia for subsequent analysis. Other preconcentration methods include the coprecipitation of metals with cobalt pyrrolidinedithiocarbamate, followed by filtration, redissolution and determination by AAS (Boyle and Edmond 1977, Muller and Kester 1991).

1.5.4.2: Inductively coupled plasma mass spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) involves the rapid sequential determination of ionised atoms from a plasma torch by mass spectrometry. Samples are aspirated into a quartz torch with a 1-2.5KW radio frequency power supply and ionised at temperatures of 5000 to 9000K (*cf* atomisation temperatures less than 3000K for GFAAS). The ions are pumped from the ICP into a low-pressure ($<10^{-5}$ torr) mass spectrometer for quantitative detection. Because of the high temperatures of the plasma torch, ionisation is more than 90% complete for most elements and intense emission is produced from many spectral lines simultaneously. Some spectral overlap occurs, but this can usually be overcome by using alternative isotopes, *eg* ^{40}Ar masks the signal from ^{40}Ca, but the less abundant ^{44}Ca isotope can be used instead (Gray 1989).

Though very expensive, ICP-MS has a number of advantages over GFAAS or voltammetric methods. Comparable or better detection limits are achieved, analysis is faster, the range of analyte elements is greater and the dynamic range of the instrument is larger, making repetitive dilutions unnecessary (Sturgeon 1990). It is necessary to separate and preconcentrate trace metals from sea water samples, however, because the sensitivity is severely reduced by high concentrations of dissolved salts (Beauchemin *et al* 1988, McLaren *et al* 1990). Some separation and preconcentration procedures used for sea water analysis by ICP-MS are given in Table 1.7. Other methods have been fully reviewed by Horváth *et al* (1991).

Table 1.7 Methods of separation and preconcentration of trace elements from sea water for subsequent analysis by ICP-MS.

Elements	Sample	Preconcentration	Reference
Ni Cu Zn Mo Cd Pb (U)	NASS-2	Silica-immobilised 8-hydroxyquinoline (x 50)	Beauchemin *et al* (1988)
Ni Cu Mo Cd Pb U	CASS-2	Silica-immobilised 8-hydroxyquinoline (x 90)	McLaren *et al* (1990)
	CASS-2	Reductive coprecipitation with Fe and Pd (x 90)	McLaren *et al* (1990)
REEs Y		Solvent extraction with HDEHP/H_2MEHP in heptane and back extraction with octyl alcohol and HNO_3 (x 200)	Shabani *et al* (1990)
REEs	Synthetic sea water	On-line continuous solvent extraction with HDEHP/H_2MEHP in heptane and back extraction with octyl alcohol and HNO_3 (x 10)	Shabani and Masuda (1991)

HDEHP is bis (2-ethylhexyl) hydrogen phosphate
H_2MEHP is 2-ethylhexyl dihydrogen phosphate
REE is rare earth elements

Detection limits and matrix interferences may be further reduced by interfacing the ICP with alternative forms of sample introduction. Electrothermal vaporisation (ETV) allows samples to be dried and some of the matrix to be driven off in a graphite furnace before injection into the ICP (Hulmston and Hutton 1990). The oxygen of injected water, for example, is one of the major interferences in the analysis of rare earth elements. Detection limits are reduced by an order of magnitude when samples are dried by ETV before analysis (Shibata *et al* 1991). Similarly, detection limits for arsenic and selenium are reduced by more than two orders of magnitude by using a hydride generator with an ICP-MS. A membrane gas-liquid separator can be used to remove the chloride ions, which normally cause spectral overlaps between $^{40}Ar^{35}Cl$ and $^{40}Ar^{37}Cl$ with ^{75}As and ^{77}Se (Hitchen *et al* 1992).

Isotope dilution ICP-MS enables low analyte concentrations to be determined accurately, without interference from the sample matrix. At least two naturally occurring stable isotopes of the analyte element must be determined by ICP-MS without interference. The isotopic ratios and volumes of the sample and spike must be known and the spiked sample must be at equilibrium before analysis. The concentration of the analyte in the original sample can be calculated from the isotope ratios in the spiked sample as determined by ICP-MS (Taylor and Garbarino 1991). This technique has been used for analysis of open ocean waters (Beauchemin *et al* 1988). ICP-MS has also been used to measure natural isotopic ratios for lead in environmental samples to determine the sources of the element (Furuta 1991).

1.5.4.3: Electrochemical methods

Differential pulse voltammetric methods have a number of advantages over atomic absorption techniques (Table 1.6). They enable analyte preconcentration to be performed electrochemically during analysis, thus eliminating the extra contamination risks associated with chemical preconcentration (Nürnberg 1984). Direct analyses can be performed on whole sea water samples since the group I and II elements do not interfere with analysis. Real-time ship-board analysis is possible and speciation studies can be performed at natural pH, with minimal sample alteration. A possible disadvantage of electrochemical methods is the necessity to break down any metal-containing colloidal material and organic complexes with UV light for determination of "total" dissolved metals (Bruland *et al* 1985). Up to six elements may be determined per run and, though the range of analyte elements in sea water has been limited (*eg* Cu, Pb, Cd, Zn, Ni and Co), new methods are being developed (*eg* Se, Sn and Sb; van den Berg *et al* 1991).

Differential pulse anodic stripping voltammetry (DPASV) involves the measurement of a current caused by the oxidation of analyte ions deposited, under carefully controlled conditions, at a mercury electrode. Detection limits are governed by the time of deposition (*ie* electrochemical preconcentration) of the elements at the mercury electrode (Nürnberg 1984). Bruland *et al* (1985) compared GFAAS methods with DPASV for the analysis of Cd, Cu and Pb in sea water. The DPASV was performed using a rotating glassy carbon electrode (*ie* a mercury-film electrode, MFE) and the GFAAS analyses were performed after chelation/solvent extraction or passing the sea water sample through a chelating column. Both methods were found to be equally sensitive for cadmium and copper, but the voltammetric method gave lower detection limits for lead. The detection limits (2σ blank values) for DPASV using deposition times of 15 minutes were 0.1ngl^{-1} for Cd, 1ngl^{-1} for Pb and 10ngl^{-1} for Cu. These can be further lowered by increasing the plating times.

Dissolved Cu, Pb and Cd can be separated into seven operationally defined fractions using a MFE (Batley and Gardner 1978). These approximate to: metal ions and unstable complexes; labile organic colloids (*eg* humic acids, organic detritus); non-labile organic colloids; labile inorganic colloids (*eg* metals associated with ferric hydroxides or clay minerals); non-labile inorganic colloids; organic complexes (*eg* cysteine and nitrilotriacetic acid) and inorganic complexes (*eg* soluble metal sulphides or silicates). In contrast, Muller and Kester (1990) distinguished between non-labile and labile fractions of Zn and Cd by measuring the time taken for each "fraction" to be oxidised at a rotating disc electrode (*ie* MFE). The effective time of measurement was varied in a controlled way between 10^{-2} and 10^{+6} seconds. It was found that the release of decreasingly labile metals was continuous throughout the experiment.

An alternative electrode for differential pulse voltammetry is the hanging mercury drop electrode (HMDE). This is less sensitive than the mercury film electrode because of its larger volume. The surface of the electrode can easily be renewed, however, by allowing a new mercury drop to form; while the MFE requires careful preparation and cleaning between measurements. A submersible *in situ* ASV system for determination of trace elements in natural waters has recently been described (Tercier *et al* 1990). This system avoids sampling and the normal requirement for sample pretreatment. It therefore reduces the possibility of contamination. Either a sessile mercury drop or a thin film mercury electrode is used in the cell; the mercury drop is preferred when memory effects are likely, since it can be renewed by increasing the flow rate of sea water through the cell. The cell has been successfully used in an anoxic lake and in oxic sea water.

During cathodic stripping voltammetry (CSV), analyte ions in the sample are complexed with specific surface active complexing agents. The concentration of the metal-complexes formed in the sample solution is determined by measuring the current as the metals are reduced at a mercury electrode. Like anodic stripping voltammetry, CSV can be used to separate labile species from total dissolved metal concentrations, *eg* for Cu and Zn (van den Berg *et al* 1987) and Ni (van den Berg *et al* 1991).

Complexing ligand concentrations in natural samples can be determined using CSV, since electrode sensitivities decrease as the natural ligands compete with the added ligands for metal ions (van den Berg *et al* 1987). Determination of specific metal complexing ligands in sea water involves the addition of known amounts of metal spike to replicate sub-samples. The part of the metal spike not complexed by the natural ligands (*ie* the excess metal) is then analysed in the normal way (Gardner and Ravenscroft 1991).

1.6: Description of the Forth and Tay estuaries.

The Forth and Tay are the two major estuaries on the east coast of Scotland (Figure 1.3). Together they carry about $12km^3yr^{-1}$ fresh water to the North Sea. Their flow rates generally vary with rainfall, though, for the Tay at least, some precipitation is retained as snow in winter and released in the February/March spates (McManus 1986). The flushing times of the estuaries are about seven times shorter in winter than in summer (Balls 1992).

The catchment areas of the Forth and Tay are $4655km^2$ (Leatherland 1987) and $7500km^2$ (West 1972) respectively. The freshwater discharge into the Tay is therefore much larger than that into the Forth. These contrasting flows give the estuaries widely differing characteristics: the Firth of Forth bears a closer resemblance to an inlet or coastal embayment than to an estuary (Dyke 1987), while the Tay is shallower, more diluted with fresh water and has stronger currents (Craig 1958).

The net water movement is anticlockwise in each Firth. The discharged water flows southwards, along with the prevailing coastal currents, and part of the water leaving the Tay is carried into the northern Firth of Forth (Craig 1958, 1972, Webb and Metcalfe 1987, West 1972).

Both estuaries are partially mixed, *ie* low-salinity (riverine) water flows over the denser high-salinity (coastal) water, causing some vertical stratification. The tidally averaged velocity profiles are seaward in the surface waters and landward in the deeper layers. This "gravitational circulation pattern" is increased by high river flows at neap tides or strong down-estuary winds. Stratification is most pronounced at slack water, since the ebb begins in the surface waters and the flood begins in the bottom waters. As tidal currents in the Tay gain strength, however, turbulent mixing reduces stratification until the water column becomes vertically well mixed.

The limit of the salinity intrusion varies seasonally, occurring higher up the estuary during low flow summer periods. The tidal limit, beyond which no diurnal rise and fall of water can be observed, is dependent on the height of the tides. It therefore varies throughout the spring-neap cycle. During periods of high flow, therefore, the tidal limit may occur further upstream than the salinity intrusion.

1.6.1: The estuary and firth of Forth

The Forth (Figure 1.4) can be divided into three main regions. The "river" is the part upstream of Stirling, which marks the approximate tidal limit. The "estuary" extends from Stirling to the Queensferry bridges with the "upper estuary" being the stretch between Stirling and Alloa; and the "firth" is the part east of the bridges with the "inner firth" extending as far as Leith (McLusky 1987). The Firth of Forth has extensive shelf areas and mudflats, though some deeper channels reach 65m below ordnance datum. The estuary shallows rapidly west of the bridges (Browne 1987).

The average freshwater flow into the tidal waters of the Forth is about $60m^3s^{-1}$ and most of this enters upstream of the Queensferry bridges (Leatherland 1987). More than 50% of the fresh water comes from the River Teith, which joins the River Forth before entering the tidal waters (McLusky 1987, McManus 1986). The Forth, Allan, Devon, Avon and Carron rivers flow into the upper estuary. Further seaward, the rivers Almond, Water of Leith, Esk and Tyne flow from the southern shore, while the Leven is the only major river flowing from the northern shore. The flushing time of the Firth of Forth under average flow conditions is estimated to be about eight months, though this would be much shorter during storms (Dyke 1987).

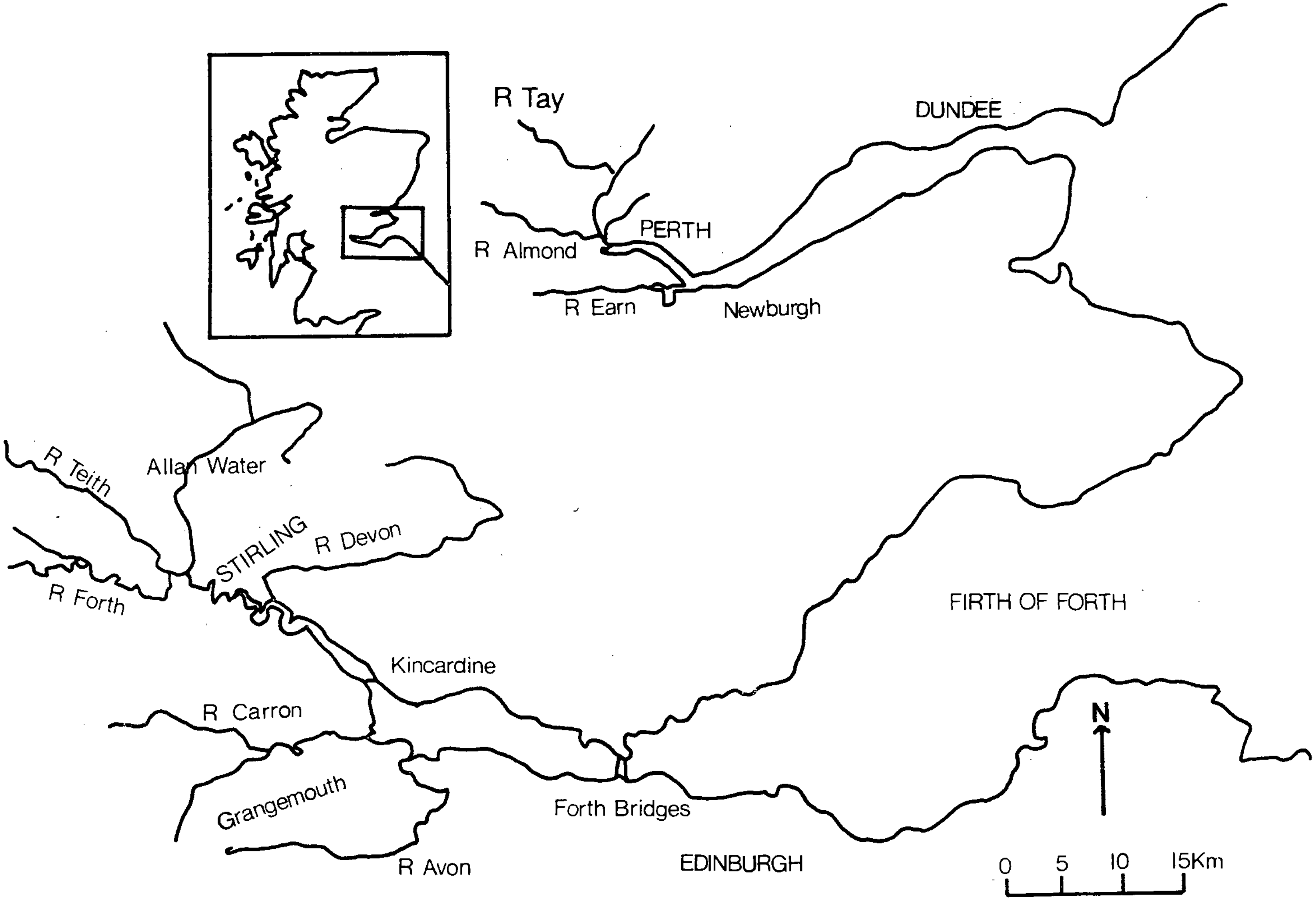

Figure 1.3. The Forth and Tay estuaries.

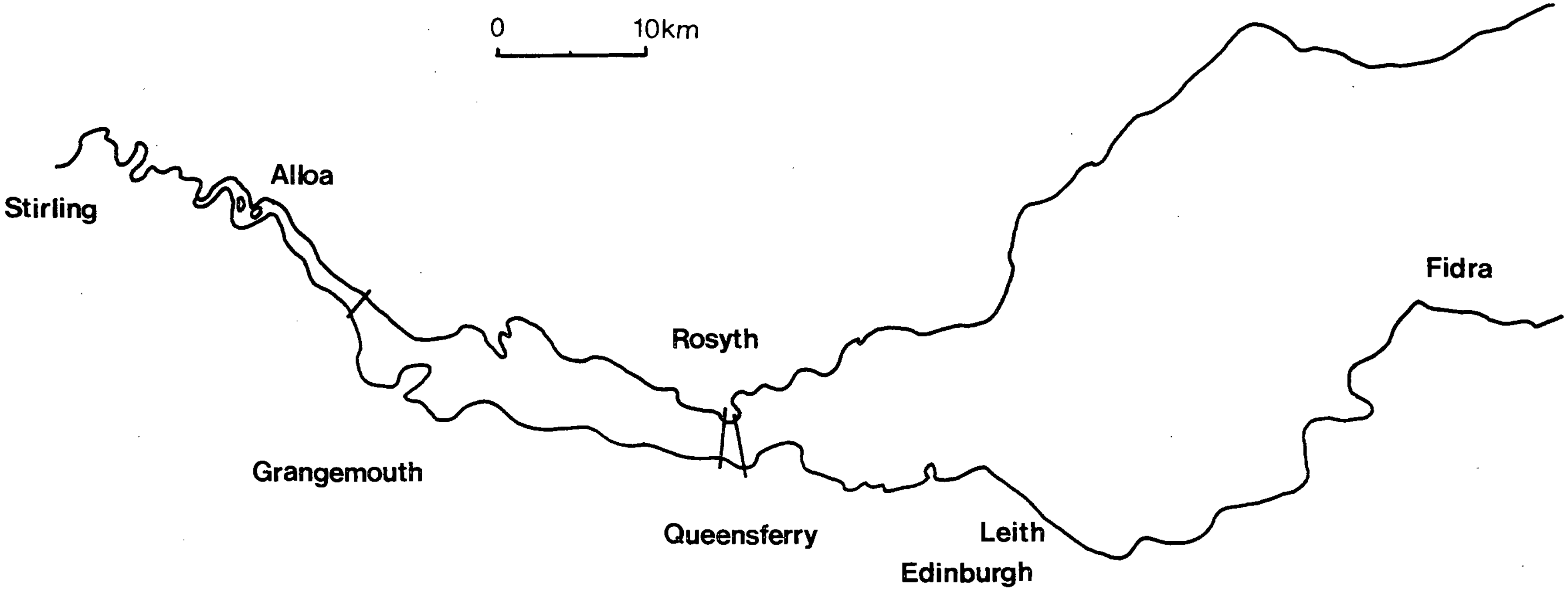

Figure 1.4. The firth and estuary of Forth

The tidal currents in the Forth Estuary are much more important than the unidirectional riverine flows. The tides are semi-diurnal and of average range for the British Isles (Webb and Metcalfe 1987). At Rosyth, the mean spring and neap ranges are 5.0m and 2.5m respectively. The large areas of mud bank on both sides of the estuary cause irregular tidal currents. Below Alloa, the duration of the flood is longer than that of the ebb and the ebb flow is correspondingly stronger. Typical peak velocities off Rosyth are 70-110cms^{-1} on the ebb and 40-70cms^{-1} on the flood. Upstream of Alloa, the tidal wave is skewed in the opposite direction, so that low water occurs later and high water earlier. In this region, the onset of the flood is so rapid that a tidal bore may develop around 6km below Alloa on the larger tides. Double high or low waters are often observed and long "stands" (periods of slack water) of up to three hours may occur in the lower reaches of the estuary (Collett 1972).

The rapid currents and the convergence of the gravitational circulation pattern cause resuspension and the development of a turbidity maximum in the upper estuary. Resuspension is highest during periods of low river flow, since the convergence penetrates the low-volume upper estuary. Suspended particulate matter loadings can vary by two orders of magnitude between spring and neap tides and loadings of over 10,000mgl^{-1} have been recorded during peak flows on large tides, though loadings of 100-3000mgl^{-1} are more usual. The turbidity maximum may account for 50-90% of the total biochemical oxygen demand (BOD) on spring tides. The major anthropogenic sources of BOD are situated at Alloa and Grangemouth. The discharged material and the natural suspended particles produce a single dissolved oxygen minimum around Alloa. The extent of this oxygen sag depends on the freshwater flow, tidal range and temperature. In summer, reduced riverine discharges increase the retention time of the upper estuary and higher temperatures increase the rate of bacterial activity. These conditions reduce dissolved oxygen concentrations in the water column. Spring tides produce the widest oxygen sags. Oxygen minima may occur in winter if very low temperatures produce drought freshwater flows by freezing springs and surface sources (Collett 1972, Griffiths 1987, Webb and Metcalfe 1987).

The main uses of the tidal Forth have been described by Griffiths (1987) and Leatherland (1987). The catchment area of the Forth holds about a quarter of Scotland's population and a significant proportion of its industry. It therefore has a long history of industrial and domestic waste disposal (Davies 1987). Solid waste from dredging and coal mining is dumped in the Firth. Effluents from chemical and petrochemical industries, food and drink manufacture, oil refining, paper making, electronics, domestic sewage and trade wastes are discharged from the major centres of population. The average freshwater flow associated with these discharges, $7.5m^3s^{-1}$, contributes significantly to the total freshwater input during periods of low run-off. Five electricity power stations use up to $170m^3s^{-1}$ of cooling water from the Firth, *ie* more than double the average riverine discharge into the Forth. The Forth is the most intensively used shipping sea area around Scotland, with 20,000 shipping movements recorded annually. There are two important ports (Leith and Grangemouth), two important oil and petrochemical terminals (Hound Point and Braefoot Bay) and a naval dockyard (Rosyth) and depot (Crombie). Large areas of the Forth are also used for conservation, recreation, angling and commercial fishing (McLusky 1987).

Concentrations of mercury, lead, cadmium, zinc and copper in the biota and sediments from the Forth have been reported to be among the highest in Scotland. This reflects the long history of metal contamination in the area (Davies 1982). Estimates of the trace metal inputs to the Forth estuary for 1984 indicate that industrial inputs are dominant for chromium, mercury and cadmium, while riverine sources are most important for copper, nickel, lead and zinc.

Atmospheric inputs of lead and zinc are also significant (Table 1.8; Davies 1987). Concentrations of dissolved and particulate copper and lead in the Firth decrease with increasing salinity. This again implies that riverine or estuarine sources are important for these metals. Concentrations of cadmium, however, are higher in the middle Firth than the inner Firth, implying that anthropogenic emissions around Leith are locally important (Balls and Topping 1987).

Table 1.8. Estimated average metal inputs to the Forth during 1984 (kg.d^{-1}).

Source	Cd	%	Cu	%	Ni	%	Pb	%	Zn	%
Riverine			137.1	61.3	63.9	85.5	39.1	42.5	142.9	31.2
Industrial	5.1	78.5	57.5	25.8	4.5	6.0	3.7	4.0	64.2	14.0
Sewage Outfalls	1.4	21.5	23.6	10.6	6.3	8.4	25.2	27.5	84.3	18.4
Atmospheric			5.1	2.3			24.0	26.0	167.0	36.4
Total	6.5		223.3		74.7		92.0		458.4	

Trace metal contamination in the Forth has been reduced during the last decade or so. Concentrations of mercury in the biota, for example, fell significantly after discharges were reduced (Davies 1980, Leatherland 1987). Cadmium concentrations were reduced after an outfall from a fertiliser plant was extended into deeper waters so that the effluent dispersal was more effective. The volume of the Firth (about 30km^3, Collett 1972) is large enough to ensure that environmental quality standards (EQS) will easily be met for small or moderate discharges as long as there is rapid dilution and dispersion of the effluent. Metal concentrations at Grangemouth are compared with the EQS for cadmium, copper, mercury, nickel, lead and zinc in Table 1.9.

Table 1.9. Dissolved trace metal concentrations at Grangemouth ($\mu g l^{-1}$) and environmental quality standards for inshore waters (Leatherland 1987).

Year	Cd	Cu	Hg	Ni	Pb	Zn
1983	0.035	1.68		1.08	<0.3	3.85
1984	0.042	2.59		1.11	<0.3	5.61
1985	0.036	1.95	0.0059	1.06	0.1	4.13
1986	0.037	2.09	0.0058	0.83	0.1	3.11
EQS	5.0	5.0	0.5	30.0	25.0	40.0

1.6.2: The estuary and firth of Tay.

The Tay has been described by Balls (1992), Craig (1958), Gunn and Yenigun (1987) and West (1972). Some of the main features are given here. The Firth of Tay, being about 5km wide at its mouth, narrows to 2km at Dundee, where it is crossed by road and rail bridges. West of the bridges, the estuary widens again to 5km, then gradually narrows to 400m at the Earn confluence (Figure 1.3). East of Dundee, the main channel varies between 6-30m deep at low water. The estuary becomes shallower further upstream and the main channel, which follows the southern shore, varies between 2-6m deep at low water. Sandbanks and mudflats, which occur throughout the firth and estuary, strongly influence the directions and strengths of tidal currents.

The mean daily freshwater flow into the Tay-Earn system is about $200 m^3 s^{-1}$. Eighty-two per cent of this comes from the Tay and 16% from the Earn. The source of the River Tay, at 625m is one of the highest in the country and its freshwater flow is larger than any other in Britain, making it one of Britain's most important aquatic systems (Maitland and Smith 1987). The tidal range at Dundee is 5m for mean spring tides and 2.2m for neaps, though water levels can be significantly affected by steady winds along the estuary or persistent low or high atmospheric pressures in the North Sea. The Tay is characterised by rapid currents, especially in the outer reaches of the Firth, where maximum spring-tide velocities may reach 1.5ms^{-1} and maximum neap-tide velocities are typically 1ms^{-1}. At Dundee, the ebb velocities are stronger than those of the flood.

The limit of salinity intrusion occurs near Newburgh during periods of high river flow. The mean spring tidal limit in the Tay is 4km upstream from Perth and in the Earn is 12km above the confluence (Nassehi and Williams 1987).

The suspended particulate matter of the Tay has been described by Hubbard and Hashim (1987) and McManus (1986). The Tay receives almost ten times as much riverine particulate material as the Forth (*ie* 1.72 x 10^{6}tyr^{-1}, compared with 0.19 x 10^{6}tyr^{-1}) and more than 50% of this may be of organic origin. Despite this, the Tay is much less turbid than the Forth. Most of the suspended load passing downstream into the inner estuary is deposited in the mudflats there and does not reach the middle estuary. Periodic increases in the suspended loads in the middle estuary are caused by the erosion of the marshes and mudflats further upstream. The sediment is therefore not directly derived from the river, but may have had a significant residence time as bottom sediments. Unlike the Forth, therefore, maximal suspended loadings occur in winter during periods of high winds and flood conditions (Weir and McManus 1987), rather than in summer during periods of low river flow. An efficient circulatory system operates in the middle Tay estuary, which retains accumulated sediment even during periods of high river flow and leaves the outer firth with very low suspended particulate matter concentrations.

Shell fragments of *Mytilus edulis* have been recognised up to 6km landwards of the most western known colonies. Used as natural tracers, these indicate that sand enters the Tay from the North Sea, migrates westward and accumulates in the intertidal flats of the upper estuary (Al-Dabbas and McManus 1987).

The population density in the Tay catchment area is low. The two major settlements are situated at Perth and Dundee. Much of the higher land is used for rough grazing or forestry, while agriculture becomes important in the lower areas (Maitland and Smith 1987). Untreated sewage and other wastes are discharged into the estuary from 36 outfalls (Hubbard and Hashim 1987). Much of this is concentrated at Dundee where it has a significant effect on the organic matter and trace metal content of suspended particles. For this reason, particulate copper and lead concentrations are elevated in the middle estuary. Zinc, however, becomes associated with dissolved organic carbon and dissolved zinc concentrations increase from the inner to the outer estuary. Dissolved copper is reported to be constant throughout the estuary.

The Tay estuary is probably one of the least contaminated major systems in Europe (Sholkovitz 1979). As such, it provides an ideal contrast with that of the Forth.

1.7: The aims of the present study.

The aim of this project is to study the behaviour of trace metals in the Forth and Tay estuaries. Because of the contrasting natures of these estuaries, the effects of freshwater flow, suspended solids loading and anthropogenic emissions can be examined. Measurements are carried out over a complete annual cycle, so that the importance of seasonal changes in trace metal geochemistry can be evaluated. Emphasis is place on the role of suspended particles. Dissolved and particulate metal concentrations are determined separately.

Of the elements chosen, lead, cadmium, copper, nickel and zinc are of anthropogenic importance and the redox cycling of manganese influences the geochemical cycles of other trace elements in the environment. This project coincides with studies of baseline contaminant concentrations in the North Sea and will aid the understanding of the role of estuaries in contaminant transport to nearshore and offshore regions.

CHAPTER 2: MATERIALS AND METHODS

2.1: Sample Collection

2.1.1: Estuarine surveys

Samples were collected from the Forth and Tay estuaries around high water on spring tides. The survey dates are listed in Table 2.1. Station positions covered the entire salinity range of each estuary. Locations are shown in Figure 2.1. The sampling commenced at the outermost station approximately two hours before high water, and terminated when fresh water was reached. The SV "FORTH RANGER" was chartered from the Forth River Purification Board (FRPB) for the outer eight stations of the Forth. The estuary was sampled in conjunction with the FRPB water quality surveys using a smaller vessel (MI21). The RV "MYA" of the Tay Estuary Research Centre was used for sampling in the Tay.

Table 2.1. Dates of Forth and Tay Estuarine Surveys

Forth	Tay
5 June 1989	4 July 1989
3 August 1989	1 August 1989
19 September 1989 *	28 September 1989
14 November 1989	28 November 1989
26 January 1990	28 February 1990
12 March 1990	26 April 1990
10 May 1990	22 June 1990

* Only the outer stations were sampled in the September survey of the Forth, due to adverse weather conditions.

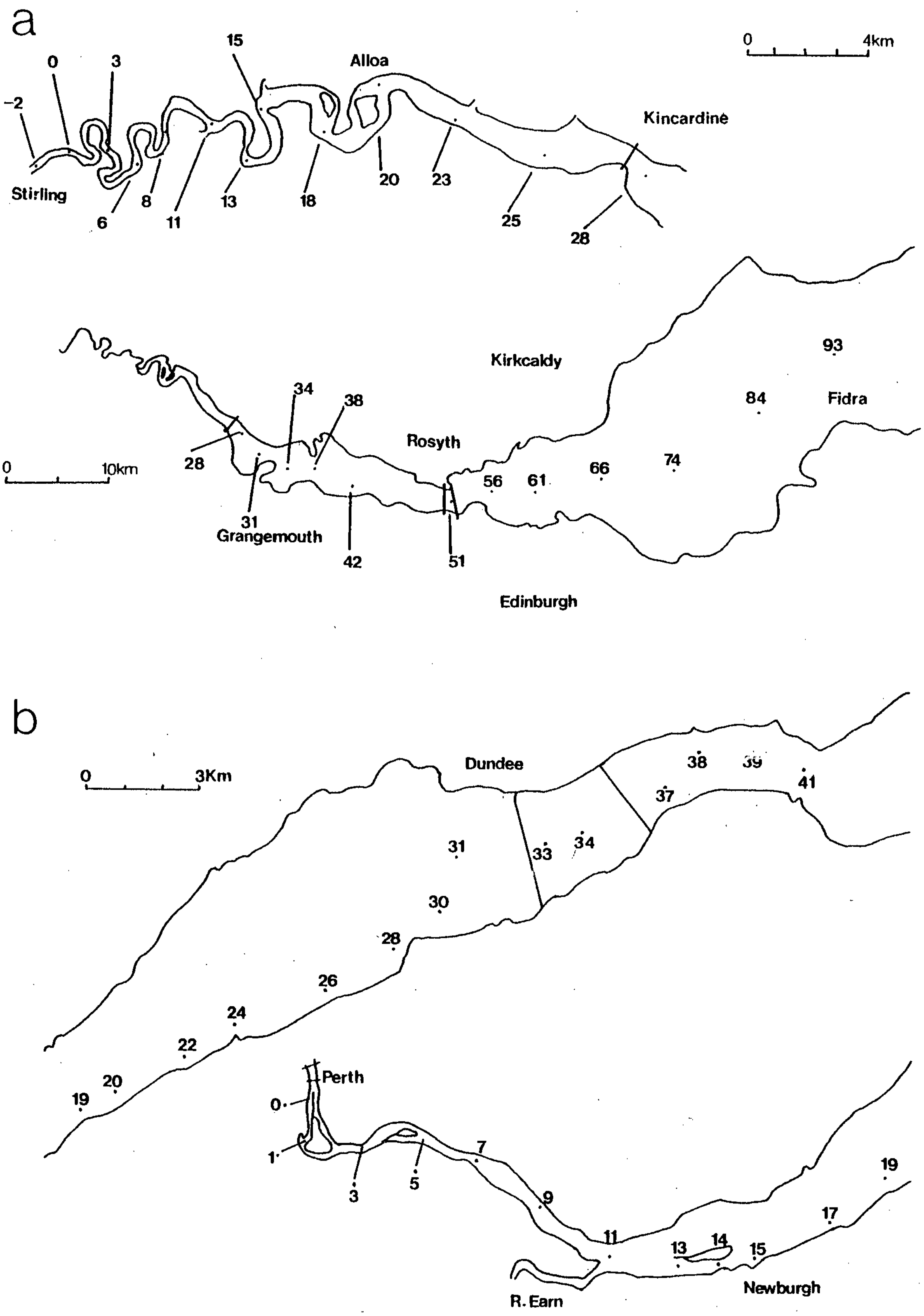

Figure 2.1. Station positions. a : Forth estuary and b : Tay estuary. Distances are in km downstream from Stirling and Perth respectively.

Sample bottles were carefully pre-cleaned by soaking in "DECON 90" and subsequently rinsing thoroughly with distilled water. The 250ml polythene bottles for the dissolved/particulate metal samples were further cleaned by filling with distilled water and adding 2.5cm^3 of concentrated nitric acid (AnalaR) from a glass dispenser. These bottles were capped, numbered, and stored full of dilute acid in resealable polythene bags. To avoid the possibility of acid leaching suspended particulate matter (SPM) and releasing trace metals, they were rinsed with distilled water before use.

Representative sampling from dynamic turbid estuaries is notoriously difficult. Firstly, because of the short-term variability of estuarine waters it is preferable to obtain samples simultaneously rather than sequentially by peristaltic pumping. Secondly, the rapid settling of suspended particles makes sub-sampling from large containers inaccurate. This can be overcome by processing entire samples (Duinker *et al* 1979b). Samples for "thin-film" XRF analysis, for which it was important not to overload membranes (see Section 2.6.1) were therefore collected in polythene bottles of various volumes to compensate for changes in water turbidity.

A sampler designed to overcome these problems, by simultaneously filling six sample bottles of varying sizes, was used in the turbid Forth and Tay estuaries (Balls and Laslett 1991). It was immersed on a Kevlar line to a depth of 1m and triggered by a Teflon coated messenger (General Oceanics). About 40 seconds were required to fill the bottles completely. The caps of the bottles were rinsed before they were replaced.

Trace metal samples from the eight outer stations of the Firth of Forth were taken using a peristaltic pump. The tubing of the pump was carefully cleaned with dilute acid and rinsed with distilled water before use. A wooden pole was used to hold the tubing away from the boat at a sampling depth of 1m. The tubing was flushed at each station before the sample bottles were filled. This method has been shown to yield uncontaminated samples for subsequent dissolved metal analysis (*eg* Balls and Topping 1987). Samples for nutrient and XRF analyses from these stations were collected with a Niskin bottle. The outer stations of the Forth are characterised by very low suspended solid loadings, and good replicate samples could be obtained by filling the various bottles sequentially.

2.1.2: Tidal cycle survey

A 12½ hour tidal cycle survey was undertaken at Alloa in the upper Forth estuary (Figure 2.1a) on 10 July 1990. Temperature and salinity readings were taken at 1m depth intervals using a probe (MCVIII, EIL). Peristaltic pumps were used to sample the water column at two depths - 1m below the surface, and 1m above the bottom. Samples were taken for dissolved and particulate trace metals and XRF analysis (also particulate carbon, dissolved organic carbon, nutrients and dissolved oxygen) using the bottles described above. Discrete salinity samples were taken to calibrate the salinometer. The samples and readings were taken at half hourly intervals.

Results from the tidal cycle survey are to be published elsewhere (Balls *et al*, in prep).

2.2: Sample processing

2.2.1: Dissolved and particulate trace metals

The following work was done with great care to avoid the problems of trace metal contamination described in Chapter 1. Disposable polythene gloves were worn, equipment was thoroughly cleaned by soaking in 1% nitric acid, and the work was performed in a Class 100 clean air cabinet.

Pre-weighed 47mm diameter 0.4μm Nuclepore polycarbonate membranes were loaded into clean numbered polycarbonate filter holders (Swin-loc, Nuclepore) fitted with silicone 0-rings. The membranes were cleaned by sequentially allowing about 50ml 1% HNO_3 and distilled water to drip, under gravity, through the holders. This procedure was demonstrated not to affect the membrane weights. The membrane-loaded filter holders were stored wrapped in cling film.

Samples were pressure filtered to reduce the possibility of micro-organism cell lysis, which may interfere with trace metal analysis (Aston 1985). The filtering system used is shown in Figure 2.2a. With the taps closed, a pressure of 1 to 2 psi was applied through the system. Each sea water sample was thoroughly shaken, and the entire sample (about 280ml) was carefully poured into a separating funnel. The funnel lid was replaced, and the pressure applied by opening the appropriate taps. The sea water was allowed to run through into the original sample bottle until the water level in the separating funnel reached the 250ml marker. The collecting bottle was rinsed out with this subsample of filtered sea water and the remaining 250ml of sea water was filtered. For samples with a high SPM loading there was a tendency for particles to settle onto the walls of the separating funnels. To avoid this the samples were periodically tapped. After filtration the water samples were acidified with 200μl sub-boiled

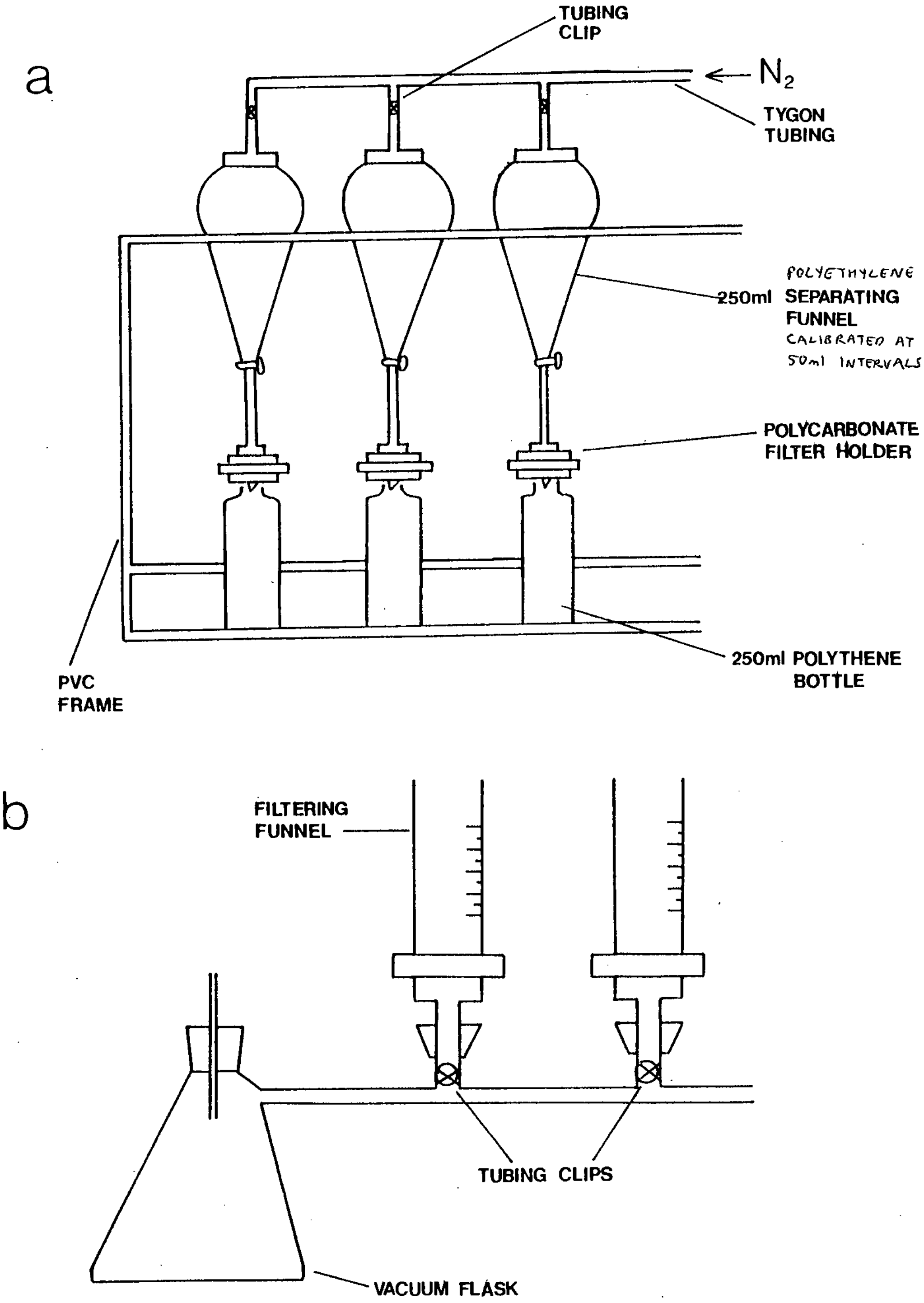

Figure 2.2. Filtration apparatus. a : Pressure filtration system for trace metal samples, and b : Polycarbonate vacuum filtration system for washing 47mm diameter Nuclepore membranes. (NB This apparatus is similar to the PTFE apparatus for filtering and washing XRF samples.)

distilled concentrated nitric acid, and were stored in resealable polythene bags prior to dissolved trace metal analysis.

The membranes were carefully transferred to polycarbonate filtering funnels (Figure 2.2b). A vacuum was applied and four aliquots of distilled water (each of 5ml) were used to wash the membranes free of salt. This washing procedure does not result in any significant loss of heavy metals (Cu, Zn, Cr, Fe, Mn or Al) from the particulate phases (Duinker *et al* 1979b). The membranes were transferred to Petri dishes and allowed to dry in a clean air cabinet. After being reweighed to an accuracy of ±0.01mg, the membranes were stored in sealed labelled Petri dishes prior to particulate analysis.

2.2.2: Major particulate elements by X-ray fluorescence analysis

Preweighed 37mm diameter 0.4μm Nuclepore polycarbonate membranes were loaded in teflon funnels (Cowie Scientific), and a vacuum was applied (*cf* Figure 2.2b). Only enough water was filtered to ideally cause a single layer of particles to be collected on the membrane (see Section 2.6.1). The volume of water filtered onto each membrane was recorded, and the salt was removed by washing with four aliquots of distilled water (5ml). The membranes were transferred to numbered Petri dishes and allowed to dry in a clean air cabinet. They were reweighed to an accuracy of ±0.01mg, and sealed in Petri dishes prior to analysis.

2.2.3: Particulate organic carbon/nitrogen, and dissolved organic carbon

Whatman GF/F membranes of 25mm diameter were heated at 500°C for about 3 hours before use. The all glass vacuum filtering apparatus was thoroughly rinsed with distilled water. A vacuum was applied, and about 5ml of sample was filtered through the system. This aliquot was used to rinse the receiving Buchner flask and was then discarded. The remainder of the sample was filtered and collected in the Buchner flask. A glass bottle (50ml medical flat) was rinsed and half filled with filtrate. These samples were stored deep frozen, then analysed for dissolved organic carbon (Technicon). ~~(technician)~~.

The membranes were carefully folded in half and stored deep-frozen, separated by labelled 42.5cm diameter GF/C filters, in a plastic vial. They were analysed for particulate organic carbon and nitrogen as described in Balls (1992).

2.2.4: Nutrients and salinity

All nutrient samples were filtered under vacuum using a Sartorius system. The cap and neck of each salinity bottle were carefully dried before storage. Salinity samples collected from the turbid upper estuarine stations were also vacuum filtered through a Whatman GF/C membrane.

Chlorophyll measurements were taken for the anchor station, the Forth May 1990 survey and the Tay June and April 1990 surveys. The analyses were performed on the 47mm diameter Whatman GF/C membranes used to filter the nutrient samples. The volume of water filtered was recorded, and the membranes were folded and stored in labelled polythene tubes in darkness, and frozen until they were analysed.

2.3: Dissolved trace metal analysis

2.3.1: Introduction

The concentrations of most dissolved heavy metals in sea or estuarine water are too low to be analysed directly by graphite furnace atomic absorption spectrometry (GFAAS). In addition, the major elements present in sea water (*eg* Na) cause severe interference problems, even when furnace "ashing" steps are carefully optimised and appropriate matrix modification is used. It is therefore beneficial to selectively preconcentrate heavy metals into a non-saline aqueous matrix for subsequent determination by GFAAS.

A liquid/liquid extraction method based on that of Statham (1985) is used here. It is a multi-element technique, suitable for determining cadmium, cobalt, copper, iron, manganese, nickel, lead and zinc in sea or estuarine water. Two chelating agents are used: ammonium pyrrolidine-dithiocarbamate (APDC) and diethylammonium diethyldithiocarbamate (DDDC). This mixture selectively complexes a number of trace metals over a wide pH range (Bruland *et al* 1979, Kinrade and Van Loon 1974). Normally a 1% (v/v) solution of each chelating agent is adequate to extract the metals, but if manganese is to be quantitatively extracted a concentration of 2% (v/v) is necessary (Statham 1985). The complexant is made up in 3.5% sodium chloride solution. This solution causes the flocculation of any metal-containing colloids present so that they can be removed by filtration (Tappin 1988). The complexant is unstable and must be made up daily (Kinrade and Van Loon 1974).

The organic solvent used is 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113, hereafter simply referred to as Freon). Freon is less toxic than other suitable solvents (Danielsson *et al* 1978), gives rapid and total phase separation with waters of all salinities (Danielsson *et al* 1982) and is readily purified

(Statham 1985). The forward extraction (*ie* metals from sea water into Freon) is repeated, to ensure that any drops of Freon left with the aqueous phase after the first separation are included with the Freon in the second. It is better to leave a drop of Freon in the aqueous phase than to include a drop of water in the organic phase since the salt contained in the water would interfere with the subsequent atomic absorption spectrometry (Danielsson *et al* 1978, Statham 1985).

The metal complexes in Freon start to break down after about eight hours (Kinrade and Van Loon 1974). This instability is overcome by back extracting the metals into dilute nitric acid (Jan and Young 1978, Schmidt and Dietl 1978), and the resulting extract is stable for at least 70 days (Danielsson *et al* 1978). The back extraction also gives a second concentration step (Magnusson and Westerlund 1981).

The liquid/liquid extraction steps are mechanised by using specifically designed polypropylene rotating tables (Statham 1985, Tappin 1988). The tables are fixed inside a clean air cabinet with the motor, timer and other fittings outside. A rotation speed of 60 rpm gives good mixing of the aqueous and organic phases, and is found to give much more reproducible results than manual shaking (Statham 1985).

During back extraction Danielsson *et al* (1978) found it necessary to rotate the samples for at least five minutes with concentrated acid before diluting with water. However, the higher complexant concentrations used here increase the stability of the metal complexes in Freon, so it is necessary to use two back extraction steps to give quantitative metal recovery (Statham 1985).

2.3.2: Apparatus

All apparatus was cleaned before use by soaking with 1% nitric acid for a few weeks, rinsing with distilled water and leaving to dry in a 'Class 100' laminar flow cabinet.

125ml	FEP separating funnels (The caps must be sealed with teflon tape) (8)
500ml	FEP separating funnel (1)
125ml	FEP bottles (4)
250ml	FEP bottle (1)
1000ml	FEP bottle (1)
2000ml	FEP bottle (1)
10ml	Polythene measuring cylinder (1)
100ml	Polythene measuring cylinder (1)
10ml	Screw capped FEP centrifuge tubes (one per sample)
1.4ml	Clear polypropylene microcentrifuge tubes (Eppendorf) (one per sample)
	Polystyrene microcentrifuge tube rack (Whatman)
	Micropipettes and clear pipette tips
	Rotating tables (see Figure 2.3)
	Teflon autosampler cups (Perkin Elmer) and polypropylene lids (BDH)

2.3.3: Reagent preparation

The reagents must be very pure to ensure that they do not become a source of contamination. Both sub-boiling distillation and solvent extraction are used to clean reagents here. Sub-boiling distillation involves the non-violent surface evaporation of a liquid reagent, so that no spray droplets of the impure liquid can be swept through the apparatus and contaminate the distillate. Solvent extraction involves the repeated mixing of the reagent with separate aliquots of an

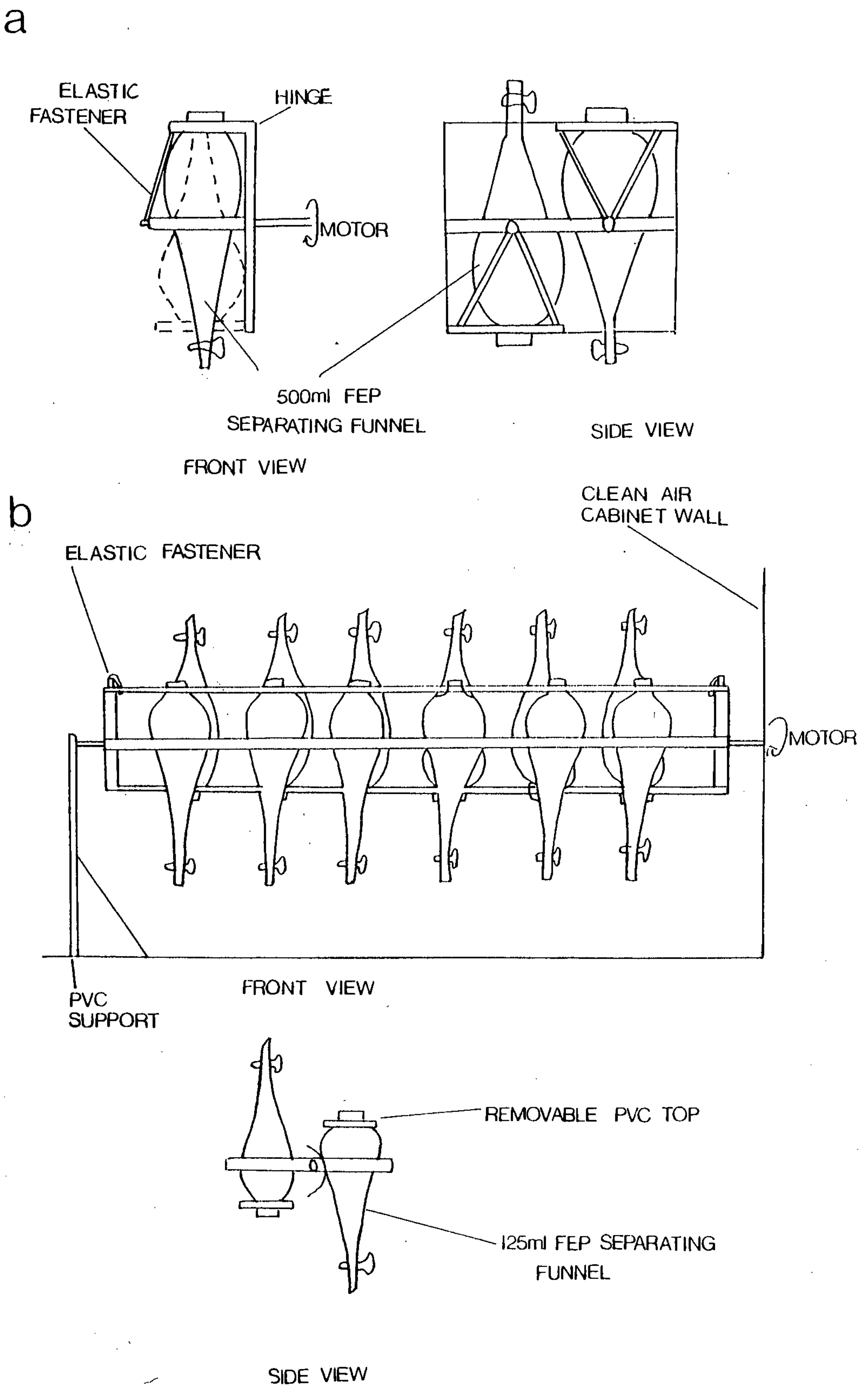

Figure 2.3. Rotating tables. a : 500ml separating funnels for cleaning Freon and complexant (after Statham 1985), b : 125ml separating funnels for forward extraction (after Tappin 1990).

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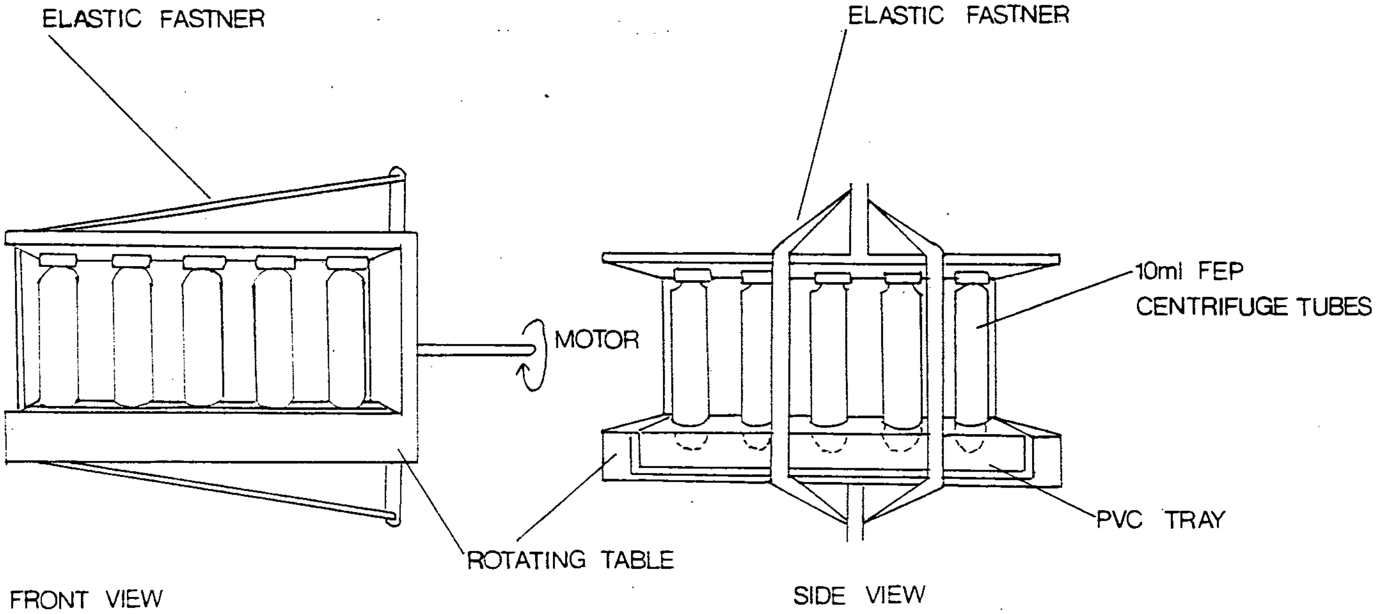


Figure 2.3.(cont.) c: 10ml centrifuge tubes for back extraction (after Tappin 1990). Tray holds 25 centrifuge tubes and slides into rotating table.

immiscible liquid in the presence of a complexing agent (Moody and Beary 1982). Methods of reagent preparation and cleaning are described below.

2.3.3.1: Sub-boiling point distilled reagents

Sub-boiling point distilled water (SBDW) was prepared from distilled water using all-teflon apparatus described by van Belle and Boelrijk (1988). Sub-boiling point distilled concentrated nitric acid was prepared in the same way from concentrated nitric acid (ARISTAR). Both reagents were stored in 1l FEP bottles. Four per cent v/v nitric acid was made up with SBDW and sub-boiled nitric acid using acid-cleaned apparatus and stored in a 250ml FEP bottle.

2.3.3.2: Ammonia solution

Ammonia solution (0.800 S.G. AnalaR) was diluted 1:1 with SBDW and stored in a 125ml FEP bottle.

2.3.3.3: Metal standards

Spectroscopic grade 1000ppm metal nitrate standards were used to make up a mixed element working standard of 0.1ppm Cu, Ni, Mn, Pb, and Zn and 0.01ppm Cd in 4% nitric acid (see above). This was stored in a 50ml polythene volumetric flask.

2.3.3.4: Freon

About 250ml Freon was placed in an acid cleaned 500ml FEP separating funnel with 1ml of concentrated sub-boiled distilled nitric acid. This was rotated, as shown in Figure 2.3a, for five minutes. About 100ml SBDW was added to the funnel and rotated for a further five minutes. The Freon was run off into a clean FEP bottle, the aqueous phase discarded and the Freon returned to the separating funnel. The procedure was repeated twice. The cleaning was completed by adding a further 100ml SBDW to the Freon, and rotating without any acid. The clean Freon was stored in a 2000ml FEP bottle.

2.3.3.5: Complexant

A 3.5% salt solution was prepared by dissolving 8.75g of sodium chloride (AnalaR) in 250ml SBDW. Five grams each of APDC (AnalaR) and DDDC (GPR) were weighed out and dissolved in the sodium chloride solution. This complexant was then filtered through a Whatman No 1 paper under a small vacuum, and stripped of trace metals by rotating for 5 minutes each with four aliquots of clean Freon (25ml) in the 500ml separating funnel (Figure 2.3a). The complexant was stored in a clean 250ml FEP bottle in a refrigerator, and used within 24 hours.

2.3.4: Analytical method

A typical batch consisted of two reagent blanks, two SBDW blanks, four standard additions, four certified reference materials, and about 20 samples.

The extraction of the metals was performed at pH 7 or higher to include the quantitative determination of manganese (Kinrade and Van Loon 1974, Statham 1985). The volume of ammonia solution necessary to neutralise the samples was determined before each batch of analysis. Small volumes of ammonia solution were added sequentially to a 30ml subsample of water. The pH of the solution was monitored after each addition using a glass electrode, and the volume of ammonia required to bring the pH to 7 or 8 was recorded. This was repeated for three sea water samples per batch, and an average volume of ammonia necessary to neutralise 60ml was calculated. The volumes required for the reference sea water, and the blanks and additions were determined separately.

The sub-samples used for these ~~texts~~ tests were discarded.

Sixty millilitres of each sea water sample was measured out using an acid cleaned 100ml polythene measuring cylinder, and poured into a 125ml separating funnel in the rotating table (Figure 2.3b). The appropriate amount of ammonia solution was added using a micropipette and the funnel was quickly shaken to prevent the formation of localised areas of high pH, which may otherwise break down the complexant when added. For standard addition purposes, a metal spike of a few tens of microlitres was added to some of the samples. To each separating funnel 6ml of Freon was added using a 10ml polythene measuring cylinder, followed by 3ml of complexant using a micropipette. The separating funnels were then rotated for five minutes.

When the two phases had fully separated, the Freon was drawn off into a 10ml screw-capped FEP centrifuge tube. Care was taken to avoid any transfer of the aqueous phase since the salt would interfere with the subsequent GFAAS determination (Danielsson *et al* 1978, Statham 1985). Another 3ml of clean Freon was then added to each funnel, and they were rotated for a further five minutes. The Freon was drawn off and added to the same tubes as previously.

The back extraction was carried out as follows: 20μl sub-boiling point distilled concentrated nitric acid was added to the Freon in the tubes which were then rotated for five minutes (Figure 2.3c), 500μl of SBDW was added and the tubes rotated for a further five minutes. The aqueous phase was then carefully drawn off using a micropipette and transferred to a 1.5ml snap-shut polypropylene micro-centrifuge tube (Eppendorf). The back extraction was repeated, and the second aliquot was added to the first.

The extracts were analysed using a Perkin-Elmer Zeeman 3030 Graphite Furnace atomic absorption spectrometer with background correction. $NH_4H_2PO_4$ was used as a matrix modifier. Where necessary the extracts were diluted with

4% HNO_3 to bring them within the calibration range of the instrument. The furnace conditions used are given in Table 2.2.

Table 2.2. HGA furnace conditions for sea water analysis.

Element	Cd	Cu	Mn	Ni	Pb	Zn
Wavelength (nm)	228.8	324.8	279.5	232.0	283.3	213.9
Slit width (nm)	0.7	0.7	0.2	0.2	0.7	0.7
Tube type	Pyro	Pyro	Pyro	Pyro	Pyro	Pyro
L'vov platform	Yes	Yes	Yes	No	Yes	Yes
Lamp type	EDL	HCL	HCL	HCL	EDL	HCL
Lamp current (mA)	10.0	10.0	15.0	15.0	10.0	10.0
Ashing temp (°C)	800	1200	1400	1200	900	700
Ashing ramp (s)	15	30	40	10	25	5
Ashing time (s)	10	10	10	30	30	10
Atomisation temp (°C)	1450	2300	2200	2500	1800	1800
Atomisation ramp (s)	1	0	0	0	1	1
Atomisation time (s)	7	4	3	3	4	3
Gas flow ($ml.min^{-1}$)	0	0	150	0	0	300

To prevent any carryover between samples the 100ml measuring cylinder was rinsed out with each sample before use and the separating funnels were cleaned before use and between each sample by rotating with 6ml of Freon and 3ml of complexant for five minutes. The micropipette tips used to transfer the aqueous phase to the micro-centrifuge tubes were rinsed with 4% nitric acid between each sample.

2.3.5: Analytical quality control

Detection limits have been defined as: "The smallest concentration of a determinand for which we can be 95% confident that the determinand will be detected by the method" (Caulcutt and Boddy 1983). The corrected reading corresponding to a limit of detection = $t_b s_b + t_d s_d$ where

s_b = standard deviation of duplicate blanks from n batches

t_b = 95% critical value from the t-distribution (with n d.f.)

s_d = standard deviation of a set of m readings near the detection limit

t_d = 95% critical value from the t-distribution (with m-1 d.f.).

To calculate the detection limits for the dissolved metals, the blanks from all 15 batches of analysis were used to estimate s_b , and the reference sea water (CASS-2, National Research Council, Canada) samples from each batch were used to calculate s_d . The detection limits for 60ml water samples are quoted in Table 2.3 along with the average and standard deviation of the CASS-2 reference material values obtained throughout the project, and coefficients of variation of ten replicate sea water samples analysed in a single batch.

The higher coefficients of variation for Zn and Mn (Table 2.3) are probably caused by the increased sample handling necessary for these elements, since dilution is required to bring them into the linear calibration range for flameless AAS. Although dilutions of two orders of magnitude are sometimes required, the sample volumes obtained from the extraction procedure are too small for analysis by flame AAS.

Table 2.3. Analytical quality control parameters for dissolved metals in sea water.

Metal	Detection Limit $(\mu g l^{-1})$	CASS-2 mean ± σ^{-1} $(\mu g l^{-1})$	n	Certified value $(\mu g l^{-1})$	C.V. (%)
Cd	0.003	0.018 ± 0.004	26	0.019 ± 0.004	5.7
Cu	0.2	0.66 ± 0.06	26	0.675 ± 0.039	3.4
Mn	0.2	1.69 ± 0.20	25	1.99 ± 0.015	12.9
Ni	0.1	0.32 ± 0.03	28	0.298 ± 0.036	5.1
Pb	0.02	0.017 ± 0.004	6	0.019 ± 0.006	4.3
Zn	0.4	1.68 ± 0.26	26	1.97 ± 0.12	10.5

2.4: Trace metal analysis of suspended particulate matter

The digestion method described here removes most trace metals associated with the suspended particulate matter, but does not attack the aluminosilicate structures of the particles. It is therefore a partial digest and, as such, is expected to give lower concentrations of metals than XRF spectrometry, or digests involving hydrofluoric acid. The method has been used in previous studies of trace metal geochemistry in nearshore environments, and has been described by Balls (1985).

2.4.1: Apparatus

10ml PTFE beakers (Azlon) (30)
Plastic tweezers
Acid dispenser (Oxford)
Enamel-topped hotplate (Corning)
Micropipettes and clear pipette tips
Nunc vials (30ml disposable polystyrene vials with screw caps)
Acid cleaned Teflon autosampler cups (Perkin Elmer) and polypropylene lids (BDH)

2.4.2: Reagent preparation

Twenty per cent v/v nitric acid was prepared from ARISTAR grade nitric acid and double distilled water, and was stored in a 2.5 litre glass bottle. A mixed element working standard was made up in 20% nitric acid from spectroscopic grade 1000ppm metal nitrate standards. The working standard contained 2.00ppm Mn, 1.00ppm Cu, Pb and Ni, 0.5ppm Zn and 0.05ppm Cd, and was stored in a 100ml polythene volumetric flask.

2.4.3: Analytical method

A typical batch consisted of about 20 samples, four membrane blanks, two reagent blanks, and three standard additions. The 10ml PTFE beakers were numbered and washed in distilled water. They were thoroughly cleaned with hot concentrated acid as follows: 5ml concentrated nitric acid (AnalaR) was added to each beaker from a glass dispenser and the beakers were placed on an enamel-topped hotplate in a clean air cabinet discharging into a fume hood. They were left at 160°C for at least an hour, so that the acid vaporised and cleaned the walls of the beakers thoroughly. The beakers were then removed and allowed to cool. Any excess acid was discarded and the beakers were rinsed with double distilled water and placed in a polythene tray covered with cling film.

Each sample membrane was removed from the Petri dish, folded and placed in the appropriate numbered PTFE beaker using clean plastic tweezers. Four unused membranes were added in the same way as blanks. 4ml concentrated nitric acid (ARISTAR) was added to each beaker using a macro-pipette and disposable pipette tips. The beakers were returned to the hotplate at 160°C as before, and were periodically swirled to ensure continued total immersion of the membranes. After boiling dry, the samples were removed and left to cool on the polythene tray covered with cling film.

Redissolution was achieved by adding 2ml 20% nitric acid using a micropipette. They were left to stand for at least five minutes and gently swirled so that the whole sample was redissolved. A micropipette was used to transfer 1ml of each sample to a labelled Nunc vial for subsequent dilution and analysis by flame atomic absorption spectrometry (elements Mn and Zn). The rest of the sample was analysed immediately by flameless atomic absorption spectrometry with $NH_4H_2PO_4$ as a matrix modifier (elements Cd, Cu, Pb and Ni). Most of the analysis was performed using a Perkin Elmer 3030 Graphite Furnace Atomic

Absorption Spectrometer, with Zeeman background correction. The last three batches were analysed using a Philips PU9200 Furnace Atomic Absorption Spectrometer, with deuterium background correction. The two instruments had quite different characteristics, and the optimum furnace conditions for each were determined separately. Furnace conditions for the Perkin Elmer instrument are given in Table 2.4. A Perkin Elmer 5000 Atomic Absorption Spectrometer was used for the flame analysis, and the conditions are given in Table 2.5.

Table 2.4. HGA furnace conditions for particulate analysis using the Perkin Elmer Zeeman 3030 atomic absorption spectrometer.

Element	Cd	Cu	Mn	Ni	Pb	Zn
Wavelength (nm)	228.8	324.8	279.5	232.0	283.3	213.9
Slit width (nm)	0.7	0.7	0.2	0.2	0.7	0.7
Tube type	Pyro	Pyro	Pyro	Pyro	Pyro	Pyro
L'vov platform	Yes	Yes	Yes	No	Yes	Yes
Lamp type	EDL	HCL	HCL	HCL	EDL	HCL
Lamp current (mA)	10.0	10.0	10.0	15.0	10.0	15.0
Ashing temp (°C)	700	1200	1400	1400	900	700
Ashing ramp (s)	15	30	40	40	10	10
Ashing time (s)	20	10	10	20	20	30
Atomisation temp (°C)	1600	2400	2500	2650	1800	1800
Atomisation ramp (s)	1	0	0	0	0	0
Atomisation time (s)	6	3	3	3	4	3
Gas flow ($ml.min^{-1}$)	0	0	0	0	0	100

2.4.4: Analytical quality control

Detection limits for the SPM analyses were calculated from the equation given by Caulcutt and Boddy (1983) (See section 2.3.5) using the blank membranes from all batches of analysis. Since no reference material was included in each batch, s_d was approximated from results of replicate samples of BCSS-1 reference sediment digested with a Nuclepore membrane. The weights

Table 2.5. Flame conditions for particulate analysis using the Perkin Elmer 5000 atomic absorption spectrometer.

Element	Mn	Zn	Fe
Wavelength (nm)	279.5	213.9	248.3
Slit width (nm)	0.2	0.7	0.2
Lamp type	HCL	HCL	HCL
Lamp current (mA)	10.0	15.0	15.0
Oxidant	Air	Air	Air
Fuel	Acetylene	Acetylene	Acetylene
Oxidant Flow	25.0	25.0	25.0
Fuel Flow	15.0	15.0	15.0

of BCSS-1 taken ranged from 0.55 to 3.39mg, and were therefore at the lower end of those generally obtained in the estuarine surveys.

The detection limits for the suspended particulate metals, along with results of the BCSS-1 reference material, are listed in Table 2.6.

Table 2.6. Analytical quality control parameters for SPM analysis.
n = number of observations

Metal	Detection Limit (5mg) (μgg^{-1})	BCSS mean ± σ^{-1} (μgg^{-1})	n	C.V. (%)	Accepted Value (μgg^{-1})
Cd	0.05	0.27 ± 0.04	10	13	0.25 ± 0.4
Cu	2	19.4 ± 4.7	9	24	18.5 ± 2.7
Mn	2	246 ± 22	9	9	229 ± 15
Ni	3	56.4 ± 6.6	8	12	55.3 ± 3.6
Pb	1	19.5 ± 2.4	10	8	22.7 ± 3.4
Zn	1	151 ± 17	9	11	119 ± 12

2.5: Major particulate metal analysis

2.5.1: Introduction

XRF spectrometry is a rapid, non-destructive technique for the simultaneous determination of a number of major elements (Mg, Al, Si, K, Ca, Ti, P, Cl, Mn and Fe) in particulate samples. The atoms of a sample are energised by being bombarded with X-rays (primary radiation). The excited electrons emit secondary radiation as they return to their ground state. The wavelength of this radiation is inversely proportional to the amount of energy released during this process and is therefore element-specific. In non-thin film analysis, where X-rays cannot penetrate the sample, the intensity of the secondary X-rays is dependent on the concentration of the element present. Under thin film conditions, *ie* where the sample thickness is small compared to the depth of penetration of the secondary X-rays, the intensity of the fluorescence is proportional to the mass of the element present (Cann and Winter 1971). XRF analysis of suspended particulate matter is particularly attractive, since no sample preparation is required, and filtration is quick because only small amounts of material are needed (Baker and Piper 1976).

The count/mass relationships of suspended particulate matter may be influenced by the mass density and sizes of particles within the sample. Sensitivities decrease with greater loadings or particle sizes, because larger proportions of the secondary X-ray are absorbed by the sample matrix (Criss 1976). Secondary X-rays with shorter wavelengths, those characteristic of the heavier elements, penetrate sample matrices to greater depths than X-rays of longer wavelengths from the lighter elements. The count/mass ratios for light elements like Si and Al start to become non-linear for samples with thicknesses greater than about $10\mu m$, or membrane loadings greater than $300\mu g cm^{-2}$. Values for the light elements on heavily loaded membranes are therefore less reliable than those for the heavy elements (Baker and Piper 1976, Cann and Winter 1971). Aluminium is primarily associated with terrigenous clay minerals. This element therefore provides a useful index for changes in the chemical or mineralogical composition of the particles. Great care must be taken when using elemental/aluminium ratios, however, since they are particularly vulnerable to particle size effects (Holmes 1981).

2.5.2: Analytical method

Analysis was performed using a chromium lamp on a Philips PW1480 Sequential X-ray Spectrometer fitted with a PW1510 sample changer. About 20 standards were used to calibrate the instrument for each element. The standards were marine and riverine suspended particulate samples which had previously been analysed. (Alternatively standards could have been prepared by spotting known amounts of ground rock standard or standard metal solution onto Nuclepore membranes.) The standards and samples should have similar grain sizes to avoid the possibility of obtaining different count/mass ratios. Blank Nuclepore membranes were used to correct for the scattering caused by the membrane material and sample holder. The analytical programs are shown in Table 2.7. Coefficients of variation for ten replicate sample readings were better than 1% for Ti, K, P, Al, Si and Mg, and 2% for Fe, Mn and Ca.

2.5.3: Correction for the presence of sea salt

Any salt crystals remaining on the particulate membranes would increase the signals for calcium, potassium, magnesium and sulphur (not determined here), and give positive chlorine results. The ratio of masses of these elements in sea salt is as follows:

1 Cl : 0.0212 Ca : 0.0202 K : 0.0665 Mg : 0.0466 S

Appropriate salt corrections were made for these elements whenever a sample was found to contain chlorine.

Table 2.7. XRF analytical program for Philips PW1480 spectrometer.

The + or - symbols represent the channels providing the background counts for the elements referred to. In addition, a separate background correction is given to Al, channel 17.

Channel number	Channel name	Units	Measurement time (s)
1	Fe-	None	10
2	Fe	μg membrane^{-1}	10
3	Mn	μg membrane^{-1}	50
4	Mn+	None	50
5	Ti	μg membrane^{-1}	10
6	Ti+	None	10
7	Ca-	None	10
8	Ca	μg membrane^{-1}	10
9	K-	None	10
10	K	μg membrane^{-1}	10
11	Cl-	None	6
12	Cl	μg membrane^{-1}	10
13	Cl+	None	6
14	P	μg membrane^{-1}	50
15	P+	None	50
16	Al-	None	50
17	Al	μg membrane^{-1}	50
18	Si	μg membrane^{-1}	50
19	Si+	None	50
20	Mg	μg membrane^{-1}	50
21	Mg+	None	50
22	OK	None	2

2.5.4: Leaching of iron/manganese oxide coatings from particles

2.5.4.1: Introduction

Iron and manganese oxides are often found as coatings on suspended particulate matter in marine environments (*eg* Jenne 1968, Olsen *et al* 1982). These phases can be selectively removed by leaching with a solution of hydroxylamine-hydrochloride in acetic acid (Tessier *et al* 1979). The amounts of iron and manganese associated with oxide coatings were determined for six membranes from November 1989 in the Forth and six from September 1989 in the Tay. These membranes were analysed by XRF spectrometry as described above, leached, dried and re-analysed in the same way.

2.5.4.2: Method

A 0.04M solution of hydroxylamine-hydrochloride in 25% acetic acid was made up as follows. 1.39g of hydroxylamine-hydrochloride ($NH_2OH.HCl$) was weighed out and put into a 500ml glass volumetric flask. The flask was then half filled with distilled water. 125ml acetic acid was measured out with a glass measuring cylinder in a fume cupboard, and poured into the volumetric flask. The volume was made up with distilled water and the solution was shaken until all the hydroxylamine-hydrochloride had dissolved.

The membranes were loaded in 37mm diameter Teflon funnels as shown in Figure 2.2b. Twenty millilitres of hydroxylamine-hydrochloride solution was poured onto each membrane, and left to stand for 45 to 55 minutes. The taps were opened and a vacuum applied to filter the solution through the system. The membranes were thoroughly washed with five aliquots of distilled water (5ml each) then returned to their numbered Petri dishes and allowed to dry in a clean air cabinet. They were subsequently re-analysed by XRF spectrometry.

CHAPTER 3: DISSOLVED TRACE METALS

3.1: Hydrography

3.1.1: Riverine flow

Fresh water discharges into the Forth and Tay estuaries varied considerably during the study period (Figure 3.1, data from FRPB and TRPB). The lowest flows occurred from May to mid-August 1989. Minimum flows for the Forth and Tay were 3.5m^3s^{-1} and 31m^3s^{-1} respectively and occurred on 21 and 25 July 1989. Flood conditions were observed from January to March 1990 with maximum flows for both estuaries occurring on 5 February. The maxima were 465m^3s^{-1} and 1554m^3s^{-1} for the Forth and Tay respectively.

3.1.2: Suspended particulate matter loading

Peak suspended particulate matter (SPM) loadings recorded in each survey are shown in Figure 3.2. Apart from the March/April 1990 surveys, the Forth had much greater SPM loadings than the Tay. The highest loadings in the Forth were observed in low flow conditions (*eg* 445mgl^{-1} in June) and the lowest loadings during high flow conditions (*eg* 37.6mgl^{-1} in March). Conversely, the highest loading in the Tay (76mgl^{-1}) was observed in February 1990 during flood conditions. The origins of these differences are discussed further in Section 1.6.

3.1.3: Dissolved oxygen

During summer, pronounced minima in the concentrations of dissolved oxygen were observed in the upper Forth estuary. These were absent in winter (Figure 3.3, data from FRPB). Oxygen minima are the consequence of removal

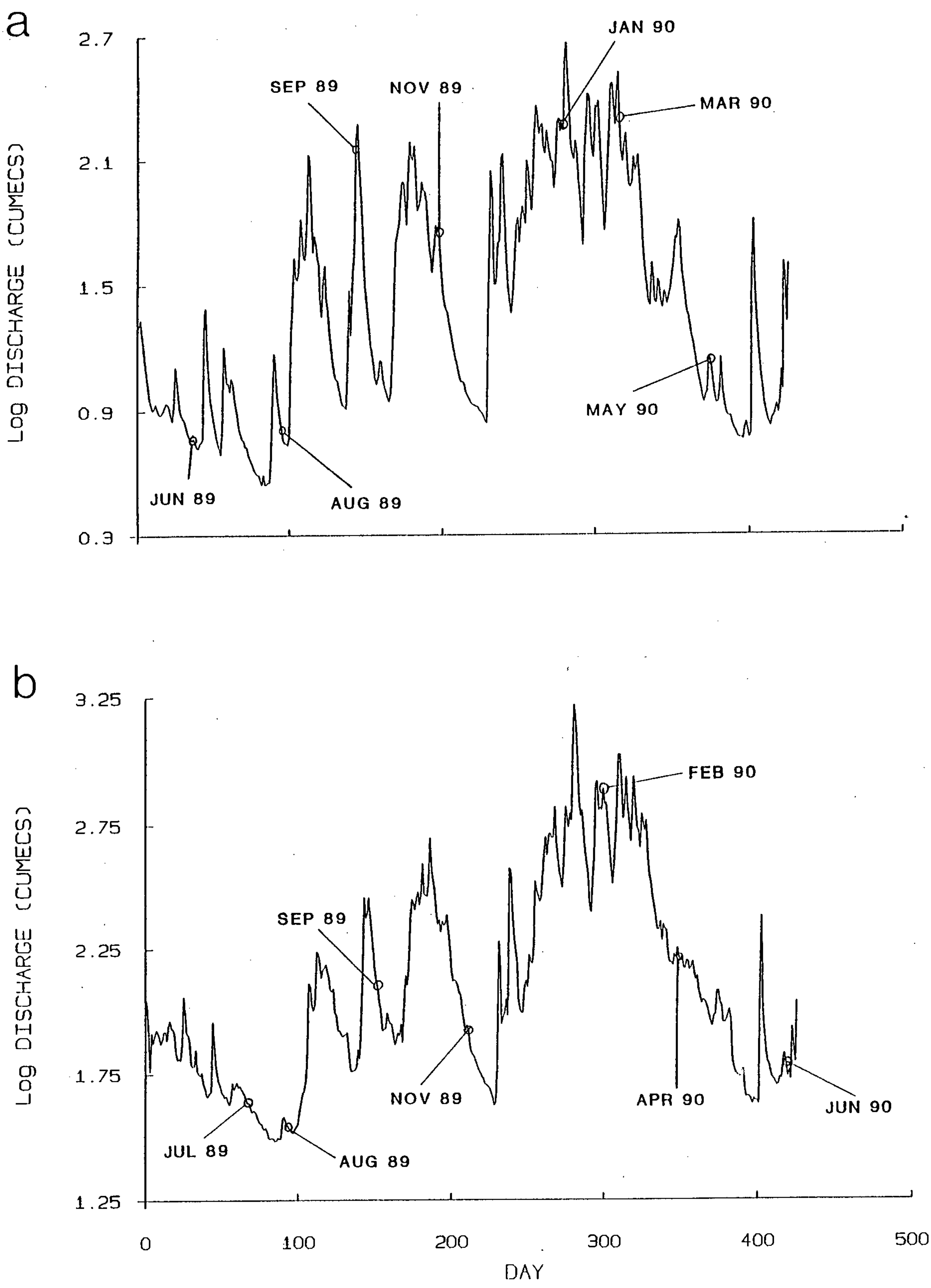


Figure 3.1. Fresh water discharges during the study period. a: Forth estuary and b: Tay estuary.

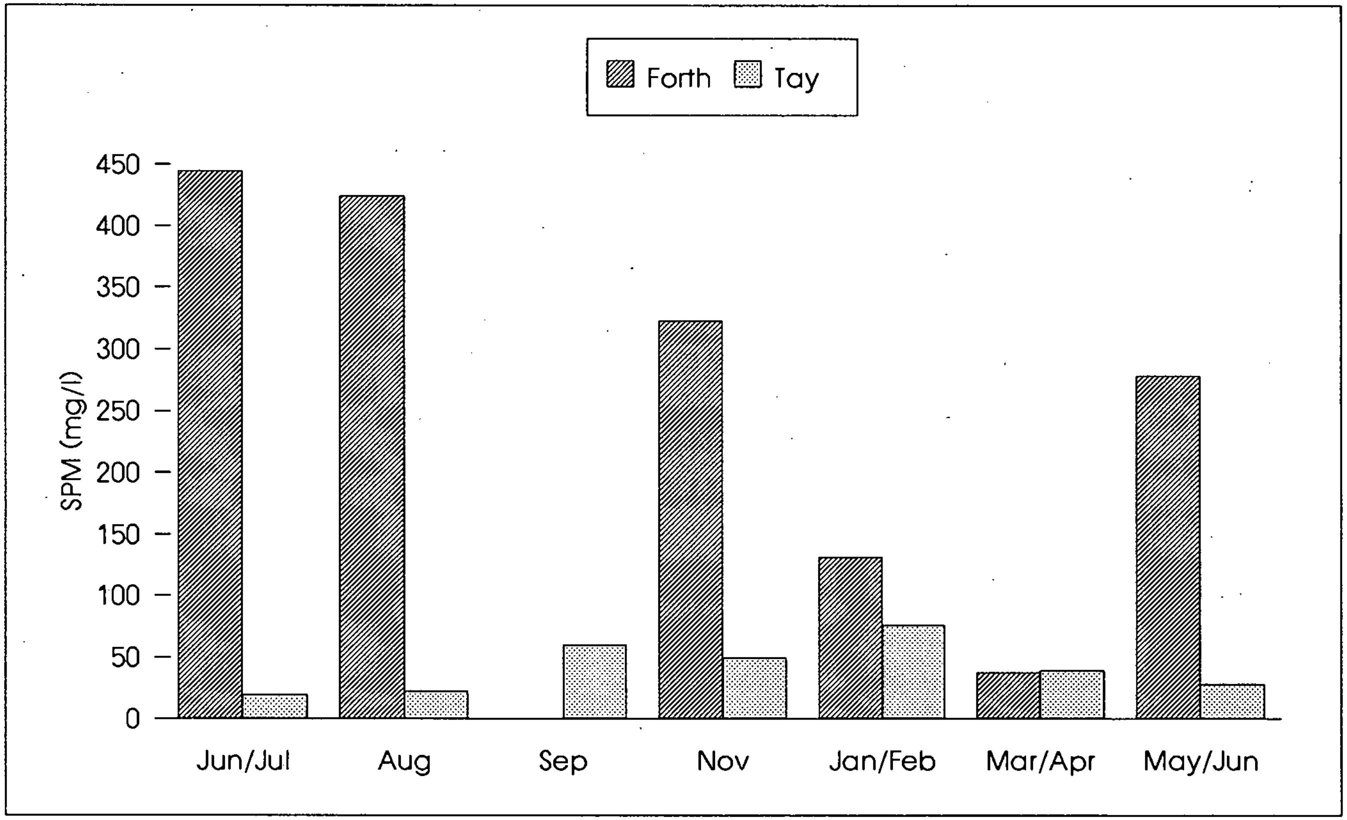


Figure 3.2. Peak suspended particulate matter loadings in the Forth and Tay estuaries

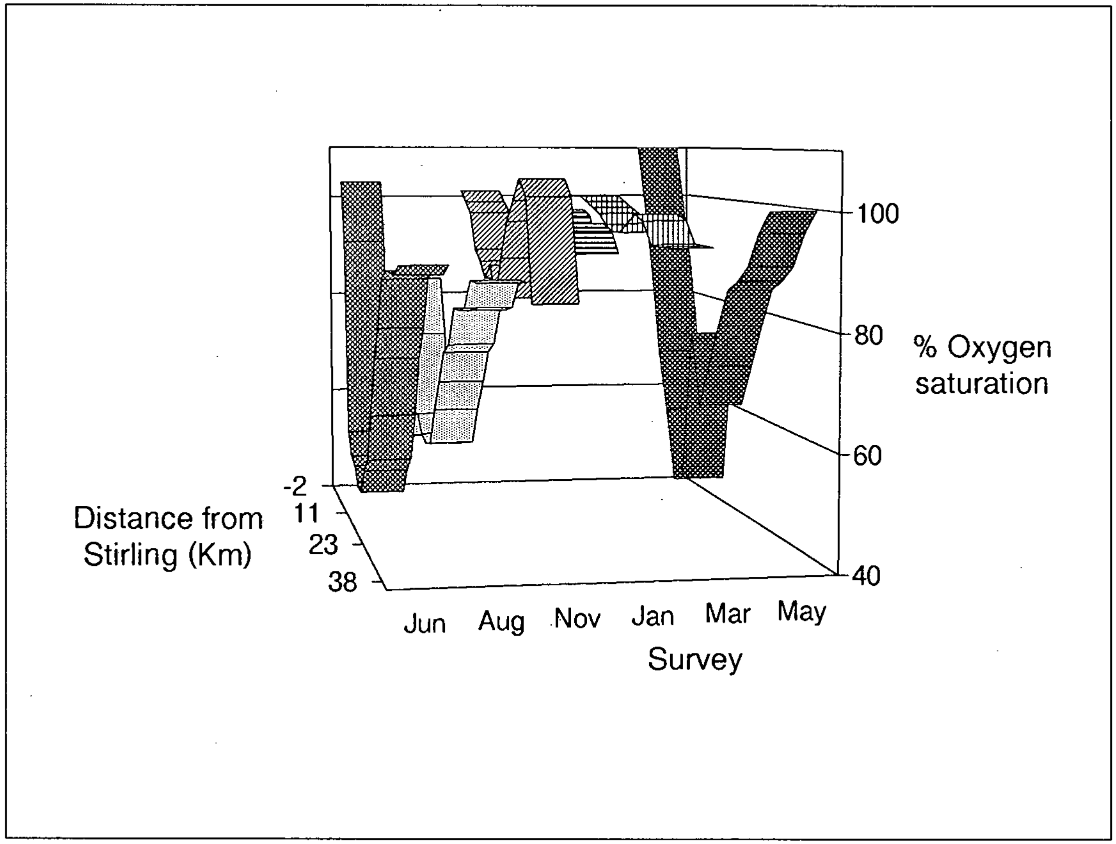


Figure 3.3. Dissolved oxygen saturation in the Forth estuary (Data from FRPB)

processes exceeding those of supply. In the case of the Forth, increased biochemical oxygen demand (BOD) is attributed to high SPM loadings and high water temperatures in summer (Table 3.1) coupled with reduced river flows, the principal source of dissolved oxygen (Forth River Purification Board 1983). The improved water quality in winter is due to the rapid flushing of the upper Forth with oxygenated riverine water, as well as reduced BOD (see Section 3.1.4). Dissolved oxygen concentrations in the Tay survey of June 1990 range from 80% to 97% saturation.

Table 3.1. Average water temperatures (°C) in the Forth and Tay surveys.

Survey	Minimum	Mean	Maximum	n
Forth				
June 1989	11.8	14.0	15.6	17
August 1989	14.8	17.4	19.0	17
November 1989	7.0	8.1	10.1	12
January 1990	3.0	4.2	4.9	10
March 1990	6.0	6.4	7.2	13
May 1990	10.8	12.5	13.8	16
Tay				
July 1989	12.8	15.4	17.1	23
August 1989	13.6	16.4	17.0	21
November 1989	2.3	4.3	6.1	20
February 1990	2.7	4.1	5.2	17
April 1990	8.2	9.0	9.6	16
June 1990	12.1	14.4	15.6	18

3.1.4: General discussion

The water renewal time for an estuary (or part of it) can be estimated from a box model, with salinity, water volume, and fresh water flow rates as inputs (Kaul and Froelich 1984, Morris 1990). This approach has been applied to the Forth and Tay estuaries in the present study (Balls 1992).

The replacement times for water in the whole of the Forth estuary range from 13 days in March to 48 days in August, while those in the Tay are much shorter, ranging from 2 days in February to 11 days in July. Chemical reactions with characteristic time scales of days are therefore more likely to produce non-conservative metal/salinity profiles in the Forth than in the Tay, and in summer than in winter.

The water quality of the upper Forth estuary is particularly vulnerable to low river flows. In summer the salt water penetrates further into the upper estuary, causing high sediment resuspension and increased BOD. The rates of dissolved oxygen consumption become fast in comparison with fresh water renewal rates. This causes the seasonal variation in oxygen profiles (Figure 3.3).

Different parts of the estuary have very different characteristic time scales. The larger volumes of water in the middle to lower estuary have the effect of damping out short-term rainfall variation. The estimated renewal time for the water held in a volume bounded by stations 42-51, for example, is about 11 days in August, though still only 3 days in March. Although time scales are longer in the outer estuary, rates of chemical reaction tend to be slower. This is because gradients of change (*eg* salinity, pH, SPM) are much smaller, and sites of reaction are usually less concentrated. Non-conservative behaviour is therefore less likely to be observed in these areas.

3.2: Dissolved manganese

3.2.1: Results

Dissolved manganese/salinity profiles in the Forth show non-conservative addition over the whole salinity range throughout the year (Figure 3.4). Concentrations at the river and sea-water end-members are less than $16\mu gl^{-1}$ and the peak concentrations range from $36\mu gl^{-1}$ in January to $155\mu gl^{-1}$ in June.

The Mn concentrations in the Tay are much lower than those in the Forth (Figure 3.5) and rarely exceed $10\mu gl^{-1}$. The November 1989 and April 1990 surveys, however, show unusually large peaks reaching $23\mu gl^{-1}$ and $21\mu gl^{-1}$ respectively. The November peak occurs at a salinity of 0.5 $^{o}/_{oo}$ and is quite sharp, while the April peak is broader and resembles the Mn profiles of the Forth.

3.2.2: Tay estuary - point sources of addition

The narrow shape of the dissolved Mn peak in the Tay in November 1989 is indicative of a point source. The rate of addition, given by the product of the daily riverine flow ($84{,}766ls^{-1}$) and the excess Mn (*ie* the amount exceeding that predicted by a conservative mixing curve, $18\mu gl^{-1}$), is approximately $132kgd^{-1}$. This is almost 3½ times greater than the fresh water input of manganese to the estuary on the same date (see Section 3.2.4) and therefore represents an important source. Unusually large peaks of dissolved Pb, Cu and Zn coincide with the Mn peak in this survey. The rates of addition for Pb, Cu and Zn are 7, 7 and $36kgd^{-1}$ respectively. The peaks are 15km downstream from Perth. Their source is unknown, though their positions would be consistent with an input from Newburgh or the River Earn.

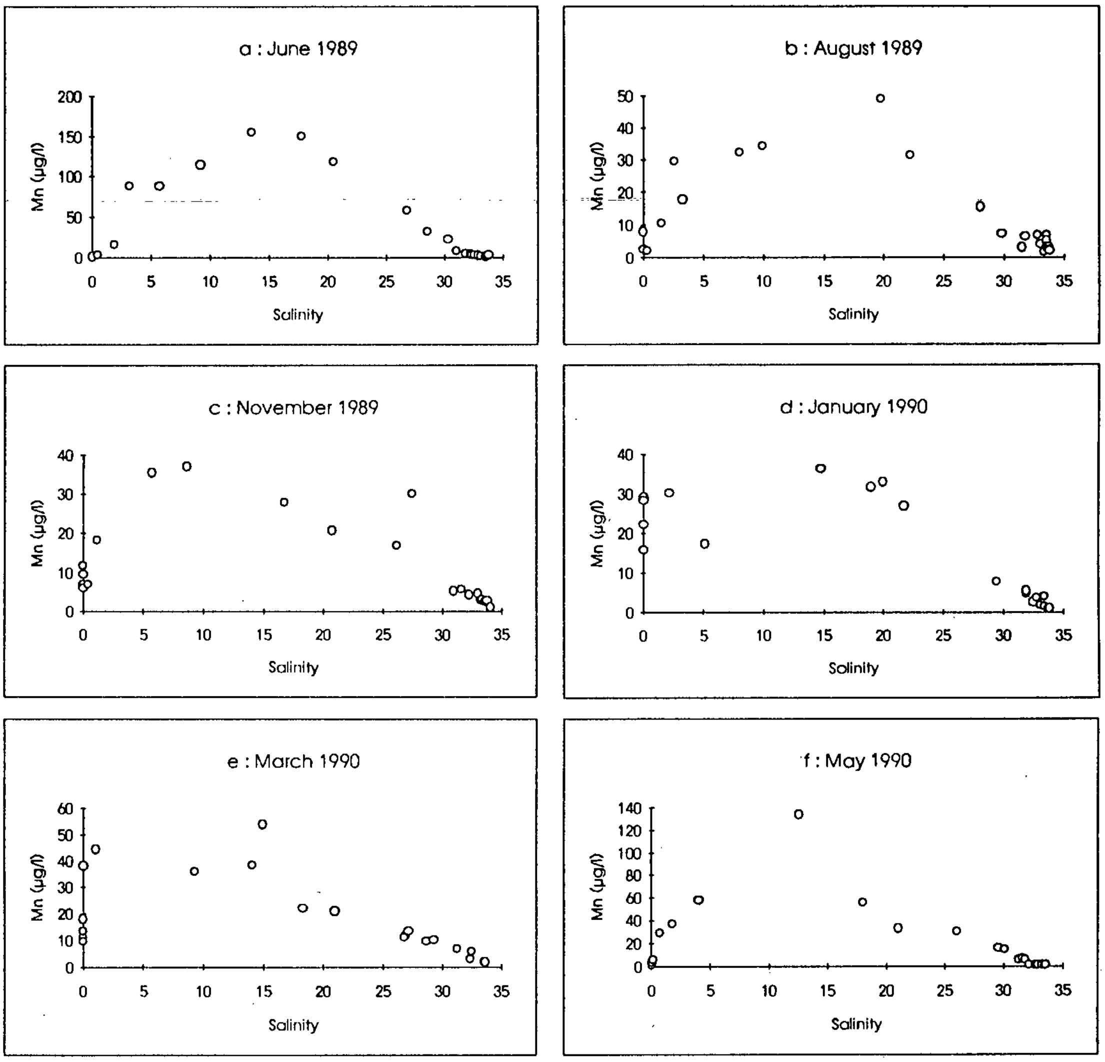


Figure 3.4. Dissolved Mn against salinity in the Forth estuary. a : June 1989, b : August 1989, c : November 1989, d : January 1990, e : March 1990, f : May 1990

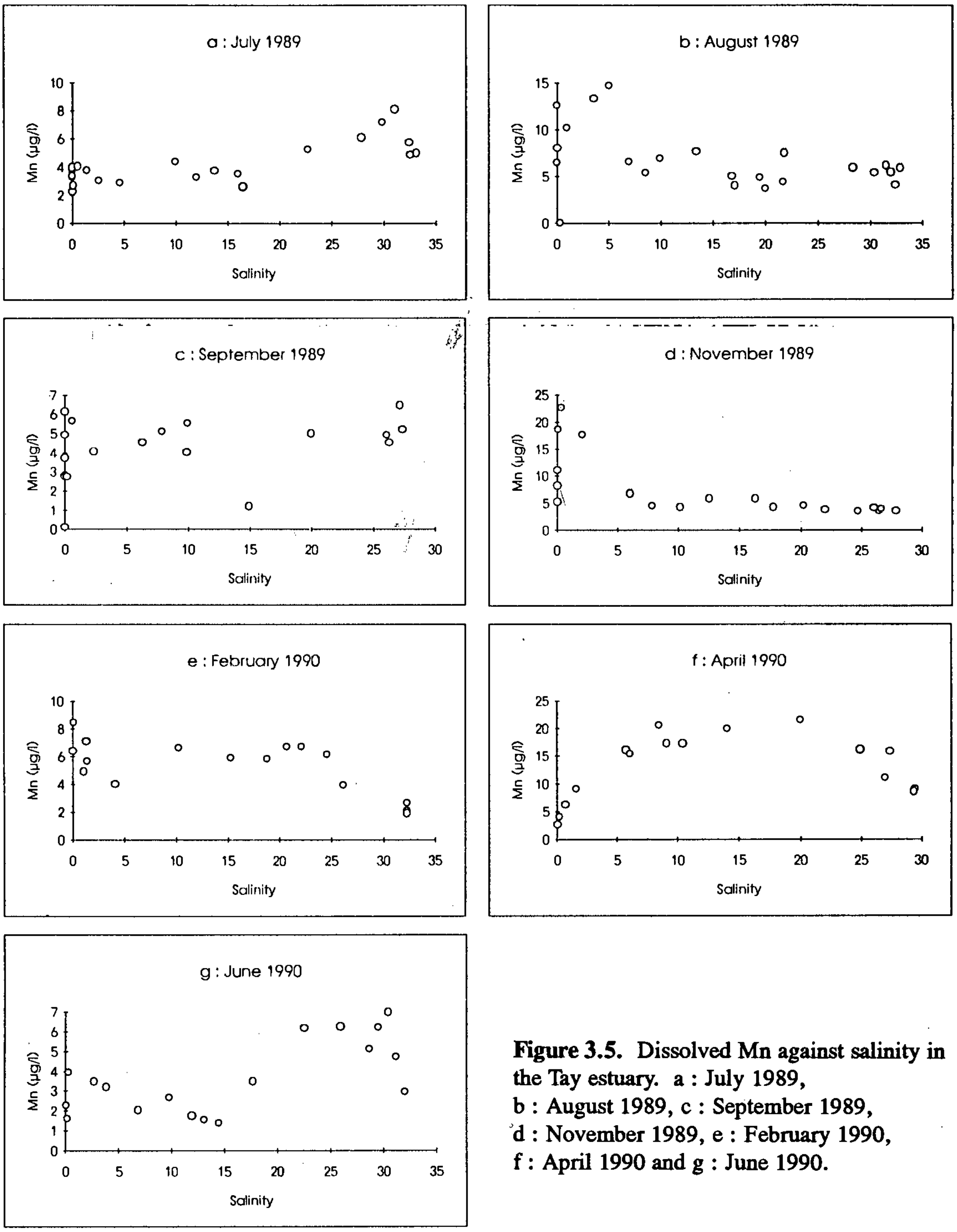


Figure 3.5. Dissolved Mn against salinity in the Tay estuary. a : July 1989, b : August 1989, c : September 1989, d : November 1989, e : February 1990, f : April 1990 and g : June 1990.

3.2.3: Riverine dissolved manganese concentrations

Fresh water end-member concentrations are taken as the mean concentration for samples at <0.1 ‰ salinity. (Analysis of variance showed that the salinities of these stations did not vary between surveys.) The end-member dissolved manganese concentrations, along with water temperatures, oxygen concentrations and suspended particulate matter loadings, are given in Table 3.2.

The Forth end-member concentrations gradually increase from a minimum of 1.11μgl^{-1} in June, to a maximum of 15.6μgl^{-1} in January. They span the "global average" riverine dissolved manganese concentration, estimated to be 8.2μgl^{-1} (Martin and Meybeck 1979).

The Mn end-member concentrations in the Tay are within the range of those in the Forth, but do not vary seasonally. Only in August did they exceed the global average riverine concentration, and then by less than 1μgl^{-1}.

3.2.3.1: Fresh water end-member manganese concentrations: seasonality

For seasonality to be observed, in the fresh water end-member of the Forth the rates of net Mn addition or removal must be comparable to water renewal rates in the upper estuary. If rates of Mn removal were much faster than water renewal rates, for example, concentrations would remain low throughout the year. If the converse were true then the effects of removal would be undetectable. The causes of seasonality in the Forth must also explain the apparent absence of seasonality in the Tay. Sources and sinks of dissolved manganese, and relevant reaction kinetics, are discussed below.

3.2.3.1.1: Manganese sources

Manganese forms 0.1% by weight of the earth's crust (Hem 1963). Terrigenous weathering is therefore an important source of manganese to the marine environment. Increased weathering, due to higher freshwater flows, may contribute to the higher dissolved manganese concentrations observed in the Forth in winter, and the large input to the Tay in February.

Table 3.2. Mn concentrations, water temperatures, O_2 concentrations and SPM loadings in the fresh water end-members of the Forth and Tay estuaries. Average values for stations of salinity <0.1 ‰ are quoted. The distance is that in km downstream from Stirling or Perth of the lowest station of salinity <0.1 ‰.

Survey date	Mn $(\mu g l^{-1})$	Distance (km)	No of samples	T (°C)	O_2 (%)	SPM mean $\pm\sigma$ $(mg l^{-1})$
Forth						
June 1989	1.11	0	2	15.2	97	144 ± 159
August 1989	5.05	0	2	18.8	78	199 ± 127
November 1989	8.49	13	4	7.2	97	83 ± 78
January 1990	15.60	15	4	3.0	95	71 ± 49
March 1990	12.98	15	4	6.0	99	17 ± 7
May 1990	2.55	6	3	12.1	98	76 ± 110
Tay						
July 1989	3.30	7	5	16.9	-	10 ± 9
August 1989	8.95	3	3	16.7	-	4 ± 4
September 1989	3.38	11	6	-	-	7 ± 6
November 1989	8.18	11	3	2.4	-	11 ± 5
February 1990	6.36	15	1	2.9	-	17
April 1990	2.70	11	1	9.2	-	17
June 1990	2.28	7	1	15.3	88	10

3.2.3.1.2: Manganese removal

The oxidative removal of dissolved Mn from the water column is essentially microbially mediated in estuaries (Sunda and Huntsman 1987, Vojak *et al* 1985, Wollast *et al* 1979), anoxic Fjords (Emerson *et al* 1979, 1982, Rosson *et al* 1984), lakes (Chapnick *et al* 1982) and coastal seawater (Wartel *et al* 1991). Removal is faster near continental margins (Table 3.3), where concentrations of nutrients and bacterial binding sites on particulate surfaces are higher (Tebo 1991).

Manganese oxidising bacteria are integrally associated with SPM. Sterilised sediment, for example, failed to cause Mn removal when returned to lake waters (Chapnick *et al* 1982). Manganese oxidation is extremely slow in the absence of SPM but increases proportionally with increasing loads, at least up to 100mgl^{-1} (Vojak *et al* 1985).

Table 3.3. Removal rates and scavenging residence times of dissolved manganese in marine environments.

Area		Maximum rate ($\mu gl^{-1}d^{-1}$)	Mn scavenging residence time	Reference
Galapagos Rift		-	51 years	Weiss 1977
Sargasso Sea	0-40m	0.013	420 days	Sunda and Huntsman 1988
	80-160m	0.119	30 days	Sunda and Huntsman 1988
	500m	0.013	100 days	Sunda and Huntsman 1988
Scheldt estuary		-	2 months	Wollast *et al* 1979
Rhine estuary		-	days	Wollast *et al* 1979
Narragansett Bay		-	2 days	Graham *et al* 1976
Saanich Inlet	Oxic layer	-	2 days	Emerson *et al* 1979, 1982
Saanich Inlet		7.27	-	Tebo and Emerson 1985
Saanich Inlet	120m	26.4	-	Rosson *et al* 1984
Newport River estuary (Summer)		4.62	0.7 days	Sunda and Huntsman 1987
Newport River estuary (Winter)		0.82	11 days	Sunda and Huntsman 1987
Black Sea; central		8.33	>9 days	Tebo 1991
Black Sea; nearshore		89.38	0.6 days	Tebo 1991
Tamar estuary		6.72	60 days	Morris and Bale 1979
Tamar estuary, fresh water		142	-	Vojak *et al* 1985
Tamar estuary, salt water		6.5	-	Vojak *et al* 1985

The SPM concentrations in the Forth end-member samples exceed 15mgl^{-1} during all surveys (Table 3.2). They are highest in summer and will therefore give the greatest Mn removal rates in summer. The average SPM loadings in the Tay end-members are lower than 12mgl^{-1} in most months, though they reach 17mgl^{-1} in February and April. Manganese removal rates in the Tay are therefore expected to be slower than in the Forth.

Manganese oxidation rates double for every 11°C rise in temperature (Yeats and Strain 1990). Optimum temperatures vary from 20°C in Saanich Inlet (Tebo and Emerson 1985) to 30°C in the Tamar (Vojak *et al* 1985) and Newport River estuaries (Sunda and Huntsman 1987). Rates decrease at higher temperatures.

The fresh water end-member temperatures of the Forth and Tay reach 19°C and 17°C in summer, but fall to 3°C and 2°C respectively in winter (Table 3.2). Removal of dissolved manganese from the Forth and Tay should therefore be at least twice as fast in summer.

3.2.3.1.3: Kinetics

Data from the fresh water end-member of the macrotidal, turbid Tamar estuary can be used to estimate Mn removal rates from the Forth and Tay. These must only be considered approximate, however, since rate constants depend both on the SPM composition and bacterial population within each estuary. The Mn oxidation rate is $0.11\mu g l^{-1} h^{-1} mg^{-1}$ of suspended sediment at 20°C in the Tamar (Vojak *et al* 1985). This is used for the summer surveys of the Forth and Tay. Since water temperatures are at least 11°C lower in winter, the rate constant is halved for the January and February surveys. Results are given in Table 3.4.

The manganese removal rates calculated for the Forth in August are very fast compared with the water renewal rates. Less removal will take place in January (and the other winter months) because removal rates are slower and water renewal rates faster. This provides a possible explanation for the seasonality observed in the Forth.

In the Tay, however, Mn removal is slower due to lower SPM loadings, while water renewal rates are faster due to larger riverine flows. During February, when SPM concentrations are highest, the water residence time in the upper estuary is reduced to hours. The situation in the Tay is unlike that in the Forth where lowest flows coincide with highest SPM loadings and water temperatures, and all factors work simultaneously to reduce manganese concentrations in summer. This is a possible explanation for the absence of seasonality in the Tay.

Table 3.4. Estimated Mn removal rates in the Forth and Tay end-members. Replacement times are estimated for the volume of water between 0 and 15km downstream from Stirling or Perth (Balls 1992).

Station No	Salinity (‰)	T (°C)	O_2 (%)	SPM (mgl^{-1})	Rate constant ($\mu gl^{-1}h^{-1}mg^{-1}$)	Mn removal ($\mu gl^{-1}d^{-1}$)	Replacement time
FORTH AUGUST							
-2	0.04	19	83	29.15	0.11	77	7 days
0	0.07	19	72	207.98	0.11	549	
FORTH JANUARY							
8	0.09	3	95	14.0	0.055	18	½ day
11	0.07	3	94	77.8	0.055	103	
TAY JULY							
0	0.03	17	-	0.64	0.11	1.7	2 days
1	0.03	17	-	0.95	0.11	2.5	
TAY FEBRUARY							
15	0.06	3	-	16.7	0.055	22	2 hours
17	0.11	3	-	40.1	0.055	53	

3.2.4: Riverine dissolved manganese fluxes

The riverine dissolved Mn fluxes are calculated by multiplying the end-member concentrations by the fresh water flows on the survey dates (Table 3.5).

Fresh water manganese fluxes in the Forth increase by over three orders of magnitude between June and March, and fall again in May (Table 3.5). This seasonality reflects the variations both in riverine run-off and in dissolved Mn end-member concentrations.

The fluxes in the Tay are much less variable, being of the same order of magnitude in all surveys except February, when flooding occurred.

Table 3.5. Fresh water manganese concentrations and riverine fluxes.

Survey date	Mn (μgl^{-1})	Flow (ls^{-1})	Mn Flux (kgd^{-1})
Forth			
June 1989	1.11	5,659	0.5
August 1989	5.05	6,378	2.8
November 1989	8.49	59,897	43.9
January 1990	15.60	123,798	167.0
March 1990	12.98	190,263	213.4
May 1990	2.55	14,005	3.1
Tay			
July 1989	3.30	47,809	13.6
August 1989	8.95	35,176	27.2
September 1989	3.38	130,879	38.2
November 1989	5.20	84,766	38.1
February 1990	6.36	463,770	255.0
April 1990	2.70	137,196	32.0
June 1990	2.28	67,784	13.3

3.2.5: Sea water end-member manganese concentrations

Sea water end-member concentrations are taken as the average of those at salinities greater than 33.6 °/₀₀. (The average end-member salinities were not significantly different between surveys.) End-member concentrations for dissolved Mn in the Forth are listed in Table 3.6. Values for the Tay are not calculated, since salinities greater than 30 °/₀₀ were not sampled. For the purpose of calculating a conservative mixing line in the Tay (Section 3.2.7.1), the sea water end-member Mn concentration was taken to be the average of all end-member concentrations in the Forth.

End-member concentrations in the Forth vary significantly (at 95% level) throughout the year. Although the seasonal trend is not as smooth as that in the fresh water end-members, the concentrations in January, March and May are lower than those of the summer and autumn surveys. This is the converse behaviour of that observed in the riverine water.

Similar seasonality in dissolved manganese concentration has been observed in the Western Baltic (Balzer *et al* 1987). Such seasonality has been attributed to sedimentary inputs of dissolved Mn to the water column. In summer, rapid sinking and degradation of newly formed organic matter causes the development of sub-oxic or anoxic conditions in the bottom sediments. These cause rapid diffusion of dissolved Mn into the water column (Dehairs *et al* 1989). The importance of newly fixed (reactive) carbon has been demonstrated using microcosms in coastal environments (Hunt 1983): benthic fluxes are lower in autumn than at comparable temperatures in spring and vary from year to year according to the amount of carbon fixed by primary productivity. In winter benthic fluxes are low due to lower temperatures and the absence of reactive organic carbon in the sediments.

3.2.6: Dissolved manganese export to the North Sea

Fluxes of dissolved constituents leaving estuaries can be calculated by multiplying the theoretical zero salinity end-member (TZSEM) concentration (Figure 3.6) by the riverine flow (GESAMP 1987). Fluxes are calculated for all Forth surveys, but only for the April survey of the Tay, since the profiles in the other Tay surveys did not exhibit clear non-point addition. Results are listed in Table 3.6.

The dissolved manganese fluxes leaving the Forth are up to more than ten times higher in winter than in summer. The river flow exerts a greater influence on the calculated flux than the variation in the TZSEM concentration. The flux leaving the Tay in April falls within the ranges of those observed in the Forth.

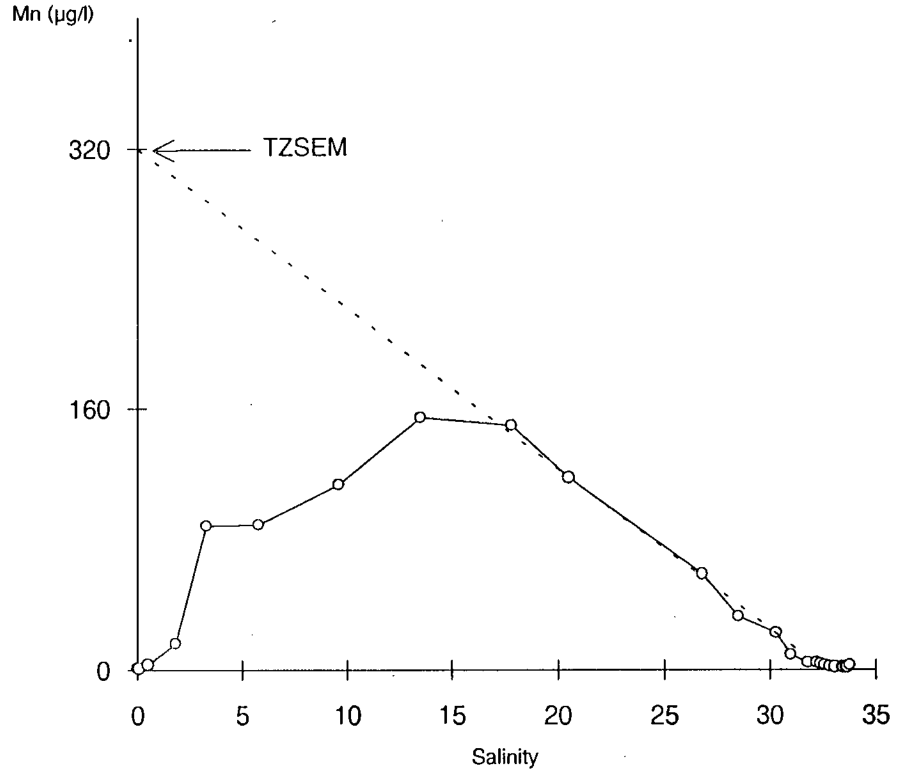


Figure 3.6. Calculation of the theoretical zero salinity end-member concentration (TZSEM), Forth estuary, June 1989.

In each survey, the amount of dissolved manganese leaving the estuary is greater than that entering from riverine sources. Both estuaries therefore contain additional sources of dissolved Mn. The output/input ratios are much larger in summer than in winter. This is partly because of the lower riverine flows in summer, but may also be influenced by the seasonality in sedimentary Mn inputs, as discussed below.

Table 3.6. Coastal water manganese concentrations and export fluxes.

Survey date	Mn (μgl^{-1})	TZSEM (μgl^{-1})	Riverine flow (ls^{-1})	Export (kgd^{-1})	Export/ Input
Forth					
June 1989	2.01	320	5,659	156	287
August 1989	2.81	120	6,378	66	23
September 1989	1.99	-	43,790	-	
November 1989	2.01	50	59,897	259	6
January 1990	0.86	75	123,798	802	5
March 1990	1.70	50	190,263	822	4
May 1990	0.60	140	14,005	169	55
Tay					
April 1990		52	137,196	616	19

3.2.7: Dissolved manganese sediment fluxes

3.2.7.1: Calculations

All the manganese/salinity profiles in the Forth, and that for April in the Tay, resemble those found in the St Lawrence (Bewers and Yeats 1979), Geum (Byrd *et al* 1990), Tamar (Knox *et al* 1981), Newport (Evans *et al* 1977), Rhine and Scheldt estuaries (Wollast *et al* 1979). The shape of the peaks in the present study, and their similarity with ammonia profiles (Balls 1992), indicate a benthic source of Mn. In order to estimate the benthic fluxes, the estuaries are divided into a number of boxes, and fluxes for each box are calculated using the following equation (Callaway *et al* 1988):

$$\text{Net flux } (\mu g cm^{-2} d^{-1}) = \frac{[\text{Excess Mn}] \times V}{A \times T}$$

where:

[Excess Mn] is the difference between the observed Mn concentration and that calculated from the theoretical dilution line joining the two end-member concentrations (μgl^{-1}). Though excess concentrations result from the competing processes of benthic addition and oxidative removal, removal rates are lower in mid-estuarine mixing zones because sea water cations compete with Mn for adsorption sites (Morris *et al* 1982, Vojak *et al* 1985).

V is the volume of the water in the box at spring tide (l) (Data from FRPB).

A is the sediment area of the box (cm^{-2}) (Data from FRPB).

T is the residence time of water in the box (d) (Data from Balls 1992).

Benthic fluxes are not calculated for the firths since estimates of A, V and T are less precise, and the small [excess Mn] values are subject to proportionally higher uncertainties.

Despite the assumptions, this method of estimation gives an indication of the relative importance of sedimentary inputs to the manganese budget of the system.

3.2.7.2: Results

The results for the Forth estuary are summarised in Figure 3.7. The highest flux, $66\mu g cm^{-2} d^{-1}$, is observed in the upper Forth in June. The peak flux in the April survey of the Tay is $17\mu g cm^{-2} d^{-1}$. These values are within the ranges of those obtained in the Tamar estuary, *ie* $5.3\text{-}53\mu g cm^{-2} d^{-1}$ by calculation and $38\text{-}92\mu g cm^{-2} d^{-1}$ from sediment cores (Knox *et al* 1981). It is interesting to note that, despite the lower concentrations of Mn observed in the Tay, the benthic fluxes are of the same order as those in the Forth.

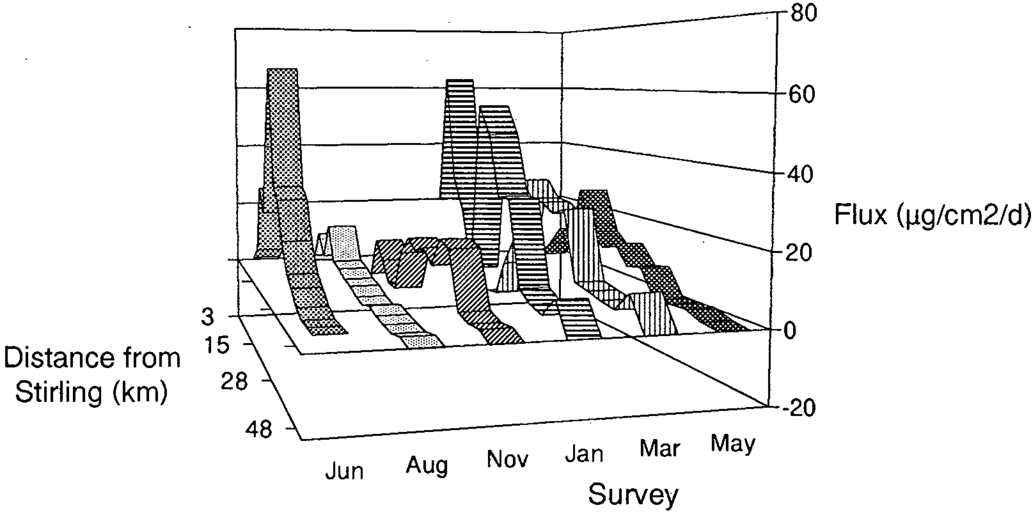


Figure 3.7. Benthic Mn fluxes in the Forth

3.2.7.3: Benthic fluxes

There are two possible mechanisms of Mn release from bottom sediments. Firstly, Mn may be released by molecular diffusion from interstitial waters. This diffusion is enhanced by higher temperatures (*eg* Aller and Benniger 1981, Elderfield *et al* 1981) or the increased production of Mn(II) caused by increased anoxia (Eaton 1979a).

Secondly, Mn fluxes may be enhanced by active bioturbation (*eg* Aller 1980), or other physical disturbances/resuspension of bottom sediments (*eg* Byrd *et al* 1990, Duinker *et al* 1982a, Sanders 1978). In the latter case elevated Mn concentrations may be accompanied by increased SPM loadings.

In the summer surveys of the Forth (June, August and May) the greatest Mn fluxes occurred in the upper estuary. They were coincident with the oxygen minima, but further downstream than the turbidity maxima (*eg* see Figure 3.8a for June). The June survey showed the highest Mn fluxes. At this time an oxygen minimum of <50% saturation extended over 8km of the upper estuary. The oxygen minimum in May was not as wide as that in June (saturations of <50% extended over 3km) and the Mn flux was correspondingly lower. Although water temperatures were highest in August, the oxygen minimum did not get below 54% saturation and the greatest Mn flux was much smaller than in the other months. Studies using coastal mesocosms indicate that summer Mn fluxes are dependent on the amount of readily metabolised organic matter in the sediments, rather than on temperature (Hunt 1983). Benthic chamber fluxes are higher in July than in August because newly produced organic matter is added to the sediments in winter and spring. The present results indicate that benthic Mn fluxes are also, at least partly, controlled by the extent of oxygen depletion in the upper Forth during low flow summer conditions.

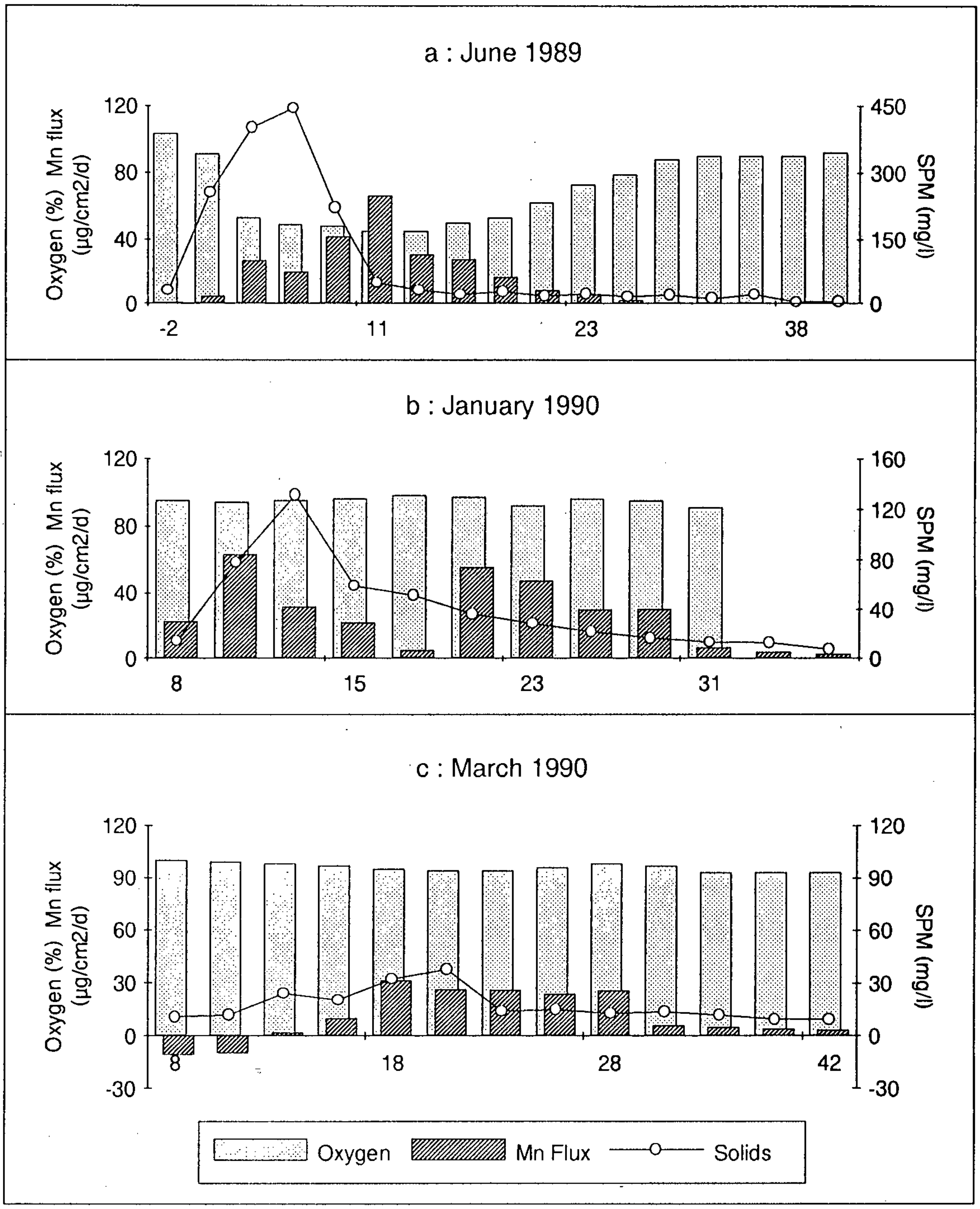


Figure 3.8. Manganese fluxes, oxygen saturations and suspended solids concentrations against station number in the Forth.
a : June 1989, b : January 1990 and c : March 1990.

Despite the absence of oxygen minima, some very large Mn fluxes are observed in winter. These peak fluxes are not limited to the low salinity regions. In the January survey of the Forth, for example, two distinct maxima of similar magnitude occurred: one in the upper estuary, and the other further downstream (Figure 3.8b). These unexpectedly high fluxes can be attributed to increased resuspension of bottom sediments, caused by wind stress. The suspended particulate matter concentrations reached $131mgl^{-1}$ in January but only $38mgl^{-1}$ in March. The peak Mn fluxes are therefore lower in March (Compare Figure 3.8b with 3.8c).

The Forth estuary therefore exhibits both diffusional benthic fluxes, controlled by sub-oxic or anoxic sediments, and non-diffusional fluxes, caused by wind-stress and sediment resuspension. These factors are seasonally and spatially variable within the estuary.

The benthic Mn fluxes in the Tay are of similar magnitude to those in the Forth. The Tay fluxes do not appear to be controlled by sub-oxic conditions or sediment resuspension. Instead, they may be affected by increased residual currents at slack water, caused by larger riverine flows. Experimental evidence suggests that an increase in water current from $0\text{-}15cms^{-1}$ causes a threefold increase in the depth of penetration of dissolved oxygen from overlying waters (Booij *et al* 1991). Since this is caused by a reduction in the thickness of the benthic boundary layer, it may be applied to the diffusion of Mn out of the sediment. Verification of this is beyond the scope of this project.

3.2.8: Estuarine manganese cycling, sources and sinks

Though the greatest benthic Mn fluxes occur in the upper estuary, this represents only a small part of the Forth. The fluxes in the outer estuary are small, but the larger sediment area means that these sediments account for more than half the total manganese added to the tidal waters (Table 3.7). The proportion of Mn(II) contributed by the upper estuary is greatest in summer, when sub-oxic conditions occur. In June and August the upper estuary accounts for almost half of the total Mn(II) added to the system. This falls to less than 10% at other times of the year. The increased importance of the upper estuary during the summer months may explain the larger output/input ratios (Mn export to the North Sea to Mn input from fresh water) observed during summer (Section 3.2.6).

Table 3.7. Percentage contributions of upper estuarine sediments, lower estuarine sediments and fresh water discharges (Section 3.2.4) to the total dissolved Mn inputs for each survey. For comparative purposes, the upper Forth estuary was taken to be that between 10 and 19km, and the lower estuary between 19 and 45km from Stirling. The upper Tay estuary was taken to be between 10 and 21km, and the lower estuary between 22 and 41km from Perth.

Survey date	River %	Upper Estuary %	Lower Estuary %
Forth			
June 1989	0.02	45	55
August 1989	0.63	34	65
November 1989	1.30	1	97
January 1990	2.13	9	89
March 1990	0.45	8	92
May 1990	0.12	2	98
Tay			
April 1990	1.00	12	87

Riverine inputs of dissolved manganese are negligible compared with sedimentary inputs in both Forth and Tay estuaries. This agrees with the observation that most of the Mn transported by rivers is associated with suspended particles, *eg* 90% in the Amazon (Gibbs 1973) and more than 98% in the Mississippi (Trefry and Presley 1982). Coastal sediments are often more important than fresh water sources of dissolved Mn to offshore waters. Sundby *et al* (1981), for example, found that an average of 14,000kgd^{-1} dissolved Mn is exported from the Gulf of St Lawrence, that is about 50% more than the amount added by fresh water. Four times as much manganese is added to Chesapeake Bay from bottom sediments than is added from the Susquehanna River (Eaton 1979a). Similarly, 40-75% of the Mn added to the abyssal waters of the Gulf of Mexico is derived from the sediments of the Mississippi Delta, the remaining 25-60% coming from riverine or oceanic sources (Trefry and Presley 1982). More dissolved Mn is exported from the Newport River estuary than is added by the river (Evans *et al* 1977), the excess again attributed to remobilisation from reducing sediments.

Total inputs (riverine and benthic) of dissolved manganese to the estuaries of the Forth and Tay are listed in Table 3.8. Fluxes are highest in winter and lowest in summer. This trend reflects the importance of physical disturbances of bottom sediments in the outer estuary rather than the riverine inputs (which are negligible) or the release associated with anoxia in the upper estuary. Meteorological events may therefore be very important in determining the amount of manganese discharged into the North Sea.

Total amounts of dissolved manganese added to each estuary are compared with those discharged into the North Sea (Section 3.2.6) in Table 3.8. Even though inputs of dissolved Mn from the firth sediments are ignored, only about 10% of the Mn added to each estuary enters the North Sea in the dissolved phase.

Manganese oxidation rates observed in the Tamar estuary are fast enough to account for the amount of "lost" manganese by oxidation onto suspended particulate matter in the water column of the firth of Forth. The manganese "lost" from the dissolved phase in the Forth is calculated from the difference between the total input and export of Mn. This is divided by the volume of the firth at spring tide (*ie* 1.3362 x 10^{13} litres between 50km and 92km downstream from Stirling, data from FRPB). The resulting removal rates range from 0.03$\mu gl^{-1}d^{-1}$ in August to 0.54$\mu gl^{-1}d^{-1}$ in January (Table 3.9).

Table 3.8. A comparison of the combined benthic and riverine dissolved Mn inputs with total dissolved Mn exports (Section 3.2.6).

Survey date	Input (kgd^{-1})	Export (kgd^{-1})	% "lost"
Forth			
June 1989	2300	160	93
August 1989	470	66	86
November 1989	3400	260	92
January 1990	8000	800	90
March 1990	4700	820	83
May 1990	3000	170	94
Tay			
April 1990	6400	620	90

Oxidation rates for saline water in the Tamar are about 0.017$\mu gh^{-1}mg^{-1}$ of particles at 20°C (Vojak *et al* 1985). Suspended particulate matter concentrations in the firth of Forth are typically about 5mgl^{-1} during all surveys. Oxidation rates in the firth of Forth may therefore be about 2.04μgd^{-1} at 20°C. Since rates double for every 11°C rise in temperature (Yeats and Strain 1990) rates at 9°C may be about 1.02μgd^{-1}, and intermediate rates at 15°C and 5°C may be about 1.5 and 0.5μgd^{-1} respectively. These rates compare favourably with observed rates of removal in the Forth (Table 3.9).

Removal of dissolved Mn onto suspended particulate matter at high salinities is a common feature in coastal waters, *eg* Rhine and Scheldt estuaries (Duinker *et al* 1979a), Peconic River estuary (Wilke and Dayal 1982) and Narragansett Bay (Graham *et al* 1976). After becoming associated with suspended particulate matter, manganese may be buried in the sediments and recycled within the coastal/estuarine circulation pattern for considerable periods of time. The fraction of Mn escaping coastal waters is mainly in the particulate form (Duinker *et al* 1979a), thus riverine manganese of terrigenous origin eventually reaches pelagic sediments (Bender *et al* 1977, Yeats *et al* 1979).

Table 3.9. A comparison of Mn "lost" from the dissolved phase of the Forth with predicted Mn oxidation rates in the firth.

Survey date	Total input (kgd^{-1})	Export (kgd^{-1})	Amount "lost" (μgd^{-1})	Amount "lost" ($\mu gl^{-1}d^{-1}$)	Water temperature (°C)	Rate estimate ($\mu gl^{-1}d^{-1}$)
June 1989	2300	160	2.14×10^{12}	0.16	12	1.0
August 1989	470	66	4.04×10^{11}	0.03	15	1.5
November 1989	3400	260	3.14×10^{12}	0.23	10	1.0
January 1990	8000	800	7.20×10^{12}	0.54	5	0.5
March 1990	4700	820	3.88×10^{12}	0.28	6	0.5
May 1990	3000	170	2.83×10^{12}	0.21	11	1.0

3.3: Nickel and zinc

3.3.1: Results

Like those for manganese, both nickel and zinc profiles in the Forth show non-conservative behaviour with wide mid-estuarine maxima (Figures 3.9 and 3.10). The highest nickel concentration (1.49μgl^{-1}) occurred in June 1989 while the lowest peak concentration (0.73μgl^{-1}) occurred in March 1990. The highest dissolved zinc concentration (9.45μgl^{-1}) occurred in January and the peak concentrations of the other surveys varied around 4μgl^{-1}.

The Ni and Zn profiles in the Tay also show non-conservative behaviour (Figures 3.11 and 3.12). The concentrations were generally lower than those in the Forth and the data therefore show more scatter. The peak nickel concentrations range from 0.43μgl^{-1} in September to 0.81μgl^{-1} in July. The mid-estuarine peaks of zinc ranged from 1.20μgl^{-1} in June to 2.17μgl^{-1} in April. An unusually high peak, reaching 7.57μgl^{-1} was observed at a salinity of 0.5 ‰ in the November 1989 survey. This peak coincided with a similar Mn peak (see Section 3.2.2).

The concentration ranges of dissolved Ni and Zn in the Forth and Tay are generally lower than those in other major, macrotidal estuaries (Table 3.10). The Severn, Mersey and Beaulieu, for example, have peak concentrations which are more than 10 times greater than the peak concentrations observed in this study. The non-industrialised Tweed has similar ranges of dissolved Ni and Zn concentrations to those observed in the Tay.

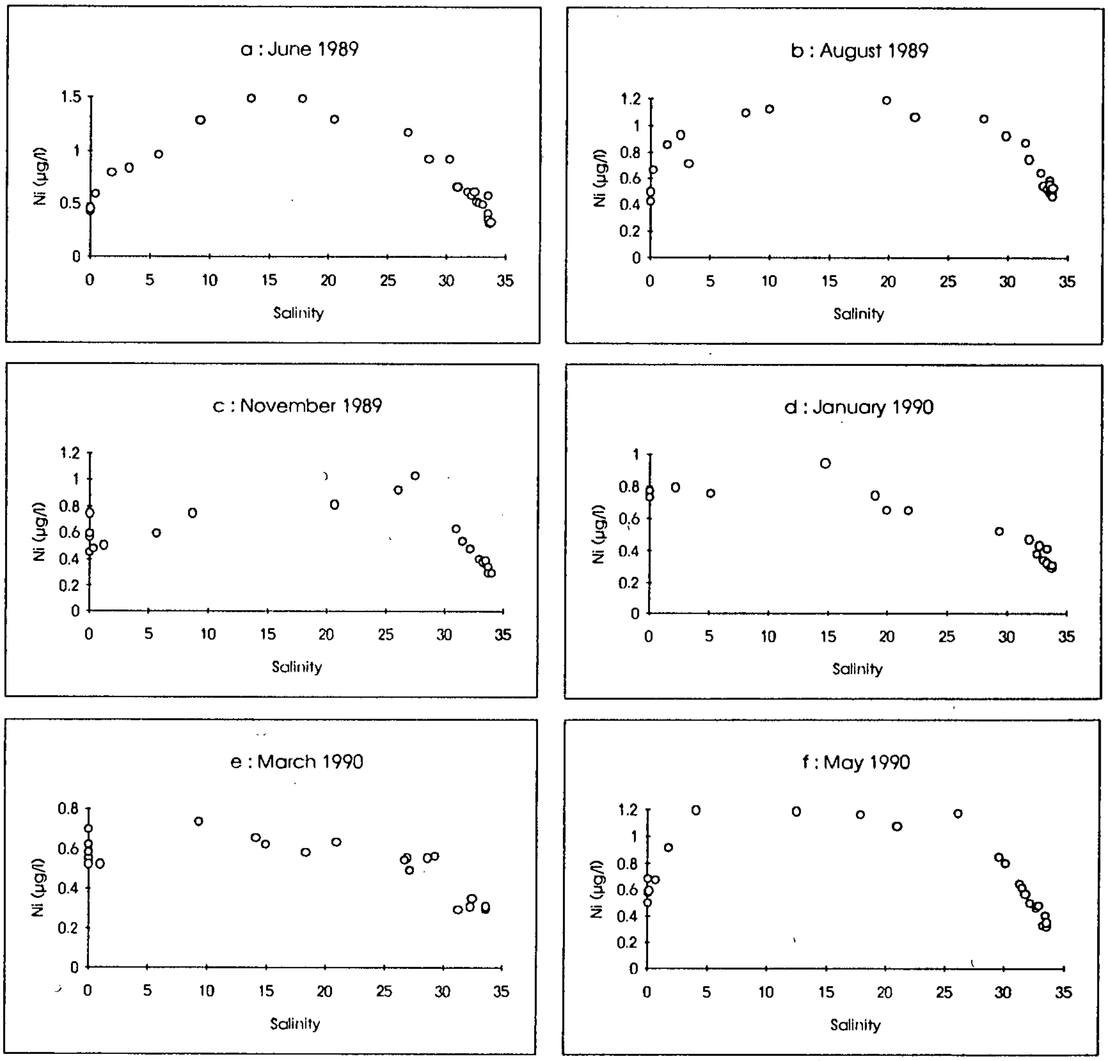


Figure 3.9. Dissolved Ni against salinity in the Forth estuary.
a : June 1989, b : August 1989, c : November 1989,
d : January 1990, e : March 1990 and f : May 1990.

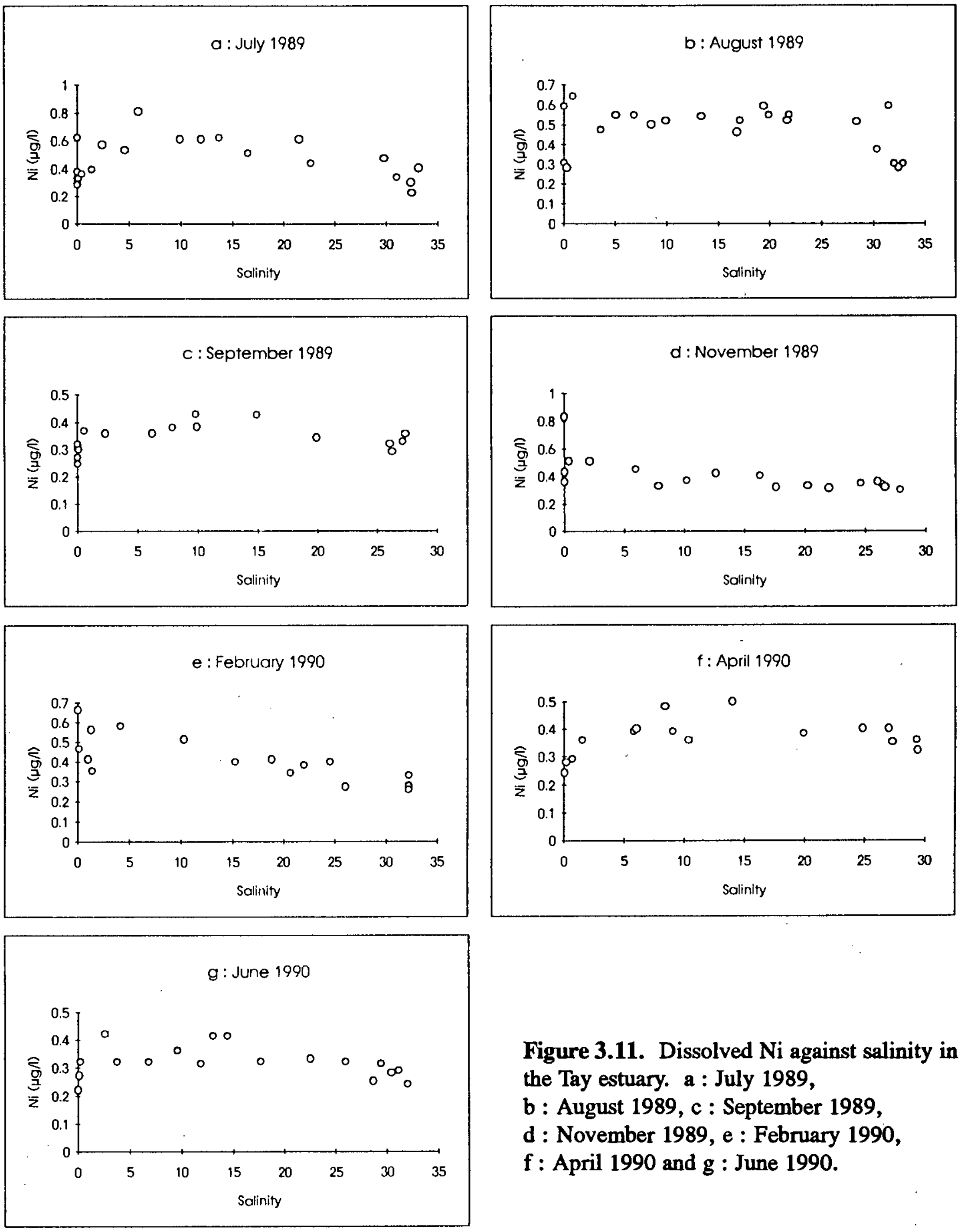


Figure 3.11. Dissolved Ni against salinity in the Tay estuary. a : July 1989, b : August 1989, c : September 1989, d : November 1989, e : February 1990, f : April 1990 and g : June 1990.

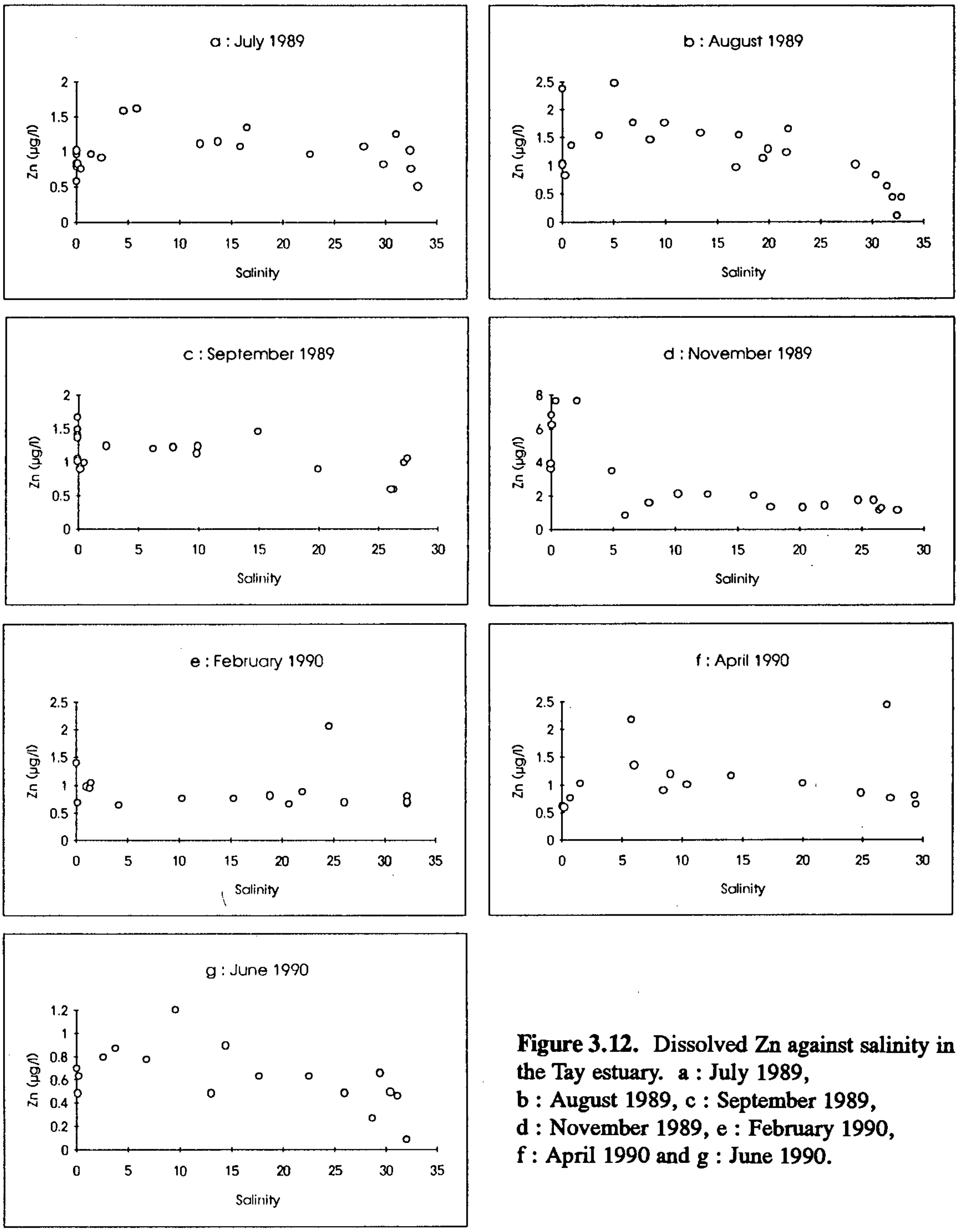


Figure 3.12. Dissolved Zn against salinity in the Tay estuary. a : July 1989, b : August 1989, c : September 1989, d : November 1989, e : February 1990, f : April 1990 and g : June 1990.

Table 3.10. Dissolved Ni and Zn concentrations in European marcrotidal estuaries

Estuary	Zinc (μgl^{-1})	Nickel (μgl^{-1})	Reference
Tweed	0.43-1.90	0.23-0.81	Law *et al* 1992
Tay	0.08-2.28	0.13-0.83	This study (Overall values)
Forth	0.12-4.92	0.29-1.49	This study (Overall values)
Göta	0.5-6	0.4-1.0	Danielsson *et al* 1983
Wear	0.50-7.53	0.30-2.93	Law *et al* 1992
Humber	3.61-14.6	0.9-6.3	Law *et al* 1992
Tyne	0.55-25.2	0.28-2.75	Law *et al* 1992
Scheldt	1-26	0.5-24	Duinker *et al* 1982c
Seine	1.37-19.9		Boughriet *et al* 1992a
Elbe		0.2-5.2	Mart *et al* 1985
Elbe	2-27		Duinker *et al* 1982c
Tees	0.7-14	0.21-1.0	Law *et al* 1992
Tees	1.0-117		Taylor 1982
Severn	1.61-17.5	0.30-15.8	Apte *et al* 1990
Severn	10-23	1.5-3.5	Morris 1984
Ems	3.6-28		Duinker *et al* 1985
Mersey	1.5-17.3	0.8-9.4	Law *et al* 1992
Mersey	4.2-55.6	0.8-17.4	Campbell *et al* 1988
Weser	4-9	2-7	Turner *et al* 1992
Weser	5-18		Duinker *et al* 1982a
Beaulieu	5-65		Holliday and Liss 1976
Rhine	5-20		Duinker and Nolting 1978
Rhine	8-70		Duinker and Nolting 1977

3.3.2: Riverine inputs and estuarine exports

Fresh water end-member concentrations, riverine inputs and estuarine exports for dissolved nickel and zinc are calculated as described for Mn in Sections 3.2.4 and 3.2.6. The results are given in Table 3.11. The end-member concentrations compare well with the estimated "world average" for Ni ($0.5\mu gl^{-1}$) but are lower than that for Zn ($30\mu gl^{-1}$) (Martin and Whitfield 1983).

Fresh water nickel and zinc fluxes in both estuaries are two orders of magnitude higher in winter than in summer. This seasonality is primarily caused by higher fresh water flows in winter.

Table 3.11. Fresh water dissolved nickel and zinc concentrations, riverine fluxes and exports to the North Sea.

Survey date	Flow (ls^{-1})	Ni (μgl^{-1})	Input (Kgd^{-1})	TZSEM (μgl^{-1})	Export (Kgd^{-1})	Export/ Input
Forth						
June 1989	5,659	0.44	0.2	4.5	2.2	10.1
August 1989	6,378	0.46	0.3	4.4	2.4	9.7
September 1989	43,970			7.0	27	
November 1989	59,897	0.59	3.1	4.1	21	6.9
January 1990	123,798	0.76	8.1	1.4	15	1.8
March 1990	190,263	0.61	10.0	0.9	15	1.5
May 1990	14,005	0.59	0.7	4.1	5.0	6.9
Tay						
July 1989	47,809	0.38	1.6			
August 1989	35,176	0.28	0.9			
September 1989	130,879	0.29	3.3			
November 1989	84,766	0.52	3.8			
February 1990	463,770	0.66	26.4			
April 1990	137,196	0.24	2.8			
June 1990	67,784	0.22	1.3			

Survey date	Flow (ls^{-1})	Zn (μgl^{-1})	Input (Kgd^{-1})	TZSEM (μgl^{-1})	Export (Kgd^{-1})	Export/ Input
Forth						
June 1989	5,659	0.95	0.5	13.02	6.4	13.7
August 1989	6,378	0.90	0.5	17.12	9.4	19.0
September 1989	43,790			62.55	236.7	
November 1989	59,897	1.95	10.1	27.03	139.9	13.9
January 1990	123,798	2.40	25.7	12.50	133.7	5.2
March 1990	190,263	3.53	58.0	4.5	74.0	1.3
May 1990	14,005	0.69	0.8	14.82	17.9	21.5
Tay						
July 1989	47,809	0.83	3.4			
August 1989	35,176	1.13	3.4			
September 1989	130,879	1.33	15.0			
November 1989	84,766	4.75	34.8			
February 1990	463,770	1.39	55.7			
April 1990	137,196	0.61	7.2			
June 1990	67,784	0.70	0.7			

Export/input ratios indicate that the Forth estuary has internal sources of dissolved Ni and Zn. These non-point sources are important and are discussed further in Section 3.3.3. Like those for Mn, the export/input ratios are higher in summer than in winter, though they vary over just one order of magnitude, while those for Mn vary over two orders (Section 3.2.6). The Forth estuary appears to be more important in augmenting the riverine metal flux than, for example, the industrialised basin of the Puget Sound, where the annual average output/riverine input ratio for Zn is estimated to be 1.51 (Paulson *et al* 1989c).

3.3.3: Addition and removal of dissolved nickel and zinc in the Forth estuary

The shapes of the nickel and zinc profiles in some surveys of the Forth are similar. When the two elements are plotted against each other, highly significant ($r > 90\%$) correlations are obtained for the June and May surveys, though this relationship breaks down in January, when the correlation coefficient falls to 69.4% (Figure 3.13). The highly significant relationships between dissolved Ni and Zn in summer suggest a common source for these elements.

The rates of net addition of nickel and zinc at each station in the Forth were calculated using the box model and equation given in Section 3.2.7.1. Results are illustrated in Figures 3.14 and 3.15 for summer and winter surveys respectively.

The amounts of Zn added to, or removed from, the dissolved phase are greater than those of Ni. This may be related to the greater abundance of Zn in suspended particulate matter (Chapter 4). Addition of both metals occurred during summer and winter surveys. Removal, however, was only observed in winter. The results for the different seasons are discussed separately below.

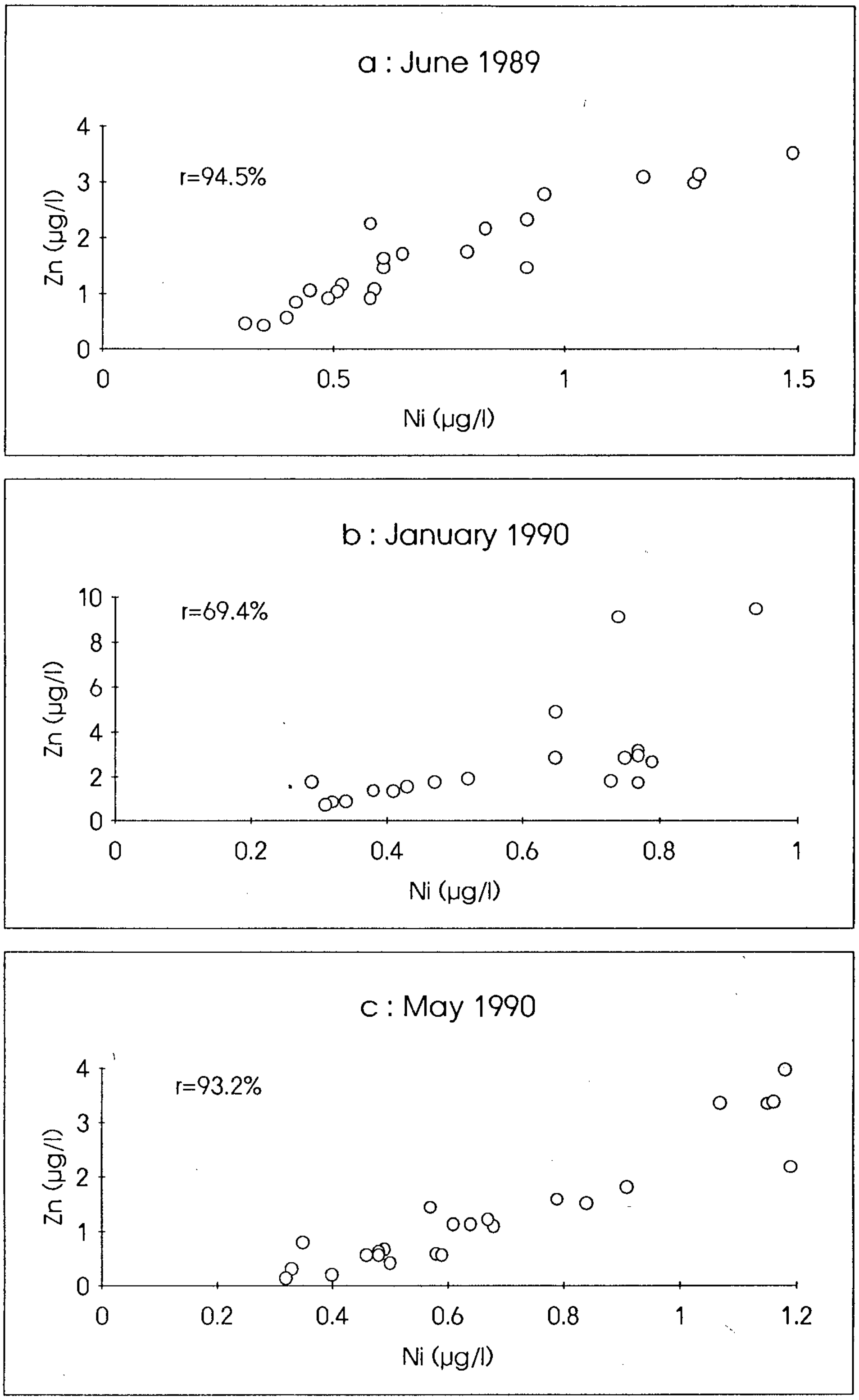


Figure 3.13. Correlations between Ni and Zn in the Forth estuary. a : June 1989, b : January 1990 and c : May 1990.

3.3.3.1: June and August surveys

In June and August the peak Ni, Zn and Mn fluxes were coincident in the upper estuary (Figure 3.14). Correlations between Ni and Zn fluxes with Mn fluxes had coefficients of 94% and 93% respectively in June and 87% and 86% respectively in August (Figure 3.16). It therefore appears that both metals are remobilised with manganese in the anoxic or sub-oxic sediments. Similar remobilisation of zinc has been reported in the St Lawrence (Bewers and Yeats 1979) and Geum estuaries (Byrd *et al* 1990).

Remobilisation of nickel with manganese oxides occurs in the pelagic (Klinkhammer 1980, 1983) and hemipelagic (Sawlan and Murray 1983) sediments of the eastern equatorial Pacific and the Guatemala Basin. Nickel is trapped with Mn oxides in the surface oxic layer, but released in the lower Mn reduction zone (Klinkhammer *et al* 1982, Rutgers van der Loeff and Waijers 1986). Nickel is strongly correlated with Mn in both the sediments and pore waters of these cores. The Ni/Mn atomic ratios in pore waters of pelagic sediments range from 0.010 to 0.018 (Klinkhammer 1980). The ratios in hemipelagic pore waters (0.0078 to 0.0124) and sediments (0.0067 and 0.0132) are very similar (Sawlan and Murray 1983).

Rates of Ni and Zn addition plotted against those of Mn in the Forth estuary give an indication of the molar ratios involved. (This, however, ignores any differences between the metal removal rates, *eg* oxidation of Mn.) The strong positive correlations obtained in June and August in the Forth (Figure 3.16) indicate that the elemental ratios remained constant within, but not between, the surveys. The elemental ratios were approximately:

June: 1 Mn : 0.012 Zn : 0.0056 Ni

August: 1 Mn : 0.041 Zn : 0.0154 Ni

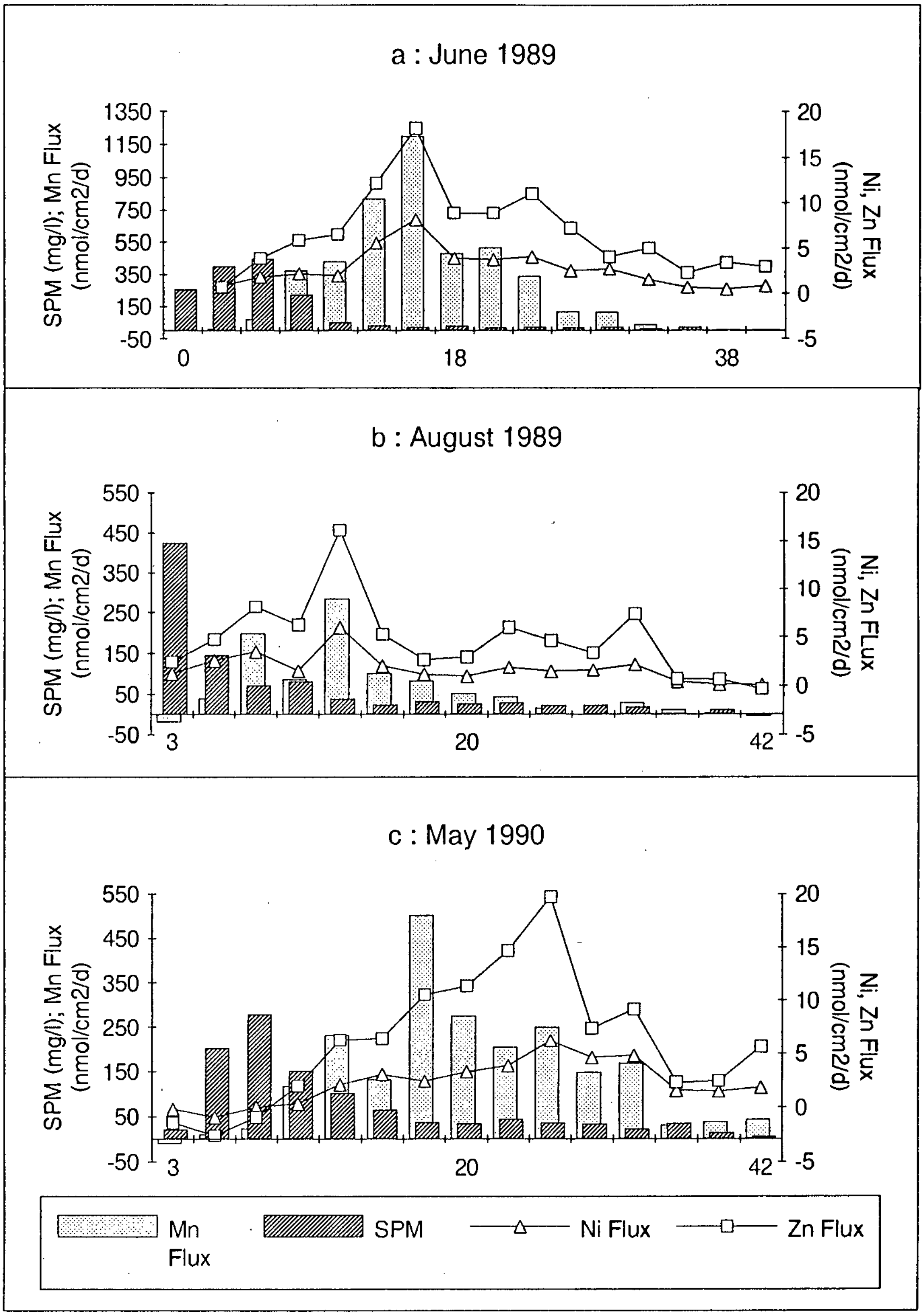


Figure 3.14. Mn, Ni and Zn fluxes and SPM loadings against station number in the Forth. Summer surveys. a : June 1989, b : August 1989 and c : May 1990.

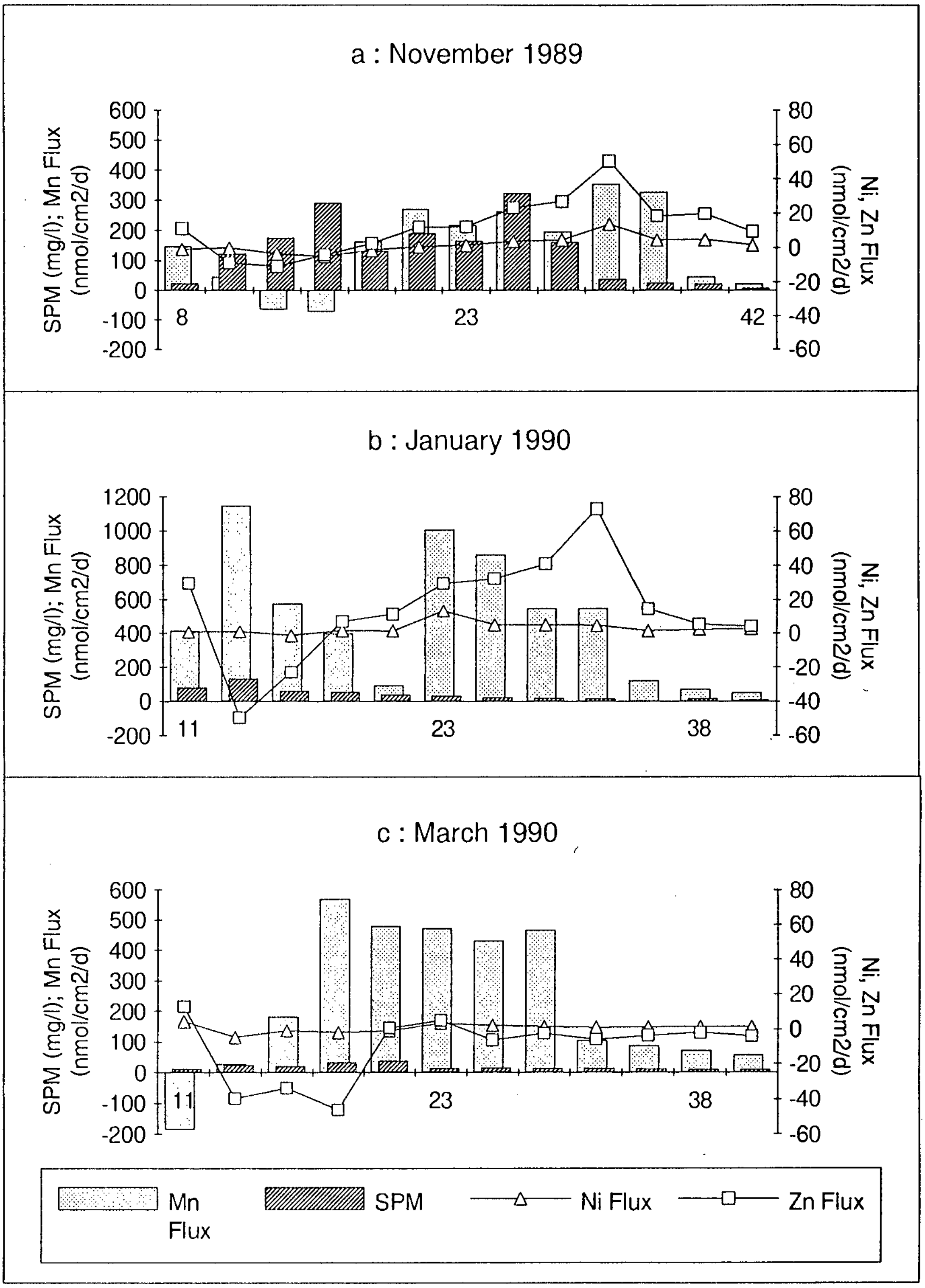
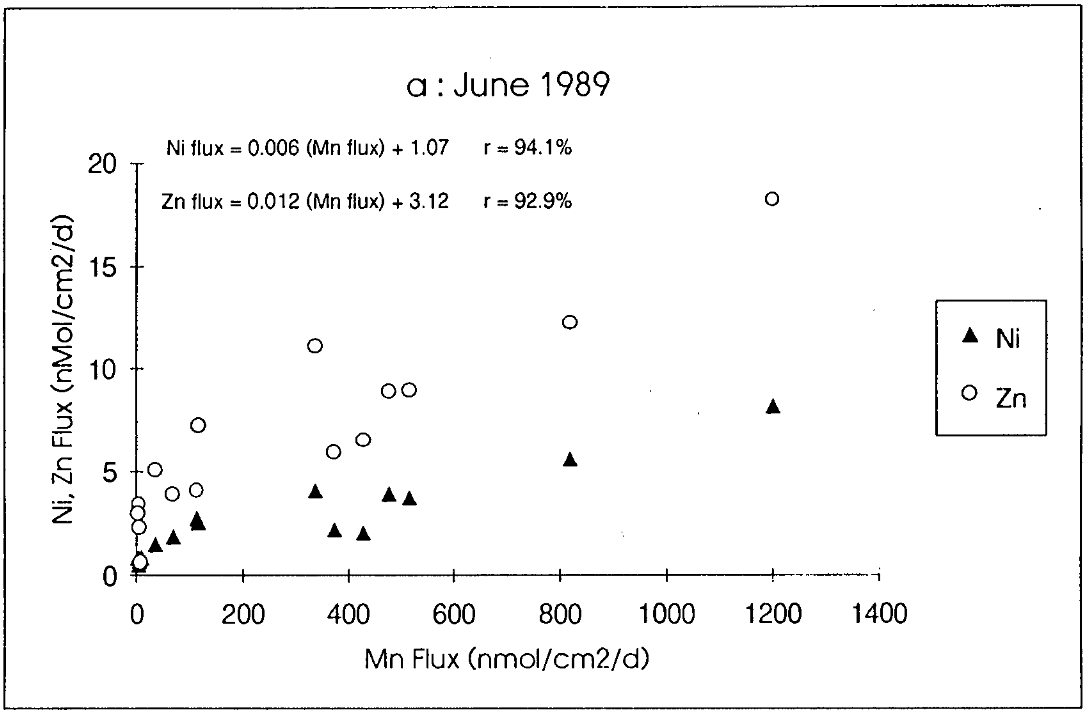


Figure 3.15. Mn, Ni and Zn fluxes and SPM loadings against station number in the Forth. Winter surveys. a : November 1989, b : January 1990 and c : March 1990.



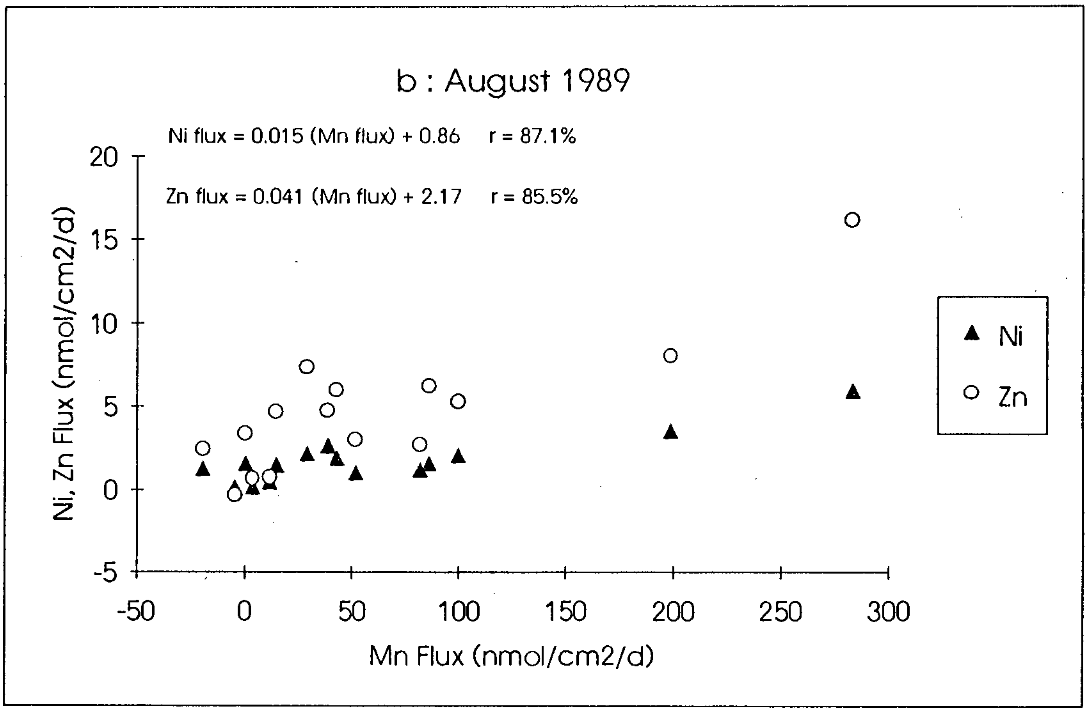


Figure 3.16. Ni and Zn fluxes against Mn flux in the Forth estuary. a : June 1989 and b : August 1989.

The Ni/Mn ratios are surprisingly close to those obtained in pore waters of the pelagic and hemipelagic sediments given above, and suggest that Ni may be incorporated in reducible Mn oxides in constant ratios in a variety of marine environments.

In the Forth, the maximum rates of Ni and Zn addition in June are similar to those in August (Figure 3.14). The varying Ni/Mn and Zn/Mn molar ratios therefore reflect the differences in Mn addition between the surveys. (Faster rates of Mn removal in August would give similar results, but this possibility is rejected below). Reasons for a lower benthic Mn flux in August have been discussed in Section 3.2.7.3. Since the rates of Ni and Zn addition are similar, however, either the elemental ratios in the solid Mn oxyhydroxides must increase throughout the season, or some Ni and Zn must be released from a source not associated with Mn remobilisation. Possible extra sources for Ni and Zn include any direct release from the breakdown of particulate organic carbon, or diffusion from the bottom sediments. An additional source of Ni and Zn during this survey may explain why the correlation coefficients are lower in August (85-85%) than in June (93-94%).

The correlations for the Zn/Mn relationships in both surveys, and the Ni/Mn relationship in June, have positive intercepts (at the 95% confidence level). In both surveys therefore, either some Zn is added from a source not associated with Mn remobilisation, and/or Mn removal is taking place within the water column. The same can be said for Ni in June. If, for the sake of argument, no Mn is being removed, then the excess nickel and zinc must be added by the alternative process(es) at rates indicated by the 95% confidence interval of the intercepts (Table 3.12). Since the confidence intervals between surveys overlap for each element, the rates of addition are not significantly different between surveys. If, on the other hand, Mn removal alone is considered, then the rate of "excess" manganese oxidation (*ie* that which is not accounted for by Ni and Zn) can be estimated by solving the correlation equations for a zero release of Ni and Zn. In this case the confidence intervals indicate that the rate of Mn removal is faster in June than in August (Table 3.12). This option would tend to make the differences in elemental/ Mn ratios, discussed above, even larger than measured. Since it is easier to envisage the addition of Ni and Zn from other sources, than to explain why excess Mn oxidation should occur without removal of these elements, this option is rejected as unlikely.

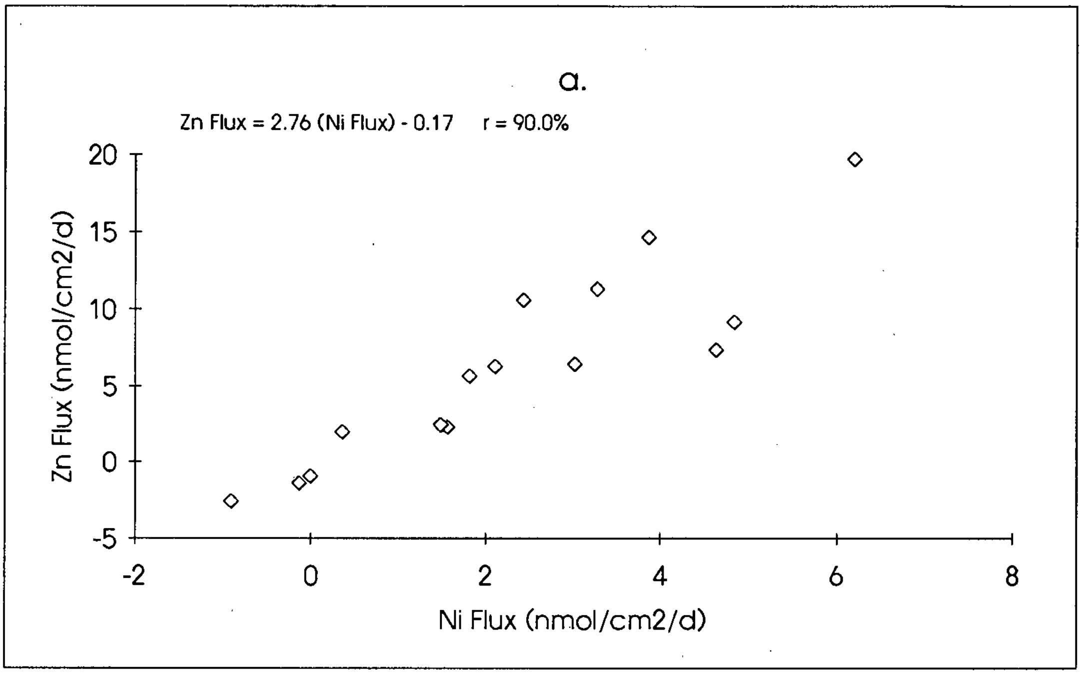
Table 3.12. 95% confidence limits for the intercepts of the Ni/Mn and Zn/Mn relationships observed in the June and August surveys of the Forth.

Correlation	95% limits for Ni or Zn addition $nmolcm^{-2}d^{-1}$	95% limits for Mn removal $nmolcm^{-2}d^{-1}$
June Ni vs Mn	0.70 to 1.44	124 to 256
June Zn vs Mn	2.25 to 3.99	186 to 330
August Ni vs Mn	-0.52 to 2.24	-34 to 145
August Zn vs Mn	1.14 to 3.21	28 to 77

3.3.3.2: May survey

In May, the peak Ni and Zn fluxes were coincident, but occurred further downstream than the peak Mn flux (Figure 3.14). Although the correlation between Ni and Zn was significant (r=90%), those between Ni/Mn and Zn/Mn were much poorer (Figure 3.17). This suggests that the common source between Ni and Zn is something other than remobilisation of Mn.

The release of Ni and Zn may be caused naturally by a physical disturbance of bottom sediments and injection of interstitial waters. Water flows were higher in May than in June or August, and average SPM concentrations



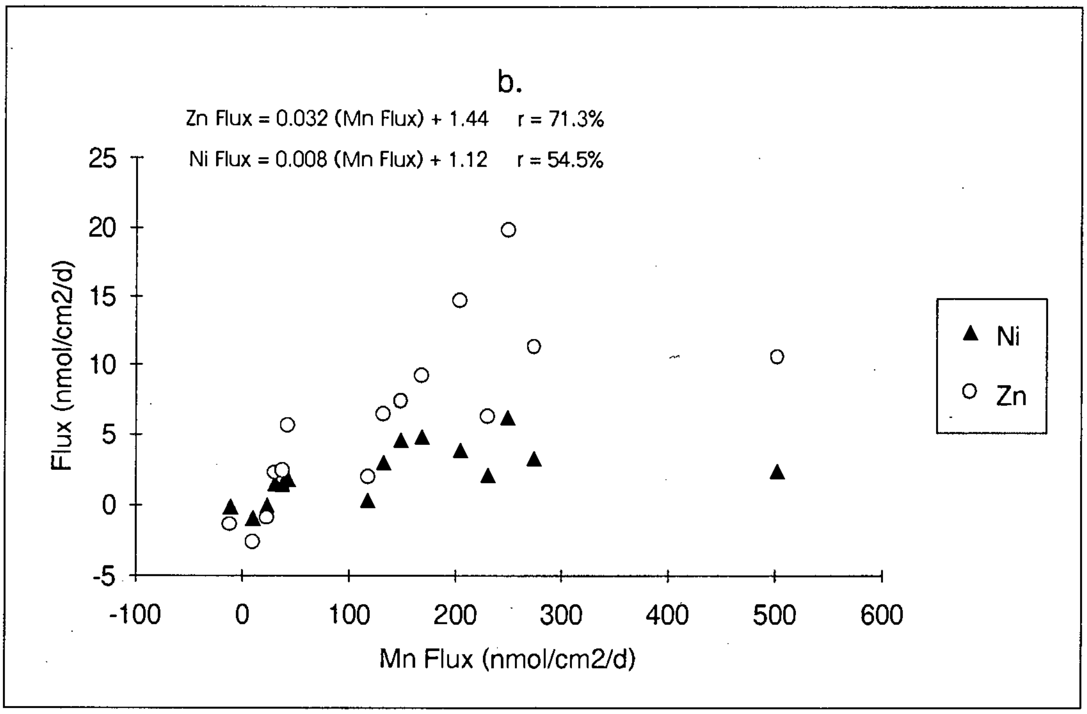


Figure 3.17. Relationships between Ni, Zn and Mn fluxes in the Forth, May 1990. a : Zn flux vs Ni flux and b : Zn and Ni fluxes vs Mn flux.

between 20 and 42km downstream from Stirling were higher in May (27.5mgl^{-1}) than in June (14.3mgl^{-1}) or August (21.3mgl^{-1}).

Alternatively, the metals may have an anthropogenic source. The greatest input of Ni and Zn occurred at a distance of 25km downstream from Stirling, that is 6km upstream from Grangemouth. The spring tidal excursion at Grangemouth is about 10km (Forth River Purification Board, 1978), so inputs from Grangemouth may be observed as far upstream as 25km.

Despite very high suspended particulate matter concentrations during the summer months, only slight Zn removal was observed in May and none in June or August. This may be because oxygen concentrations are low enough to prevent the formation of Fe/Mn oxyhydroxides and scavenging of the metal, or because removal is masked by greater amounts of addition. Removal is discussed more fully in the following section.

3.3.3.3: November, January and March surveys

In the winter surveys, the rates of addition of Ni and Zn do not correlate with Mn, and the patterns of addition down the estuary are different for each element (Figure 3.15). In all three surveys, there is pronounced removal of zinc in the upper estuary. Zinc removal has also been observed in the low salinity zones of the Elbe (Duinker *et al* 1982b), Rhine (Duinker and Nolting 1978), Fraser (Grieve and Fletcher 1977) and Tamar estuaries (Morris 1986). In the November and January surveys of the Forth, zinc removal is coincident with a large turbidity maximum. In January, however, manganese is being added to, not removed from, the water column. It may be that both elements are being added from the bottom sediments (*eg* by sediment resuspension) but are removed, with different reaction rates and by different mechanisms, onto the high concentrations of SPM. If Mn removal by oxidation is slower than zinc removal by scavenging, the effects of zinc removal will be more apparent.

A model describing removal of metals by particle scavenging in the turbidity maximum of the Tamar (Morris 1986) can be applied to the Forth. The model predicts the influence of the turbidity maximum on the uptake of dissolved riverine metals in the very low salinity region of the estuary, according to the following equation:

$$\frac{C}{C_R} = \frac{[1 + K_d P_R]}{[1 + K_d P_R + K_d P_S(1 - \alpha)]}$$

where: C = dissolved metal concentration in the turbidity maximum
C_R = dissolved metal concentration in the river water
K_d = partition coefficient of the metal
P_R = suspended particulate matter loading in river water
P_S = the additional suspended load in the turbidity maximum
α = the fraction of exchangeable metal on the added particles relative to ultimate equilibrium

Solving this equation for α in the Forth will give an indication of how close the particles in the turbidity maximum are to sorptive equilibrium. The partition coefficients used in the calculation were those measured for the upper Forth estuary for each survey (see Chapter 5). Table 3.13 lists the measured values and calculated results for each survey.

The estimated values for α in November and January are, perhaps, typical for turbid estuaries (*eg* Morris 1986), though the value for March is much lower. The partition coefficients, C/C_R and C_R values for March are very similar to those for January. The cause of the large difference in the value for α, therefore, is the much smaller amount of added suspended particulate material in the turbidity maximum. The predicted value for α suggests that only a quarter of the adsorptive-equilibrium zinc concentration is associated with these particles. Since some of the particles in turbidity maxima originate from further downstream, then some very strong removal process must be taking place in the lower estuary for this amount of depletion to be observed.

Table 3.13. Estimated fractions of exchangeable zinc, relative to equilibrium, on the suspended particles in the turbidity maxima of the Forth (from the adsorption equilibrium model of Morris 1986). River water values are taken from station 6 in November, station 8 in January, and stations 8 and 11 in March. Turbidity maximum values are taken from stations 11, 13 and 15 in November, 13 in January and 13, 15 and 18 in March.

Survey	K_d	C (μgl^{-1})	C_R (μgl^{-1})	Measured C/C_R	P_R (mgl^{-1})	P_S (mgl^{-1})	α (%)
Nov	$10^{5.0}$	1.17	3.88	0.30	11.00	184.8	86.1
Jan	$10^{4.7}$	1.71	3.14	0.55	14.00	117.2	90.2
Mar	$10^{4.7}$	2.17	4.36	0.51	11.24	14.41	25.0

Alternatively, processes other than sorptive equilibrium may be controlling the partitioning of zinc during this survey. The maximum removal of zinc in March does not coincide with very large SPM concentrations. Removal may instead be caused by, for example, coprecipitation with Fe-containing colloids. This mechanism has been proposed for zinc removal in the low salinity zones of the Geum (Byrd *et al* 1990), Rhine (Duinker and Nolting 1978) and Fraser estuaries (Grieve and Fletcher 1977). It has been discussed in Section 1.4.3.

Zinc removal is not observed in the outer Forth, since SPM concentrations are low, and iron hydroxide precipitation is not important at high salinities.

Instead, sediment resuspension in January (peak SPM $>40\text{mgl}^{-1}$) causes Mn, Zn and, to a lesser extent, Ni to be added to the water column. (Zinc addition was not observed in the March survey, where sediment resuspension did not occur to the same extent.) A similar mechanism has been proposed for simultaneous increases of SPM, Cd, Zn, Cu, Mn and Fe during the strong spring tidal currents in the Weser estuary (Duinker *et al* 1982a). The peak rates of addition of Ni and Zn in the Forth in January are, respectively, two and four times greater than those in June. Addition of these metals by physical disturbance of the bottom sediment may therefore be more important than remobilisation with Mn, and subsequent diffusion from the bottom sediments.

3.3.4: Nickel and zinc in the Tay

No relationship between rates of addition of Ni, Zn, and Mn is observed in the April survey of the Tay. Nickel and zinc concentrations in the Tay do not appear to be controlled by Mn remobilisation from the sediments, or by sediment resuspension and mixing of metal-rich pore waters into the overlying water. Instead, many of the features of the Ni and Zn estuarine profiles are also observed in the metal/salinity plots for Cd, Cu and Pb during all Tay surveys. These features include removal at low salinity, which will be discussed in Chapter 5, and point source addition from the vicinity of Dundee, which will be discussed in Section 3.4.4.

3.4: Dissolved copper

3.4.1: Results

The concentration ranges of dissolved Cu in the Forth and Tay are generally lower than those in other major, macrotidal estuaries (Table 3.14). The Tees, for example, has peak concentrations almost an order of magnitude greater than those observed in this study. The fresh water end-members for the Forth (0.87-1.53) and Tay (0.55-1.56) are similar to the estimated "world average" river water concentration of 1.5μgl^{-1} (Martin and Whitfield 1983). Fresh water Cu inputs to the Forth range from 0.54kgd^{-1} in June to 14.3kgd^{-1} in March. Inputs

Table 3.14. Dissolved Cu concentrations in European macrotidal estuaries.

Estuary	Copper (μgl^{-1})	Reference
Tay	0.23-1.63	This study (overall values)
Wear	0.33-1.35	Law *et al* 1992
Tyne	0.30-1.61	Law *et al* 1992
Göta	0.4-1.6	Danielsson *et al* 1983
Forth	0.27-2.43	This study (overall values)
Humber	0.75-3.64	Law *et al* 1992
Humber	0.32-3.3	Balls 1985
Mersey	1.28-3.30	Law *et al* 1992
Weser	1.5-3.5	Turner *et al* 1992
Weser	2-7	Duinker *et al* 1982a
Tweed	0.49-4.67	Law *et al* 1992
Tweed	0.5-4.6	Gardner and Ravenscroft 1991
Severn	0.5-5.0	Apte *et al* 1990
Severn	1.2-4.2	Morris 1984
Severn	1.7-4.7	Harper 1991
Rhine	2-5	Golimowski *et al* 1990
Rhine	1-7	Duinker and Nolting 1978
Tees	0.49-10.3	Law *et al* 1992
Tees	0.5-10.0	Taylor 1982
Ems	1-11	Duinker *et al* 1985
Elbe	0.5-7	Mart *et al* 1985
Elbe	3-13	Duinker *et al* 1982c

are generally higher in the Tay, ranging from 1.85kgd^{-1} in August to 62.5kgd^{-1} in February.

Dissolved copper/salinity profiles show non-conservative behaviour in both the Forth and the Tay estuaries (Figures 3.18 and 3.19 respectively). Many Forth surveys, as well as the summer/autumn surveys of the Tay, have a dissolved copper peak in the very low salinity regions as well as a second peak at higher salinities. These features are discussed separately below.

3.4.2: Upper estuary inputs of dissolved copper

The copper peaks in the upper Forth estuary occur in the narrow reaches between 3 and 15km downstream from Stirling. The peaks in the Tay occur between distances of 9 and 17km downstream from Perth.

The dissolved Cu peaks in the upper Forth are often accompanied by nutrient (NH_4 , NO_3 , PO_4 , SiO_4 , DOC) maxima and dissolved oxygen minima. Nutrient maxima are also found in the upper Tay during the late summer/autumn surveys (Balls 1992). These observations are consistent with the bacterial breakdown of riverine organic matter entering saline waters. The ratios of the excess dissolved copper (*ie* the peak concentration less the riverine concentration) to excess dissolved inorganic nitrogen (NO_3, NO_2 and NH_4) were therefore investigated and compared with the ratios found in phytoplankton, marine plants, water and sewage sludge (Table 3.15). The Cu/N ratios in the Forth and Tay are too high to be attributed to the breakdown of phytoplankton alone, but are similar to those found in higher plants. The salt-marsh cord-grass *Spartina alterniflora*, for example, has a Cu/N ratio as high as 3.8×10^{-3} (Windom *et al* 1982). *Spartina* species colonise tidal mud-flats, which are common along the northern bank of the Tay. These mud-flats are periodically eroded by strong water currents and high riverine run-off (Hubbard and Hashim 1987), thus providing a

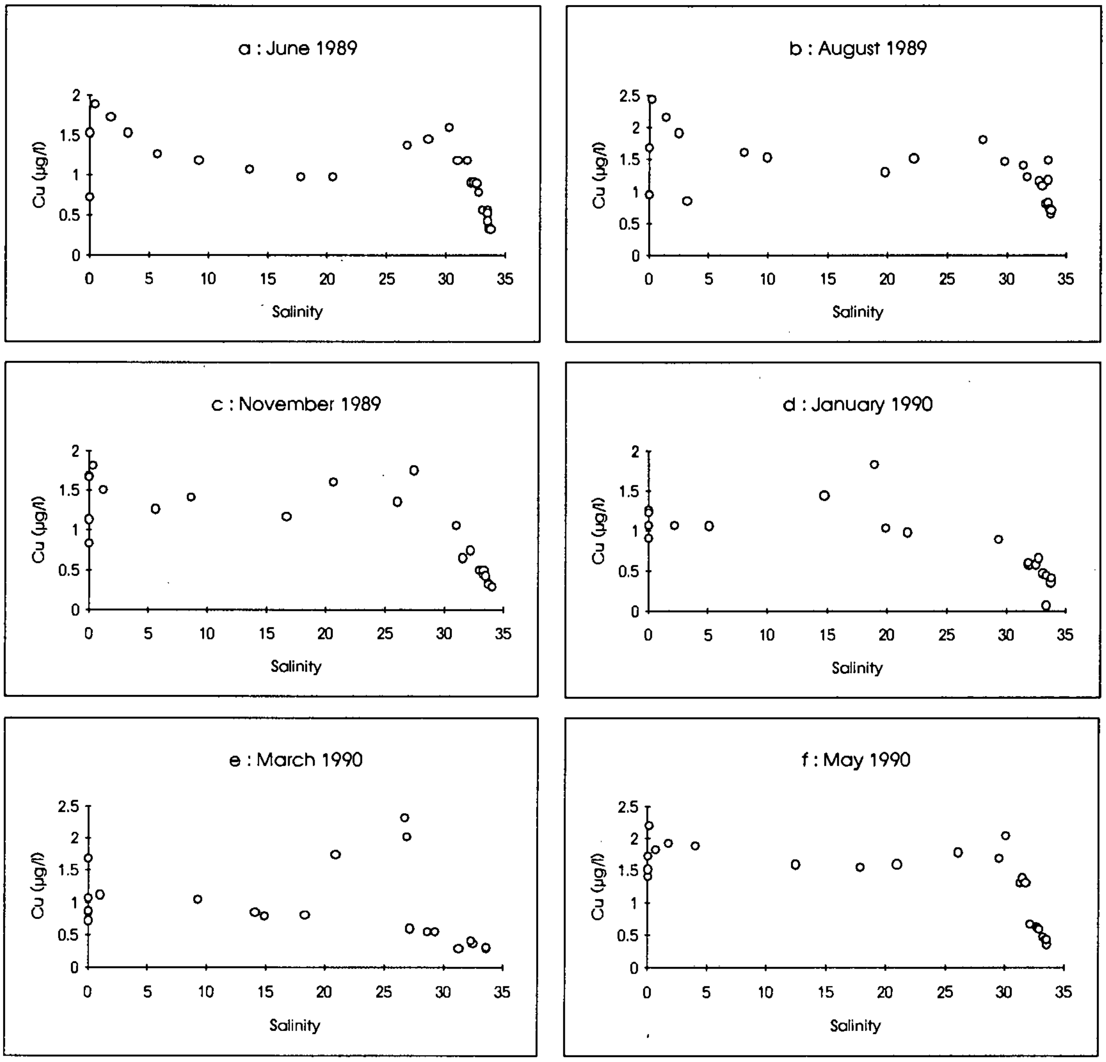


Figure 3.18. Dissolved Cu against salinity in the Forth estuary. a : June 1989, b : August 1989, c : November 1989, d : January 1990, e : March 1990 and f : May 1990.

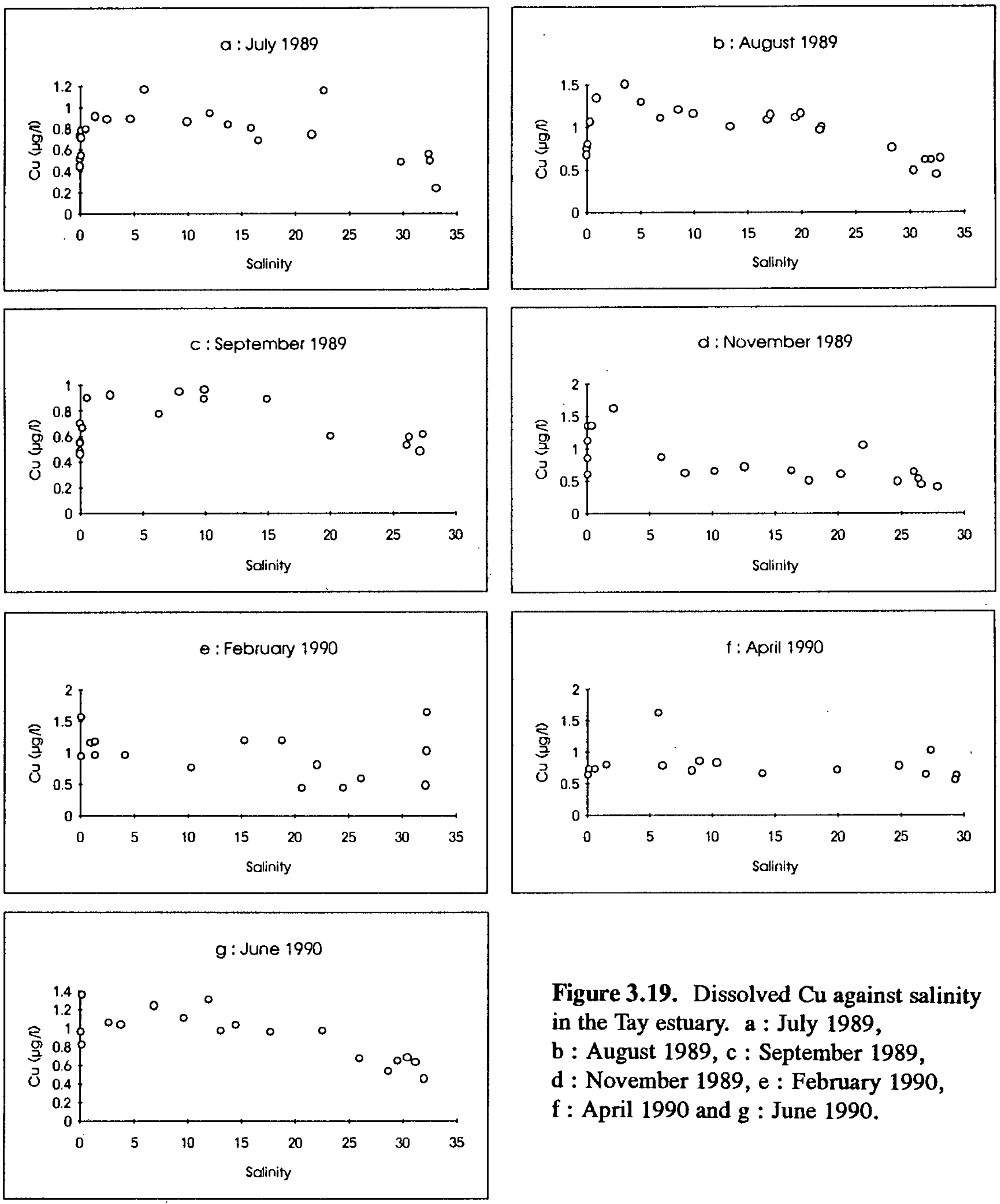


Figure 3.19. Dissolved Cu against salinity in the Tay estuary. a : July 1989, b : August 1989, c : September 1989, d : November 1989, e : February 1990, f : April 1990 and g : June 1990.

source of organic material to the upper estuary. Sewage inputs from Stirling and Perth are a further source of organic matter. The Cu/N ratio of sewage sludge is higher than those measured in the water of the Forth and Tay. Degradation (specifically nitrification, Balls 1992) of organic matter from a mixture of authigenic, detrital and anthropogenic inputs may account for the simultaneous release of Cu and N in the upper Forth and Tay, and the varying Cu/N ratios observed.

Table 3.15. Approximate dissolved Cu/N ratios in the upper Forth and Tay, and comparison with ratios in other marine materials.

Survey	Cu/N (10^{-3})	Reference
Forth		
June 1989	0.35	Present study
August 1989	0.60	Present study
November 1989	0.85	Present study
January 1990	0.41	Present study
May 1990	0.80	Present study
Tay		
July 1989	0.51	Present study
August 1989	1.11	Present study
September 1989	0.24	Present study
November 1989	0.78	Present study
Savannah (USA), July	0.10	Windom *et al* 1991
Medway (Canada), September	0.071	Windom *et al* 1991
Maeklong (Thailand), September	0.10	Windom *et al* 1991
Maeklong (Thailand), March	0.095	Windom *et al* 1991
Oceanic phytoplankton	0.025	Bruland *et al* 1991
Organic matter degradation	0.14 to 0.21	Gerringa 1990
Red seaweeds	0.30 to 1.56	Windom *et al* 1982
Brown seaweeds	0.13 to 0.58	Windom *et al* 1982
Ulva lactuca	0.47	Windom *et al* 1982
Spartina alterniflora	3.80	Windom *et al* 1982
Sewage sludge	5.76	Murray *et al* 1980

Relationships between Cu and other nutrients have been reported in a number of marine environments. Strong Cu/Si relationships, for example, were observed in the Medway, Savannah and Maeklong estuaries. These had identical Cu/Si ratios to continental rocks (about 6 x 10^{-5}) and were attributed to weathering (Windom *et al* 1991). The Cu/Si ratios in the oceans are lower, *eg* 2.3 x 10^{-5} in the North East Atlantic (Nolting *et al* 1991 and references within) suggesting that Si is preferentially remobilised in the oceans. Relationships of Cu with P have been observed in the Pacific Ocean, both in the dissolved phase (Bruland 1980) and in phytoplankton (Collier and Edmond 1984). These relationships are caused by the biological control of dissolved Cu inputs in the open oceans. No relationship between Cu and P or Si was observed in the Forth or Tay. This suggests that Cu concentrations in these estuaries are controlled by anthropogenic inputs from point sources rather than by weathering or biological activity.

3.4.3: Lower estuary inputs of dissolved copper in the Forth

In the Forth, the second peak of dissolved copper generally occurred at 28-31km from Stirling, though moved further upstream in August during low flow conditions, and further seaward in March after spate conditions. The peak is attributed to anthropogenic inputs from an industrial source at Grangemouth, some 31km downstream from Stirling. The magnitude of the input is estimated by multiplying the excess copper concentration (see Figure 3.20) by the box volume and dividing by the box flushing time from the "fresh water age" model (Balls 1992). They range from 2kgd^{-1} in August to 144kgd^{-1} in March (Table 3.16). The point sources at Grangemouth are therefore larger than the fresh water inputs of dissolved copper to the estuary (Section 3.4.1).

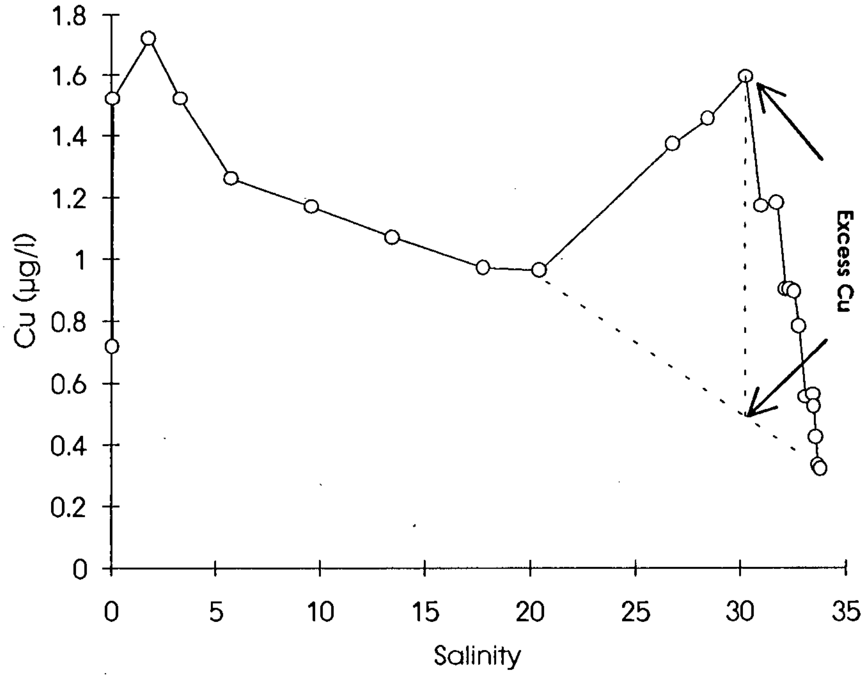


Figure 3.20. Calculation of excess Cu at Grangemouth, Forth estuary, June 1989.

Table 3.16. Dissolved Cu inputs at Grangemouth.

Survey	Distance (km)	Box Volume (l)	Excess Cu (μgl^{-1})	Time (d)	Input (Kgd^{-1})
June 1989	28	1.58×10^{10}	1.09	1.88	9
August 1989	23	6.23×10^{9}	0.89	2.31	2
November 1989	28	1.58×10^{10}	1.13	1.14	16
January 1990	28	1.58×10^{10}	0.70	0.42	26
March 1990	42	1.95×10^{11}	1.73	2.34	144
May 1990	31	3.36×10^{10}	1.42	0.63	76

3.4.4: Lower estuary inputs of dissolved metals in the Tay

The dissolved Cu peaks in the lower Tay estuary coincide with peaks in dissolved Cd, Mn, Ni, Pb and Zn as well as phosphate and ammonia (Table 3.17). These peaks are attributed to sewer inputs from Dundee (Balls 1992), which is approximately 33km downstream from Perth. When discussing dissolved Cu behaviour in the Tay, it is instructive to draw some comparisons with the Tweed estuary on the southern Scottish border. Like the Tay, the Tweed has a sparsely-populated catchment area, with a single large community (Berwick) at its mouth. Dissolved copper-complexing ligands directly control the Cu concentrations in the estuarine water (Gardner and Ravenscroft 1991). An increase in the concentration of dissolved Cu-complexing ligands in the outer Tweed is attributed to sewage inputs from Berwick. The authors tested this hypothesis by experimentally diluting sewage effluent with sea water. The resulting concentrations of complexing ligands were of the right order of magnitude to explain a sewage-related increase in the Tweed. Other mixing experiments indicate that as much as 25% of the total Cu in sewage effluent may be remobilised after an initial period of flocculation (Paulson *et al* 1991). Different studies, however, suggest that remobilisation of Cu from sewage effluent does not always take place (Paulson *et al* 1984). Sewage effluent may even enhance flocculation of Cu and other metals, thus increasing suspended particulate and sediment concentrations, but decreasing dissolved metal concentrations (Feely *et al* 1983).

In the Tay, one of the greatest peaks of dissolved Cu ($0.40\mu gl^{-1}$) occurs in February at 38km downstream from Perth. Given a "Box Volume" of $6.60 \times 10^{10}l$ and a water residence time of 0.37d, the corresponding Cu flux is $71Kgd^{-1}$. This is greater than the riverine input during the same survey (Section 3.4.1), but is only about half the greatest flux observed in the outer Forth (Section 3.4.3).

Table 3.17. Dissolved metal and nutrient peaks in the outer Tay.

Survey	Distance (km)	Metal peaks (This study)	Nutrient peaks (Balls 1992)
July	33	Cu Cd Ni	NH_4 PO_4
August	33	Cu Cd Mn Ni Pb Zn	NH_4 PO_4
September	28	Cu Mn Ni Pb	NH_4 NO_3
November	33		
February	38	Cu Cd Mn Ni Zn	NH_4
April	37	Cu Cd Mn Pb	NH_4
June	39	Cu Cd Mn Ni Pb Zn	NH_4

3.5: Dissolved cadmium and lead

The concentration ranges for Cd and Pb in the Forth and Tay are similar to those recently reported for other macrotidal estuaries (Table 3.18). The peak values observed in the Tay are bigger than those in the Forth. For lead, though, this can be attributed to the unusually high point source peak observed in November 1989.

Table 3.18. Dissolved Cd and Pb in various European macrotidal estuaries.

Estuary	Sampling date	Cd (μgl^{-1})	Pb (μgl^{-1})	Reference
Tweed	1991/92	0.007-0.033	0.040-0.169	Law *et al* 1992
Tweed	1990	<0.02-0.06		Gardner and Ravenscroft 1991
Weser	1989		0.25-0.12	Turner *et al* 1992
Göta	1980/81	0.009-0.025	0.01-0.20	Danielsson *et al* 1983
Wear	1991/92	0.013-0.058	0.058-0.547	Law *et al* 1992
Mersey	1991/92	0.009-0.061	0.032-0.877	Law *et al* 1992
Forth	1989/90	<0.003-0.088	0.02-0.40	This study (overall values)
Tay	1989/90	<0.003-0.108	0.02-0.23 (1.03)	This study (overall values)
Tees	1991/92	0.015-0.097	0.054-0.820	Law *et al* 1992
Rhine	1984	0.03-0.10	0.05-0.30	Golimowski *et al* 1990
Thames	1987	0.01-0.07	0.01-0.11	Harper 1988
Tyne	1991/92	0.011-0.126	0.057-1.087	Law *et al* 1992
Humber	1991/92	0.049-0.224	0.023-0.618	Law *et al* 1992
Humber	1983	0.026-0.60	0.010-0.055	Balls 1985
Gironde	1982	0.05-0.4		Elbaz-Poulichet *et al* 1987
Severn	1988	0.05-0.45		Apte *et al* 1990
Severn	1987	0.01-0.14	0.02-10.00	Harper 1991
Elbe	1977/83	0.01-0.24	0.04-0.40	Mart *et al* 1985

3.5.1: Cadmium

The lowest riverine dissolved Cd end-members in the Forth and Tay occur in June and September respectively. In both cases, they are below the detection limit (0.003μgl^{-1}). The highest end-member concentrations occur in May in the Forth and November in the Tay (Table 3.19). The end-members are reasonably close to the estimated "world average" river concentration for Cd ($0.02\mu gl^{-1}$) (Martin and Whitfield 1983). Fresh water fluxes range from $<1gd^{-1}$ to $181gd^{-1}$ in the Forth and $<34gd^{-1}$ to $801gd^{-1}$ in the Tay. In both estuaries the greatest fluxes occur in winter, and are caused by increased fresh water discharge.

Table 3.19. Fresh water end-member concentrations and riverine inputs of dissolved Cd and Pb to the Forth and Tay estuaries.

Survey date	Flow (ls^{-1})	Cd (μgl^{-1})	Cd Flux (kgd^{-1})	Pb (μgl^{-1})	Pb Flux (kgd^{-1})
<u>Forth</u>					
June 1989	5,659	<0.003	<0.001	0.141	0.069
August 1989	6,378	0.005	0.003	0.088	0.049
November 1989	59,897	0.006	0.031	0.192	0.994
January 1990	123,798	0.012	0.128	0.135	1.440
March 1990	190,263	0.011	0.181	0.169	2.790
May 1990	14,005	0.016	0.019	0.142	0.172
<u>Tay</u>					
July 1989	47,809	0.020	0.083	0.104	0.430
August 1989	35,176	0.014	0.043	0.330	1.000
September 1989	130,879	<0.003	<0.034	0.043	0.486
November 1989	84,766	0.028	0.205	0.415	3.040
February 1990	463,770	0.020	0.801	0.059	2.360
April 1990	137,196	0.007	0.083	0.081	0.960
June 1990	67,784	0.006	0.035	0.097	0.568

Dissolved cadmium concentrations increase with increasing salinity in both Forth and Tay estuaries (Figures 3.21 and 3.22 respectively). Similar results have been observed in the Gironde, Rhône, Huanghe (Elbaz-Poulichet *et al* 1987) and Changjiang (Edmond *et al* 1985, Elbaz-Poulichet *et al* 1987) estuaries. This behaviour has been attributed to chloro-complexation, as discussed in Section 1.4.2.

The dissolved Cd vs salinity profiles for the June survey of the Forth and the July survey of the Tay are similar to those for phosphate (Figure 3.23). This

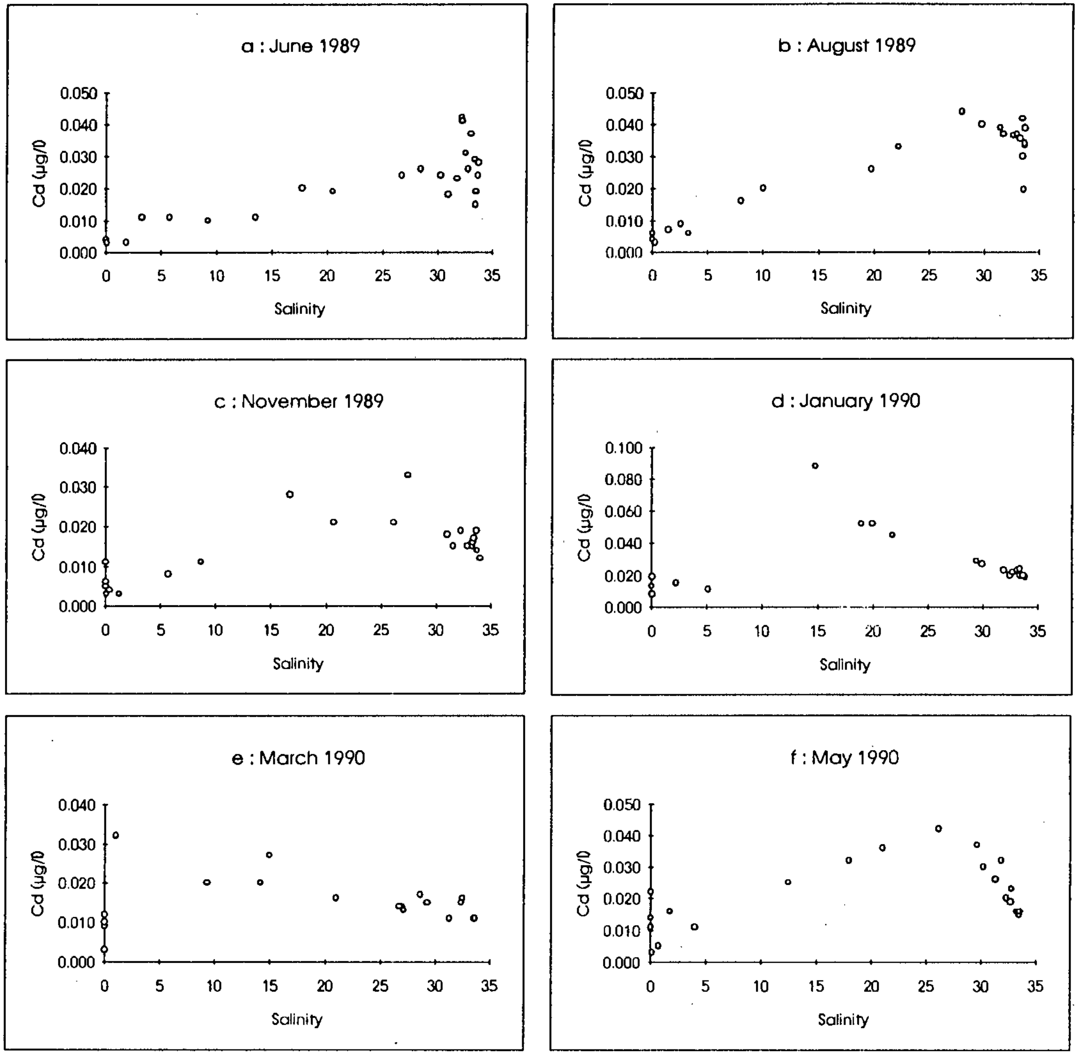


Figure 3.21. Dissolved Cd against salinity in the Forth estuary.
a : June 1989, b : August 1989, c : November 1989,
d : January 1990, e : March 1990 and f : May 1990.

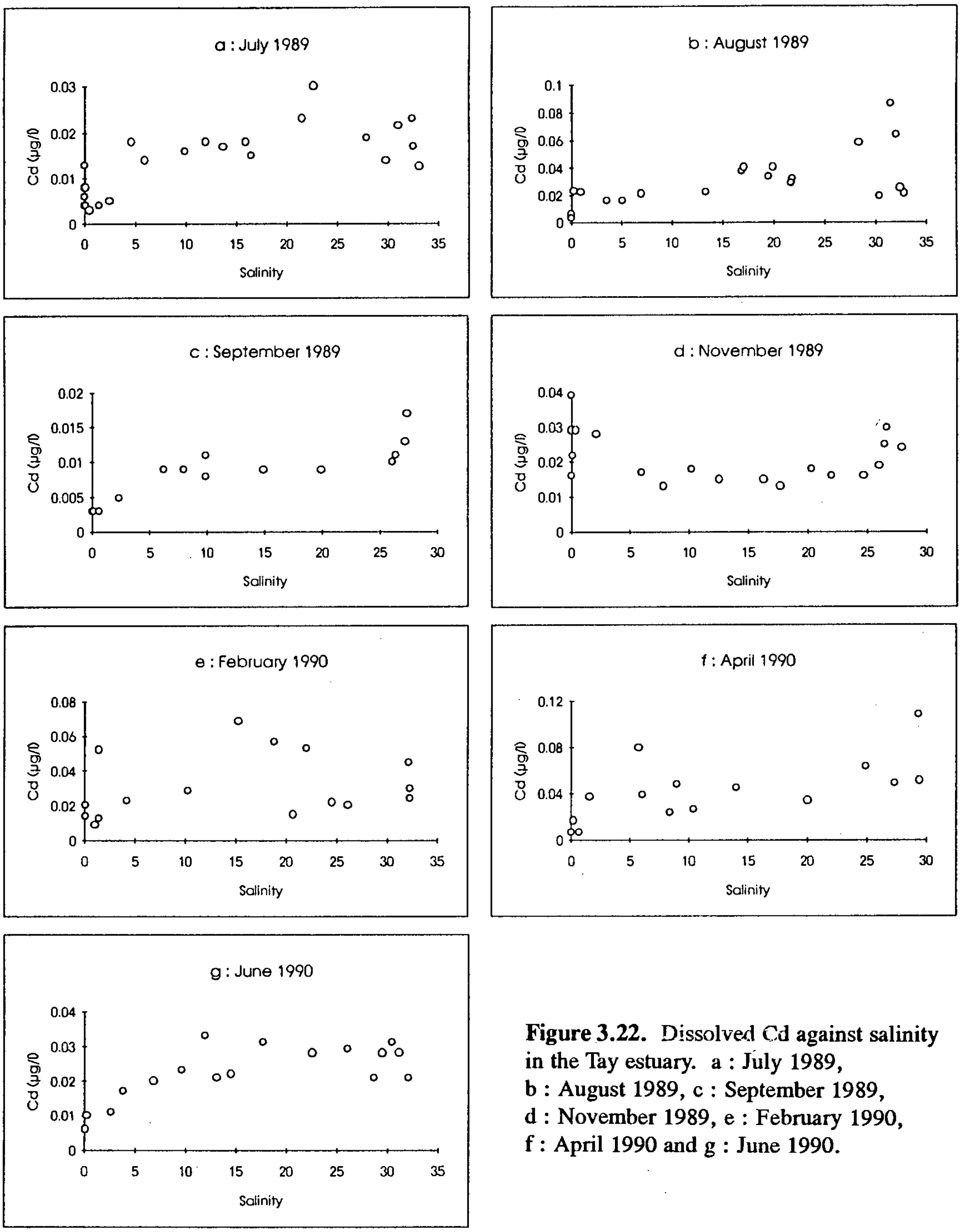


Figure 3.22. Dissolved Cd against salinity in the Tay estuary. a : July 1989, b : August 1989, c : September 1989, d : November 1989, e : February 1990, f : April 1990 and g : June 1990.

suggests that Cd and P may be released simultaneously from the particulate phase before undergoing complexation in the dissolved phase. These processes have been observed during the experimental breakdown of biological material by bacteria (Gerringa 1990) and also occur during the sinking of biogenic particulate matter in oceanic environments (*eg* Bruland 1983).

The relationships between Cd and PO_4 in the Forth and Tay have correlation coefficients of 90% and 82% respectively (Figure 3.24). The Cd/P molar ratios are similar to those observed in the water of the Savannah, Maeklong and Medway estuaries (Windom *et al* 1991) and the plankton of Monterey Bay (Martin and Knauer 1973). They are considerably lower than those observed in the Delaware estuary and in oceanic environments (Table 3.20). The variations in Cd/PO_4 ratios may be caused by differences in the phytoplankton populations present. Since Cd uptake depends on the amount of PO_4 available, ratios may vary seasonally as well as spatially (Abe and Matsunaga 1988, Danielsson *et al* 1985).

Table 3.20. Ratios of Cd to P in marine environments.

Area	Cd/P ($\times 10^{-3}$)	Reference
Tay estuary	0.040	This study
Savannah estuary	0.045	Windom *et al* 1991
Maeklong estuary	0.045	Windom *et al* 1991
Medway estuary	0.046	Windom *et al* 1991
Forth estuary	0.052	This study
Atlantic Ocean	0.091	Kremling 1985
Indian Ocean	0.15	Saager *et al* 1992
N Atlantic Ocean	0.19	Danielsson *et al* 1985
N E Tasman Sea	0.31	Hunter and Ho 1991
N Pacific Ocean	0.35	Bruland 1980
N Pacific Ocean	0.38	Collier and Edmond 1984
Delaware estuary	0.35	Church 1986
Delaware estuary	0.39	Sharp *et al* 1984
Southern Ocean	0.64	Nolting *et al* 1991

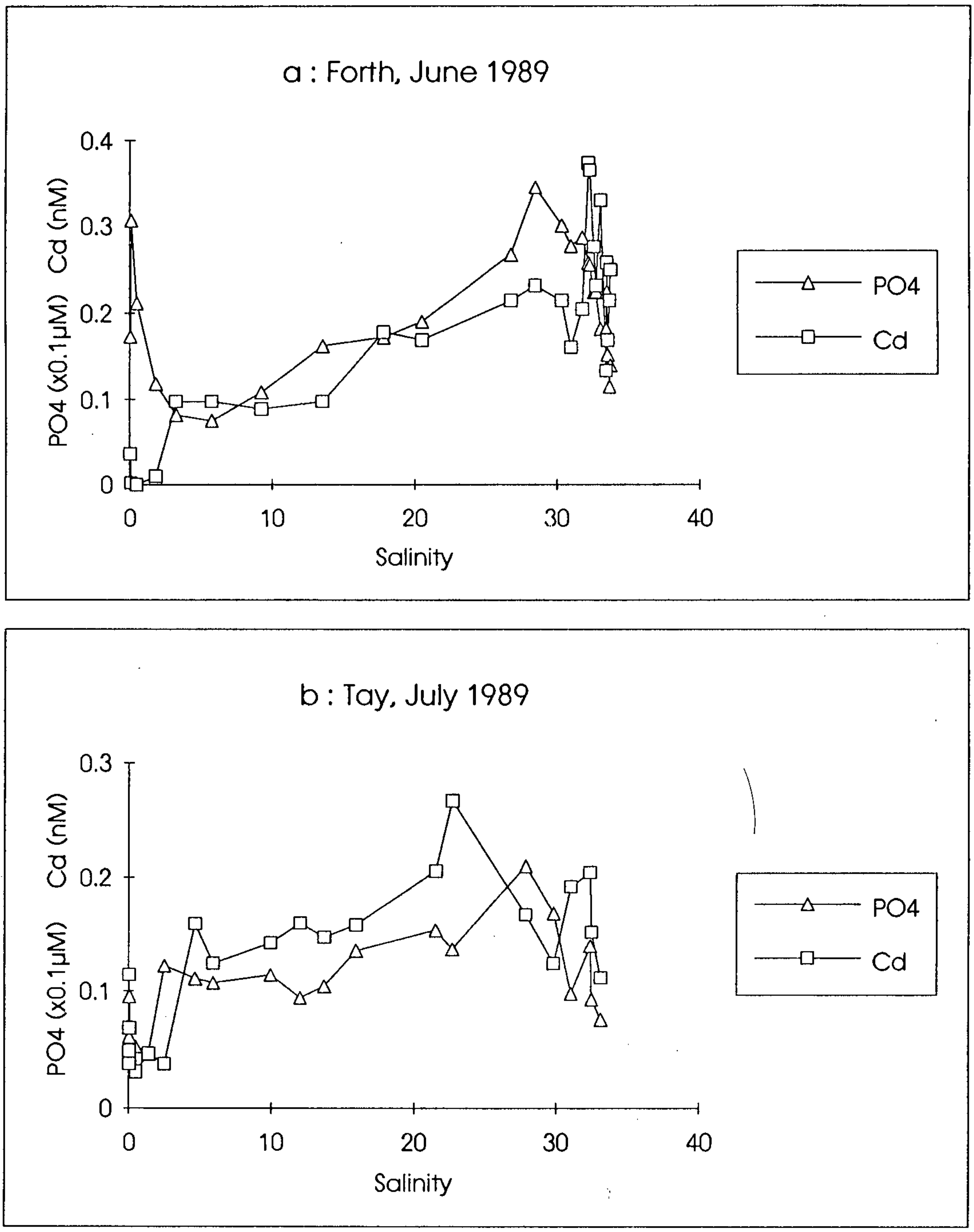


Figure 3.23. Relationships between Cd, PO_4 and salinity. a : Forth, June 1989 and b : Tay, July 1989.

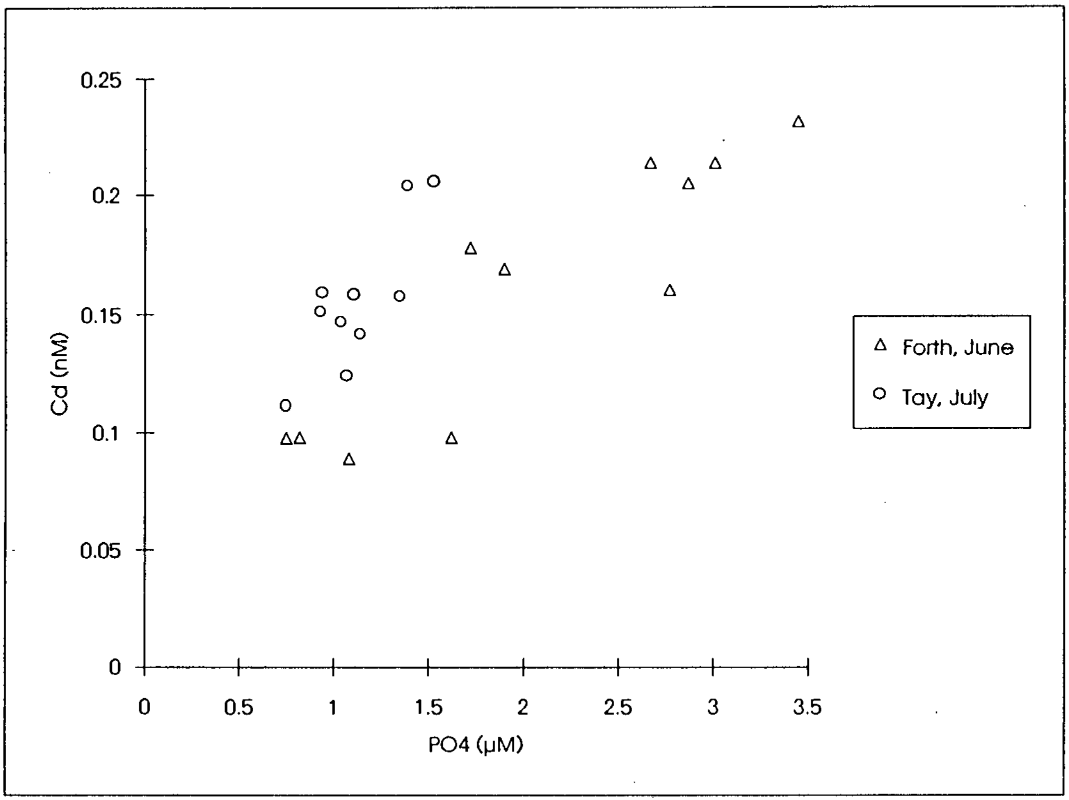


Figure 3.24. Relationships between Cd and PO_4 in the Forth and Tay estuaries. Values at salinities <3 ‰ or >32 ‰ in the Forth are excluded, as are values influenced by sewage inputs in the outer Tay.

No relationship between Cd and P was observed at other times in the Forth and Tay when water residence times were shorter and conditions less stable. During these surveys, the increase in dissolved Cd with salinity may be caused by direct competition for the element between surface sites and dissolved Cl^- ions. Experimental evidence suggests that this process is most important at salinities lower than 6 to 12 °/∞ (Comans and van Dijk 1988), though Cd concentrations in the Forth and Tay generally increase until salinities of about 25 °/∞ are reached. An alternative mechanism for the release of Cd involves ion exchange reactions between adsorbed Cd and dissolved Ca^{2+} ions. This process has been demonstrated in fresh water systems (Comans 1987).

3.5.2: Lead

In the Forth, the dissolved Pb end-members range from $0.088\mu gl^{-1}$ in August to $0.192\mu gl^{-1}$ in November. In the Tay, they range from 0.043 in September to 0.415 in November. These span the estimated "world average" river concentration for Pb ($0.1\mu gl^{-1}$) (Martin and Whitfield 1983). Fresh water fluxes range from $0.049kgd^{-1}$ to $2.79kgd^{-1}$ in the Forth and $0.43kgd^{-1}$ to $3.04kgd^{-1}$ in the Tay (Table 3.19). Riverine inputs show a strong seasonal trend in the Forth, with highest fluxes coinciding with periods of highest fresh water flow. In the Tay, however, the fluxes are not as variable as those in the Forth, and do not appear to be linked so strongly with run-off data.

Dissolved lead/salinity profiles for the Forth and Tay (Figures 3.25 and 3.26 respectively) show considerable scatter. Although no clear pattern of addition or removal can be identified in either estuary, this is not a unique situation. Large changes in dissolved lead concentrations within short distances have been reported in the Severn (Harper 1991) and Elbe (Mart *et al* 1985) estuaries. In both cases, the high concentrations are attributed to anthropogenic discharges from point sources. Rapid removal of Pb from the dissolved phase causes concentrations to decrease within very short distances from the source.

In other estuaries overall patterns of removal are observed. In the Göta (Danielsson *et al* 1983) and Weser (Turner *et al* 1992) Pb removal is coincident with removal of iron from the dissolved phase. This is attributed to the destabilisation of colloids and high rates of Pb scavenging by newly-formed iron-rich particles. In the Weser, removal may also be caused by high ($>50 mgl^{-1}$) SPM loadings in the upper estuary. Because of its high particle-reactivity, the distribution of Pb in coastal waters is controlled by suspended particulate matter concentrations (Balls and Topping 1987, Paulson *et al* 1989c). In the Humber estuary, for example, the ratio of dissolved to particulate lead decreases by over 3 orders of magnitude with increasing turbidity (Balls 1985).

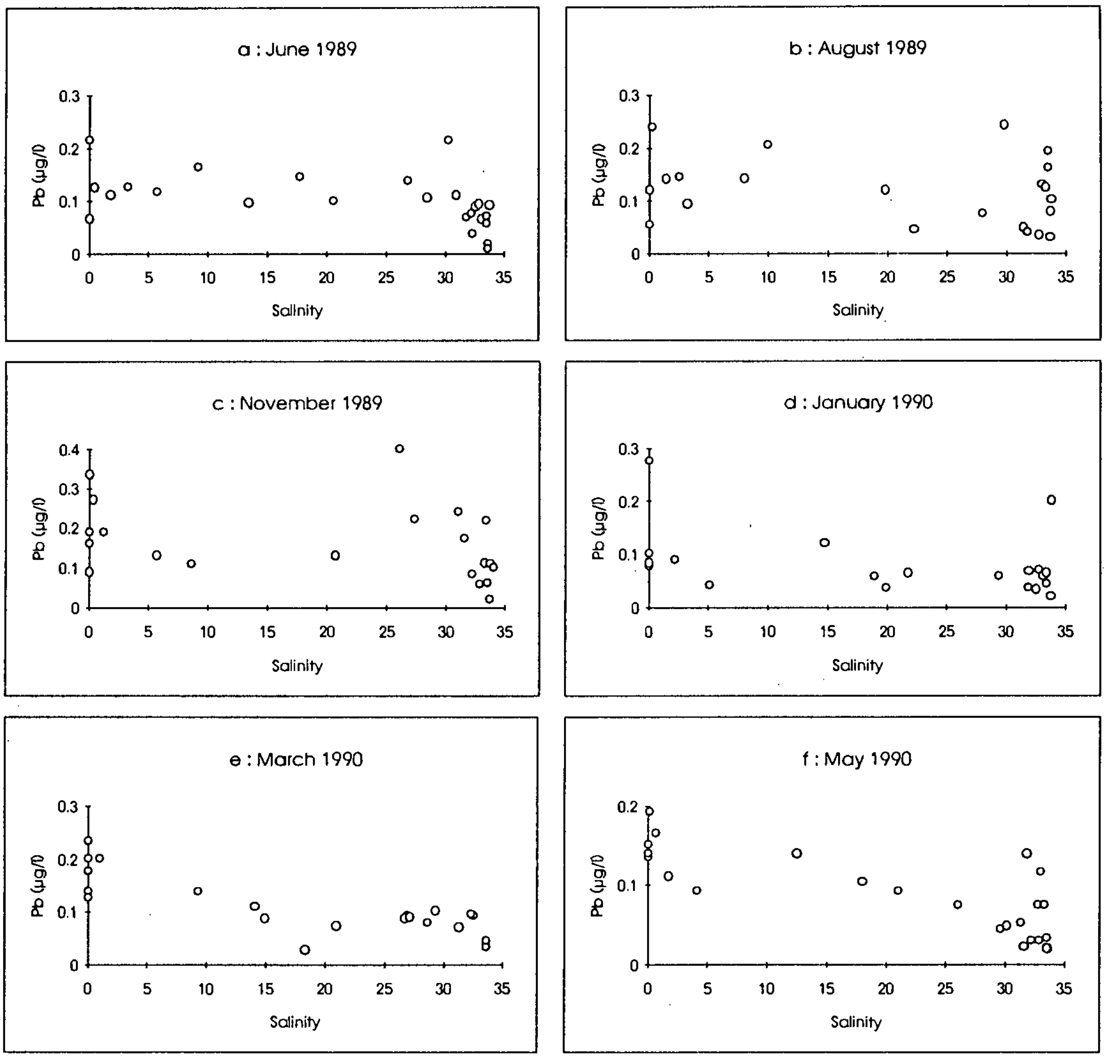


Figure 3.25. Dissolved Pb against salinity in the Forth estuary.
a : June 1989, b : August 1989, c : November 1989,
d : January 1990, e : March 1990 and f : May 1990.

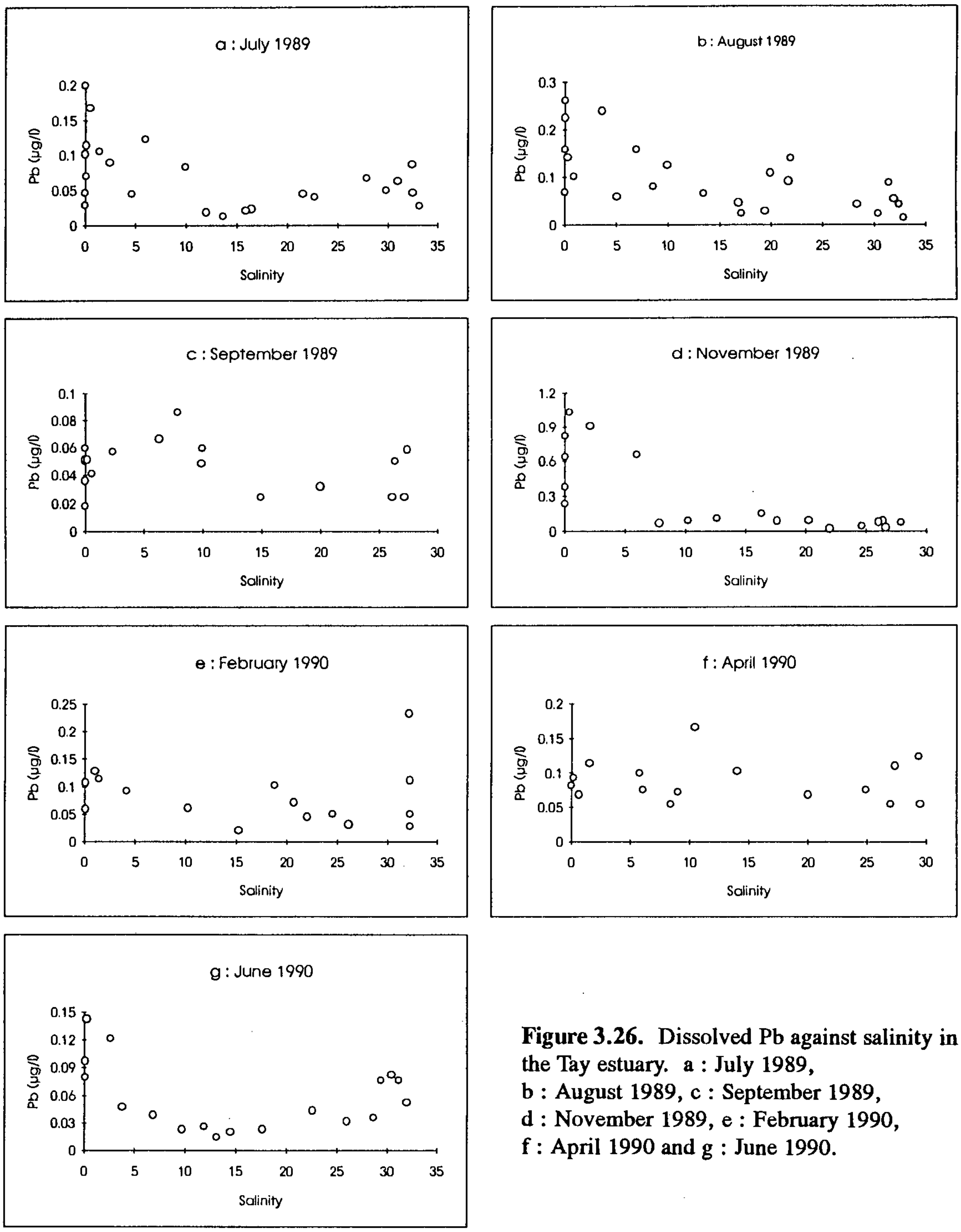


Figure 3.26. Dissolved Pb against salinity in the Tay estuary. a : July 1989, b : August 1989, c : September 1989, d : November 1989, e : February 1990, f : April 1990 and g : June 1990.

3.6: Summary

Dissolved manganese profiles from the Forth and Tay estuaries show broad mid-estuarine maxima, indicating that reduced manganese is being added to the water column from the bottom sediments. Peak dissolved Mn concentrations are higher in summer than in winter, and are higher in the Forth than the Tay. Highest benthic fluxes of Mn occur in the upper Forth estuary and coincide with dissolved oxygen minima in summer. High fluxes are also observed in January, and are attributed to increased resuspension of bottom sediments. Benthic fluxes in the Tay are similar to those in the Forth.

Only 10% of the dissolved Mn added to the estuarine waters is exported to the North Sea in the dissolved phase. The remaining 90% can be accounted for by the oxidative scavenging and removal of Mn by suspended particulate material. Riverine inputs of dissolved manganese are negligible compared with the sedimentary input. Both estuaries are therefore net sources of manganese to the North Sea. The Tay is the larger source, because of its higher flow rates.

Dissolved nickel and zinc profiles in the Forth are similar to those of Mn. In the June and August surveys Ni and Zn are remobilised with Mn in the oxygen minimum zone. Possible additional sources of Ni and Zn in May include release from disturbed bottom sediments or anthropogenic emissions. These sources are more important than any sinks of Ni and Zn in the estuary, and add to the metal load carried by the rivers to the North Sea. Removal of dissolved Ni and Zn in winter can be predicted by a particulate scavenging model (Morris 1986). Nickel and zinc profiles in the Tay are dominated by sewage inputs from Perth and Dundee, rather than remobilisation of Mn, or release from bottom sediments.

Dissolved copper profiles show non-conservative addition in both estuaries. Many Forth surveys, and the summer/autumn surveys of the Tay have a dissolved Cu peak in the very low salinity zone, as well as a second peak at higher salinities. The dissolved Cu peaks in the upper estuaries are accompanied by nutrient maxima. They are attributed to the bacterial breakdown of organic matter from authigenic, detrital or sewage-derived inputs. Lower estuary inputs are attributed to discharges from chemical works at Grangemouth in the Forth, and inputs of sewage from Dundee in the Tay. Inputs at Grangemouth are more important than riverine fluxes of dissolved Cu to the Forth.

Dissolved cadmium concentrations increase with increasing salinity in both estuaries. This behaviour is attributed to chloro-complexation. In the June and July surveys of the Forth and Tay, Cd/P ratios are constant. This suggests that the elements are simultaneously remobilised from particulate, possibly organic, material. Such relationships are not observed in the other surveys, when water residence times are shorter and conditions less stable.

Concentrations of dissolved Pb in the Forth and Tay are similar to those recently reported for other macrotidal estuaries. Riverine inputs of dissolved Pb show a strong seasonal trend in the Forth, with highest fluxes coinciding with periods of highest fresh water flow. Riverine Pb fluxes in the Tay are not linked as strongly with discharge. Dissolved lead/salinity profiles for the Forth and Tay show considerable scatter; no clear pattern of addition or removal can be identified. Because of its high particle-reactivity, the Pb distribution in coastal waters is controlled by suspended particulate matter concentrations.

CHAPTER 4: SUSPENDED PARTICULATE METALS

4.1: Major elements

4.1.1: Results

Data from the XRF spectrometer, calibrated as μg per membrane, were corrected for the presence of sea salt as described in Section 2.5.3. Since the major element concentrations (mgl^{-1}) reflect the trend in SPM loadings, results are expressed as percentage weight of their oxide in SPM. The following oxides were used: Al_2O_3 , CaO, SiO_2 , TiO_2 , K_2O, MgO, Fe_2O_3 , P_2O_5 . Results for the lighter elements (*ie* Si, Al, Mg and P) are only presented for membranes with less than 2mg particulate material. This avoids artefacts caused by decreasing counts/mass ratios for these elements at higher membrane loadings (Section 2.5.1). Suspended particulate metal contents are normalised to Al, since this element mainly exists in clays (Hirst 1962) and is geochemically unreactive (Sholkovitz 1979). In some cases, the heavier elements were normalised to Ti to avoid any artefacts of thin film XRF analysis.

Results are in general agreement with those reported from other areas (Table 4.1). They are discussed in more detail below.

4.1.2: Carbon and aluminium

Results for particulate organic carbon (POC) and Al_2O_3 are summarised in Table 4.2.

The statistical significance of differences in mean suspended particulate POC and Al_2O_3 contents between surveys was examined. Since one of the major requirements for the F-test, that for normally distributed data, was not fulfilled

Table 4.1. Comparison of major element contents with those reported in the literature.

Area	Al (%)	Si (%)	Fe (%)	Mg (%)	Ca (%)	K (%)	Ti (%)	Mn (%)	P (%)	Reference
Crustal average	8.23	28.15	5.63	2.33	4.15	2.09	0.57	0.095	0.105	Taylor 1964
World river SPM average	9.4	28.5	4.8	1.18	2.15	2	0.56	0.105	0.061	Martin and Meybeck 1979
Forth estuary	4.32-19.56	10.7-38.6	2.47-11.69	1.02-3.54	0.49-2.99	0.82-4.13	0.22-1.22	0.037-0.391	0.16-0.63	This study
Tay estuary	3.29-12.81	16.3-35.5	2.58-10.48	1.00-3.59	0.30-5.26	0.69-3.94	0.11-0.91	0.045-0.446	0.12-0.72	This study
Tamar estuary	6.2-12.0	13.7-26.7	4.57-8.42	0.58-1.33	0.44-3.93			0.062-0.130		Loring et al 1983
St Lawrence estuary	11.5-30.2	11.5-30.2	2.48-6.39					0.042-0.197		Yeats and Loring 1991
Rhine-Meuse estuary	4-6	12-20	4-6	1-2	3-9	0.2-0.4	0.5-1.2	0.05-0.16		Nolting et al 1990
North Sea	0.56-5.80		0.30-3.32		1.05-7.60			0.015-0.091		Kersten et al 1991
North Sea		3.5-20.8	0.98-4.64					0.021-0.275		Nolting and Eisma 1988
Baltic Sea	4-6		2.5-3.0		0.8			0.20-1.25		Bernhard et al 1989

here, the non-parametric Kruskal-Wallis ANOVA procedure (a χ^2 approximation) was used. This procedure does not require the data to be normally distributed, (SAS INSTITUTE Inc. 1985).

Table 4.2. Suspended POC and Al_2O_3 contents in the Forth and Tay estuaries.
n = number of observations.

Survey		POC% Mean ± σ (n)	Al_2O_3 Mean ± σ (n)
Forth			
	June 1989	8.57 ± 3.55 (20)	22.14 ± 7.79 (7)
	August 1989	9.84 ± 2.19 (24)	25.43 ± 2.08 (8)
	November 1989	11.45 ± 5.37 (21)	26.79 ± 3.83 (9)
	January 1990	17.08 ±10.98 (19)	
	March 1990	11.01 ± 3.65 (20)	29.33 ± 4.87 (14)
	May 1990	13.67 ± 7.22 (24)	21.67 ± 9.66 (6)
	Test Statistic (χ^2)	12.164 (DF=5)	5.53 (DF=4)
	90% Critical Value	9.24	7.78
	Conclusion	Significant	Not Significant
Tay			
	July 1989	9.29 ± 4.06 (23)	15.46 ± 4.74 (15)
	August 1989	10.11 ± 4.46 (22)	17.30 ± 5.73 (12)
	September 1989	8.27 ± 2.17 (19)	18.76 ± 2.86 (7)
	November 1989	10.86 ± 3.96 (20)	
	February 1990	6.38 ± 2.14 (17)	21.01 ± 1.37 (3)
	April 1990	6.23 ± 1.41 (16)	22.19 ± 0.58 (4)
	June 1990	9.52 ± 1.94 (17)	17.33 ± 3.41 (7)
	Test Statistic (χ^2)	37.344 (DF=6)	10.16 (DF=5)
	90% Critical Value	10.64	9.24
	Conclusion	Significant	Significant

POC contents vary significantly ($P < 0.10$) between the surveys in both estuaries. In the Tay, they are lowest in February and April. This reflects:

i low rates of organic carbon input from primary productivity during winter/ early spring;

ii increased importance of non-biogenic sediment resuspension during periods of large river flows and high winds.

In the Forth, however, the lowest POC contents occurred in June and August, when turbidity maxima were most important (Section 3.1.2). This reflects:

i the high proportions of terrigenous resuspended sediment in the turbidity maximum;

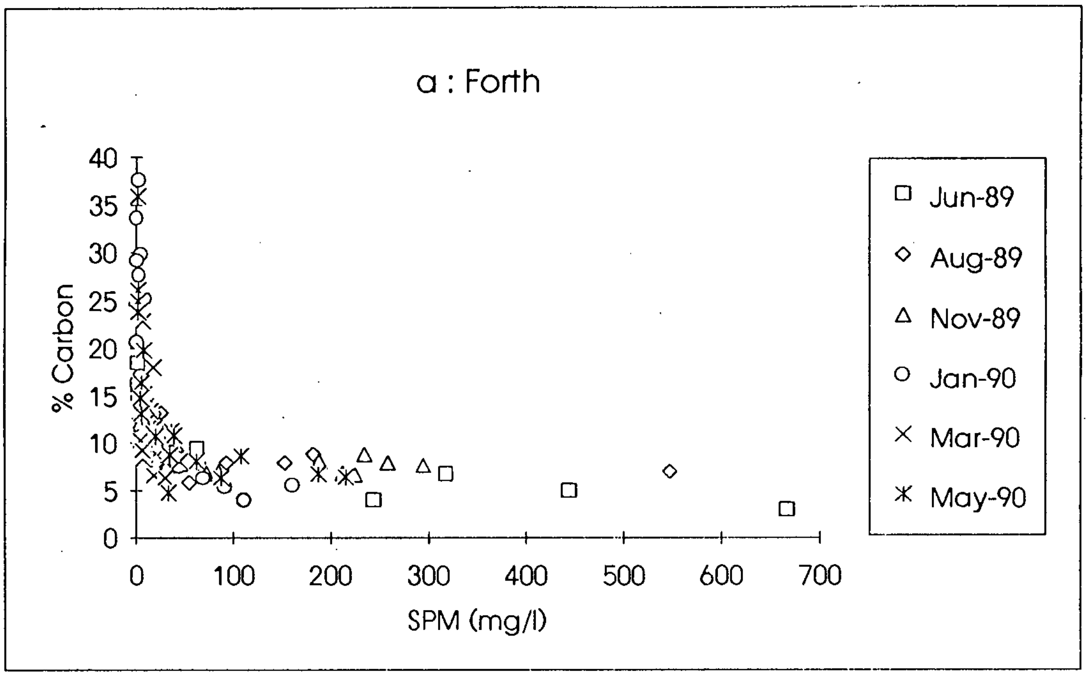
ii the lower rates of primary productivity at times of increased turbidity.

Inverse relationships between POC and SPM are therefore observed in both estuaries (Figure 4.1). Conversely, low suspended particulate Al_2O_3 contents occur in samples with low SPM loadings (Figure 4.2). Similar results have been obtained for the North Sea (Kersten *et al* 1991, Nolting and Eisma 1988), Weser estuary (Duinker *et al* 1982a) and, for POC, in the Clyde estuary and Sea Lochs (Balls 1990).

Suspended particulate Al_2O_3 contents in the Tay are similar to the crustal average (15.55% as Al_2O_3 , Taylor 1964) though those in the Forth are generally greater. These results indicate that there is a greater proportion of fine-grained alumino-silicates in the lower-energy régime of the Forth. In the Tay, suspended particulate Al_2O_3 contents vary significantly ($P < 0.10$) between surveys, being highest in winter. This reflects the importance of non-biogenic terrigenous minerals in resuspended particles. There is no significant ($P < 0.10$) seasonal difference in the percentage of suspended particulate aluminium in the Forth.

4.1.3: Calcium

The CaO contents in the low salinity regions of the Forth and Tay are slightly higher than ~~similar to~~ those found in granitic rocks (*ie* 0.71% as CaO, Turekian and Wedepohl 1961). These increase at salinities higher than 25 ‰ to peak values of 4.18% and 7.36% in the Forth and Tay (Figures 4.3 and 4.4 respectively).



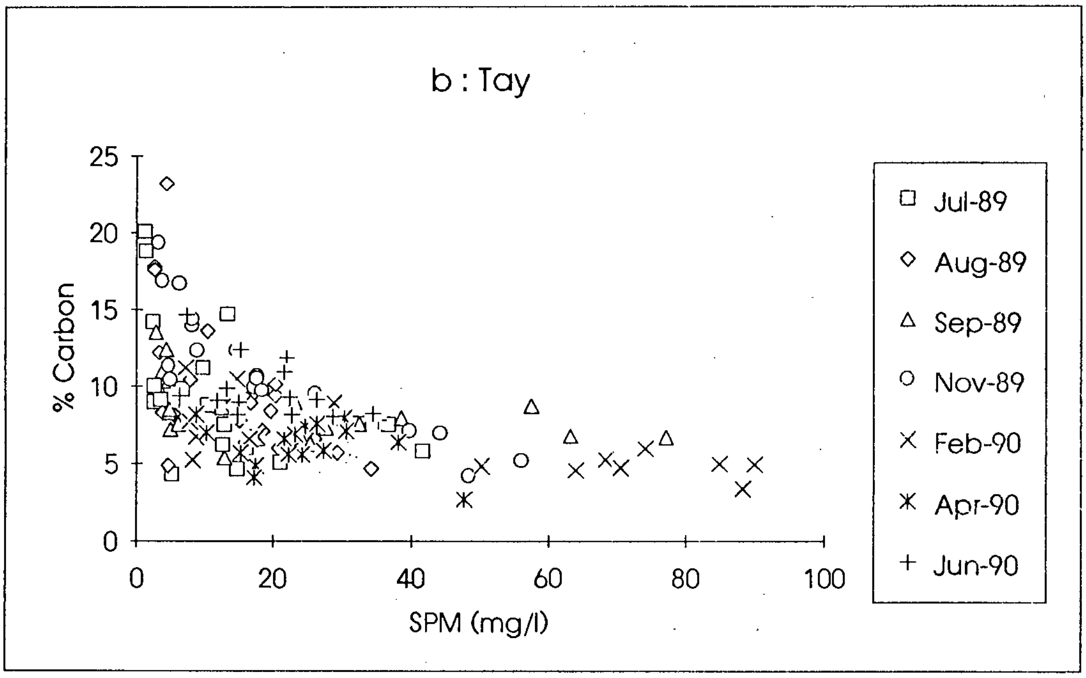
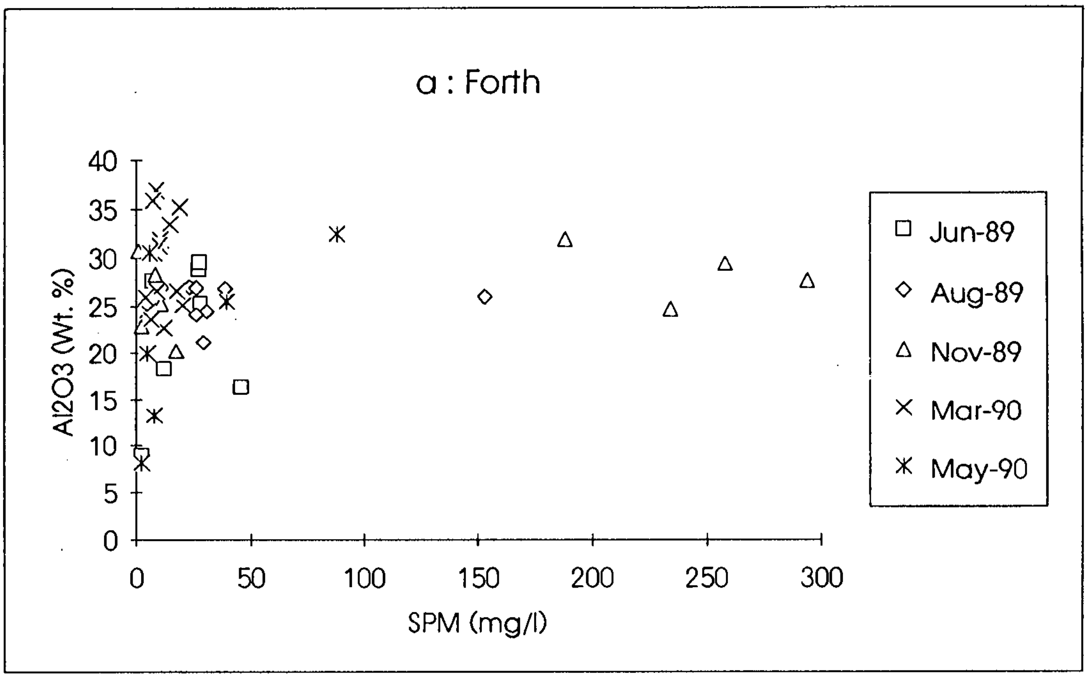


Figure 4.1. Particulate organic carbon contents against SPM. a : Forth and b : Tay.



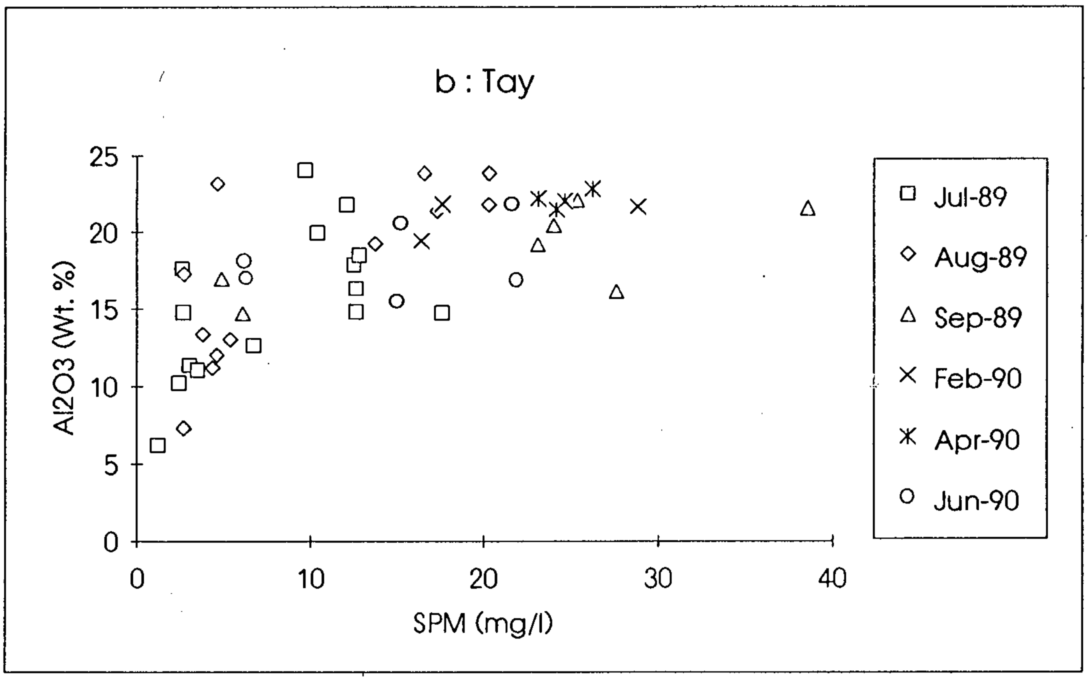


Figure 4.2. Suspended particulate Al_2O_3 contents against SPM. a : Forth and b : Tay.

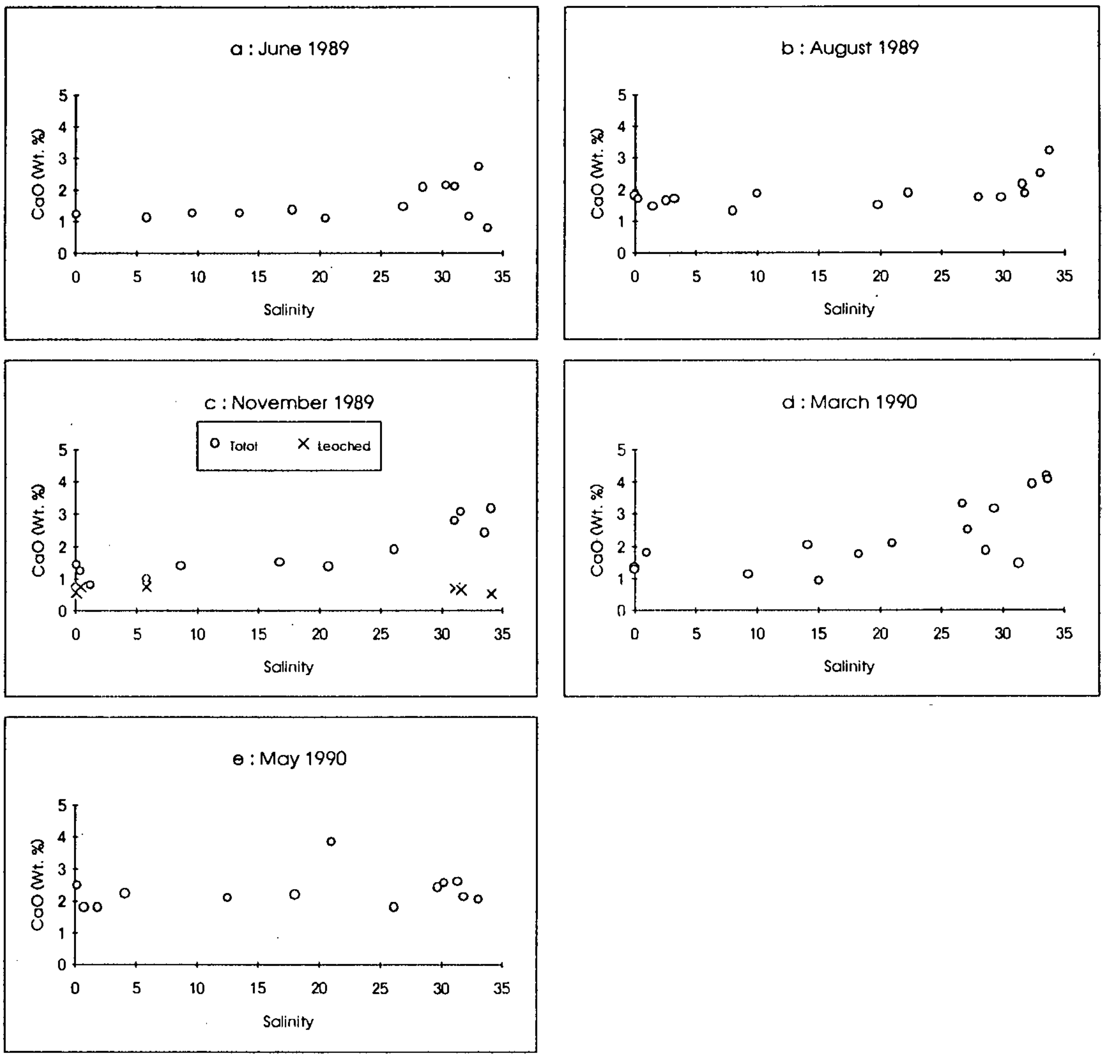


Figure 4.3. Suspended particulate CaO contents against salinity in the Forth.
a : June 1989, b : August 1989, c : November 1989,
d : March 1990 and e : May 1990.

NB. The "leached" values refer to the CaO contents of the particles after leaching.

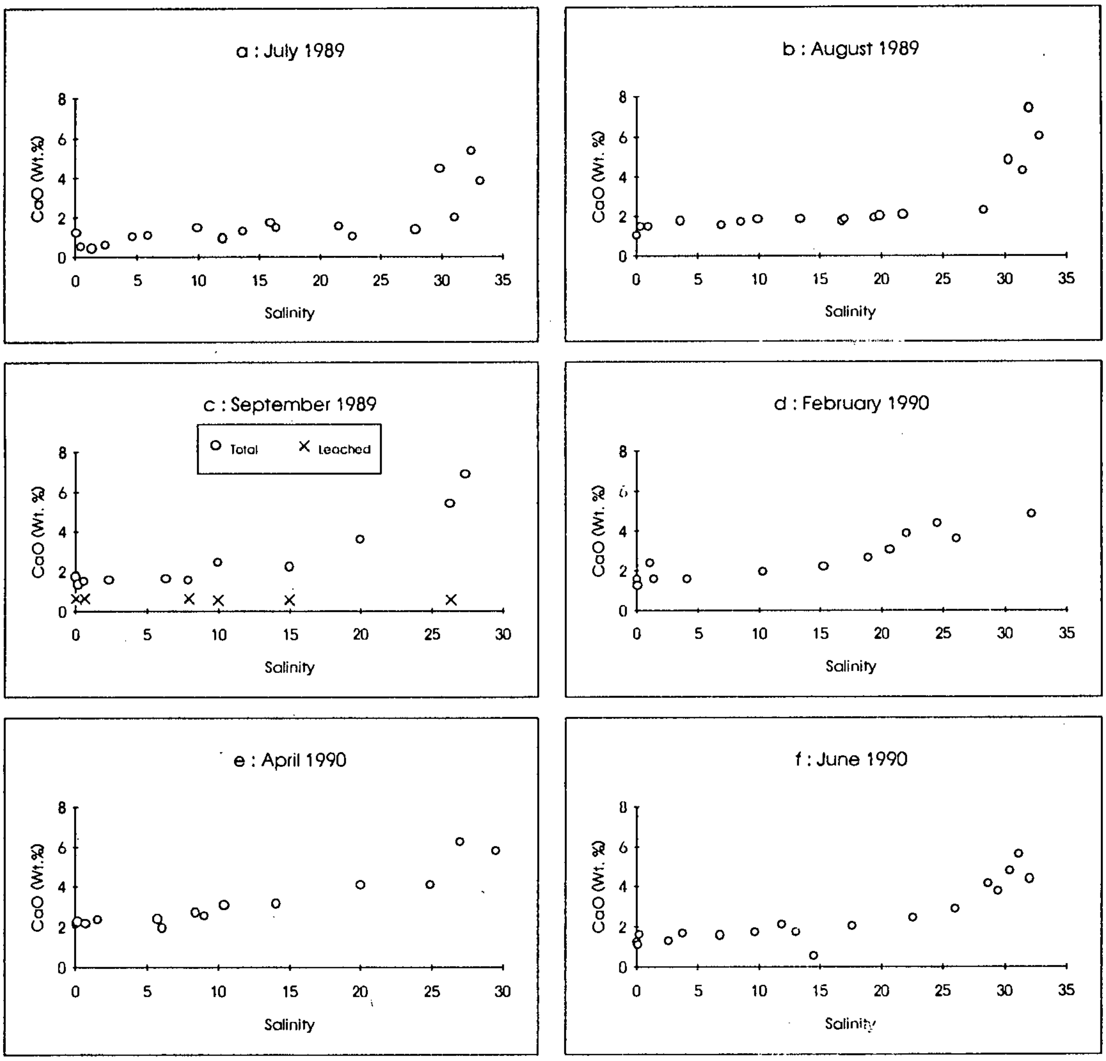


Figure 4.4. Suspended particulate CaO contents against salinity in the Tay. a : July 1989, b : August 1989, c : September 1989, d : February 1990, e : April 1990 and f : June 1990.

NB. The "leached" values refer to the CaO contents of the particles after leaching.

Increasing CaO contents with salinity have also been observed in the Tamar estuary (up to 3.5% as CaO, Loring *et al* 1983), Baltic Sea (up to 3.5% as CaO, Bernhard *et al* 1989) and Rhine-Meuse estuary (up to 14-15% as CaO, Nolting *et al* 1989, Paalman and van der Weijden 1992). The marine environment is therefore acting as a source of $CaCO_3$ to these areas. The landward movement of $CaCO_3$ from marine mollusc shells (*eg* of *Mytilus edulis*) has previously been observed in the Tay (Al-Dabbas and McManus 1987). The amount of $CaCO_3$ entering the Tay seems to be greater than that entering the Forth. This may be caused by the higher fresh water flow rates in the Tay, and correspondingly higher counter-flow of bottom water.

The $CaCO_3$ fractions of the sediment were effectively removed by the acetic acid/hydroxylamine-hydrochloride leaching procedure described in Section 2.5.4 (Figures 4.3c and 4.4c for Forth and Tay respectively).

what about the low S
samples

4.1.4: Silicon, titanium, potassium and magnesium

The suspended particulate SiO_2/Al_2O_3 , TiO_2/Al_2O_3 , K_2O/Al_2O_3 , MgO/Al_2O_3 and Fe_2O_3/MgO relationships are illustrated in Figures 4.5 to 4.9. The regression equations and 95% confidence intervals are given in Table 4.3.

The SiO_2/Al_2O_3 relationships in both estuaries have large intercepts (SiO_2 = 18-20%) which arise from the presence of quartz. The slope of the SiO_2/Al_2O_3 relationship in the Tay (2.22) is lower than previously reported for coastal waters (Table 4.4). It is, however, higher than that in the Forth, indicating that particles are generally coarser in the Tay. This observation is consistent with the higher tidal currents in the estuary.

The TiO_2/Al_2O_3 ratio in the Tay is reasonably close to that observed in Loch Etive, but slightly lower than those of other estuaries (Table 4.4). The higher ratios in the Tay than the Forth again reflect the coarser grain sizes in the

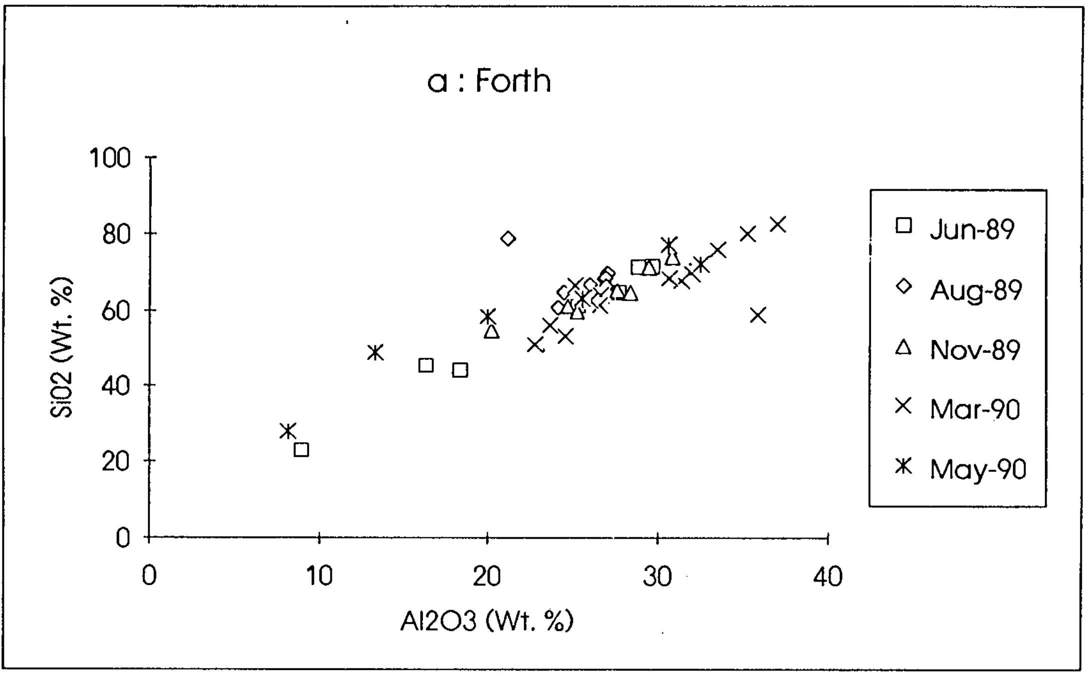
Tay. This is attributed to the presence of metamorphic/igneous detritus, *eg* ilmenite ($FeTiO_3$), rather than Carboniferous sediments (Calvert 1976, Chester and Aston 1976).

Table 4.3. Correlation relationships between major element oxides in the Forth and Tay.
n = number of observations, C.I. = confidence interval, F = Forth, T = Tay.

Element pairs	n	Intercept (Wt. %)	95% C.I.	Slope	95% C.I.	Significance	Corr. Coeff.	R^2 %
F SiO_2: Al_2O_3	44	19.8	11.4 to 28.1	1.66	1.35 to 1.98	0.0000	0.85	73%
T SiO_2: Al_2O_3	48	17.8	12.2 to 23.4	2.22	1.91 to 2.53	0.0000	0.91	83%
F TiO_2: Al_2O_3	44	0.304	0.053 to 0.554	0.044	0.035 to 0.054	0.0000	0.83	68%
T TiO_2: Al_2O_3	48	0.122	-0.018 to 0.263	0.054	0.046 to 0.061	0.0000	0.90	81%
F K_2O: Al_2O_3	44	0.499	-0.047 to 1.043	0.120	0.099 to 0.140	0.0000	0.88	77%
T K_2O: Al_2O_3	48	0.383	0.022 to 0.745	0.165	0.145 to 0.185	0.0000	0.93	86%
F MgO: Al_2O_3	44	0.675	0.279 to 1.071	0.140	0.125 to 0.154	0.0000	0.95	89%
T MgO: Al_2O_3	45	0.197	-0.178 to 0.573	0.221	0.200 to 0.241	0.0000	0.96	92%
F Fe_2O_3: MgO	44	2.60	0.44 to 4.72	2.32	1.83 to 2.81	0.0000	0.83	69%
T Fe_2O_3: MgO	45	2.14	0.70 to 3.59	2.12	1.78 to 2.46	0.0000	0.89	79%
F Fe_2O_3: TiO_2	73	1.80	0.84 to 2.75	7.37	6.74 to 8.00	0.0000	0.94	88%
T Fe_2O_3: TiO_2	95	1.02	0.20 to 1.85	8.97	8.24 to 9.71	0.0000	0.93	86%

Table 4.4. Suspended particulate metal oxide/Al_2O_3 ratios in coastal waters.

Area	SiO_2/Al_2O_3	TiO_2/Al_2O_3	K_2O/Al_2O_3	MgO/Al_2O_3	Reference
Loch Etive	2.64-10.8	0.029-0.64	0.15-0.27	0.17-0.36	Price and Calvert 1973
Ems	4.0-5.1	0.06-0.08			Duinker *et al* 1985
Elbe	5.7	0.06		0.013	Duinker *et al* 1982b
Weser	4.0	0.07		0.18	Duinker *et al* 1982a
Tagus	2.4-5.2			0.05-0.11	Vale 1990



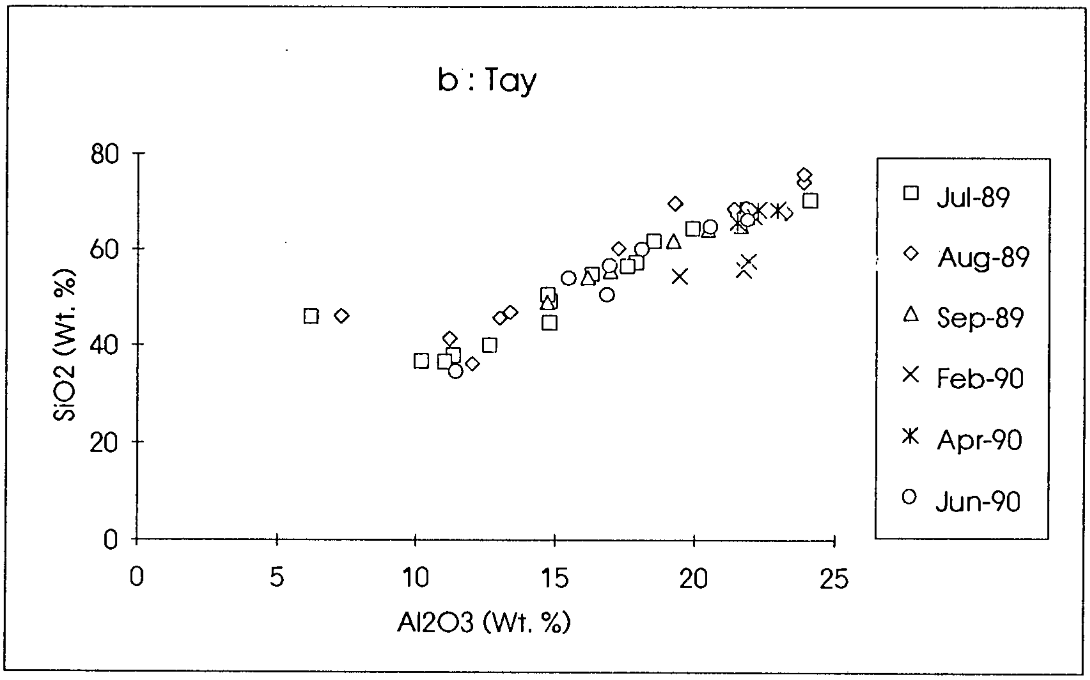
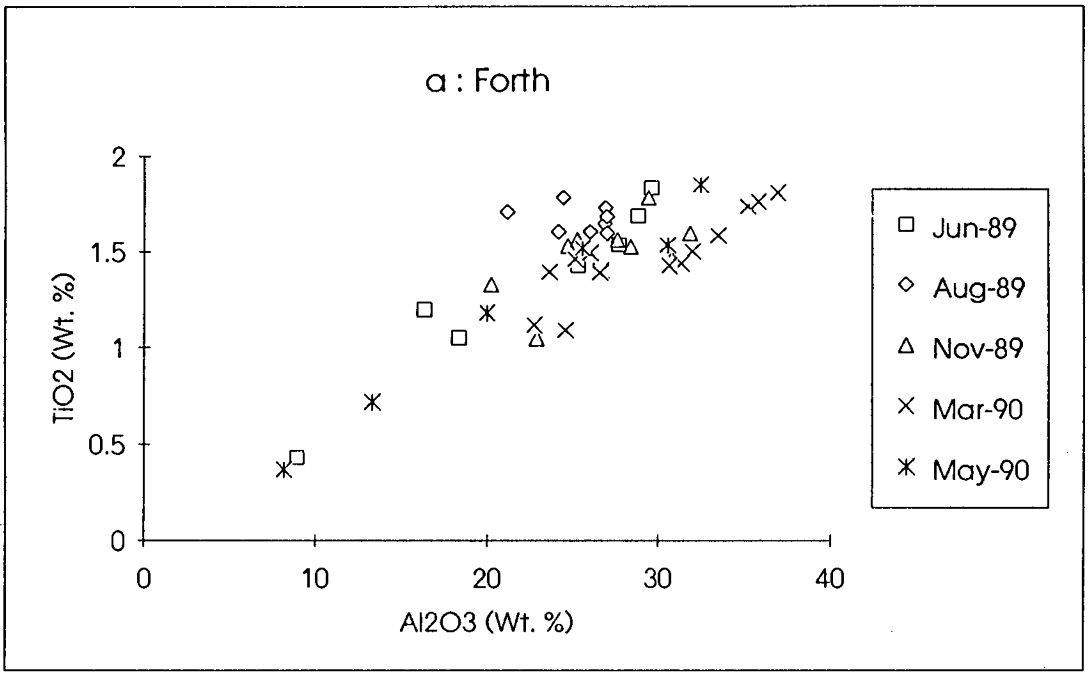


Figure 4.5. Relationships between SiO_2 and Al_2O_3 in SPM. a : Forth and b : Tay.



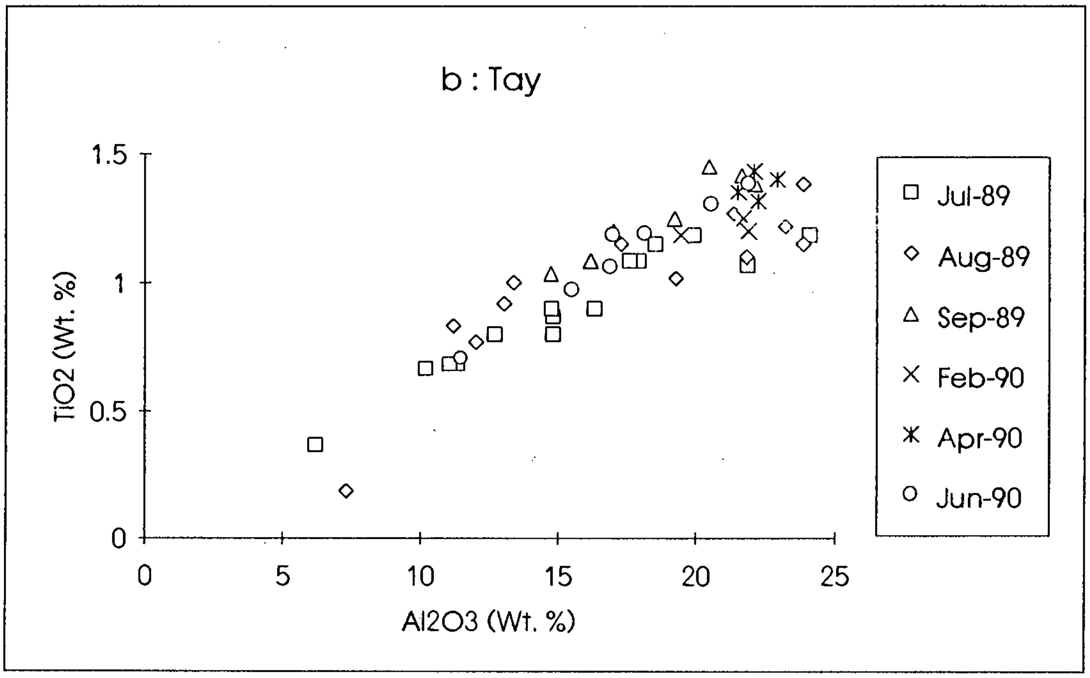
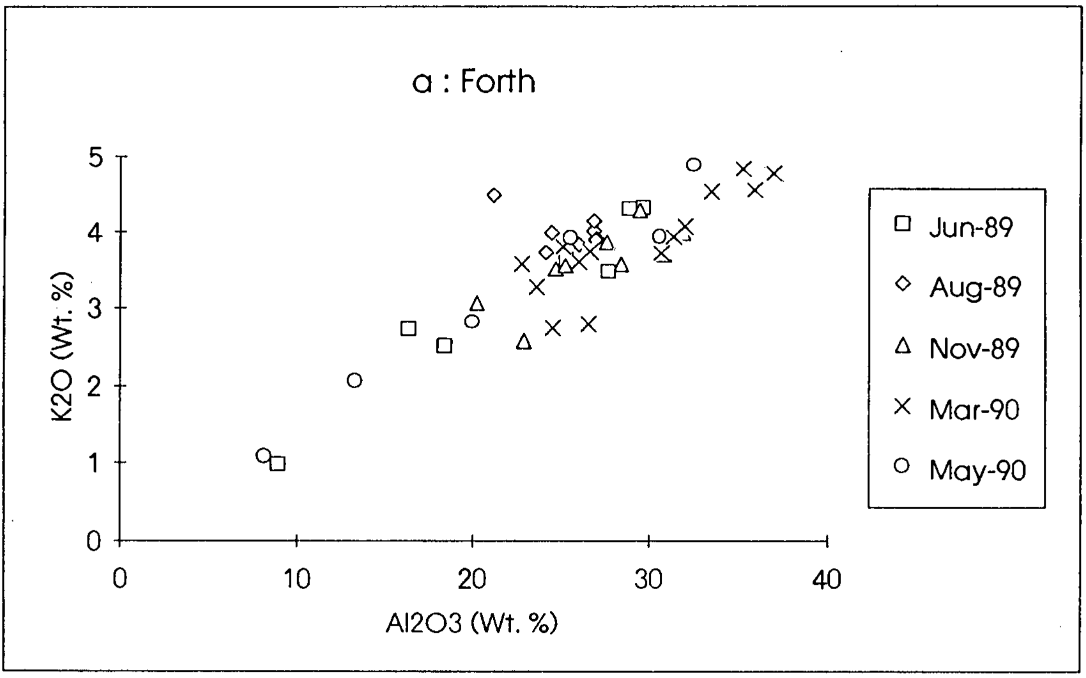


Figure 4.6. Relationships between TiO_2 and Al_2O_3 in SPM. a : Forth and b : Tay.



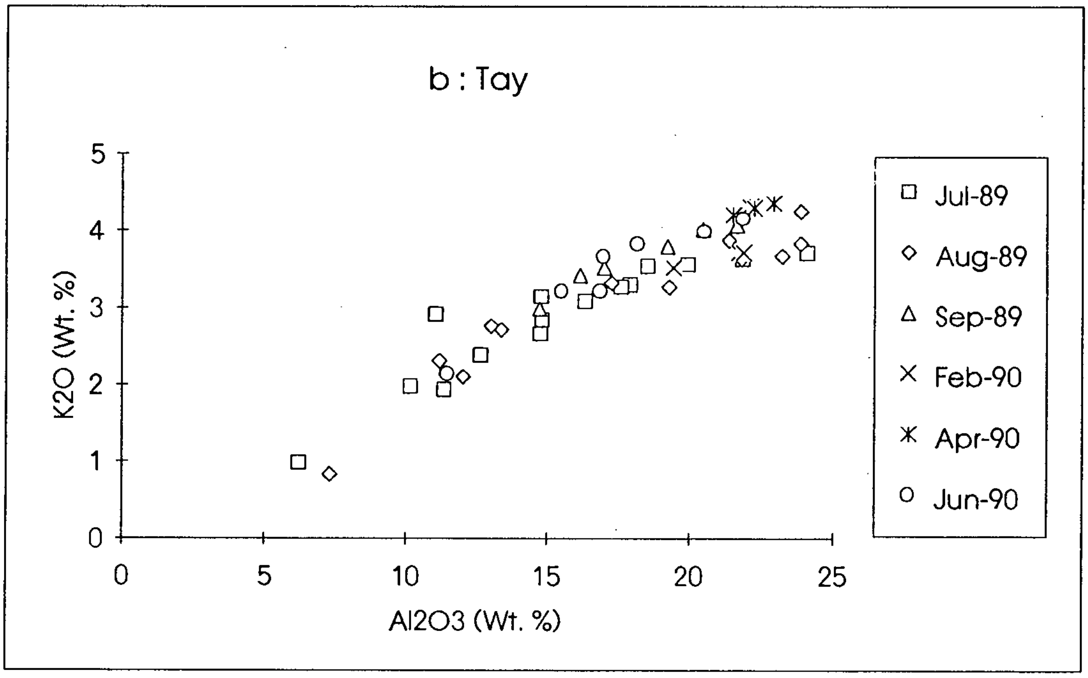
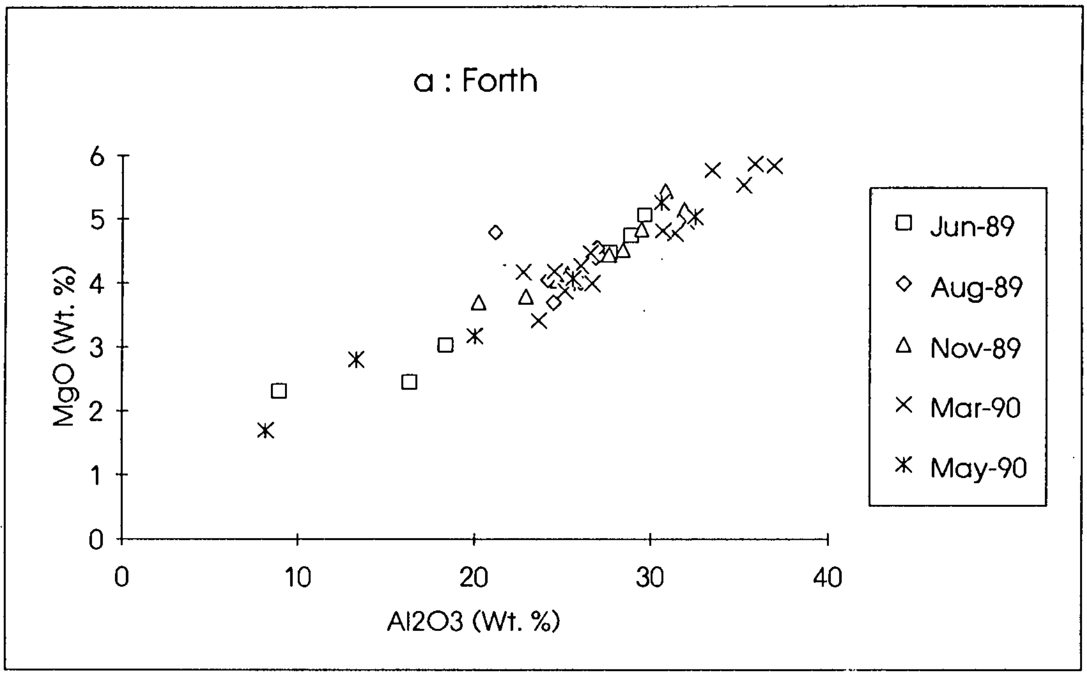


Figure 4.7. Relationships between K_2O and Al_2O_3 in SPM. a : Forth and b : Tay.



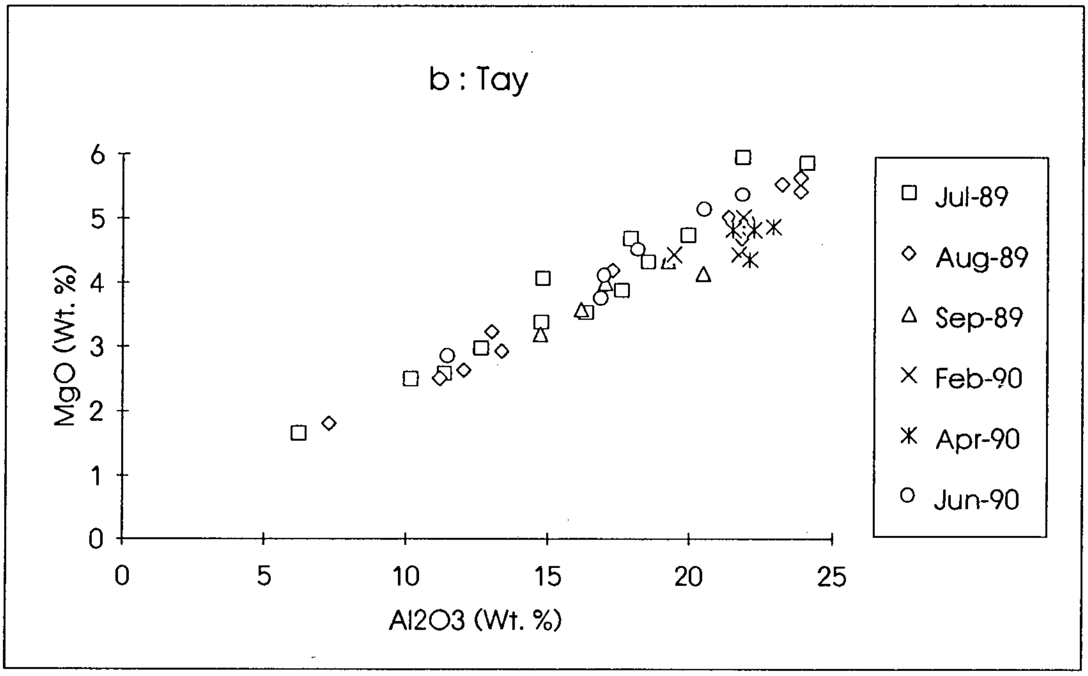
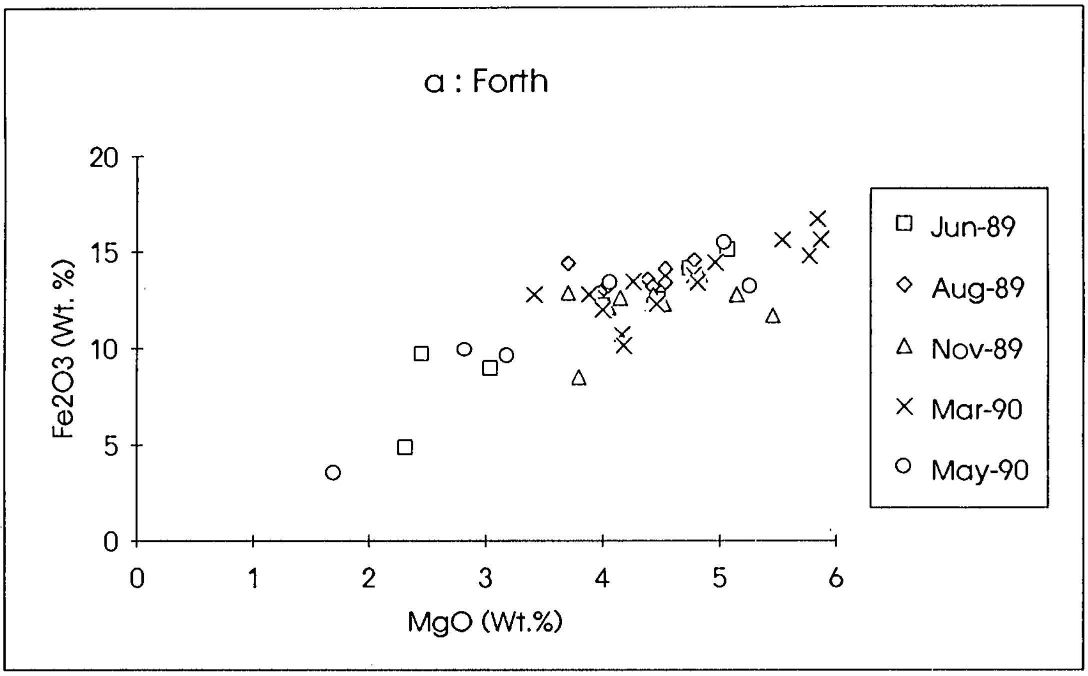


Figure 4.8. Relationships between MgO and Al_2O_3 in SPM. a : Forth and b : Tay.



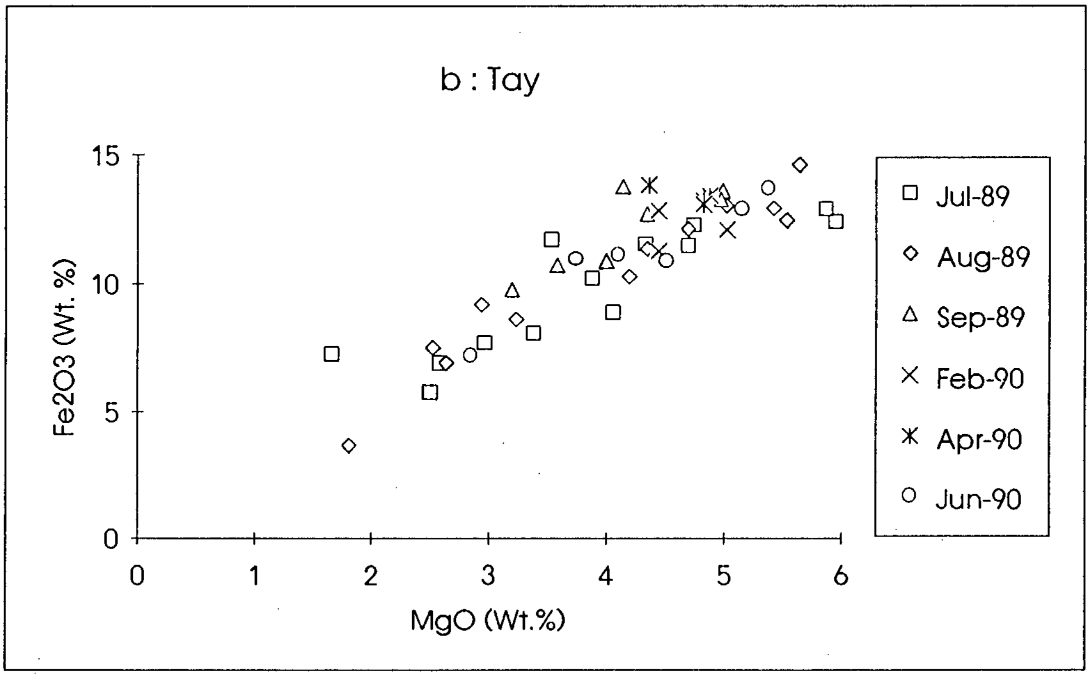


Figure 4.9. Relationships between Fe_2O_3 and MgO in SPM. a : Forth and b : Tay.

The K_2O/Al_2O_3 ratio in the Tay is similar to that observed in Loch Etive and is close to the ratio estimated for average crustal material (0.16, Taylor 1964). The K_2O/Al_2O_3 ratio in the Forth , however, is significantly lower than the crustal average. Potassium feldspars ($KAlSi_3O_8$) ~~are~~ may therefore be more important in the Tay than the Forth.

The MgO/Al_2O_3 ratios in both estuaries are lower than those expected for average crustal material (0.25, Taylor 1964), though this is not unusual in coastal SPM (Table 4.4). The ratio in the Tay is higher than that in the Forth. The constant Fe_2O_3/MgO ratios between the Forth and Tay arise from the constant ratios of these elements in ferromagnesian silicates (*ie* about 3). Higher suspended particulate MgO/Al_2O_3 ratios in the Tay therefore indicate that ferromagnesian silicates are more important in the Tay than the Forth.

Ratios of MgO/Al_2O_3 in marine sediments are generally higher than those of K_2O/Al_2O_3 (*eg* in Loch Etive, Price and Calvert 1973; Gulf of Paria, Hirst 1962). The SPM contents of the Forth and Tay, however, show the opposite trend. This may indicate that the suspended particles of both estuaries are rich in feldspars, which originate from a poorly weathered metamorphic/ igneous terraine.

4.1.5: Phosphorus

The relationships between P_2O_5 and Al_2O_3 in both estuaries are poor (Figure 4.10). The P_2O_5/Al_2O_3 ratios are higher than expected for average crustal material (0.016 as *oxides*, Taylor 1964). This is because phosphorus is present in organic matter and iron hydroxides (Hirst 1962, Stumm and Morgan 1970) as well as in detritus (*eg* as apatite).

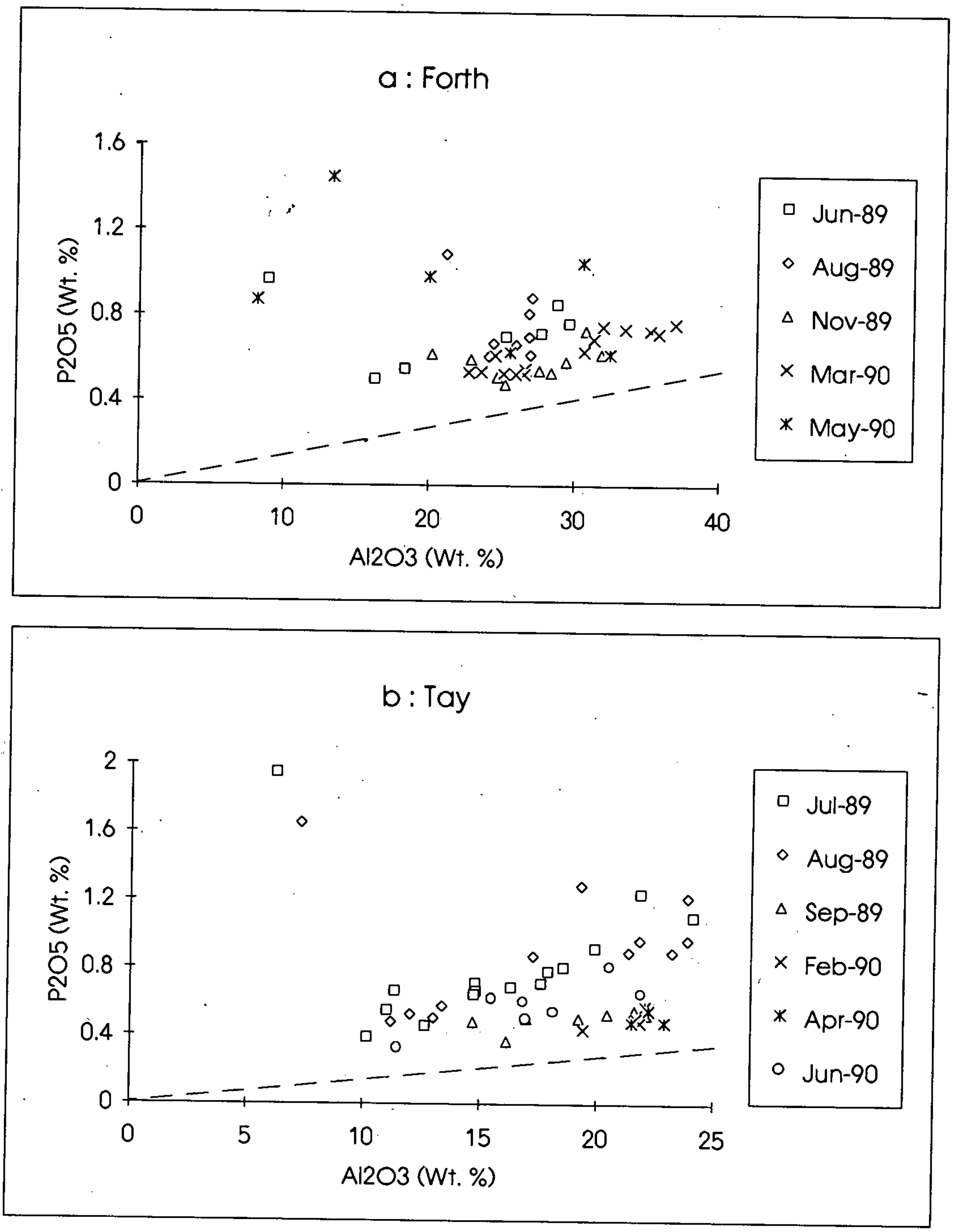


Figure 4.10. Relationships between P_2O_5 and Al_2O_3 in SPM. Broken line indicates ratio expected in detrital material. a : Forth and b : Tay.

Excess phosphorus concentrations (mgl^{-1}) were calculated by subtracting the alumino-silicate phosphorus (assuming a P/Al *elemental* ratio of 0.013, Taylor 1964) from the total phosphorus concentrations. In both estuaries, highest non-detrital concentrations are observed at low salinity during summer (Figure 4.11). They decrease with increasing salinity, approaching zero in the outer estuary. Excess concentrations in winter are lower, and remain fairly constant throughout the estuary. These observations are consistent with the observed removal of phosphate from the dissolved phase in the summer surveys of the Forth and Tay (Balls 1992). This removal is attributed to uptake by newly produced particulate organic matter.

The acetic acid/hydroxylamine-hydrochloride leaching procedure used effectively removed the 'excess' phosphorus from the suspended particles (Figure 4.11). This indicates that much of the non-detrital phosphorus is associated with the organic or hydroxide phases.

4.1.6: Iron

The suspended particulate Fe_2O_3 contents are normalised to TiO_2 to avoid the artefacts caused by comparing the heavy atomic mass of Fe with the lighter mass of Al. The Fe_2O_3/TiO_2 relationships in the Forth and Tay are illustrated in Figure 4.12. The regression parameters are given in Table 4.3.

The Fe_2O_3/TiO_2 ratios in the Tay are similar to those estimated for average crustal material (8.47, Taylor 1964). Significantly lower Fe_2O_3/TiO_2 ratios in the Forth may be due to the lower dissolved oxygen concentrations in this estuary at certain times of the year. Lower oxygen concentrations may

i limit the extent of oxidation of dissolved iron from benthic or anthropogenic sources;

ii cause remobilisation of suspended particulate iron entering estuarine waters.

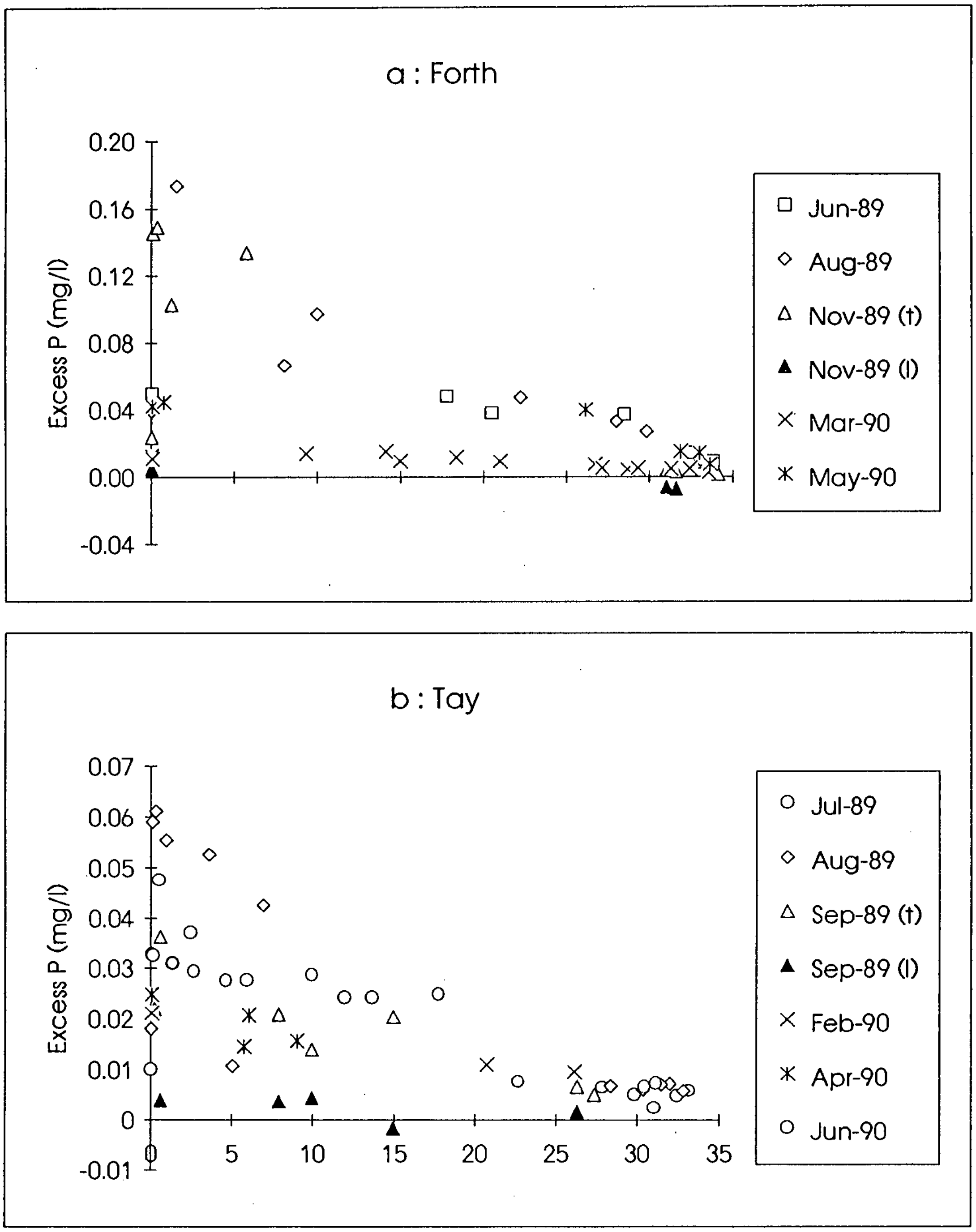
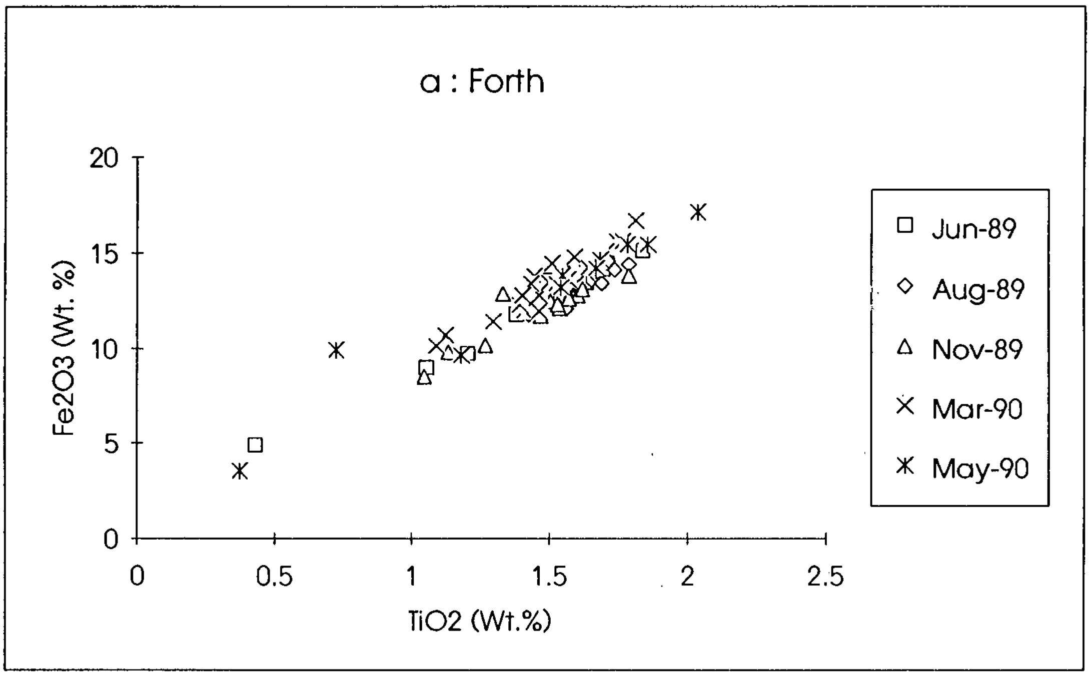


Figure 4.11. Non-detrital suspended particulate P against salinity. (t = total, l = leached) a : Forth and b : Tay.



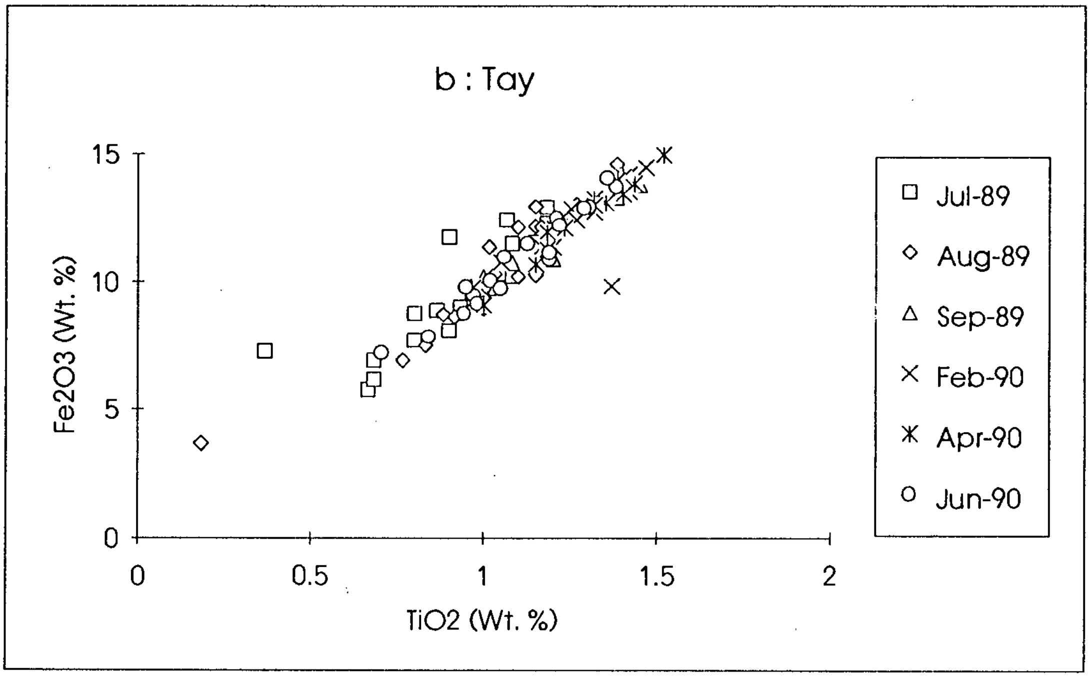


Figure 4.12. Relationships between Fe_2O_3 and TiO_2 in SPM. a : Forth and b : Tay.

Ratios of Fe_2O_3/TiO_2 are plotted against salinity for the Forth and Tay (Figures 4.13 and 4.14 respectively) to indicate which areas of each estuary had the highest particulate Fe contents.

Some of the highest Fe_2O_3/TiO_2 ratios occurred at the river water end-members of the Forth (*eg* November and May surveys) and Tay (July and August surveys). These high values may be caused by the breakdown and subsequent precipitation of Fe-containing colloidal material encountering saline waters (Section 1.4.3).

The high fresh water Fe_2O_3/TiO_2 ratios decrease rapidly in the turbidity maximum zones, TMZ (Figure 4.15). There are two possible reasons for this. Firstly, suspended solids in these zones may be coarser than those in other parts of the estuary. The smaller specific surface areas may reduce the surface sites available for iron adsorption. Secondly, material in the TMZ has a relatively short residence time in the water column. This may limit the time available for adsorption. Suspended particulate Fe_2O_3/TiO_2 minima are also observed at low salinity in the August survey of the Forth and the February and June surveys of the Tay. They agree with the findings of Sholkovitz (1979).

Ratios of Fe_2O_3/TiO_2 in suspended particles tend to increase towards the mid-salinity zones of the estuaries (*eg* June, August, November and March in the Forth; September and June in the Tay). This may be a result of the increase in residence time of the SPM so that oxidation can proceed to a greater degree.

Suspended particulate Fe contents were reduced by the acetic acid/ hydroxylamine-hydrochloride leaching procedure (Figures 4.13c and 4.14c for Forth and Tay respectively). This demonstrates that some of the Fe is associated with the non-detrital fraction of the particles.

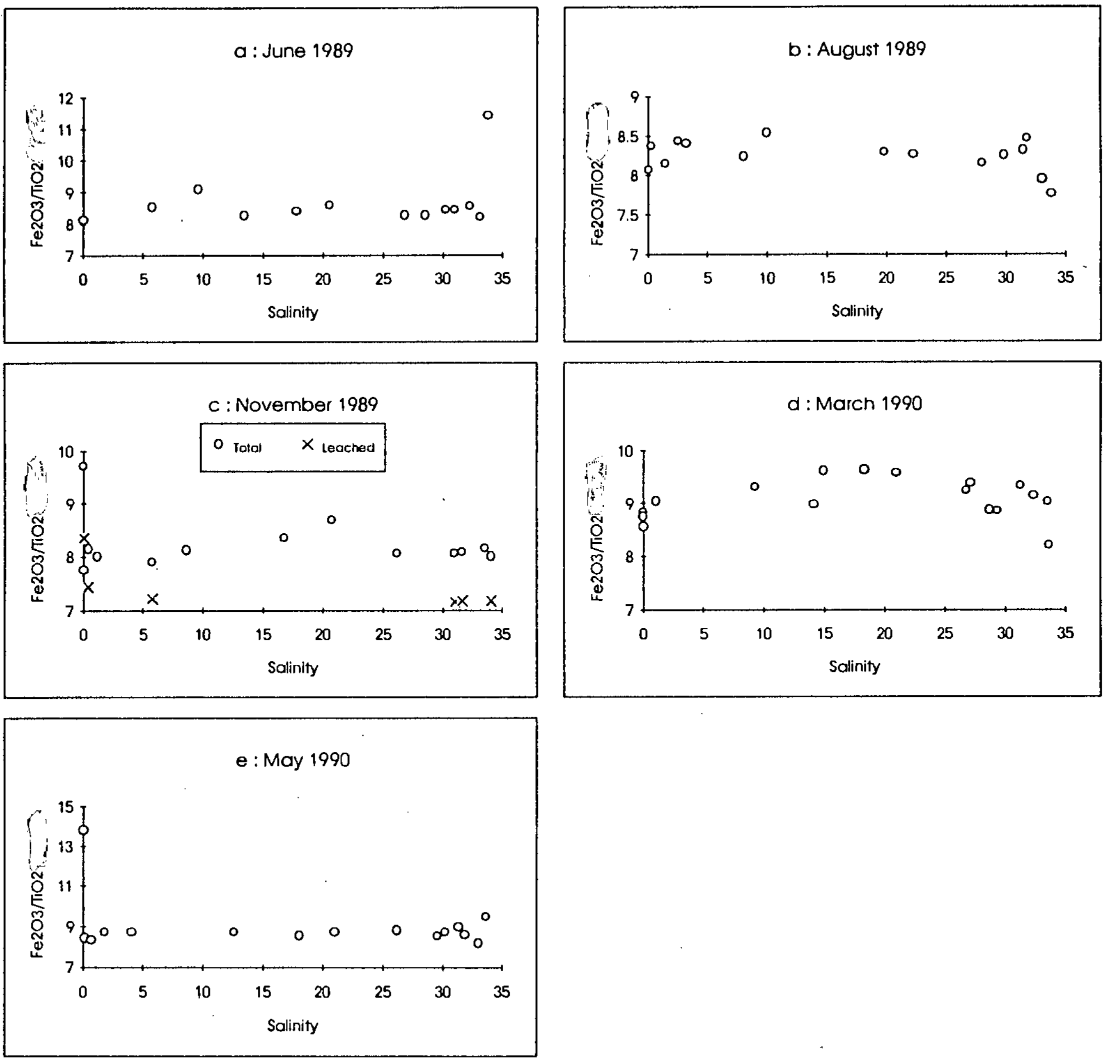


Figure 4.13. Suspended particulate Fe_2O_3/TiO_2 ratios against salinity in the Forth. a : June 1989, b : August 1989, c : November 1989, d : March 1990 and e : May 1990.

NB. The "leached" values refer to the Fe_2O_3/TiO_2 ratios of the particles after leaching

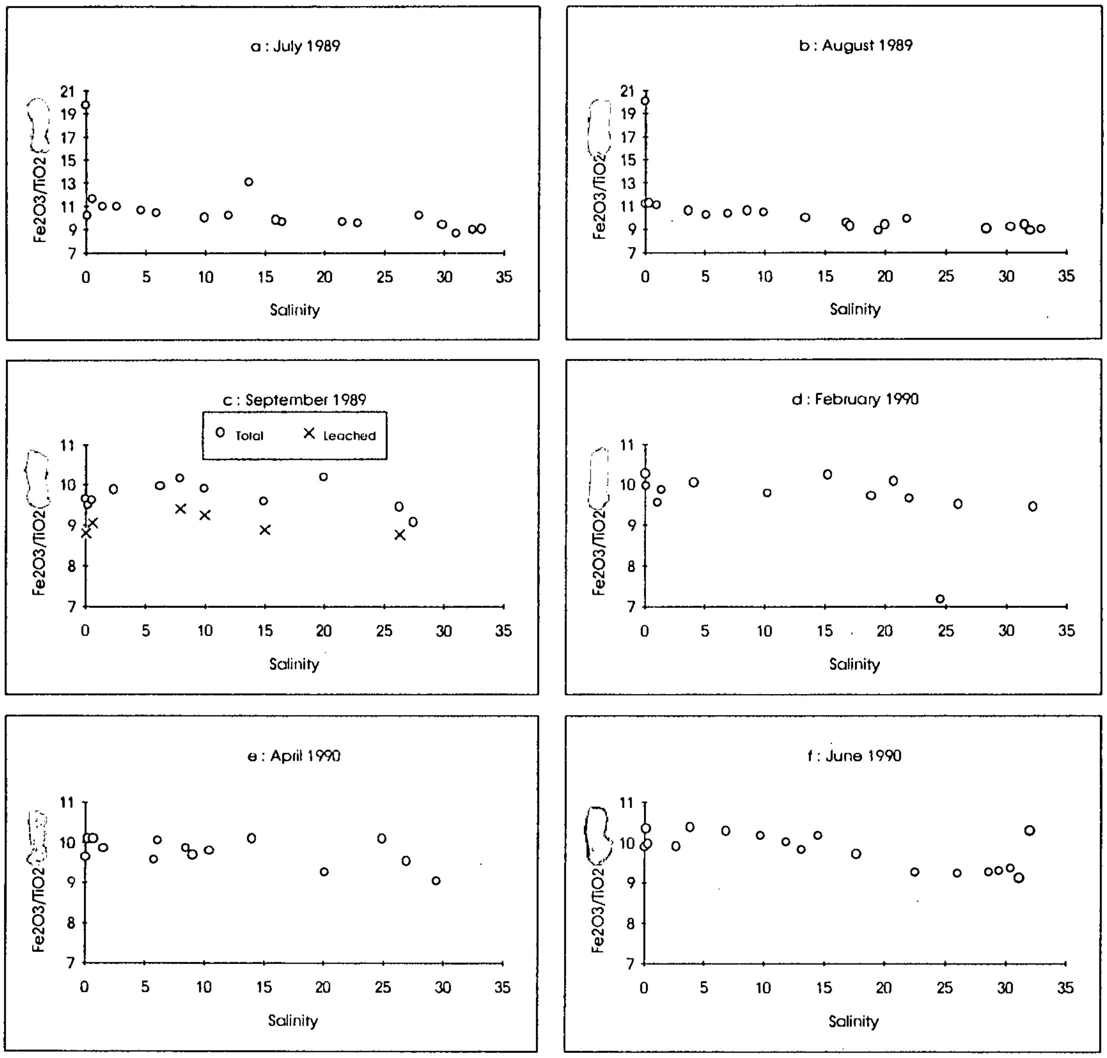


Figure 4.14. Suspended particulate Fe_2O_3/TiO_2 ratios against salinity in the Tay. a : July 1989, b : August 1989, c : September 1989, d : February 1990, e : April 1990 and f : June 1990.

NB. The "leached" values refer to the Fe_2O_3/TiO_2 ratios of the particles after leaching.

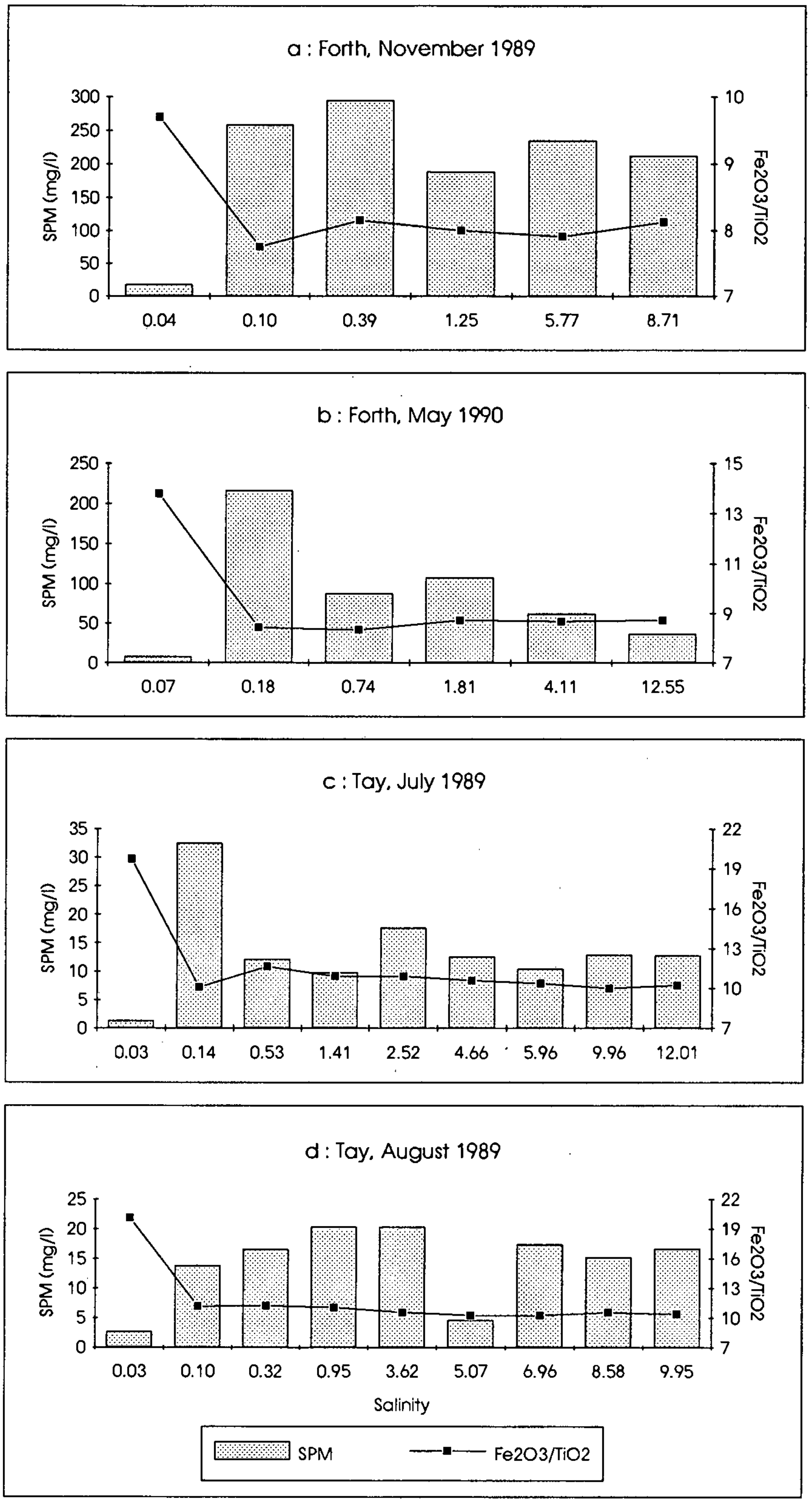


Figure 4.15. Variations in Fe_2O_3/TiO_2 ratios and SPM concentrations in the low salinity regions of the Forth and Tay. a : Forth November 1989, b : Forth May 1990, c : Tay July 1989 and d : Tay August 1989.

4.1.7: Manganese

The suspended particulate Mn results from the XRF analysis, HNO_3 digests and the acetic acid/hydroxylamine-hydrochloride leaching procedure are summarised in Figure 4.16. Results from the XRF analysis are consistently higher than those from the HNO_3 digests, while the leached particulate contents are lowest. This suggests that a proportion of the manganese may be associated with the non-detrital fraction of the particles. In the Seine river and estuary, for example, particulate Mn was associated with a) calcite lattices, b) Fe (III) oxides and c) organic matter (Boughriet *et al* 1992b).

Suspended particulate Mn contents are generally higher in the Tay than the Forth. This variation, like that for Fe, is attributed to the lower dissolved oxygen concentrations during some surveys of the Forth. Seasonal variations are observed in both estuaries, with higher average Mn concentrations occurring in summer. Non-parametric analysis of variance (HNO_3 data) indicates that the seasonal variations are significant ($P < 0.05$). Higher summer-time Mn concentrations have previously been observed in the river and estuary of the Rhine (Paalman and van der Weijden 1992, van der Weijden and Middelburg 1989) and the Humber and Scheldt estuaries (Turner *et al* 1991). They are attributed to increased concentrations of Mn (II), and the rapid oxidative precipitation of this species to Mn (IV) at higher water temperatures (see discussion, Section 3.2.3.1.2).

There are no significant ($P < 0.05$) relationships between suspended particulate Mn and Ti in the Forth or Tay. Instead Mn/Ti ratios vary considerably within each survey (Figures 4.17 and 4.18). The Mn/Ti ratio estimated for 'average' crustal material is 0.167 (Taylor 1964). The ratios in the winter surveys of the Forth are often lower than this value, and never exceed 0.3. (Depletion of Mn in suspended particulate matter has previously been observed in the 1-16 ‰ salinity region of the Hudson River estuary [Klinkhammer and

Bender 1981] though no reason has been given for this.) In the June and May surveys of the Forth Mn/Ti ratios increase to values of 1.5 and 0.5 respectively at salinities greater than 25 ‰ . Increases in suspended particulate Mn/Al ratios have been observed at salinities greater than 15 ‰ in the Seine estuary (Boughriet *et al* 1992a). They have been attributed to changes in the nature of the particles in the outer estuary. In the Forth, the increases in Mn contents coincide with decreases in Ti and Al. Since manganese is stable in calcite lattices (Boughriet *et al* 1992a, 1992b, Wartel *et al* 1990, 1991) these observations may, in part, be caused by the increases in suspended particulate CaO contents in the Forth (Section 4.1.3). Despite the greater importance of suspended particulate CaO in the outer Tay, coincident increases in Mn/Ti ratios are not observed here. The increases in the outer Forth may therefore partly be caused by the oxidation and precipitation of dissolved Mn. Such removal was suggested by the dissolved Mn budgets for the estuary (Section 3.2.8) and has previously been observed in the Scheldt (Duinker *et al* 1979a, 1982c), Yaquina (Callaway *et al* 1988) and Newport (Evans *et al* 1977) estuaries.

In the Tay, highest Mn/Ti ratios are observed in the riverine end-members (*eg* in July, August and September). Like those for Fe, and possibly for similar reasons (Section 4.1.7), the ratios fall in the low salinity high turbidity zones. Mid-estuarine increases in Mn/Ti ratios are observed in the September, February and June surveys of the Tay. They are attributed to oxidative removal of dissolved Mn from the water column. Such removal is not limited to the outer estuary, since dissolved oxygen concentrations remain high throughout the mixing zone of the Tay.

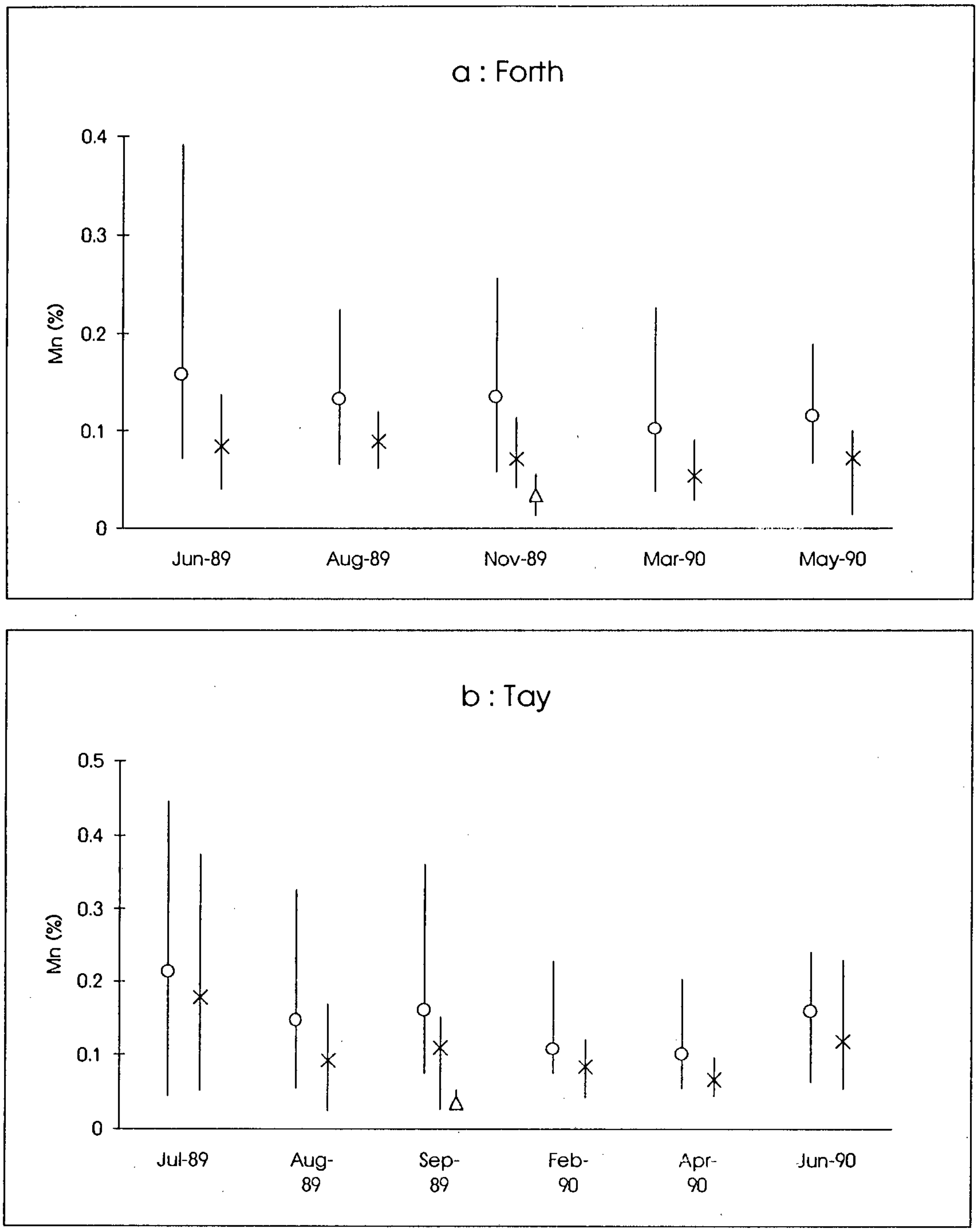


Figure 4.16. Suspended particulate Mn concentrations in each survey (minimum, maximum and mean). Circle = XRF data, star = HNO_3 data, triangle = leached data. a : Forth and b : Tay.

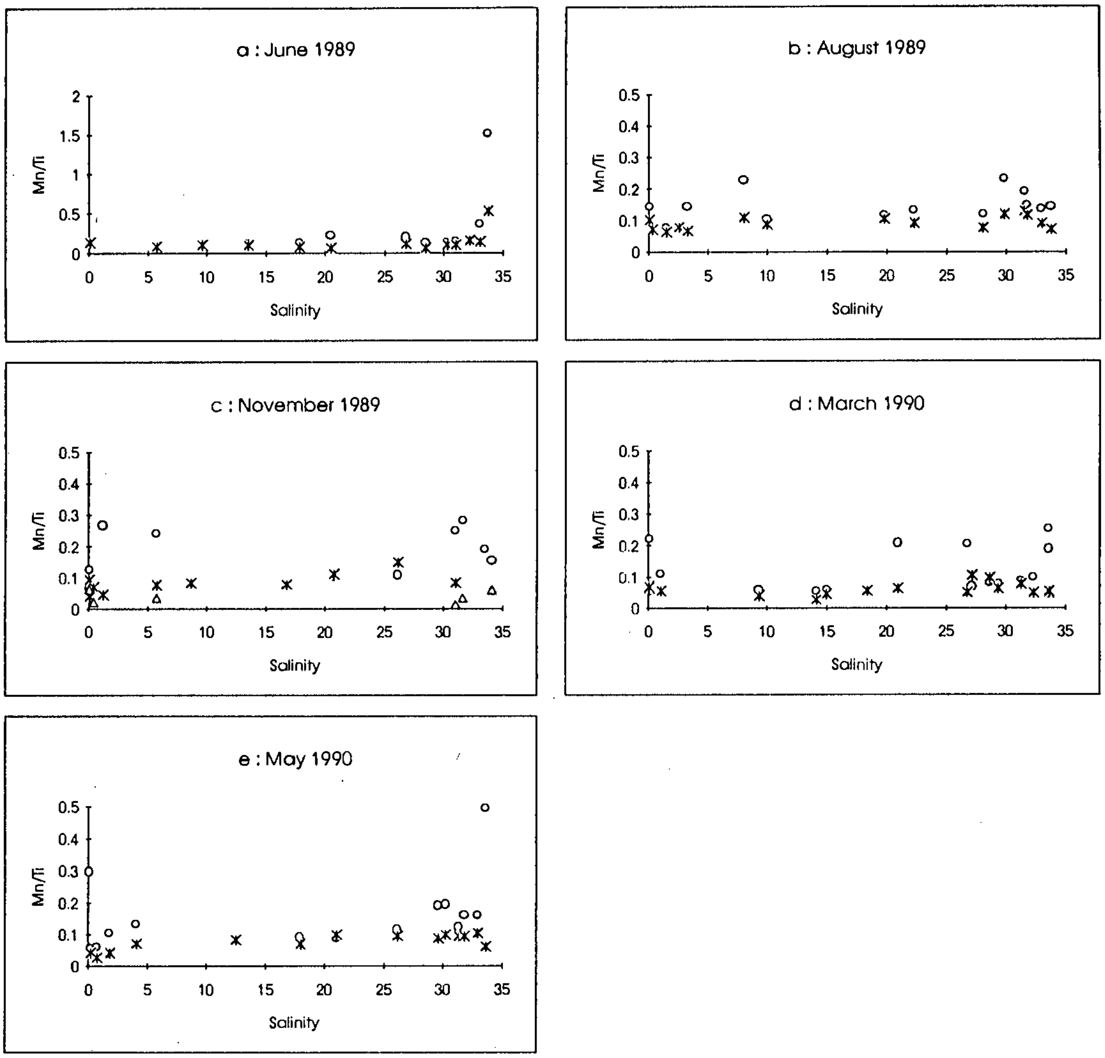


Figure 4.17. Suspended particulate Mn/Ti ratios against salinity in the Forth. Circle = XRF data, star = HNO_3 data, triangle = leached data. a : June 1989, b : August 1989, c : November 1989, d : March 1990 and e : May 1990.

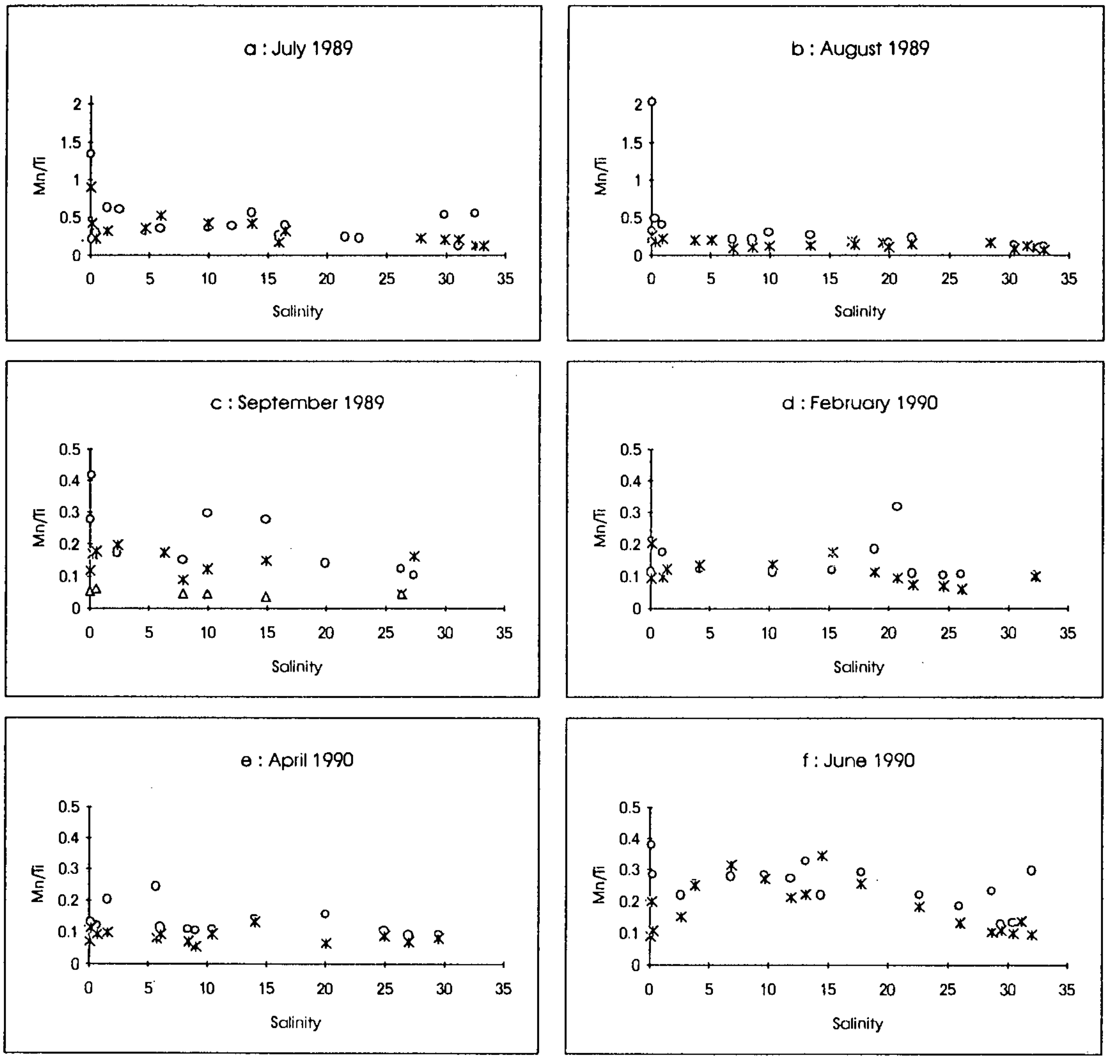


Figure 4.18. Suspended particulate Mn/Ti ratios against salinity in the Tay. Circle = XRF data, star = HNO_3 data, triangle = leached data. a : July 1989, b : August 1989, c : September 1989, d : February 1990, e : April 1990 and f : June 1990.

4.2: Trace elements

4.2.1: Suspended particulate trace metal contents

Results from the nitric acid SPM digests for the Forth and Tay are summarised in Tables 4.5 and 4.6 respectively.

Suspended particulate cadmium contents show significant seasonal variations (99% confidence) in both estuaries. The highest mean values occur in the June and July surveys of the Forth and Tay respectively. They are attributed to the binding of Cd to phytoplankton cells (Section 1.1.2.2). In the June survey of the Forth, for example, the increase in suspended particulate Cd contents in the outer estuary is accompanied by an increase in chlorophyll-a contents (Figure 4.19). Similarly, high suspended particulate Cd contents have been attributed to phytoplankton binding in the Rhine-Meuse (Golimowski *et al* 1990) and Scheldt (Valenta *et al* 1986) estuaries. This is discussed further in Section 4.2.2.1.

Average suspended particulate Cu contents are consistently higher in the Forth than in the Tay. This is attributed to the influence of anthropogenic Cu discharges in the Forth. Like those for dissolved Cu (Section 3.4.3), suspended particulate Cu profiles show clear peaks at distances ranging from 25 to 34km downstream from Stirling (Figure 4.20). The spring tidal excursion at Grangemouth (31km from Stirling) is about 10km (Forth River Purification Board 1978). The peaks in suspended particulate Cu are therefore attributed to inputs from industrial sources at Grangemouth.

Average suspended particulate trace metal concentrations tend to be lower in winter than in summer (*eg* Cu, Pb and Zn in the Forth; Zn in the Tay, $P < 0.10$). This variation may be caused by increased residence time of suspended particles during low flow periods, and by the increased scavenging of metals by the higher particulate Mn concentrations in summer (Section 4.1.7).

Table 4.5. Summary of suspended particulate trace metal contents (μgg^{-1}) in the Forth.

	Jun	Aug	Nov	Jan	Mar	May
<u>Cadmium</u>						
Minimum	0.37	0.10	0.02	0.04	0.05	0.08
Mean	3.13	0.48	1.11	0.40	0.61	0.67
Maximum	7.67	2.58	3.09	1.62	2.10	3.90
St. dev.	2.11	0.66	0.87	0.46	0.73	1.16
No. of obs.	15	13	13	13	17	13
Kruskal-Wallace test P=0.0001						
<u>Copper</u>						
Minimum	46	32	30	9	26	22
Mean	88	77	65	51	55	87
Maximum	135	104	146	149	145	267
St. dev.	25	24	27	34	29	61
No. of obs.	17	15	14	14	16	15
Kruskal-Wallace test P=0.0008						
<u>Nickel</u>						
Minimum	20	18	23	11	24	21
Mean	38	32	34	29	32	34
Maximum	68	45	56	45	43	71
St. dev.	12	8	10	9	8	12
No. of obs.	17	15	14	14	17	15
Kruskal-Wallace test P=0.3099						
<u>Lead</u>						
Minimum	43	62	50	3	64	5
Mean	105	86	83	65	85	85
Maximum	162	112	150	120	102	149
St. dev.	31	15	28	39	12	33
No. of obs.	17	15	14	14	17	15
Kruskal-Wallace test P=0.0225						
<u>Zinc</u>						
Minimum	120	80	74	52	83	79
Mean	182	137	153	128	156	130
Maximum	290	227	260	210	280	262
St. dev.	55	43	46	56	45	49
No. of obs.	17	15	14	14	17	15
Kruskal-Wallace test P=0.0607						

Table 4.6. Summary of suspended particulate trace metal contents (μgg^{-1}) in the Tay.

	Jul	Aug	Sep	Nov	Feb	Apr	Jun
Cadmium							
Minimum	0.49	0.10	0.20	0.10	0.13	0.18	0.02
Mean	1.63	0.75	0.47	1.02	0.46	0.56	0.44
Maximum	3.99	1.97	0.87	3.23	0.95	0.98	1.10
St. dev.	1.09	0.46	0.25	1.01	0.32	1.19	0.26
No. of obs.	14	20	10	17	11	14	18
Kruskal-Wallace test P=0.0006							
Copper							
Minimum	16	21	12	23	29	29	27
Mean	40	32	42	35	40	42	40
Maximum	95	53	133	51	57	65	71
St. dev.	22	8	33	8	7	12	13
No. of obs.	16	20	10	17	13	14	18
Kruskal-Wallace test P=0.0649							
Nickel							
Minimum	10	9	11	18	30	19	19
Mean	27	28	30	32	36	38	38
Maximum	47	56	48	44	53	58	63
St. dev.	10	11	10	9	9	12	15
No. of obs.	16	20	10	17	13	14	18
Kruskal-Wallace test P=0.0344							
Lead							
Minimum	21	18	33	36	47	51	53
Mean	73	65	67	63	61	70	68
Maximum	127	191	123	97	72	90	70
St. dev.	33	36	25	14	7	13	11
No. of obs.	16	20	10	17	13	14	18
Kruskal-Wallace test P=0.5376							
Zinc							
Minimum	75	115	74	53	63	66	80
Mean	203	181	131	143	154	154	184
Maximum	443	283	366	248	470	274	333
St. dev.	96	50	87	60	106	53	67
No. of obs.	16	20	10	17	13	14	18
Kruskal-Wallace test P=0.0179							

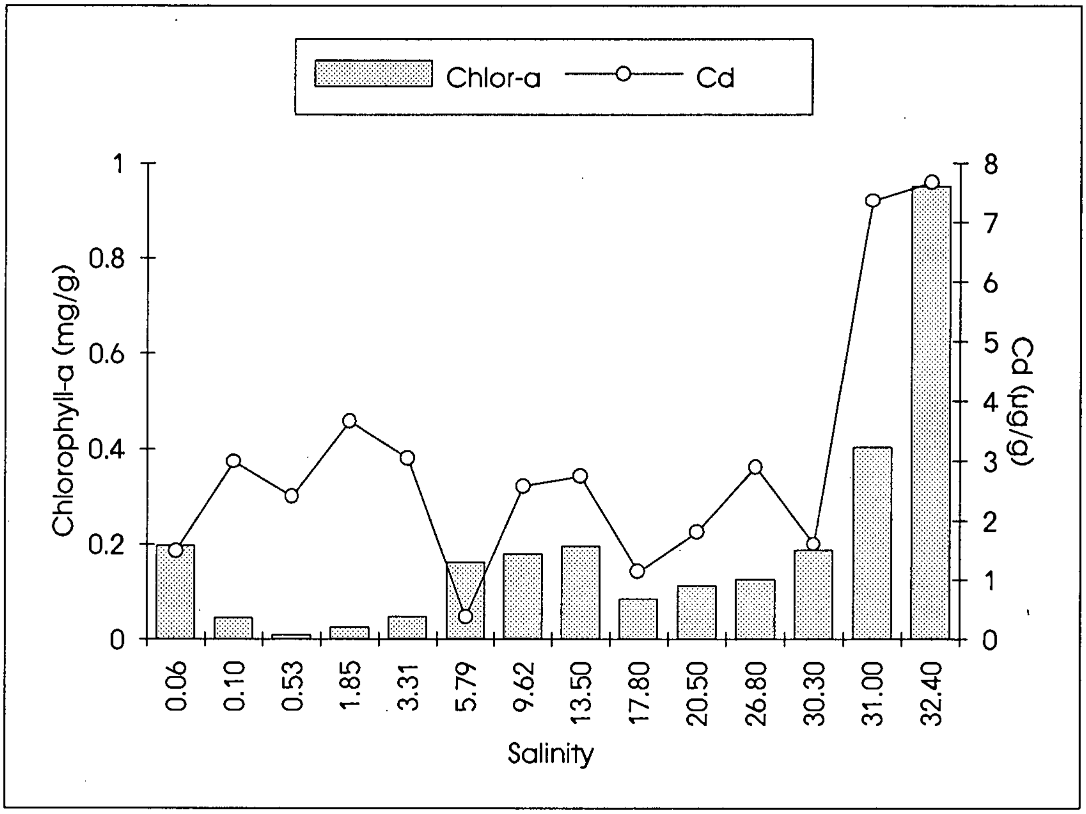


Figure 4.19. Suspended particulate Cd and chlorophyll-a contents in the Forth, June 1989.

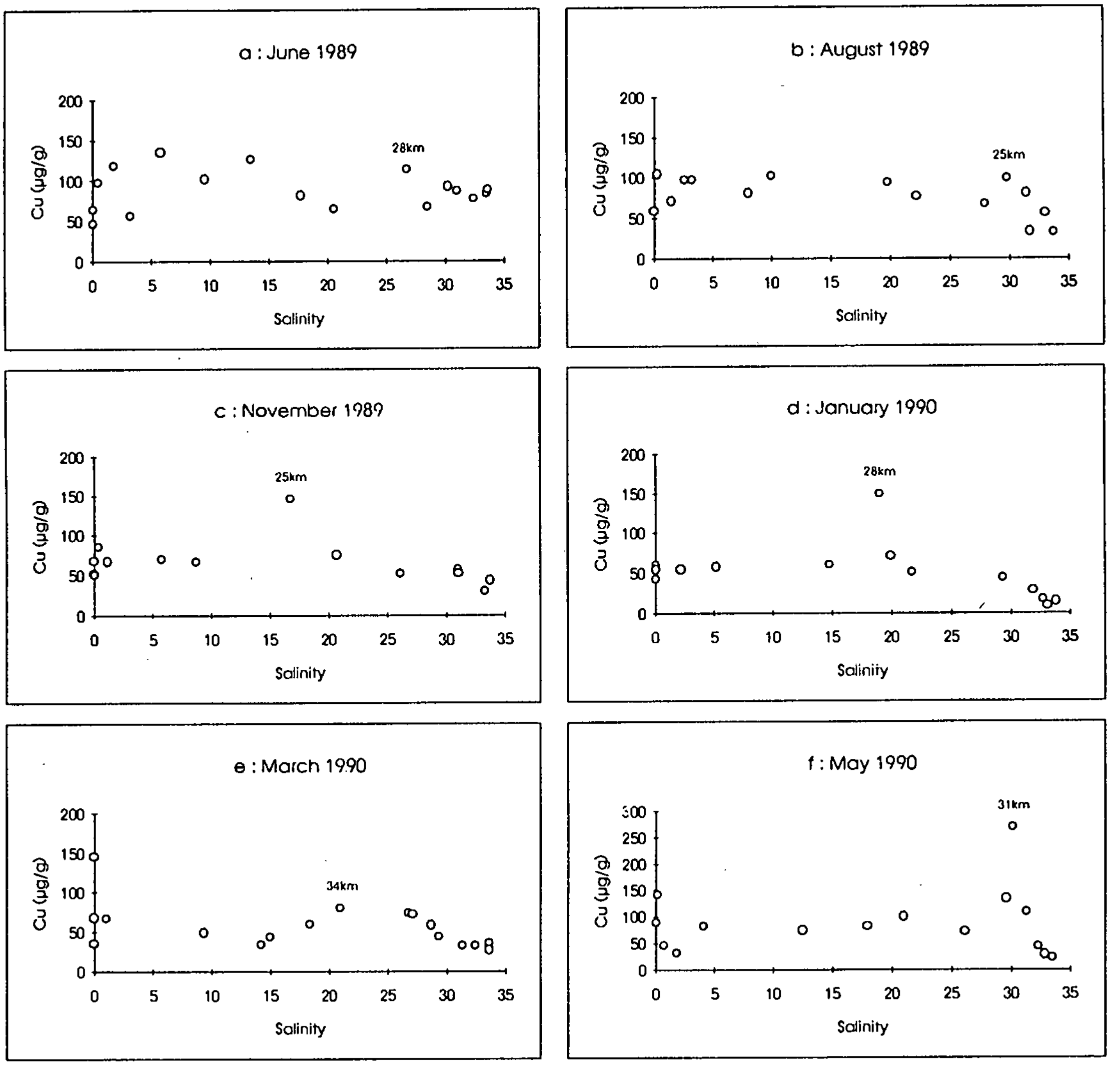


Figure 4.20. Suspended particulate Cu contents against salinity in the Forth.
a : June 1989, b : August 1989, c : November 1989,
d : January 1990, e : March 1990 and f : May 1990.

Forth tend to 'dilute' the anthropogenic metals entering the estuary. This may also explain why, at the top of the range, suspended particulate Pb and Zn contents in the less turbid Tay are greater than those in the Forth.

4.2.2: Trace element/aluminium ratios

Metal/Al ratios give an approximate indication of how enriched the suspended particles are, with respect to trace metals, over and above the detrital fraction (*eg* Klinkhammer and Bender 1981).

The overall ranges of Cd/Al, Cu/Al, Ni/Al, Pb/Al and Zn/Al presented here are compared with those in the literature in Table 4.8. They are summarised in Figures 4.21 and 4.22 for the Forth and Tay respectively. Ratios in this study are likely to be underestimated, since a partial HNO_3 digestion technique was used. The fraction of the metal content leached by HNO_3 is expected to vary from element to element, and from sample to sample. An intercomparison exercise has indicated that results from both HNO_3 and HF digestion techniques were comparable for Cd, Zn, and possibly Pb, but differed for Cu and Ni (Hovind and Skei 1992).

The ranges of the metal/Al ratios given in the literature span at least one order of magnitude for each element (Table 4.7). As expected, the lower end of the ranges for each metal in the Forth and Tay are below the values estimated for continental rock and riverine SPM. The Cd/Al relationships are discussed in Section 4.2.2.1 and those for the other elements in Section 4.2.2.2.

4.2.2.1: Cadmium

The upper ends of the Cd/Al ranges for all the estuaries are much higher than the value estimated for continental rock (Table 4.8). The Cd enrichment in the Rhine/Meuse estuary has been attributed to industrial or atmospheric inputs

(Paalman and van der Weijden 1992) and that in the Hudson to sewage discharges (Klinkhammer and Bender 1981).

Table 4.8. Comparison between suspended particulate metal/Al ratios in this study with those in other estuaries, riverine SPM and continental rock. A partial digestion technique was used in the present study. All other studies used total HF digestion or neutron activation analysis.
[a] This study, [b] Boughriet *et al* 1992a, [c] Paalman and van der Weijden 1992, [d] Vale 1990, [e] Klinkhammer and Bender 1981, [f] Martin and Whitfield 1983.

	Cd/Al (μgg^{-1})	Cu/Al (μgmg^{-1})	Ni/Al (μgmg^{-1})	Pb/Al (μgmg^{-1})	Zn/Al (μgmg^{-1})
Forth[a]	0.2-23.3	0.18-3.80	0.12-0.20	0.27-1.00	0.36-1.90
Tay[a]	1.7-93.0	0.21-1.58	0.14-1.04	0.36-0.52	0.60-13.47
Seine[b]					4.06-38.3
Rhine/Meuse[c]	100-300	0.60-2.20		1.0-3.0	5-17
Tagus[d]	20-40	0.4-1.2		0.70-4.0	3.4-8.1
Hudson[e]	10-170	0.5-7.0	0.1-1.7		1.0-9.0
Continental Rock[f]	2.9	0.46	0.71	0.23	1.83
Riverine SPM[f]		1.06	0.96	1.06	2.66

Like the Cd contents in the Forth and Tay, the Cd/Al ratios vary with season, being generally higher in summer than in winter (Figures 4.21 and 4.22). The affinity of Cd for biological particulate matter is well documented (Slauenwhite and Wangersky 1991, and references therein). It is therefore suggested that phytoplankton blooms are affecting the particulate Cd contents in the Forth and Tay. Evidence for this comes from examination of the Cd/P ratios in the estuaries, and comparison with those in biogenic and non-biogenic particulate matter (Table 4.9). Biogenic particles produced in nutrient-rich oceanic surface waters have Cd/P ratios of 0.4-0.7 x 10^{-3}. They are not dependent on the Cd/P ratios in the dissolved phase and have been attributed to "Redfield-like" ratios in phytoplankton (Collier and Edmond 1984). This ratio also appears

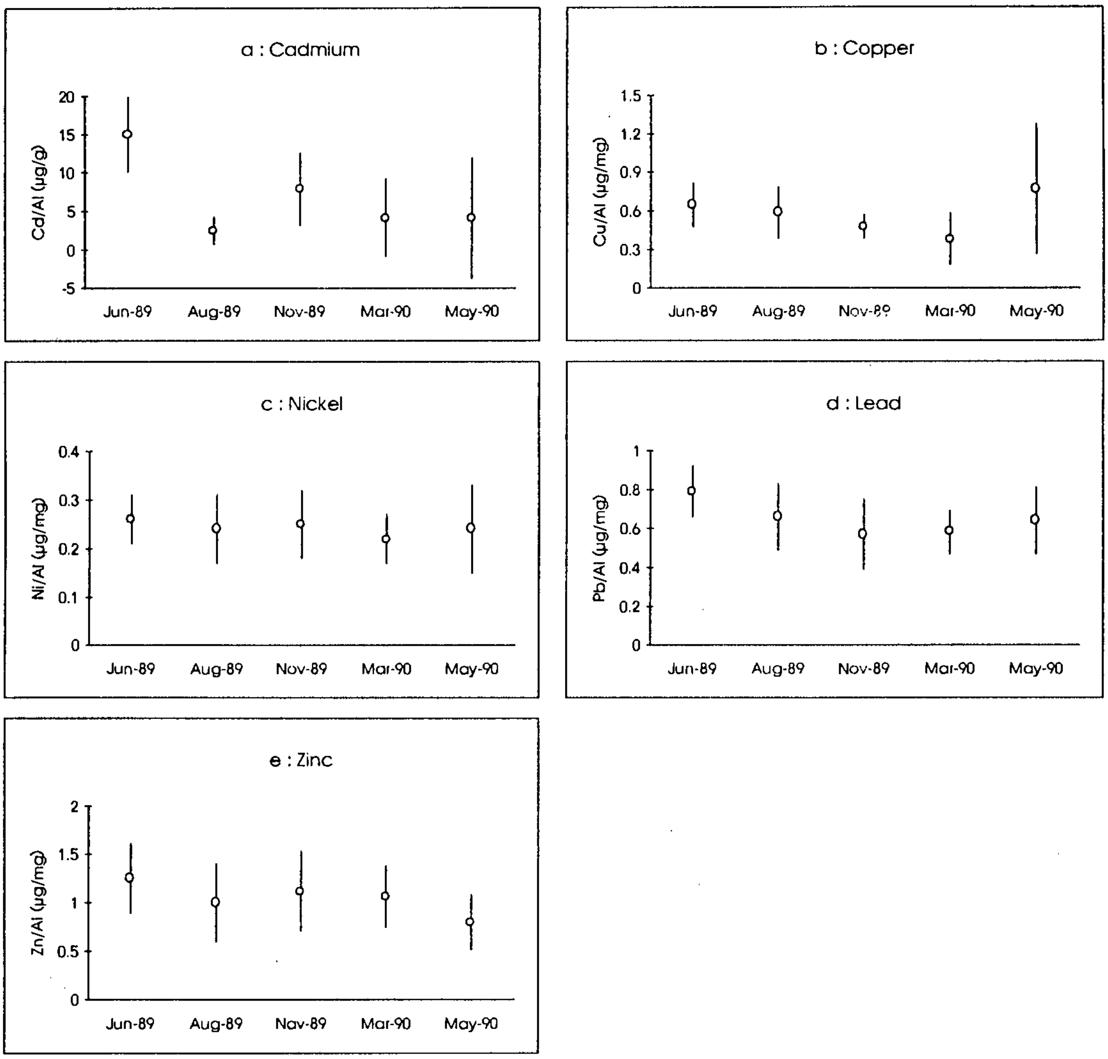


Figure 4.21. Means and standard deviations of metal/Al ratios in the Forth.
a : Cd, b : Cu, c : Ni, d : Pb and e : Zn.

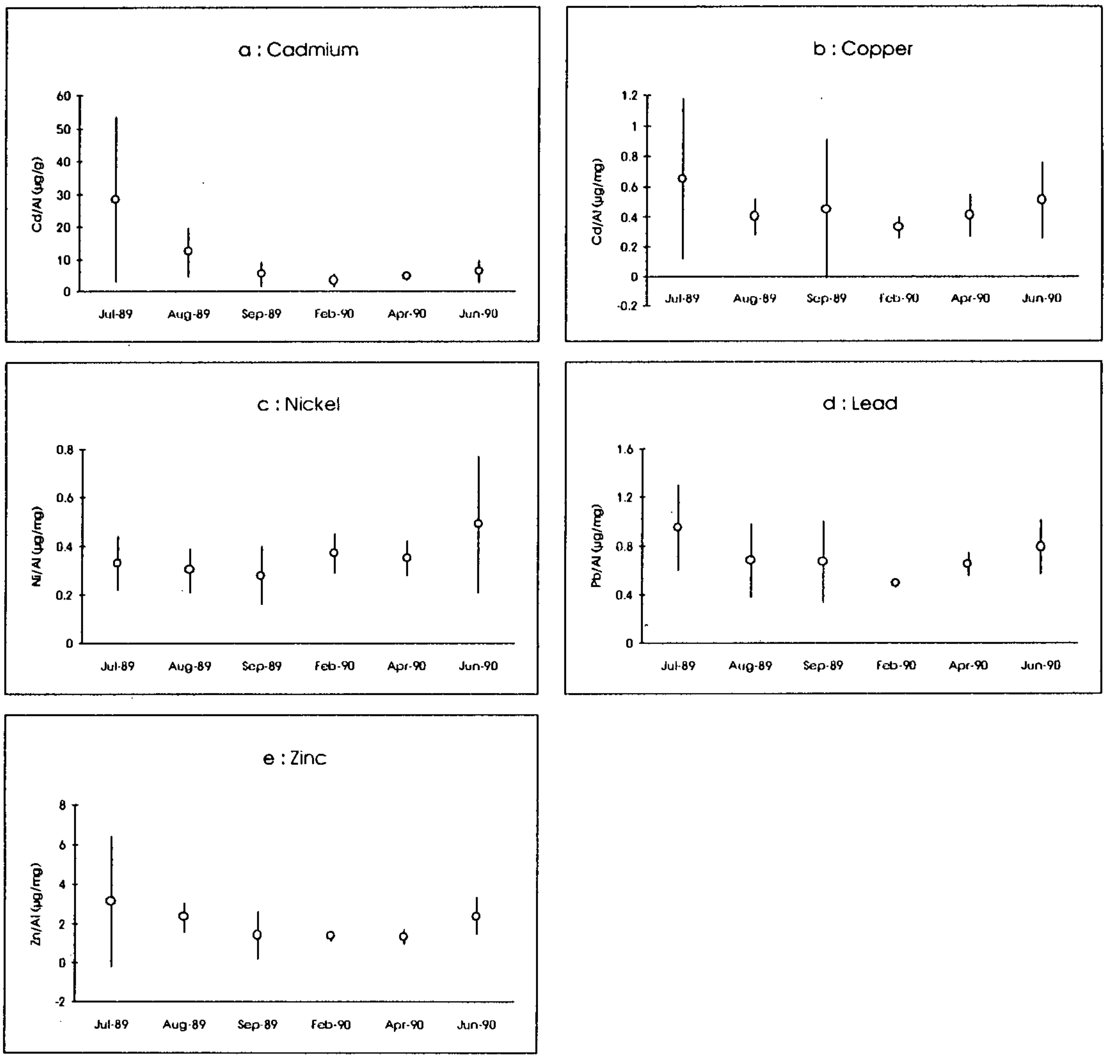


Figure 4.22. Means and standard deviations of metal/Al ratios in the Tay. a : Cd, b : Cu, c : Ni, d : Pb and e : Zn.

to apply to coastal phytoplankton. During a phytoplankton bloom in Funka Bay for example, a Cd/P ratio of 0.5×10^{-3} was observed (Noriki *et al* 1985). The high Cd/P ratios in the June and July surveys of the Forth and Tay are similar to these values. The ratios in the other surveys are more typical of non-biogenic particulate matter (Table 4.9).

Table 4.9. Cadmium/phosphorus ratios in marine SPM and continental rock.
n = number of observations

	Cd/P (10^{-3}) Mean (n)	Reference
Forth		Present study
June	0.51 (4)	
August	0.10 (7)	
November	0.48 (6)	
March	0.25 (17)	
May	0.03 (1)	
Tay		Present study
July	0.56 (10)	
August	0.27 (12)	
November	0.23 (7)	
February	0.18 (3)	
April	0.24 (4)	
June	0.24 (7)	
Funka Bay SPM (1m depth)		Noriki *et al* 1985
January	0.06 (1)	
February	0.06 (1)	
March	0.05 (4)	
May 6th	0.50 (1)	
May 19th	0.22 (1)	
Phytoplankton		Collier and Edmond 1984
Galapagos	0.89	
MANOP C	0.55	
MANOP S	0.66	
Detritus		Martin and Whitfield 1983
Continental rock	0.33	
Riverine SPM	0.17	
Deep sea clays	0.16	

4.2.2.2: Copper, nickel, lead and zinc

The upper ends of the estuarine Cu/Al, Zn/Al and Pb/Al ranges are greater than the average ratios in continental rock (Table 4.8). In the Forth, however, Ni/Al ratios are lower than the continental rock and riverine SPM values. Enrichments for these four metals in the Hudson and Rhine/Meuse estuaries are again attributed to anthropogenic inputs (Paalman and van der Weijden 1992, Klinkhammer and Bender 1981). Lower Zn/Al and Ni/Al ratios in the Forth may result from the partial leaching of these elements, as well as relatively low enrichment factors due to high suspended particulate loadings in the estuary.

The ratios of Cu/Al in the Forth, Zn/Al in the Tay and Pb/Al in both estuaries vary seasonally (Figures 4.21 and 4.22). Like those for Mn (Section 4.1.7), highest trace metal contents occur in summer. These variations may be attributed to the scavenging nature of Mn oxide coatings. Suspended particulate Pb, for example, has been shown to covary very closely with Mn oxide phases in the Rhine/Meuse estuary (Paalman and van der Weijden 1992). Like cadmium, nickel and zinc fall into the "biologically recycled" category of trace elements (Collier and Edmond 1984). Some of the enrichment of these elements during the summer surveys may therefore be biologically mediated. Because of the partial nature of the HNO_3 leaching procedure used here, however, it seems inappropriate to compare the Cu/P and Zn/P ratios obtained here with those in the literature.

4.2.3: Summary

The suspended particulate major element contents in this study are in general agreement with those reported in the literature.

Particulate organic carbon (POC) contents decrease with increasing SPM loading in both estuaries. The converse is true for Al_2O_3 contents. In the Tay, POC contents are lowest in winter when primary productivity is low. In the Forth, however, POC contents are lowest in summer when resuspension is most important. Suspended particulate Al_2O_3 contents in the Forth are higher than those in the Tay. This indicates that there is a greater proportion of fine-grained alumino-silicates in the lower-energy régime of the Forth.

The CaO contents in both estuaries increase with increasing salinity. The North Sea therefore acts as a source of $CaCO_3$ to the estuaries.

Positive SiO_2/Al_2O_3 intercepts in both estuaries indicate the presence of quartz. Higher SiO_2/Al_2O_3 and TiO_2/Al_2O_3 ratios in the Tay indicate that the suspended sediments are coarser here. This is consistent with the greater tidal velocities in the Tay. Higher K_2O/Al_2O_3 and MgO/Al_2O_3 ratios in the Tay indicate respectively that potassium feldspars and ferromagnesian silicates are more important in the Tay than the Forth.

Much of the suspended particulate phosphorus is associated with non-detrital phases in both estuaries. Highest non-detrital concentrations occur at low salinity during summer. They are attributed to the incorporation of phosphorus into particulate organic matter. In winter, excess concentrations remain low throughout the estuaries.

Lower particulate Fe and Mn contents in the Forth than the Tay are attributed to the lower dissolved oxygen concentrations in the Forth at certain times of the year. High Fe_2O_3/TiO_2 ratios at the river water end-members of both estuaries are attributed to the breakdown and subsequent precipitation of

Fe-containing colloidal material encountering saline waters. Lower suspended particulate Fe_2O_3/TiO_2 ratios in the turbidity maxima are attributed to the lower specific surface areas of the particles and their rapid deposition-resuspension cycling within this zone.

Higher summertime Mn contents in both estuaries are attributed to increased rates of precipitative oxidation at higher water temperatures. Mn/Ti ratios increase with increasing salinity in the summer surveys of the Forth. Such increases may be associated with (i) increases in suspended particulate CaO contents, and/or (ii) precipitative oxidation of Mn, as suggested by the dissolved Mn budgets for the estuary. Highest Mn/Ti ratios in the Tay are observed at the riverine end-members. Like those for Fe, these ratios decrease in the low salinity high turbidity zones.

Suspended particulate cadmium contents in both estuaries are higher in summer than in winter. This seasonality is attributed to the binding of Cd to phytoplankton cells. In the June survey of the Forth, for example, the increase in suspended particulate Cd contents in the outer estuary is accompanied by an increase in chlorophyll-a content. The Cd/P ratios in the summer surveys agree with those previously found in marine phytoplankton, while those in the other surveys are more typical of detrital material.

In general, suspended particulate trace metal contents are lower in winter than in summer. This variation may be caused by the increased scavenging of metals by the higher particulate Mn concentrations in summer. The ranges of metal concentrations in the Forth are often lower than those observed in other major estuaries. This may be because the high SPM concentrations of the Forth tend to 'dilute' the anthropogenic metals entering the estuary.

CHAPTER 5: PARTICLE-WATER INTERACTIONS

5.1: Introduction

This chapter uses partition coefficients to summarise the dissolved and suspended particulate trace metal data presented in Chapters 3 and 4. The calculation and use of partition coefficients has been discussed in Section 1.3. To reiterate, partition coefficients are the ratios of trace metal contents in the particulate phase to the concentrations in the dissolved phase. Since the coefficients range from about 10^3 to 10^7, they are conveniently expressed as $\log_{10} K_d$ values.

5.2: Results

The $\log_{10} K_d$ results in each data set (by metal, survey and estuary) were not normally distributed at the 99% confidence level (Shapiro-Wilk test, SAS Institute Inc. 1985). The non-parametric Kruskal-Wallis test was therefore used to analyse for differences between surveys and between estuaries. The partition coefficients and ANOVA results are summarised by survey in Tables 5.1 and 5.2 for the Forth and Tay respectively. Overall averages for each estuary are compared in Table 5.3.

Table 5.1. Summary of partition coefficients in the Forth.

	Jun	Aug	Nov	Jan	Mar	May
$\mathrm{Log}_{10}\ K_d$ Cd						
Minimum	4.53	3.41	3.08	3.23	3.61	3.28
Mean	5.29	4.18	4.74	3.99	4.42	4.14
Maximum	6.07	5.93	5.83	5.10	5.28	6.11
St. dev.	0.44	0.67	0.82	0.58	0.56	0.77
No. of obs.	14	13	13	13	16	13
Kruskal-Wallace test P > Chi-sq = 0.0001						
$\mathrm{Log}_{10}\ K_d$ Cu						
Minimum	4.48	4.44	4.49	4.31	4.61	4.21
Mean	4.89	4.72	4.75	4.73	4.85	4.72
Maximum	5.43	5.06	5.11	5.68	5.09	5.12
St. dev.	0.22	0.15	0.18	0.31	0.16	0.21
No. of obs.	17	15	14	14	16	15
Kruskal-Wallace test P > Chi-sq = 0.0335						
$\mathrm{Log}_{10}\ K_d$ Mn						
Minimum	3.64	4.26	4.31	4.07	3.75	3.80
Mean	4.68	4.90	4.84	4.43	4.59	4.75
Maximum	5.95	5.59	5.56	4.97	5.45	5.78
St. dev.	0.86	0.46	0.40	0.26	0.51	0.68
No. of obs.	17	15	14	14	17	15
Kruskal-Wallace test P > Chi-sq = 0.2163						
$\mathrm{Log}_{10}\ K_d$ Ni						
Minimum	4.33	4.23	4.55	4.51	4.60	4.32
Mean	4.66	4.58	4.74	4.66	4.80	4.64
Maximum	5.34	4.81	5.20	4.84	4.99	5.11
St. dev.	0.25	0.17	0.17	0.09	0.13	0.25
No. of obs.	17	15	14	14	17	15
Kruskal-Wallace test P > Chi-sq = 0.0159						
$\mathrm{Log}_{10}\ K_d$ Pb						
Minimum	5.30	5.58	5.27	4.70	5.54	5.14
Mean	6.01	5.89	5.72	5.85	5.96	5.99
Maximum	7.01	6.27	6.83	6.45	6.48	6.58
St. dev.	0.38	0.21	0.40	0.47	0.28	0.38
No. of obs.	17	15	14	14	17	15
Kruskal-Wallace test P > Chi-sq = 0.1241						
$\mathrm{Log}_{10}\ K_d$ Zn						
Minimum	4.54	4.37	4.38	4.29	4.37	4.32
Mean	4.95	4.84	4.86	4.66	4.98	4.94
Maximum	5.47	5.90	5.47	4.87	5.93	5.66
St. dev.	0.25	0.37	0.30	0.17	0.35	0.42
No. of obs.	16	15	14	13	17	15
Kruskal-Wallace test P > Chi-sq = 0.0522						

Table 5.2. Summary of partition coefficients in the Tay.

	Jul	Aug	Sep	Nov	Feb	Apr	Jun
Log_{10} K_d Cd							
Minimum	4.43	3.66	4.28	3.54	3.37	3.60	3.30
Mean	5.06	4.49	4.74	4.51	4.15	4.22	4.26
Maximum	5.71	5.60	5.32	5.27	4.61	4.89	4.65
St. dev.	0.40	0.61	0.38	0.51	0.36	0.36	0.32
No. of obs.	13	18	9	17	11	13	18
Kruskal-Wallace test P > Chi-sq = 0.0001							
Log_{10} K_d Cu							
Minimum	4.42	4.26	4.38	4.28	4.27	4.60	4.37
Mean	4.64	4.51	4.66	4.67	4.66	4.73	4.64
Maximum	5.00	4.90	5.34	5.08	5.11	4.85	5.05
St. dev.	0.18	0.15	0.28	0.20	0.22	0.09	0.19
No. of obs.	14	20	10	17	13	14	18
Kruskal-Wallace test P > Chi-sq = 0.0171							
Log_{10} K_d Mn							
Minimum	5.01	4.57	4.78	4.44	4.92	4.31	4.95
Mean	5.56	5.11	5.39	5.10	5.17	4.75	5.53
Maximum	6.05	5.44	6.02	5.55	5.58	5.39	6.05
St. dev.	0.36	0.21	0.34	0.34	0.19	0.34	0.38
No. of obs.	15	18	10	17	13	14	18
Kruskal-Wallace test P > Chi-sq = 0.0001							
Log_{10} K_d Ni							
Minimum	4.40	4.40	4.58	4.74	4.78	4.68	4.76
Mean	4.76	4.76	4.92	4.92	4.94	4.99	5.05
Maximum	5.15	5.01	5.13	5.17	5.14	5.26	6.05
St. dev.	0.24	0.14	0.16	0.12	0.12	0.19	0.38
No. of obs.	14	20	9	17	13	14	18
Kruskal-Wallace test P > Chi-sq = 0.0001							
Log_{10} K_d Pb							
Minimum	5.72	5.42	5.81	4.60	5.58	5.69	5.57
Mean	6.07	5.91	6.08	5.64	5.98	5.94	6.19
Maximum	6.95	6.32	6.41	6.54	6.45	6.14	7.15
St. dev.	0.31	0.24	0.22	0.58	0.24	0.13	0.36
No. of obs.	16	20	10	16	13	14	18
Kruskal-Wallace test P > Chi-sq = 0.0251							
Log_{10} K_d Zn							
Minimum	4.87	4.86	4.68	3.90	4.92	4.76	5.15
Mean	5.26	5.21	5.03	4.78	5.18	5.15	5.52
Maximum	5.67	6.06	5.54	5.35	5.54	5.66	6.31
St. dev.	0.24	0.28	0.22	0.48	0.19	0.24	0.28
No. of obs.	15	20	10	17	13	14	17
Kruskal-Wallace test P > Chi-sq = 0.0001							

5.2.1: Seasonal variations

There are significant ($P < 0.01$) seasonal variations in $\log_{10} K_d$ values for Cd in both estuaries. Values are highest in the June and July surveys of the Forth and Tay respectively. These variations are caused by the increased binding of Cd to phytoplankton cells during the summer months, as discussed in Section 4.2.2.1. Similar increases in the partition coefficients of Cd during phytoplankton bloom periods have been observed in the Rhine and Waal (Golimowski *et al* 1990) and Scheldt estuaries (Valenta *et al* 1986).

Significant variations in $\log_{10} K_d$ values between surveys are observed for Mn, Ni and Zn in the Tay, though not in the Forth.

For Ni, the partition coefficients increase throughout the study period in the Tay. The overall range of $\log_{10} K_d$ values for Ni (0.38) is the narrowest of all the elements. Although, therefore, the seasonal variation is statistically significant, it is not considered to be of practical importance or theoretical significance.

The average partition coefficient for Zn is particularly low in the November survey of the Tay. This low value is a result of the unusually high dissolved Zn concentrations from an unknown point-source in the upper estuary (Section 3.2.2). These results suggest that the dissolved Zn input is not yet at equilibrium with the suspended particulate phase.

The low mean $\log_{10} K_d$ value for Mn in the April survey of the Tay is a consequence of the higher dissolved Mn concentrations from non-point sources in this survey (Section 3.2.7).

There are no significant variations in $\log_{10} K_d$ values for Cu or Pb in either estuary at the 99% confidence level.

5.2.2: Variations between estuaries

Partition coefficients of Cd and Pb do not vary significantly (99% confidence) between the Forth and Tay (Table 5.3).

The $\log_{10} K_d$ values for Cu are significantly higher in the Forth than the Tay. Since Cu has a strong affinity for particulate organic carbon (*eg* Collier and Edmond 1984, Valenta *et al* 1986) this difference may be linked to the higher particulate organic carbon contents in the Forth (Section 4.1.2). There is, however, no simple linear relationship between $\log_{10} K_d$ Cu and POC contents.

Table 5.3. Analysis of variance for overall mean $\log_{10} K_d$ values in the Forth and Tay.

Estuary	Cd	Cu	Mn	Ni	Pb	Zn
Forth	4.47	4.78	4.70	4.68	5.91	4.88
Tay	4.48	4.64	5.23	4.90	5.97	5.16
Significance	0.4985	0.0001	0.0001	0.0001	0.0979	0.0001

Partition coefficients for Mn, Ni and Zn are higher in the Tay than the Forth. This is attributed to the greater rates of Mn oxidation caused by higher dissolved oxygen concentrations in the Tay. Nickel and zinc are, to some extent, associated with and trapped in the recycling pattern of Mn (Section 3.3).

The partition coefficients in the Forth and Tay decrease in the following order:

$$Pb > Mn, Zn > Ni > Cu > Cd$$

This is in general agreement with the patterns observed in other estuaries (Table 5.4).

Table 5.4. Comparison of $\log_{10} K_d$ values obtained in the Forth and Tay with those in other estuaries.

Area	$\log_{10} K_d$ Cd	$\log_{10} K_d$ Cu	$\log_{10} K_d$ Pb	Reference
Forth	3.08-6.11	4.21-5.68	5.14-7.01	This study
Tay	3.30-5.71	4.26-4.85	5.42-7.15	This study
Rhine	4.7-5.6	4.1-5.0	5.7-6.4	Golimowski *et al* 1990
Waal	4.4-5.7	3.7-5.3	5.8-6.8	Golimowski *et al* 1990
Maas	5.5-6.5	4.7-5.8	5.8-7.1	Golimowski *et al* 1990
Scheldt	3.7-5.0	4.4-5.3	5.6-6.6	Valenta *et al* 1986
Weser (means)	-	4.15	6.27	Turner *et al* 1992

Area	$\log_{10} K_d$ Ni	$\log_{10} K_d$ Zn	$\log_{10} K_d$ Mn	Reference
Forth	4.23-5.34	4.29-5.93	3.64-5.95	This study
Tay	4.40-4.78	3.90-6.31	4.31-6.05	This study
Seine	-	4.15-5.41	3.10-5.57	Boughriet *et al* 1992a
Rhine	-	4.0-5.2	-	Golimowski *et al* 1990
Waal	-	4.0-5.3	-	Golimowski *et al* 1990
Maas	-	4.9-5.4	-	Golimowski *et al* 1990
Weser (means)	4.29	4.77	6.23	Turner *et al* 1992

5.2.3: Relationships of partition coefficients with SPM and salinity.

5.2.3.1: Variation with SPM

Relationships between $\log_{10} K_d$s and SPM loadings have been discussed in Section 1.3.1.4. For the present data, best fit eye-drawn lines suggest possible decreases in the $\log_{10} K_d$s for Pb in the Forth and Cd in the Tay (see Figures 5.1 and 5.2 respectively).

Decreasing partition coefficients with increasing SPM loadings are common for particle-reactive elements (Balls 1989, Nevissi 1986) and have recently been observed for Pb in the Weser estuary (Turner *et al* 1992). In the

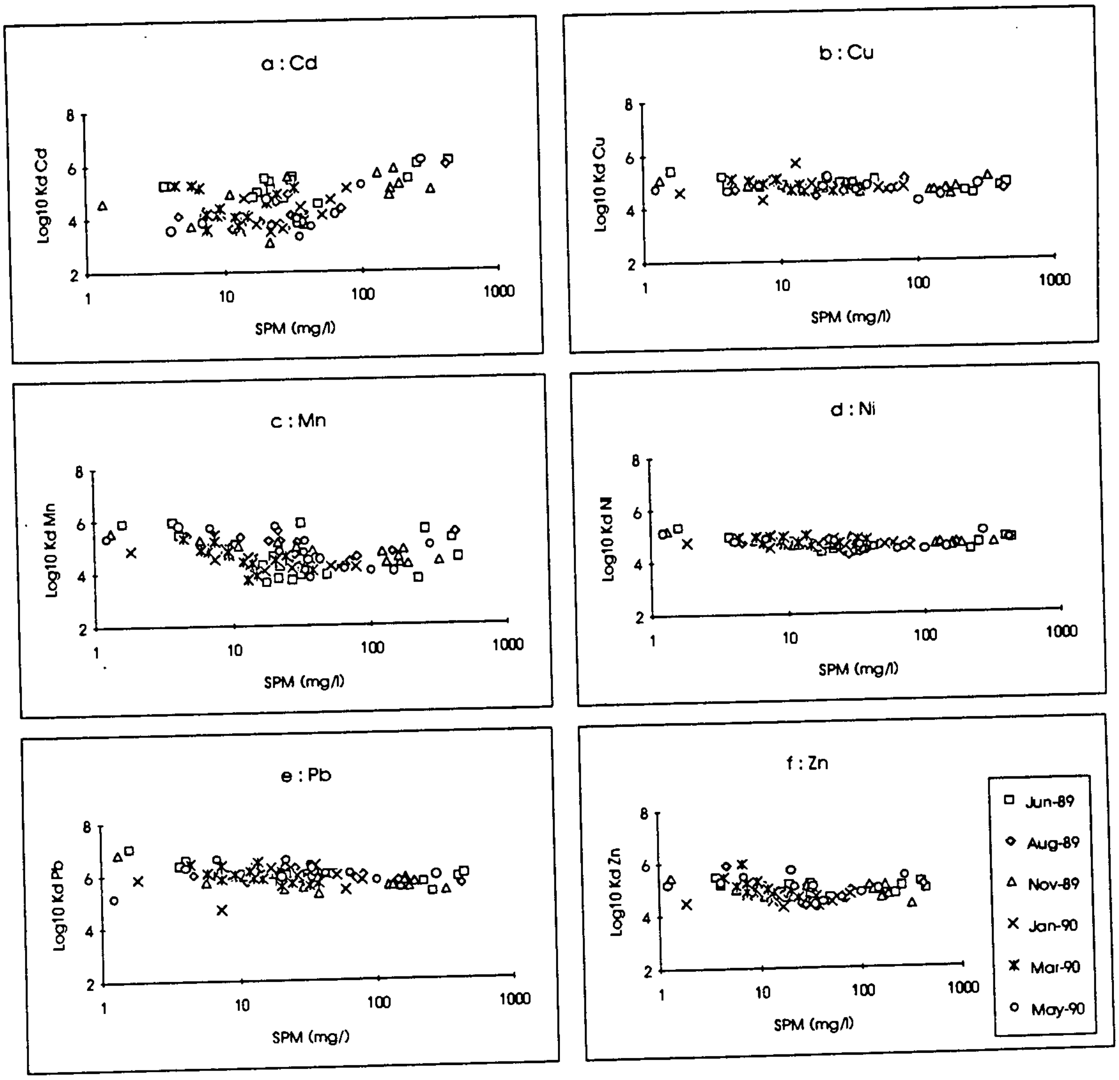


Figure 5.1. Relationships between partition coefficients and SPM in the Forth. a : Cadmium, b : Copper, c : Manganese, d : Nickel, e : Lead and f : Zinc.

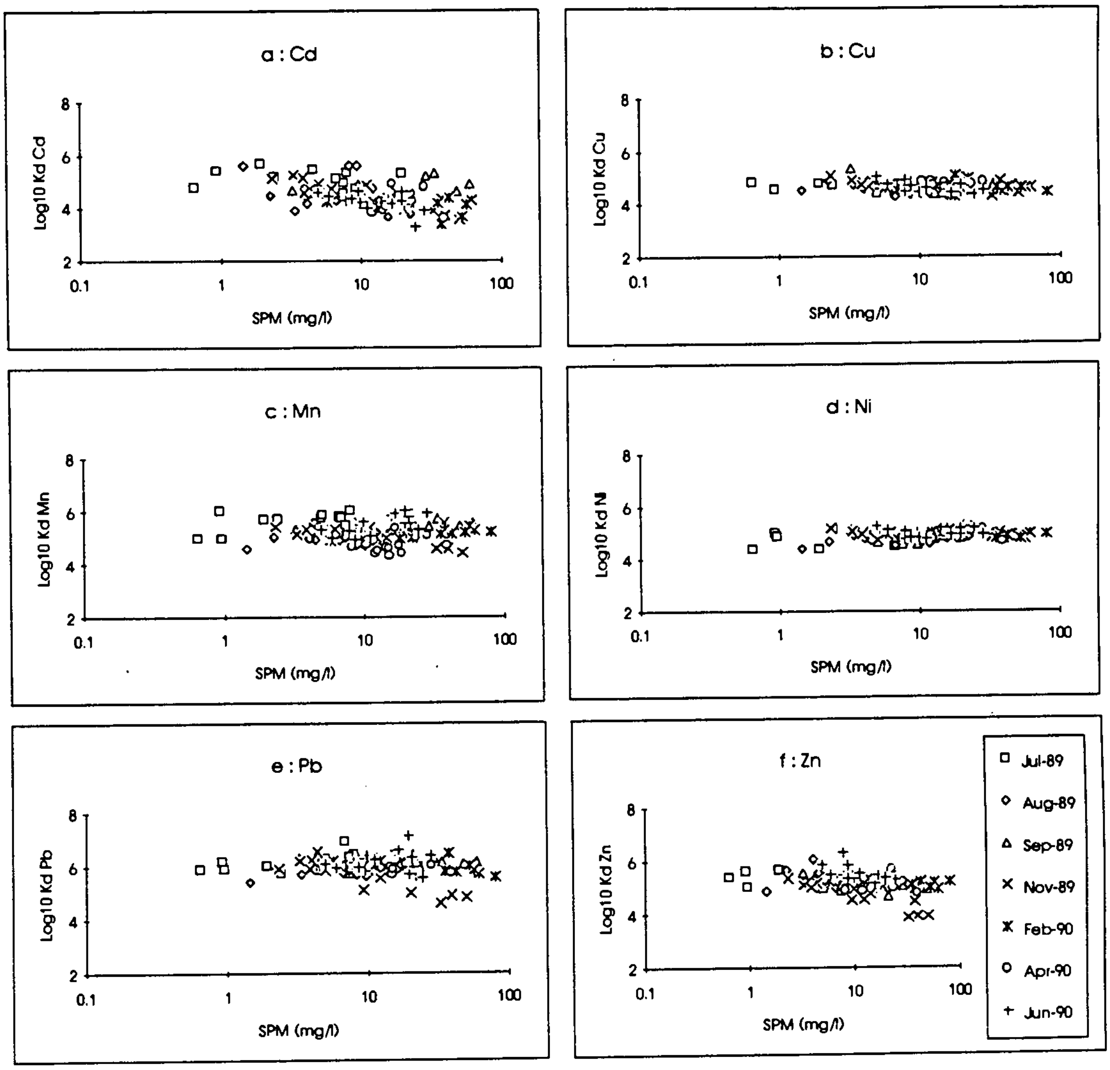


Figure 5.2. Relationships between partition coefficients and SPM in the Tay. a : Cadmium, b : Copper, c : Manganese, d : Nickel, e : Lead and f : Zinc.

Forth, the partition coefficient for Pb decreases by about one order of magnitude over an SPM range of three orders of magnitude. The extent of this variation agrees with the theoretical predictions of Duursma and Hoede (1967). No clear relationship is observed in the Tay because of the smaller range of SPM loadings and the scatter of the data.

For cadmium in the Tay, decreasing $\log_{10} K_d$ values with increasing SPM loadings result from the seasonality of this element (Section 5.2.1). Suspended particulate matter loadings in the Tay are lowest in summer when primary productivity is important. Partition coefficients are consequently high at low SPM loadings when a high proportion of the material is of biogenic origin. By contrast, in the Forth during summer when primary productivity is high and K_d values might be anticipated to be high, SPM loadings also tend to be at their greatest (Section 3.1.2). This combination of factors conceals any possible relationship between $\log_{10} K_d$ Cd values and SPM concentration in the Forth.

There are no clear relationships between $\log_{10} K_d$ and SPM for Mn, Ni, Zn and Cu in either estuary. Factors other than SPM concentration therefore dominate the partitioning behaviours of these elements.

Since the partition coefficients do not vary with SPM, increased particulate loadings must be balanced by removal of dissolved metals for partitioning equilibrium to be maintained. Such removal of Zn in the Forth was described by the adsorption model of Morris (1986) in Section 3.3.3.3. The model is now applied to Cd, Cu, Mn, Ni and Zn in the Tay. Lead is excluded since no removal was observed in the turbidity maximum for this element. Results are listed in Table 5.5.

There is evidence that the fraction of metal adsorbed on added particles relative to final equilibrium, α, is approximately equal to the acetic acid/ hydroxylamine-hydrochloride ($NH_2OH.HCl$ HOAc) leachable proportion (Turner *et al* 1992). No experimental data were obtained in the present study, but the predicted values for α (Table 5.5) are within the ranges of leachable Cd, Cu, Mn and Zn observed in other North Sea estuaries (Table 5.6). For Ni in the Tay, the model predicts that added particles are much closer to equilibrium than suggested by the $NH_2OH.HCl$ HOAc leachable Ni in the Scheldt or Weser estuaries. Either the assumption that α is approximately equal to the leachable proportion does not hold for Ni, or greater proportions of Ni would be leached by $NH_2OH.HCl$ HOAc in the Tay than in the Weser of Scheldt estuaries. More work needs to be done to examine this.

Table 5.5. Application of equilibrium adsorption model (Morris 1986) to trace metal removal in the Tay.
C = dissolved metal concentration in turbidity maximum, C_R = dissolved metal concentration in river water, K_d = partition coefficient, P_R = suspended load in the river water, P_S = additional suspended load in the turbidity maximum and α = fraction of exchangeable metal on the added particles relative to ultimate equilibrium. River water values are taken from Stations 0 in July and August, Station 5 in September and Station 15 in February. Turbidity maximum values are taken from Stations 3 in July, 5 and 6.5 in August, 15 and 17 in September and 20 and 22 in February.

	Survey	K_d	C (μgl^{-1})	C_R (μgl^{-1})	Measured C/C_R	P_R (mgl^{-1})	P_S (mgl^{-1})	Predicted α (%)
Cd	Jul	$10^{5.5}$	0.004	0.006	0.76	0.64	18.66	99
	Feb	$10^{4.4}$	0.011	0.020	0.55	16.70	50.27	73
Cu	Jul	$10^{4.8}$	0.51	0.73	0.70	0.64	18.66	99
	Feb	$10^{4.5}$	1.06	1.56	0.68	16.70	50.27	84
Mn	Jul	$10^{5.7}$	3.28	3.69	0.89	0.64	18.66	100
	Feb	$10^{5.2}$	5.29	6.36	0.83	16.70	50.27	93
Ni	Jul	$10^{4.8}$	0.37	0.62	0.60	0.64	18.66	98
	Feb	$10^{4.9}$	0.38	0.66	0.58	16.70	50.27	76
Zn	Jul	$10^{5.5}$	0.78	0.95	0.82	0.64	18.66	99
	Aug	$10^{5.2}$	1.09	2.37	0.46	1.45	7.37	77
	Sep	$10^{5.1}$	0.94	1.66	0.56	3.29	27.97	91
	Feb	$10^{5.1}$	1.01	1.39	0.72	16.70	50.27	88

For all five metals, the added particles are closer to equilibrium in July than in February. There are two possible reasons for this. Firstly, longer water residence times in summer (Section 3.1.4) are expected to allow adsorptive equilibrium to be approached more closely. Secondly, the adsorption model does not account for differences in the quality of particles (Turner *et al* 1993), so the seasonal difference may be an artefact of particle size. As resuspension becomes more important (in February) mean particle sizes increase and specific surface areas are likely to decrease. Particles with fewer adsorption sites are likely to have smaller concentrations of leachable metals.

In the Tay, (*eg* in February) the percentages of leachable metals follow the order: Mn > Zn > Cu > Ni > Cd. This is close to the order of decreasing partition coefficients (Section 5.2.2).

Table 5.6. Proportions of leachable metals on SPM in some North Sea estuaries.
[1] Turner 1990, [2] Turner *et al* 1992, [3] Duinker *et al* 1982a, [4] Duinker *et al* 1982b.
n = number of observations.

Estuary	n	Cd (%)	Cu (%)	Mn (%)	Ni (%)	Zn (%)	Method
Scheldt[1]	37		19	61	41	59	$NH_2OH.HCl$ HOAc
Weser[2]	14		27	85	28	60	$NH_2OH.HCl$ HOAc
Weser[3]	22	61-100	50-100	80-100		50-82	0.1N HCl
Elbe[4]	22	80-100	25-80	90-100		80-100	0.1N HCl

5.2.3.2: Variation with salinity

Relationships between $\log_{10} K_d$ values and salinity are illustrated in Figures 5.3 and 5.4 for the Forth and Tay respectively.

The partition coefficients for Cd in the Forth decrease with increasing salinity. This is attributed to the desorption of Cd as it forms chloro-complexes at high salinities (Section 3.5.1) and has been observed in mixing experiments using water from the Humber (Turner *et al* 1993). There is no clear decrease in $\log_{10} K_d$ values with increasing salinity in the Tay; the wide range of the values, resulting from the seasonality of the element, makes any variation with salinity difficult to see.

The relationship of $\log_{10} K_d$ Mn with salinity in the Forth has a pronounced 'U'-shape. The lower $\log_{10} K_d$ values in the mid-salinity zones are caused by the low dissolved oxygen concentrations at certain times of the year. Partition coefficients increase in the outer estuary as higher oxygen concentrations allow oxidative precipitation to proceed (Section 4.1.7). Similar increases have been observed at high salinity in water from the Humber (Turner *et al* 1993). The greatest increase in the partition coefficients occurs in June. This may be a consequence of increasing Mn oxidation rates at higher water temperatures. The $\log_{10} K_d$ values for Mn span three orders of magnitude in June, but less than one order in January.

The $\log_{10} K_d$ Ni and Zn relationships with salinity in the Forth are also slightly 'U'-shaped. This is a consequence of the association of these elements with manganese oxides (Section 3.3.3).

The ranges of $\log_{10} K_d$ values for Cu and Pb increase at salinities greater than 25 ‰ in the Forth. The increased ranges may be associated with inputs of Cu and Pb from industrial sources at Grangemouth, and suggest that the metals are not at partitioning equilibrium here. In the Tay, abnormally low $\log_{10} K_d$ values for Cd, Mn, Pb and Zn are observed at low salinity in November. These are a consequence of the high dissolved concentrations from an unknown transient source in the upper estuary (Section 3.2.2). The absence of any relationships between the $\log_{10} K_d$s for Cu, Mn, Ni, Pb and Zn with salinity in either estuary suggests that salinity is not an important control on the partitioning behaviours of these elements.

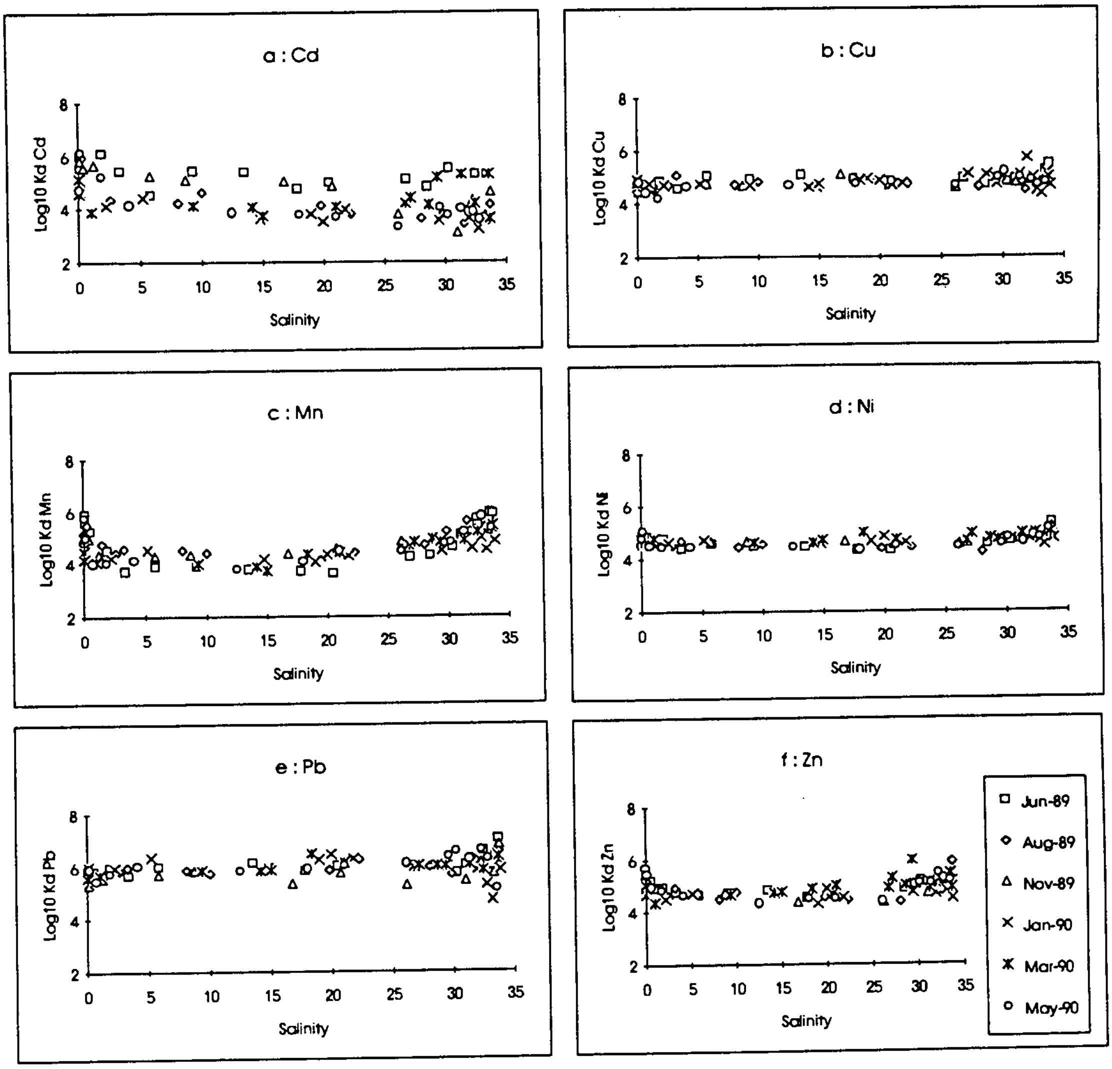


Figure 5.3. Relationships between partition coefficients and salinity in the Forth. a : Cadmium, b : Copper, c : Manganese, d : Nickel, e : Lead and f : Zinc.

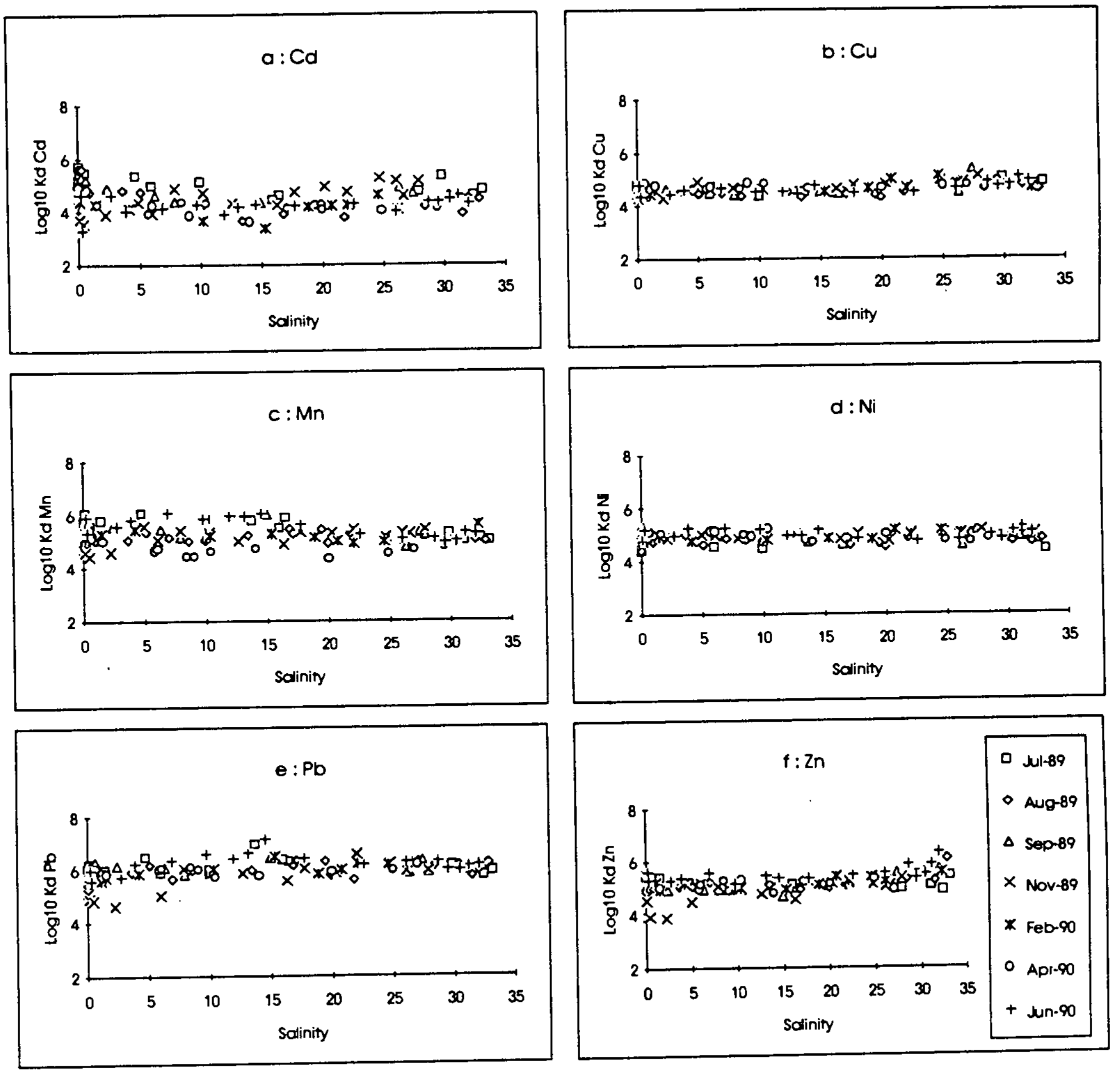


Figure 5.4. Relationships between partition coefficients and salinity in the Tay. a : Cadmium, b : Copper, c : Manganese, d : Nickel, e : Lead and f : Zinc.

5.3: Flux estimates

5.3.1: Calculations

5.3.1.1: Dissolved trace metals

The fluxes of dissolved metals entering the North Sea from the Forth and Tay are estimated using the method described in Section 3.2.6 (GESAMP 1987). Briefly, the theoretical zero salinity end-members (TZSEM), estimated from the dissolved metal profiles at high salinities, are multiplied by the fresh water flows.

To obtain an estimate of the annual average TZSEM for each metal, a single regression analysis was performed on the appropriate data for all surveys undertaken in each estuary. This method ignores any seasonal variations in the dissolved metal fluxes, which, for Mn, Ni and Zn, have been discussed in Sections 3.2.8 and 3.3.2. Since many of the metal/salinity profiles in the Forth showed mid-estuarine maxima centred around 15 °/₀₀ (Chapter 3), data at salinities greater than 20 °/₀₀ were used. Mid-estuarine maxima in the Tay were generally less pronounced, therefore data at salinities greater than 10 °/₀₀ were used. The regression equations are summarised in Table 5.7. The regression relationships are not statistically significant for dissolved Cd or Pb. This is because these data show considerable variability at higher salinities. Caution must therefore be taken when discussing the results of the flux calculations for these metals. The relationships for Cu, Mn, Ni and Zn are statistically significant at the 95% confidence level, giving more credence to these estimates.

The total fresh water flows during the sampling year were 1.82×10^{12} la^{-1} and 6.75×10^{12} la^{-1} for the Forth and Tay respectively (data from Forth River Purification Board and Tay River Purification Board). Calculated dissolved metal discharges are listed in Table 5.8.

Table 5.7. Regression analysis of dissolved metal vs salinity relationships in the outer Forth and Tay. For the Forth estuary, all results at salinities >20°/oo were used. Results at salinities >10°/oo were used for the Tay and the April data were omitted.

n = number of observations, C.I. = confidence interval, F = Forth, T = Tay.

	Metal	n	Intercept ($\mu g l^{-1}$)	95% C.I.	Slope	95% C.I.	Significance	Corr. Coeff.	R^2 %
F	Cd	44	0.038	0.016 to 0.060	-0.0004	-0.0011 to 0.0003	0.2398	0.18	3
T	Cd	55	0.023	0.008 to 0.038	0.0003	-0.0004 to 0.0009	0.4250	0.11	1
F	Cu	44	3.36	2.32 to 4.41	-0.080	-0.115 to -0.045	0.0000	0.58	34
T	Cu	55	1.16	0.97 to 1.35	-0.019	-0.027 to -0.011	0.0000	0.54	29
F	Mn	44	115	82 to 148	-3.42	-4.52 to -2.33	0.0000	0.68	49
T	Mn	50	3.18	1.63 to 4.73	0.069	0.003 to 0.134	0.0402	0.29	8
F	Ni	44	2.00	1.54 to 2.46	-0.046	-0.061 to -0.030	0.0000	0.68	46
T	Ni	54	0.52	0.44 to 0.61	-0.006	-0.009 to -0.003	0.0005	0.46	21
F	Pb	44	0.214	0.055 to 0.371	-0.004	-0.010 to 0.001	0.1106	0.24	6
T	Pb	57	0.069	0.037 to 0.100	-0.001	-0.002 to -0.001	0.4467	0.10	1
F	Zn	43	7.27	5.65 to 8.88	-0.171	-0.235 to -0.127	0.0000	0.73	53
T	Zn	56	1.69	1.25 to 2.13	-0.029	-0.046 to -0.011	0.0024	0.40	16

Table 5.8. Dissolved and suspended particulate trace metal fluxes entering the North Sea from the Forth and Tay estuaries.

TZSEM = theoretical zero salinity end-member concentration for dissolved metals
EMC = end-member concentration for particulate metals

	Cd	Cu	Mn	Ni	Pb	Zn
Forth dissolved						
TZSEM ($\mu g l^{-1}$)	0.038	3.4	120	2.0	0.21	7.3
Discharge ($t a^{-1}$)	0.07	6	200	4	0.4	10
Forth particulate						
EMC ($\mu g g^{-1}$)	1.5	70	580	30	80	150
Discharge ($t a^{-1}$)	0.3	10	100	6	15	30
Tay dissolved						
TZSEM ($\mu g l^{-1}$)	0.023	1.2	3.2	0.52	0.069	1.7
Discharge ($t a^{-1}$)	0.2	8	20	4	0.5	10
Tay particulate						
EMC ($\mu g g^{-1}$)	0.7	40	1100	30	70	180
Discharge ($t a^{-1}$)	1.2	70	1900	50	120	300

5.3.1.2: Suspended particulate trace metals

The suspended particulate trace metal fluxes leaving the Forth and Tay are estimated using the method of Turner *et al* (1991). Briefly, the suspended particulate metal contents at the fresh water end-members are combined with the rate of supply of SPM to the estuaries. Two assumptions are made. Firstly, it is assumed that the amount of sediment entering the estuary from riverine sources leaves the estuary by natural circulation and/or dredging processes. The calculations would therefore not take into account any particles produced by primary productivity within the mixing zones. These uncertainties are, however, considered to be negligible when compared with the greater approximations associated with the calculation. The second assumption is that solid/solution processes have negligible overall effects on suspended particulate metal contents. The data presented here show that SPM composition does not vary greatly within each estuary, so this assumption generally holds. Although particulate Mn contents increase in the outer Forth as a result of precipitative oxidation (Section 4.1.7) and effects of Cu inputs are observed in the particulate phase at Grangemouth (Section 4.2.1), the particulate metal contents change by less than an order of magnitude in each case.

End-member particulate metal contents for each estuary are estimated by averaging results at <0.2 °/₀₀ salinity obtained throughout the year. The masses of particulate material entering the Forth and Tay estuaries are 0.19×10^6 ta^{-1} and 1.72×10^6 ta^{-1} respectively (McManus 1986). Results are listed in Table 5.8.

5.3.2: Discussion

The annual average dissolved Ni and Zn discharges for the Forth are within the ranges of those given in Section 3.3.2, *ie* 0.8-9.9ta^{-1} and 2.3-86.3ta^{-1} respectively. The average discharges for Mn, however, appear to be overestimated for the Forth, since the discharges calculated for separate surveys range from 0.2-78ta^{-1} (Section 3.2.8). This is attributed to a bias in the average TZSEM towards higher concentrations, a consequence of more frequent summer than winter surveys. Summer surveys represent essentially atypical and extreme conditions relative to the generally higher flow rates associated with the rest of the year. In the Tay, the TZSEMs do not show such wide variability. In consequence, the annual average estimate presented here is within the range of discharges given previously, namely 4.85-93ta^{-1}. It was not possible to refine these calculations further by estimating the fluxes from individual surveys, since data on the daily riverine SPM discharge were not available.

The partitioning behaviour of Cd is consistent between the Forth and Tay; about five times as much Cd is discharged in the particulate phases as the dissolved phases. For the other five metals, however, affinities for the particulate phases are greater in the Tay than the Forth. This is particularly true for Mn. The amount of dissolved Mn discharged from the Forth is of the same order as that discharged in the suspended particulate phase. In the Tay, however, the particulate phase is 200 times more important than the dissolved phase. This marked difference is caused by the response of the element to differing redox conditions, and has been a constant theme throughout the thesis.

The greater affinities of Ni, Zn, Pb and Cu for the particulate phases in the Tay than the Forth result from the scavenging behaviour of particulate Mn oxides.

The relative contributions of the dissolved and suspended particulate trace metals from each estuary are illustrated in Figure 5.5. The Forth and Tay discharge approximately equal amounts of dissolved Cd, Cu, Ni, Pb and Zn to the North Sea, though the Forth is the greater source of dissolved Mn. Particulate discharges of all six elements are 4 to 19 times more important in the Tay than the Forth. The greater overall input of metals from the Tay reflects its larger catchment area. Similar relationships between catchment area and particulate metal discharge have previously been observed for other North Sea estuaries (Turner *et al* 1991). The discharges calculated here are not directly comparable with those obtained previously, since Turner *et al* (1991) used a weaker leaching agent. The fluxes presented here therefore seem high when compared with those of the other estuaries (Table 5.9).

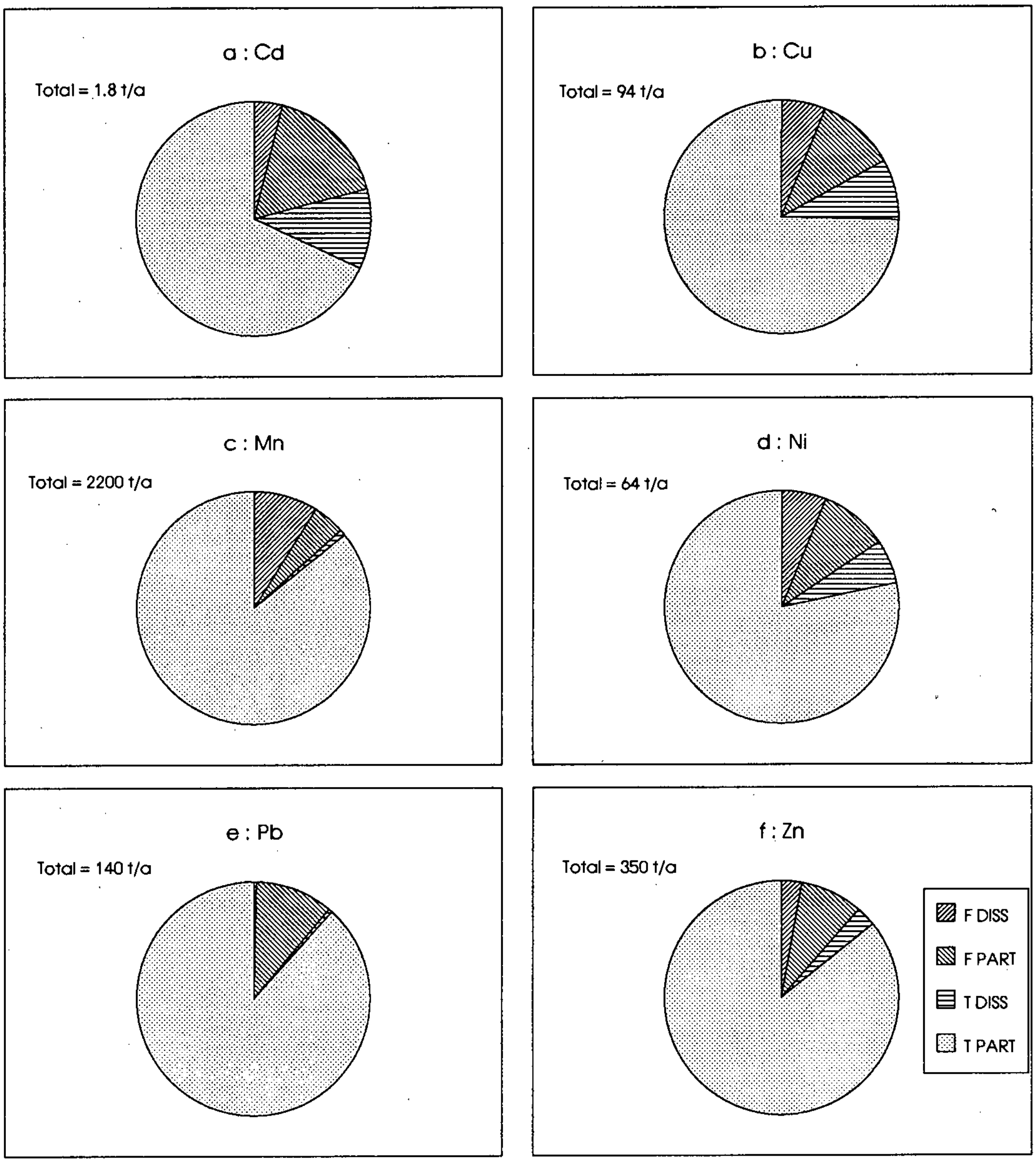


Figure 5.5. Relative dissolved and suspended particulate trace metal fluxes from the Forth and Tay into the North Sea. F = Forth, T = Tay, DISS = dissolved and PART = particulate. a : Cd, b : Cu, c : Mn, d : Ni, e : Pb and f : Zn.

Table 5.9. Particulate metal discharges from North Sea estuaries
[a] Turner *et al* 1991 (weak leaching agent), [b] Present study (strong leaching agent), [c] West 1972, [d] Leatherland 1987, [e] Maitland and Smith 1987.

Estuary	Catchment Area (km^2)	Mean river flow (m^3s^{-1})	Cu flux (ta^{-1})	Mn flux (ta^{-1})	Ni flux (ta^{-1})	Pb flux (ta^{-1})	Zn flux (ta^{-1})
[a]Elbe	148,500	726	13	2,000	20	40	390
[a]Weser	44,304	326	8	1,200	7	15	150
[a]Humber	27,000	246	10	200	4	7	60
[a]Scheldt	21,580	100	4	60	4	6	80
[a]Thames	9,900	82	3	70	3	6	50
[b]Tay	[c]7,500	[e]200	70	1,900	50	120	300
[b]Forth	[d]4,655	[d]60	10	100	6	15	30

5.4: Particle-water interactions - summary of main conclusions

There are significant seasonal variations in $\log_{10} K_d$ values for Cd in both estuaries. Higher values during the June and July surveys are caused by an increase in the proportion of biogenic material, and the affinity of Cd for phytoplankton cells.

Significantly higher $\log_{10} K_d$ values for Cu in the Forth than the Tay are attributed to the higher POC contents in the Forth. Higher partition coefficients for Mn, Ni and Zn in the Tay are attributed to the greater rates of Mn oxidation and precipitation, and the subsequent scavenging of Ni and Zn, a consequence of higher dissolved oxygen concentrations.

The order of decreasing partition coefficients, Pb > Mn, Zn > Ni > Cu > Cd, is similar in the Forth and Tay to those observed in other estuaries.

The partition coefficients for Pb in the Forth decrease with increasing SPM loadings. Similar findings are reported in the literature. Partition coefficients for Cd in the Tay are high at low SPM loadings because these coincide with the peak phytoplankton bloom periods. No other clear relationships between K_d and SPM are observed in the Forth or Tay.

To maintain partitioning equilibrium, metals must be removed from solution as SPM concentrations increase. This redistribution can be used in an adsorption model to calculate the proportion of metals on the added SPM relative to ultimate equilibrium (Morris 1986). For Cd, Cu, Mn and Zn in the Tay, this estimated proportion is similar to the leachable fractions observed in other North Sea estuaries.

The adsorption model also indicates that particles are closer to equilibrium in July than in February. This may partly be a consequence of longer water residence times in summer. Since resuspension is more important in February, particles are likely to be coarser and have lower specific surface areas. Such particles are likely to have smaller concentrations of leachable metals.

The calculated percentages of leachable metals on SPM in the Tay follow the order of decreasing partition coefficients.

In the Forth, $\log_{10} K_d$ Cd values decrease with increasing salinity. This is attributed to the desorption of Cd as it forms soluble chloro-complexes at higher salinities. The relationship of $\log_{10} K_d$ Mn with salinity is 'U'-shaped in the Forth. Lower $\log_{10} K_d$ values in the mid-salinity zones are a consequence of low dissolved oxygen concentrations at certain times of the year. Increases in the outer estuary are caused by the oxidative precipitation of Mn. This is most important during summer. The $\log_{10} K_d$ Ni and Zn relationships with salinity in the Forth are also slightly 'U'-shaped. This is probably a result of the association of these elements with manganese oxides.

Fluxes of dissolved and suspended particulate metals discharged by the Forth and Tay estuaries have been estimated. Each estuary discharges about five times as much Cd in the particulate phase as the dissolved phase. The affinities of Cu, Mn, Ni, Pb and Zn for the particulate phases are greater in the Tay than the Forth. This is attributed to the greater importance of Mn oxides in the Tay.

The Forth and Tay discharge approximately equal amounts of dissolved Cd, Cu, Ni, Pb and Zn. Particulate discharges of all six elements are 4 to 19 times more important in the Tay than the Forth. Overall, the Tay is the greater source of trace metals to the North Sea, and this reflects the larger catchment area of the estuary.

CHAPTER 6: CONCLUDING DISCUSSIONS

The estuarine biogeochemistries of six trace elements have been examined. Two adjacent, contrasting estuaries were selected so that the effects of riverine discharge, hydrodynamic régime and particulate phase composition could be assessed. Sampling throughout an annual cycle enabled seasonal differences in primary productivity and meteorological conditions to be included. Simultaneous nutrient determinations and fresh water flow measurements were used to help interpret the metal data. Determination of metal concentrations in both suspended particulate and dissolved phases enabled the partitioning behaviour of each metal to be examined.

The contrasting trace metal behaviours in the Forth and Tay are summarised in Section 6.1. Implications for the transport of dissolved and particulate metals from the two estuaries to the North Sea are discussed in Section 6.2. Suggestions for future work are given in Section 6.3.

6.1: Partitioning behaviour of the elements

The possible interchanges of trace metals between dissolved and particulate phases in estuarine environments are summarised in Figure 6.1 (master model). Not all elements will undergo every process, and different processes will dominate the behaviour of each element according to its particular biogeochemistry. The master model is used as a basis for summarising the contrasting behaviours of the metals studied in the Forth and Tay. All observed processes are given, though some are seasonal and others occur only in parts of an estuary. Anthropogenic inputs are included if their effects are observed in

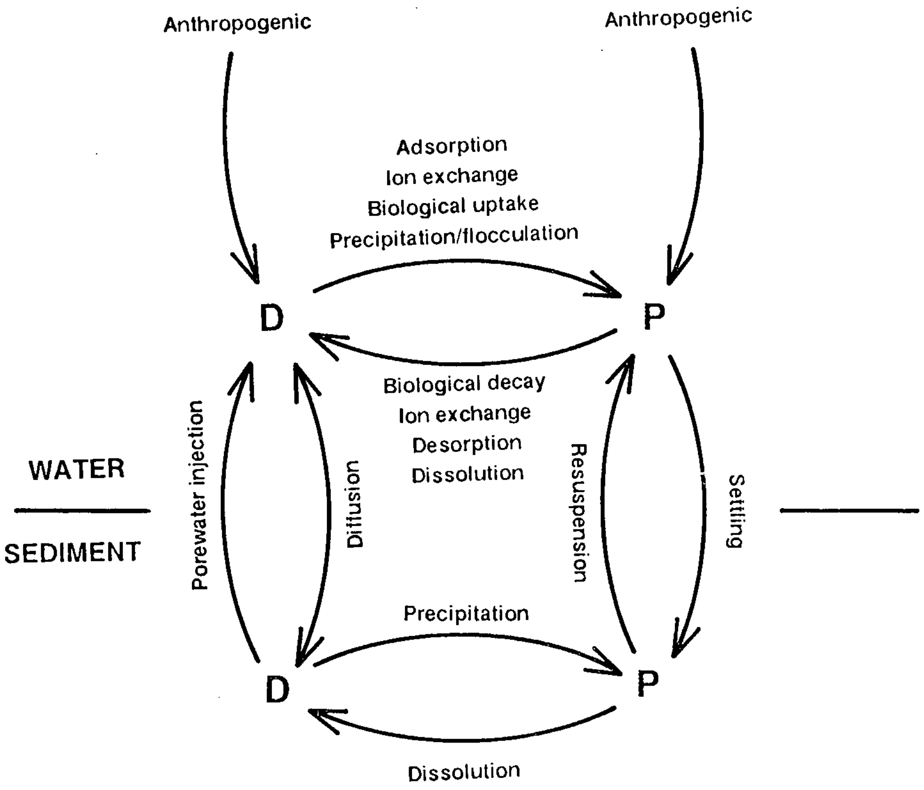


Figure 6.1. Metal partitioning processes in estuarine environments - master model.

either phase. Interchanges within the sediments, where given, are inferred, since no data were collected here.

6.1.1: Manganese, nickel and zinc

The behaviours of Mn, Ni and Zn in the Forth and Tay are linked. They are represented together in Figure 6.2a. Each process is discussed separately below.

The cycling between particulate and dissolved phases within the sediments is inferred from the wide mid-estuarine maxima in dissolved Mn, Ni and Zn distributions. The inputs to the water column from the sediments are a consequence of the remobilisation of Mn oxides, and associated elements, in sub-oxic conditions. This is most important during summer when particulate organic inputs (carbon and nitrogen) and water temperatures are high.

The mechanisms whereby dissolved Mn, Ni and Zn enter the water column are diffusion and/or sediment resuspension and pore water injection into the water column. Calculations presented in this study indicate that benthic Mn fluxes ($\mu g\ cm^{-2}\ d^{-1}$) are highest in the upper Forth estuary in early summer. They coincide with pronounced oxygen minima but are further downstream than the turbidity maxima. These benthic fluxes are therefore dominated by diffusional processes. High sediment inputs are also observed in January, when anoxic conditions are less important and water temperatures are lower. In January, fluxes of Mn, Ni and Zn into the water column are attributed to sediment resuspension associated with turbidity maxima. Similar processes may operate in the Tay, where anoxic conditions are less prevalent. Since inputs caused by sediment resuspension are not limited to the small-area upper estuary, they are more important than diffusional fluxes for the overall input of dissolved Mn, Ni and Zn to the water column.

In the water column, there are two mechanisms whereby dissolved Mn, Ni and Zn can be removed to the particulate phase. Adsorption in the turbidity maximum zone is observed in the Forth and Tay, but only for some of the elements on some occasions. Oxidative Mn precipitation and scavenging of Ni and Zn appears to be the more important process, since it occurs over larger areas of the estuaries. Large-scale removal of dissolved Mn from the water column was theoretically predicted from the dissolved profiles in each estuary. Calculated benthic Mn fluxes were consistently greater than dissolved Mn discharges from each estuary. The 'lost' Mn was attributed to removal by oxidative precipitation onto suspended particulate material. Rates of Mn oxidation increase with higher oxygen concentrations and water temperatures. Particulate Mn contents, and partition coefficients, are therefore higher in summer than winter, and higher in the well-oxygenated Tay than the Forth. Removal of dissolved Mn, indicated by increasing partition coefficients, is most important in the outer Forth during summer. Many of the above observations are also true for Ni and Zn in the Forth, since they are scavenged from the dissolved phase by newly formed particulate Mn oxides.

In the Tay, dissolved Ni and Zn peaks generally coincide with those of ammonia and phosphate. They are attributed to sewage discharges from Dundee. Large dissolved Mn and Ni peaks in the low salinity zone of the November survey of the Tay are attributed to a transient input of unknown origin. Anthropogenic inputs therefore influence the dissolved Ni and Zn profiles in the Tay. Calculations suggest that inputs of Ni and Zn to the water column of the Forth are sometimes greater than can be explained by Mn remobilisation. These excesses are also attributed to anthropogenic inputs.

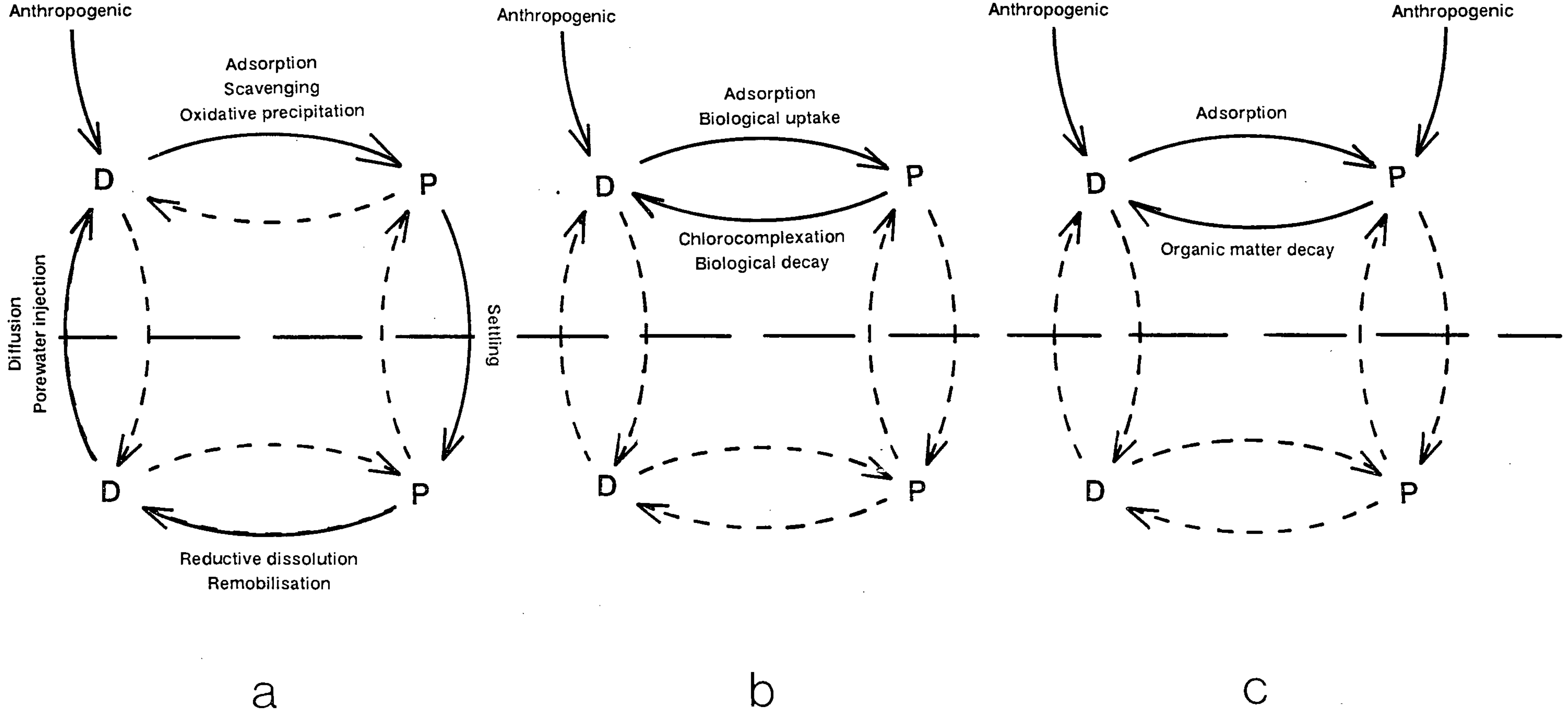


Figure 6.2. Partitioning behaviours of trace metals in the Forth and Tay. a : Mn, Ni and Zn, b : Cd and c : Cu.

6.1.2: Cadmium

Although cadmium is the least particle reactive of the elements studied, two processes cause its removal from the dissolved phase in the water column (Figure 6.2b). Firstly, adsorption is observed in the turbidity maximum zones of the July and February surveys of the Tay. Secondly, incorporation into newly produced biogenic particles during summer results in higher particulate cadmium contents and K_ds in both estuaries. Particulate Cd/P ratios during summer are similar to those of marine phytoplankton. At other times of the year ratios are more typical of detrital material.

There are two mechanisms for the remobilisation of cadmium from particulate to dissolved phases. Firstly, Cd is released during the decay of biogenic particulate matter. Such release is suggested by constant dissolved Cd/P ratios during the summer surveys of the Forth and Tay. The second, and more important, process is that of chloro-complexation. This is observed during most surveys of the Forth and Tay. The strong soluble complexes formed with Cl^- ions at high ionic strengths cause dissolved Cd concentrations to increase, and K_ds to decrease, with increasing salinity.

Anthropogenic inputs of dissolved Cd are observed in the outer Tay. Like those for Ni and Zn, they are attributed to sewage discharges from Dundee.

6.1.3: Copper

The cycling of copper is illustrated in Figure 6.2c. In the water column, Cu is removed from the dissolved to the suspended particulate phase by adsorption. This is observed in the turbidity maxima of the February and June surveys of the Tay. Like cadmium, copper is remobilised from particulate to dissolved phases by the decay of particulate organic matter, evidenced by the occurrence of nitrification. Dissolved Cu peaks coincide with nutrient peaks in the low salinity zones of many Forth surveys, and the summer/autumn surveys of the Tay.

Anthropogenic inputs influence the Cu profiles of each estuary. In the Forth, inputs from industrial sources at Grangemouth result in increased variability in Cu K_ds at high salinities. Anthropogenic effects are clearly seen in the metal/salinity profiles of both phases. In the Tay, dissolved Cu peaks in the outer estuary are attributed to wastewater discharges from Dundee. Large dissolved Cu peaks are also observed at low salinity in the November survey, though the source of this feature is unknown.

6.1.4: Lead

Only about 5% of the lead is present in the dissolved phase. It is therefore difficult to detect any changes in the partitioning behaviour of this element. Anthropogenic inputs do, however, influence the dissolved Pb profiles in each estuary. In the Forth, inputs from industrial sources at Grangemouth result in increased variability in Pb K_ds at high salinities. In the Tay, effects of anthropogenic discharges are observed in the dissolved phase at Dundee, and at low salinity in the November survey.

6.2: Fluxes

The partitioning behaviour of trace metals in estuarine environments affects their ultimate fates. The contrasting characteristics of the Forth and Tay estuaries result in more subtle variations on the basic partitioning behaviour of individual metals. To illustrate, partition coefficients in both estuaries decrease in the order Pb > Mn, Zn > Ni > Cu > Cd. The greater oxygen concentrations in the Tay cause many of the partition coefficients to be higher in this estuary than in the Forth. Since these increases are not constant for all elements, the ratios of dissolved to particulate metals discharged from each estuary vary.

The effects of these differences are particularly pronounced for Mn. The Forth discharges about twice as much Mn in the dissolved phase as the particulate phase, while the Tay discharges 200 times more Mn in the particulate phase than the dissolved phase. Although the Forth and Tay discharge approximately equal amounts of dissolved Cd, Cu, Ni, Pb and Zn to the North Sea, particulate discharges from the Tay are greater than those from the Forth by factors of 4 for Cd, 7 for Cu, 8 for Ni and Pb, 10 for Zn and 19 for Mn. The Tay is therefore the greater overall source of these metals to the North Sea. This reflects the larger catchment area of the estuary.

The fluxes presented in this study suggest that the combined metal discharges from the Forth and Tay are approximately 2, 90, 2000, 60, 100 and 350 tonnes per year for Cd, Cu, Mn, Ni, Pb and Zn respectively.

6.3: Suggestions for future work

This project demonstrates the need for simultaneous determinations of nutrient and major particulate element concentrations, as well as flushing dynamics, to fully interpret dissolved trace metal data from estuaries. The importance of sampling throughout a whole year is also demonstrated, since a number of seasonal factors affect metal geochemistries. Future estuarine research would therefore usefully be conducted along similar lines.

I would recommend, however, that both total (HF soluble) and leachable particulate metal contents be determined. Total digestion techniques have a number of advantages over the HNO_3 digestion procedure used here. Firstly, the data obtained are directly comparable with those from other studies using total methods of analysis. Secondly it enables certified reference materials to be used for analytical quality control purposes. Inclusion of reference materials with each batch would give an indication of the analytical variability encountered. Thirdly, since HF techniques attack the mineral lattices, unambiguous trace metal/Al ratios can be obtained on the same digest. It must be stated, however, that this technique would substantially increase the time required for particulate metal analysis by furnace atomic absorption spectrometry. Not only would the number of elements per batch be increased (involving about a day per element per batch) but analysis of, say, Al and Cd on the same digest would require time-consuming dilutions of the sample. Matrix problems are also greater for HF digests. Some of these problems would be overcome if an inductively-coupled plasma mass spectrometer were available. This rapid technique would reduce the time required for analysis and, since the dynamic range of the instrument is larger, would minimise the requirement for dilutions. The lower detection limits of the instrument would allow samples to be diluted to reduce matrix problems.

I would recommend the use of the hydroxylammonium-hydrochloride leaching procedure for the trace elements, as well as the major elements. This would allow direct analysis of the non-detrital (Fe/Mn-oxide, carbonate, or organic) metals in the particulate materials.

It would also be instructive to examine the rôle of colloidal material, in particular colloidal organic carbon, in estuarine metal partitioning behaviour. Experimental evidence suggests that colloidal material acts as an intermediate step during the adsorption of metals onto suspended particulate material. Higher concentrations of colloidal material would therefore be expected to speed adsorption reactions (Honeyman and Santschi 1989). While some 10-15% of oceanic "dissolved" organic carbon, aluminium and thorium is associated with colloidal material, this proportion rises to about 50% in coastal waters (Moran and Moore 1989).

This study has demonstrated that the estuarine behaviours of, for example, Mn, Ni and Zn are affected by sediment disturbance/resuspension. Single dramatic events may therefore dominate estuarine metal discharges to coastal zones. Further research would usefully examine the importance of flood conditions to the overall annual metal budgets to coastal zones. Furthermore, since sediment resuspension is likely to be less important during neap tides, estimated annual fluxes of dissolved Mn, Ni and Zn may be reduced if data from neap tides were included.

Both the Forth and Tay are partially mixed temperate macrotidal estuaries. Further research would usefully examine metal behaviours in

i) stratified estuaries (*eg* Krka, Croatia) where buoyant riverine plumes overlie more saline waters;

ii) microtidal estuaries (*eg* Rhône, France) where turbidity maxima are absent, and estuarine plumes extend over the sea surface;

iii) tropical estuaries (*eg* Bang Pakong, Thailand) where little reactive dissolved organic carbon remains, having undergone intense decomposition within the tropical watershed (Windom *et al* 1988).

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APPENDIX 1 DISSOLVED AND SUSPENDED PARTICULATE TRACE METAL CONCENTRATIONS AND PARTITION COEFFICIENTS

			SPM	POC	Cadmium			Copper			Manganese			Nickel			Lead			Zinc		
Survey	Stn.	Salinity	mg/l	µg/l	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd
F 6'89	-2.00	0.060	31.40	3535	0.004	1.48	5.5682	0.72	64	4.9488	1.25	980	5.8943	0.42	25	4.7747	0.066	66	6.0000	0.84	130	5.1897
F 6'89	0.00	0.102	256.00	21140	0.003	2.99	5.9985	1.52	46	4.4809	0.97	399	5.6142	0.45	20	4.6478	0.215	43	5.3010	1.05	121	5.0616
F 6'89	3.00	0.533	400.30	22250	.	2.40	.	1.89	98	4.7148	3.12	558	5.2525	0.59	42	4.8524	0.125	83	5.8222	1.07	172	5.2061
F 6'89	6.00	1.851	444.60	20380	0.003	3.66	6.0864	1.72	117	4.8327	15.90	529	4.5221	0.79	48	4.7836	0.111	104	5.9717	1.73	159	4.9634
F 6'89	8.00	3.309	221.30	9660	0.011	3.04	5.4415	1.52	55	4.5585	88.10	466	3.7234	0.83	20	4.3820	0.127	56	5.6444	2.06	125	4.7830
F 6'89	11.00	5.787	48.50	5890	0.011	0.37	4.5268	1.26	135	5.0300	88.70	740	3.9213	0.96	37	4.5859	0.118	113	5.9812	2.77	124	4.6509
F 6'89	13.00	9.259	31.00	.	0.010	2.58	5.4116	1.17	101	4.9361	113.70	910	3.9033	1.28	39	4.4839	0.165	111	5.8278	2.96	150	4.7048
F 6'89	15.00	13.540	21.40	2380	0.011	2.74	5.3964	1.07	126	5.0710	154.60	930	3.7793	1.49	44	4.4703	0.097	141	6.1624	3.50	239	4.8343
F 6'89	18.00	17.808	27.00	2150	0.020	1.13	4.7520	0.97	80	4.9163	149.80	790	3.7221	1.49	32	4.3320	0.147	100	5.8327	3.50	120	4.5351
F 6'89	20.00	20.506	17.60	2130	0.019	1.80	4.9765	0.96	64	4.8239	117.90	520	3.6445	1.29	28	4.3366	0.101	103	6.0085	3.12	145	4.6672
F 6'89	23.00	26.777	22.00	2630	0.024	2.90	5.0822	1.37	113	4.9164	58.20	1040	4.2521	1.17	45	4.5850	0.139	134	5.9841	3.07	232	4.8783
F 6'89	25.00	28.496	16.40	1950	0.026	1.60	4.7891	1.45	67	4.6647	32.20	670	4.3182	0.92	32	4.5414	0.106	104	5.9917	2.31	166	4.8565
F 6'89	28.00	30.328	19.60	2350	0.024	7.37	5.4873	1.59	92	4.7624	22.20	960	4.6359	0.92	41	4.6490	0.215	113	5.7206	1.46	211	5.1599
F 6'89	31.00	30.983	10.40	1750	0.018	.	.	1.17	86	4.8663	8.81	1050	5.0762	0.65	37	4.7553	0.111	120	6.0339	1.68	210	5.0969
F 6'89	34.00	31.791	21.20	2000	0.023	.	.	1.18	.	.	4.37	.	.	0.61	.	.	0.071	.	.	1.46	.	.
F 6'89	38.00	32.243	3.10	1070	0.042	.	.	0.90	.	.	4.30	.	.	0.58	.	.	0.076	.	.	2.24	.	.
F 6'89	42.00	32.300	4.10	.	0.041	7.67	5.2720	0.90	76	4.9266	3.43	1010	5.4690	0.61	41	4.8275	0.038	136	6.5538	1.62	230	5.1522
F 6'89	48.00	32.575	.	920	0.031	.	.	0.89	.	.	2.84	.	.	0.52	.	.	0.090	.	.	1.16	.	.
F 6'89	51.00	32.767	.	953	0.026	.	.	0.78	.	.	2.11	.	.	0.51	.	.	0.094	.	.	1.03	.	.
F 6'89	56.00	33.089	.	660	0.037	.	.	0.55	.	.	1.63	.	.	0.49	.	.	0.066	.	.	0.92	.	.
F 6'89	66.00	33.461	3.70	.	0.029	5.18	5.2519	0.56	83	5.1709	1.53	1350	5.9456	0.58	51	4.9441	0.073	162	6.3462	0.92	270	5.4676
F 6'89	61.00	33.519	3.70	632	0.015	.	.	0.52	.	.	1.21	.	.	0.40	.	.	0.059	.	.	0.06	.	.
F 6'89	74.00	33.558	1.60	444	0.019	.	.	0.42	.	.	1.56	.	.	0.35	.	.	0.019	.	.	0.42	.	.
F 6'89	84.00	33.706	1.60	.	0.024	.	.	0.33	88	5.4260	1.63	1370	5.9245	0.31	68	5.3411	0.010	103	7.0128	.	290	.
F 6'89	93.00	33.757	1.40	404	0.028	.	.	0.32	.	.	2.84	.	.	0.31	.	.	0.092	.	.	0.47	.	.
F 8'89	-2.00	0.040	29.15	2240	0.006	0.47	4.8939	0.94	59	4.7977	7.77	1080	5.1430	0.42	23	4.7385	0.121	76	5.7980	0.88	110	5.0969
F 8'89	0.00	0.071	207.98	16010	0.004	.	.	1.67	.	.	2.32	.	.	0.49	.	.	0.055	.	.	0.92	.	.
F 8'89	3.00	0.277	424.24	38330	0.003	2.58	5.9345	2.43	104	4.6314	2.18	673	5.4896	0.66	43	4.8139	0.239	91	5.5806	1.33	173	5.1142
F 8'89	6.00	1.516	145.09	12150	0.007	.	.	2.15	71	4.5188	10.40	614	4.7711	0.85	28	4.5177	0.142	77	5.7342	1.72	158	4.9631
F 8'89	8.00	2.585	70.78	5067	0.009	0.20	4.3468	1.90	96	4.7035	29.29	740	4.4025	0.92	30	4.5133	0.146	100	5.8356	2.13	88	4.6161
F 8'89	11.00	3.277	79.92	7360	0.006	.	.	0.85	98	5.0618	17.68	659	4.5714	0.71	34	4.6802	0.094	89	5.9763	2.06	169	4.9140
F 8'89	13.00	8.050	37.63	4225	0.016	0.27	4.2272	1.60	80	4.6990	32.24	1090	4.5290	1.09	30	4.4397	0.142	103	5.8605	2.93	91	4.4922
F 8'89	15.00	10.013	23.74	3277	0.020	0.80	4.6021	1.52	102	4.8268	34.32	890	4.4138	1.12	38	4.5306	0.205	110	5.7296	2.96	163	4.7409
F 8'89	18.00	19.785	30.57	3843	0.026	0.33	4.1035	1.28	94	4.8659	49.05	890	4.2588	1.18	28	4.3753	0.121	84	5.8415	3.03	110	4.5600

APPENDIX 1 (cont.)

			SPM	POC	Cadmium			Copper			Manganese			Nickel			Lead			Zinc		
Survey	Stn.	Salinity	mg/l	µg/l	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd
F 8'89	20.00	22.246	25.58	2656	0.033	0.20	3.7825	1.50	77	4.7104	31.54	880	4.4456	1.06	28	4.4219	0.045	80	6.2499	3.24	90	4.4437
F 8'89	23.00	28.034	27.95	3466	0.044	0.19	3.6353	1.79	67	4.5732	15.25	780	4.7088	1.05	18	4.2341	0.076	65	5.9321	3.45	80	4.3653
F 8'89	25.00	29.832	22.08	2793	0.040	0.23	3.7597	1.44	99	4.8373	7.07	1160	5.2150	0.92	45	4.6894	0.243	112	5.6636	3.00	227	4.8789
F 8'89	28.00	31.517	21.38	2146	0.039	0.10	3.4089	1.39	80	4.7601	3.05	1200	5.5949	0.87	38	4.6403	0.049	91	6.2688	2.44	177	4.8606
F 8'89	31.00	31.778	18.30	2476	0.037	0.28	3.8790	1.20	33	4.4393	6.24	1040	5.2218	0.74	40	4.7328	0.042	62	6.1691	2.51	164	4.8152
F 8'89	34.00	32.729	34.73	3030	0.037	.	.	1.15	.	.	6.62	.	.	0.64	.	.	0.035	.	.	1.82	.	.
F 8'89	38.00	33.047	11.41	1315	0.037	0.16	3.6359	1.07	56	4.7188	3.92	910	5.3658	0.54	28	4.7148	0.132	70	5.7245	1.79	130	4.8611
F 8'89	42.00	33.320	9.01	1350	0.036	.	.	0.80	.	.	1.66	.	.	0.51	.	.	0.125	.	.	1.45	.	.
F 8'89	50.00	33.602	13.11	1596	0.020	.	.	1.48	.	.	3.12	.	.	0.49	.	.	.	.	.	2.68	.	.
F 8'89	51.00	33.570	14.95	1818	0.030	.	.	0.81	.	.	4.99	.	.	0.55	.	.	0.163	.	.	1.88	.	.
F 8'89	52.00	33.559	10.21	1525	0.042	.	.	1.16	.	.	6.48	.	.	0.58	.	.	0.194	.	.	2.10	.	.
F 8'89	56.00	33.713	4.75	717	0.034	.	.	0.66	.	.	3.16	.	.	0.46	.	.	.	.	.	1.40	.	.
F 8'89	57.00	33.725	4.66	713	0.034	0.44	4.1120	0.65	32	4.6922	2.46	670	5.4351	0.46	24	4.7175	0.080	78	5.9890	1.16	930	5.9040
F 8'89	59.00	33.785	5.19	653	0.039	.	.	0.07	.	.	2.18	.	.	0.52	.	.	0.104	.	.	1.13	.	.
F 9'89	34.00	30.622	35.44	4140	0.031	.	.	0.97	.	.	7.90	.	.	0.78	.	.	0.200	.	.	2.63	.	.
F 9'89	38.00	31.431	19.26	4360	0.027	.	.	0.85	.	.	7.49	.	.	0.65	.	.	0.110	.	.	1.59	.	.
F 9'89	42.00	31.831	24.81	1830	0.021	.	.	0.84	.	.	6.59	.	.	0.70	.	.	0.220	.	.	1.98	.	.
F 9'89	48.00	32.281	12.23	1340	0.022	.	.	0.76	.	.	3.21	.	.	0.60	.	.	0.240	.	.	1.75	.	.
F 9'89	51.00	32.464	19.15	1050	0.016	.	.	0.75	.	.	2.05	.	.	0.56	.	.	0.150	.	.	1.65	.	.
F 9'89	56.00	32.682	8.87	1090	0.022	.	.	0.65	.	.	1.94	.	.	0.53	.	.	0.120	.	.	1.73	.	.
F 9'89	61.00	33.063	6.61	718	0.008	.	.	0.45	.	.	1.07	.	.	0.35	.	.	0.150	.	.	1.11	.	.
F 9'89	66.00	33.517	4.91	699	0.010	.	.	0.41	.	.	1.21	.	.	0.31	.	.	0.180	.	.	0.78	.	.
F 9'89	74.00	33.912	2.23	517	0.010	.	.	0.32	.	.	1.39	.	.	0.28	.	.	0.100	.	.	0.50	.	.
F 9'89	84.00	33.972	3.71	629	0.019	.	.	0.36	.	.	0.25	.	.	0.28	.	.	0.120	.	.	0.78	.	.
F 9'89	93.00	33.835	3.25	598	0.035	.	.	0.52	.	.	2.05	.	.	0.40	.	.	0.130	.	.	1.65	.	.
F 11'89	6.00	0.035	11.02	1780	0.011	0.89	4.9080	0.83	52	4.7969	6.76	740	5.0393	0.74	32	4.6359	0.089	84	5.9749	3.88	210	4.7334
F 11'89	8.00	0.039	23.80	3060	0.006	.	.	1.12	.	.	11.61	.	.	0.57	.	.	0.334	.	.	1.73	.	.
F 11'89	11.00	0.057	122.16	10790	0.005	.	.	1.67	68	4.6098	9.53	558	4.7675	0.59	27	4.6605	0.190	67	5.5473	1.20	161	5.1276
F 11'89	13.00	0.102	174.56	20280	0.003	2.05	5.8346	1.66	51	4.4875	6.07	415	4.8349	0.45	23	4.7085	0.160	50	5.4949	0.98	123	5.0987
F 11'89	15.00	0.395	290.60	22290	0.004	1.45	5.5593	1.80	85	4.6741	6.85	647	4.9752	0.47	39	4.9190	0.270	82	5.4825	1.33	165	5.0936
F 11'89	18.00	1.249	131.98	15010	0.003	1.33	5.6467	1.51	67	4.6471	18.37	436	4.3754	0.50	27	4.7324	0.190	71	5.5725	1.60	142	4.9482
F 11'89	20.00	5.765	189.08	20590	0.008	1.46	5.2613	1.25	70	4.7482	35.36	721	4.3094	0.59	27	4.6605	0.130	64	5.6922	2.81	154	4.7388
F 11'89	23.00	8.706	164.35	14450	0.011	1.32	5.0792	1.41	66	4.6703	36.83	808	4.3412	0.74	33	4.6493	0.110	77	5.8451	3.25	174	4.7287
F 11'89	25.00	16.757	322.97	18100	0.028	3.09	5.0428	1.16	146	5.0999	27.65	722	4.4168	1.18	56	4.6763	0.560	126	5.3522	6.02	151	4.3994

APPENDIX 1 (cont.)

			SPM	POC	Cadmium			Copper			Manganese			Nickel			Lead			Zinc		
Survey	Stn.	Salinity	mg/l	µg/l	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd
F 11'89	28.00	20.725	160.57	15400	0.021	1.43	4.8331	1.59	75	4.6737	20.45	761	4.5707	0.81	30	4.5686	0.130	74	5.7553	3.61	154	4.6300
F 11'89	31.00	26.162	37.74	4580	0.021	0.13	3.7917	1.35	52	4.5857	16.81	1140	4.8313	0.92	33	4.5547	0.400	75	5.2730	3.12	74	4.3751
F 11'89	34.00	27.443	25.90	5920	0.033	.	.	1.73	.	.	30.16	.	.	1.03	.	.	0.223	.	.	5.66	.	.
F 11'89	38.00	32.262	21.17	2230	0.019	0.02	3.0830	1.05	56	4.7270	5.20	790	5.1816	0.63	36	4.7570	0.240	66	5.4393	2.11	108	4.7091
F 11'89	42.00	31.038	7.13	1250	0.018	0.35	4.2888	0.74	52	4.8468	4.19	800	5.2809	0.47	35	4.8720	0.084	112	6.1249	1.65	170	5.0130
F 11'89	48.00	31.601	4.40	880	0.015	.	.	0.64	.	.	5.69	.	.	0.54	.	.	0.174	.	.	1.29	.	.
F 11'89	51.00	32.930	5.00	846	0.015	.	.	0.49	.	.	4.56	.	.	0.40	.	.	0.057	.	.	1.24	.	.
F 11'89	56.00	33.304	5.76	747	0.015	0.09	3.7533	0.44	30	4.8337	2.77	480	5.2388	0.37	25	4.8297	0.112	59	5.7216	1.02	97	4.9782
F 11'89	61.00	33.354	4.20	684	0.016	.	.	0.50	.	.	3.09	.	.	0.38	.	.	0.216	.	.	1.20	.	.
F 11'89	66.00	33.807	15.20	400	0.014	.	.	0.31	.	.	2.77	.	.	0.30	.	.	0.109	.	.	0.71	.	.
F 11'89	74.00	34.089	0.90	320	0.012	.	.	0.27	.	.	0.90	.	.	0.29	.	.	0.102	.	.	0.48	.	.
F 11'89	84.00	33.501	2.30	390	0.017	.	.	0.42	.	.	2.48	.	.	0.39	.	.	0.064	.	.	0.91	.	.
F 11'89	93.00	33.720	1.31	380	0.019	0.76	4.6021	0.33	43	5.1150	2.36	850	5.5565	0.34	54	5.2009	0.022	150	6.8337	0.89	260	5.4656
F 1'90	8.00	0.087	13.96	1620	0.019	1.14	4.7782	0.89	42	4.6739	15.60	530	4.5312	0.77	35	4.6576	0.079	76	5.9832	3.14	210	4.8253
F 1'90	11.00	0.070	77.81	4360	0.013	1.62	5.0956	1.06	59	4.7455	22.10	350	4.1997	0.77	27	4.5449	0.101	59	5.7665	2.95	185	4.7973
F 1'90	13.00	0.085	131.20	8900	0.008	.	.	1.25	.	.	28.93	.	.	0.77	.	.	0.084	.	.	1.71	.	.
F 1'90	15.00	0.091	59.08	4880	0.008	0.38	4.6767	1.22	54	4.6460	27.99	450	4.2062	0.73	32	4.6418	0.276	70	5.4042	1.81	82	4.6561
F 1'90	18.00	2.236	51.45	4290	0.015	0.19	4.1027	1.06	54	4.7071	29.99	500	4.2220	0.79	33	4.6209	0.089	76	5.9314	2.64	84	4.5027
F 1'90	20.00	5.170	35.87	3350	0.011	0.28	4.4058	1.05	57	4.7347	17.16	590	4.5363	0.75	37	4.6931	0.042	91	6.3358	2.78	140	4.7021
F 1'90	23.00	14.796	28.60	2810	0.088	0.38	3.6353	1.43	59	4.6155	36.23	530	4.1652	0.94	36	4.5832	0.119	106	5.9498	.	150	.
F 1'90	25.00	19.980	21.70	2410	0.052	0.17	3.5144	1.05	72	4.8361	32.85	730	4.3468	0.65	45	4.8403	0.037	104	6.4488	2.84	210	4.8689
F 1'90	28.00	18.977	16.90	2040	0.052	0.32	3.7891	1.82	149	4.9131	31.46	370	4.0704	0.74	33	4.6493	0.060	106	6.2472	9.07	178	4.2928
F 1'90	31.00	21.758	13.30	1860	0.045	0.42	3.9700	0.97	50	4.7122	26.78	550	4.3126	0.65	28	4.6342	0.065	120	6.2663	4.91	170	4.5394
F 1'90	38.00	29.437	13.00	2090	0.029	0.10	3.5376	0.88	44	4.6990	7.80	240	4.4881	0.52	27	4.7154	0.058	52	5.9526	1.91	100	4.7190
F 1'90	42.00	29.943	7.40	1130	0.027	.	.	0.57	.	.	4.68	.	.	.	.	.	0.068	.	.	1.57	.	.
F 1'90	48.00	31.929	12.80	1340	0.023	0.10	3.6160	0.06	28	5.6763	5.35	200	4.5727	0.47	26	4.7429	0.037	24	5.8120	1.73	81	4.6704
F 1'90	51.00	32.530	.	1010	0.020	.	.	0.57	.	.	2.60	.	.	0.38	.	.	0.034	.	.	1.34	.	.
F 1'90	56.00	32.735	.	800	0.022	0.04	3.2258	0.65	17	4.4175	3.54	330	4.9695	0.43	21	4.6888	0.070	13	5.2688	1.52	91	4.7772
F 1'90	61.00	33.132	7.63	750	0.023	0.08	3.5574	0.46	9	4.3104	1.65	54	4.5149	0.34	11	4.5099	0.060	3	4.6990	0.89	54	4.7830
F 1'90	66.00	33.437	5.30	350	0.020	.	.	0.44	.	.	1.37	.	.	0.32	.	.	0.044	.	.	0.82	.	.
F 1'90	74.00	33.815	1.84	246	0.019	.	.	0.35	14	4.6021	0.78	55	4.8483	0.29	16	4.7417	0.020	14	5.8451	1.74	52	4.4755
F 1'90	84.00	33.686	2.50	236	0.020	.	.	0.41	.	.	0.94	.	.	0.31	.	.	0.020	.	.	0.69	.	.
F 1'90	93.00	33.396	2.00	330	0.024	.	.	0.60	.	.	3.78	.	.	0.41	.	.	0.065	.	.	1.31	.	.
F 3'90	8.00	0.038	10.80	1603	0.012	.	.	0.85	.	.	10.90	.	.	0.62	.	.	0.137	.	.	4.92	.	.

APPENDIX 1 (cont.)

			SPM	POC	Cadmium			Copper			Manganese			Nickel			Lead			Zinc		
Survey	Stn.	Salinity	mg/l	µg/l	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd
F 3'90	11.00	0.037	11.67	1210	0.012	.	.	0.71	.	.	9.80	.	.	0.69	.	.	0.128	.	.	3.79	.	.
F 3'90	13.00	0.037	24.13	1890	0.009	0.69	4.8846	0.86	35	4.6096	13.30	550	4.6165	0.55	26	4.6746	0.177	81	5.6605	2.98	140	4.6719
F 3'90	15.00	0.040	20.40	1810	0.010	0.37	4.5682	1.06	68	4.8072	17.90	560	4.4953	0.58	35	4.7806	0.234	82	5.5446	2.44	196	4.9049
F 3'90	18.00	0.054	32.43	3220	0.003	0.41	5.1357	1.66	145	4.9413	38.00	570	4.1761	0.52	36	4.8403	0.201	77	5.5833	1.10	120	5.0378
F 3'90	20.00	1.041	37.63	3580	0.032	0.25	3.8928	1.11	67	4.7808	44.10	520	4.0716	0.52	33	4.8025	0.199	93	5.6696	3.52	83	4.3725
F 3'90	23.00	9.335	14.00	1940	0.020	0.25	4.0969	1.03	49	4.6774	35.80	370	4.0143	0.73	32	4.6418	0.139	96	5.8393	3.41	153	4.6519
F 3'90	25.00	14.161	14.80	2160	0.020	0.24	4.0792	0.84	34	4.6072	38.30	290	3.8792	0.65	26	4.6021	0.109	72	5.8199	2.34	126	4.7312
F 3'90	28.00	14.976	12.77	1390	0.027	0.15	3.7447	0.79	42	4.7256	53.80	300	3.7463	0.62	31	4.6990	0.087	64	5.8667	2.55	140	4.7396
F 3'90	31.00	18.356	13.67	1440	.	0.45	.	0.81	59	4.8624	21.70	510	4.3711	0.58	56	4.9848	0.028	85	6.4823	1.64	123	4.8751
F 3'90	34.00	20.984	11.87	1410	0.016	0.19	4.0746	1.73	80	4.6650	20.90	570	4.4357	0.63	34	4.7321	0.073	100	6.1367	1.80	170	4.9752
F 3'90	38.00	26.957	9.39	826	0.014	.	.	2.01	.	.	11.80	.	.	0.55	.	.	0.094	.	.	2.02	.	.
F 3'90	42.00	26.745	9.37	865	0.014	0.22	4.1963	2.32	.	.	10.90	560	4.7108	0.54	24	4.6478	0.087	76	5.9413	1.69	130	4.8861
F 3'90	48.00	28.662	8.90	1070	0.017	0.23	4.1313	0.55	58	5.0231	9.40	820	4.9407	0.55	33	4.7782	0.080	84	6.0212	1.96	200	5.0088
F 3'90	51.00	27.163	9.30	680	0.013	0.32	4.3912	0.59	72	5.0865	13.50	910	4.8287	0.49	43	4.9433	0.090	100	6.0458	1.53	280	5.2625
F 3'90	56.00	29.322	6.63	693	0.015	2.10	5.1461	0.55	44	4.9031	10.10	670	4.8218	0.56	28	4.6990	0.101	100	5.9957	0.24	205	5.9315
F 3'90	61.00	31.314	5.90	585	0.011	2.10	5.2808	0.29	32	5.0428	6.40	510	4.9014	0.29	25	4.9355	0.070	81	6.0634	1.21	152	5.0991
F 3'90	66.00	32.494	5.70	494	0.016	.	.	0.36	.	.	5.70	.	.	0.35	.	.	0.092	.	.	1.21	.	.
F 3'90	74.00	33.561	4.40	560	0.011	2.10	5.2808	0.29	35	5.0817	2.00	440	5.3424	0.29	24	4.9178	0.033	87	6.4210	0.56	155	5.4421
F 3'90	84.00	33.656	7.40	606	0.011	0.05	3.6118	0.30	26	4.9379	1.70	480	5.4508	0.31	30	4.9858	0.045	102	6.3554	1.96	150	4.8838
F 3'90	93.00	32.399	7.40	623	0.015	0.23	4.1761	0.40	32	4.9031	2.80	440	5.1963	0.31	28	4.9558	0.097	66	5.8328	0.83	130	5.1949
F 5'90	0.00	0.066	5.43	1530	0.022	.	.	1.39	.	.	2.43	.	.	0.68	.	.	0.151	.	.	1.09	.	.
F 5'90	3.00	0.067	20.60	1950	0.011	0.55	4.6990	1.50	88	4.7684	1.75	1000	5.7570	0.58	37	4.8048	0.135	108	5.9031	0.57	262	5.6624
F 5'90	6.00	0.080	202.40	13540	0.014	.	.	1.71	.	.	3.47	.	.	0.50	.	.	0.140	.	.	0.40	.	.
F 5'90	8.00	0.184	278.30	17860	0.003	3.90	6.1139	2.20	141	4.8068	5.59	508	4.9585	0.59	71	5.0804	0.192	149	5.8899	0.55	162	5.4692
F 5'90	11.00	0.743	150.80	9550	0.005	.	.	1.82	46	4.4027	28.43	296	4.0175	0.67	21	4.4961	0.166	47	5.4520	1.21	108	4.9506
F 5'90	13.00	1.813	102.00	9260	0.016	2.46	5.1868	1.92	31	4.2081	36.57	389	4.0268	0.91	24	4.4212	0.111	61	5.7400	1.80	125	4.8416
F 5'90	15.00	4.107	64.70	3240	0.011	0.15	4.1347	1.87	82	4.6420	58.09	760	4.1167	1.19	33	4.4430	0.093	89	5.9809	2.18	91	4.6206
F 5'90	18.00	12.549	36.70	4130	0.025	0.17	3.8325	1.58	73	4.6647	133.23	840	3.7997	1.18	32	4.4333	0.139	94	5.8301	3.97	82	4.3150
F 5'90	20.00	18.013	34.00	3210	0.032	0.19	3.7736	1.53	82	4.7291	55.62	680	4.0873	1.15	24	4.3195	0.104	83	5.9020	3.34	100	4.4763
F 5'90	23.00	20.998	43.10	3580	0.036	0.17	3.6741	1.58	99	4.7970	32.88	980	4.4743	1.07	34	4.5021	0.092	93	6.0047	3.36	97	4.4604
F 5'90	25.00	26.153	35.40	3170	0.042	0.08	3.2798	1.76	72	4.6118	29.81	870	4.4652	1.16	31	4.4269	0.075	91	6.0840	3.38	79	4.3687
F 5'90	28.00	29.622	32.80	3010	0.037	0.40	4.0339	1.66	132	4.9005	14.91	880	4.7710	0.84	29	4.5381	0.045	98	6.3380	1.51	150	4.9971
F 5'90	31.00	30.194	22.00	2150	0.030	0.15	3.6990	2.02	267	5.1212	14.60	930	4.8041	0.79	46	4.7651	0.028	95	6.5306	1.58	181	5.0590
F 5'90	34.00	31.341	34.10	1580	0.026	0.24	3.9652	1.30	107	4.9154	5.84	870	5.1731	0.64	26	4.6088	0.052	89	6.2334	1.13	120	5.0261

APPENDIX 1 (cont.)

			SPM	POC	Cadmium			Copper			Manganese			Nickel			Lead			Zinc		
Survey	Stn.	Salinity	mg/l	µg/l	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd
F 5'90	38.00	29.622	13.70	1230	0.037	.	.	1.66	.	.	14.91	.	.	0.84	.	.	0.045	.	.	1.51	.	.
F 5'90	42.00	31.862	4.93	970	0.032	.	.	1.30	.	.	5.47	.	.	0.57	.	.	0.139	.	.	1.43	.	.
F 5'90	48.00	32.300	6.97	845	0.020	0.14	3.8451	0.66	43	4.8139	1.69	870	5.7116	0.49	35	4.8539	0.030	113	6.5760	0.64	180	5.4491
F 5'90	51.00	32.742	6.00	720	0.019	.	.	0.62	.	.	1.26	.	.	0.46	.	.	0.075	.	.	0.55	.	.
F 5'90	56.00	32.800	4.13	771	0.023	0.08	3.5414	0.60	27	4.6532	1.20	730	5.7841	0.48	29	4.7812	0.030	54	6.2553	0.61	100	5.2147
F 5'90	61.00	32.998	4.03	709	.	.	.	0.58	.	.	1.17	.	.	0.48	.	.	0.116	.	.	0.54	.	.
F 5'90	66.00	33.303	3.07	678	0.016	.	.	0.46	.	.	0.71	.	.	0.33	.	.	0.075	.	.	0.29	.	.
F 5'90	74.00	33.608	2.10	547	0.016	.	.	0.35	.	.	0.52	.	.	0.32	.	.	0.020	.	.	0.12	.	.
F 5'90	84.00	33.455	1.70	467	0.015	.	.	0.42	.	.	0.55	.	.	0.40	.	.	0.020	.	.	0.19	.	.
F 5'90	93.00	33.500	1.23	428	0.016	.	.	0.42	22	4.7192	0.68	140	5.3136	0.35	45	5.1091	0.034	5	5.1406	0.78	110	5.1493
T 7'89	0.00	0.029	1.91	241	0.006	3.06	5.7076	0.73	48	4.8179	3.69	1980	5.7296	0.62	16	4.4117	0.046	50	6.0362	0.95	443	5.6687
T 7'89	1.25	0.032	1.06	224	0.008	.	.	0.44	.	.	3.96	.	.	0.29	.	.	0.029	.	.	1.01	.	.
T 7'89	3.00	0.034	2.16	2740	0.004	.	.	0.51	.	.	3.28	.	.	0.37	.	.	0.101	.	.	0.78	.	.
T 7'89	5.00	0.041	2.08	1950	0.013	.	.	0.54	.	.	3.34	.	.	0.28	.	.	0.199	.	.	0.58	.	.
T 7'89	6.50	0.060	2.40	2410	0.004	0.64	5.2041	0.71	40	4.7508	2.25	1180	5.7197	0.33	47	5.1536	0.114	63	5.7424	0.83	180	5.3362
T 7'89	8.75	0.138	0.92	2450	0.008	2.16	5.4314	0.78	30	4.5850	2.67	2910	6.0374	0.33	35	5.0256	0.070	109	6.1923	0.82	348	5.6278
T 7'89	11.00	0.532	4.56	1050	0.003	0.88	5.4674	0.79	48	4.7836	4.00	1420	5.5502	0.36	37	5.0119	0.168	127	5.8785	0.74	180	5.3860
T 7'89	13.00	2.516	11.27	1090	0.005	.	.	0.88	.	.	3.02	.	.	0.57	.	.	0.089	.	.	0.91	.	.
T 7'89	13.25	1.411	4.88	1170	0.004	.	.	0.91	39	4.6320	3.76	2230	5.7731	0.39	38	4.9887	0.105	96	5.9611	0.95	250	5.4202
T 7'89	14.00	4.662	7.92	1070	0.018	3.99	5.3457	0.88	31	4.5469	2.92	3260	6.0478	0.53	31	4.7671	0.044	120	6.4357	1.58	251	5.2010
T 7'89	15.00	5.956	7.56	931	0.014	1.34	4.9810	1.16	31	4.4269	.	3739	.	0.81	29	4.5539	0.123	91	5.8691	1.61	262	5.2115
T 7'89	17.00	9.962	6.61	965	0.016	2.20	5.1383	0.86	26	4.4805	4.37	2950	5.8293	0.61	19	4.4934	0.083	76	5.9617	.	200	.
T 7'89	19.00	12.012	4.45	793	0.018	.	.	0.94	.	.	3.26	.	.	0.61	.	.	0.018	.	.	1.11	.	.
T 7'89	20.00	13.681	6.82	.	0.017	.	.	0.83	27	4.5123	3.76	2240	5.7751	0.62	30	4.6847	0.013	116	6.9505	1.14	200	5.2441
T 7'89	22.00	16.481	4.98	965	0.015	0.60	4.6021	0.68	18	4.4228	2.59	1905	5.8666	0.51	21	4.6146	0.023	43	6.2717	1.34	125	4.9698
T 7'89	23.50	15.921	7.35	1070	0.018	0.49	4.4349	0.80	23	4.4586	3.51	1120	5.5039	.	18	.	0.021	46	6.3405	1.06	140	5.1208
T 7'89	26.00	21.536	10.32	690	0.023	.	.	0.74	.	.	.	.	.	0.61	.	.	0.044	.	.	.	.	.
T 7'89	28.00	22.695	8.55	655	0.030	.	.	1.15	.	.	5.26	.	.	0.44	.	.	0.040	.	.	0.96	.	.
T 7'89	29.50	27.875	9.08	283	0.019	1.08	4.7547	.	95	.	6.08	948	5.1929	.	20	.	0.067	45	5.8271	1.07	93	4.9391
T 7'89	31.00	29.840	19.51	260	0.014	2.93	5.3207	0.47	47	5.0000	7.16	1340	5.2722	0.47	29	4.7903	0.049	64	6.1160	0.81	240	5.4717
T 7'89	33.00	32.426	7.42	233	0.023	0.85	4.5677	0.55	31	4.7510	5.74	716	5.0960	0.30	18	4.7782	0.086	45	5.7187	1.01	75	4.8707
T 7'89	36.50	32.530	19.26	264	0.017	.	.	0.49	.	.	4.87	.	.	0.22	.	.	0.046	.	.	0.75	.	.
T 7'89	37.75	31.044	0.95	341	.	1.73	.	.	82	.	8.10	850	5.0209	0.34	27	4.8999	0.062	51	5.9152	1.24	132	5.0272
T 7'89	40.75	33.142	0.64	283	0.013	0.80	4.8062	0.23	16	4.8424	4.97	510	5.0112	0.40	10	4.3979	0.027	21	5.8909	0.50	129	5.4116

APPENDIX 1 (cont.)

			SPM	POC	Cadmium			Copper			Manganese			Nickel			Lead			Zinc		
Survey	Stn.	Salinity	mg/l	µg/l	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd
T 8'89	0.00	0.031	1.45	481	0.003	1.20	5.6021	0.75	26	4.5399	6.41	240	4.5734	0.31	8	4.4007	0.069	18	5.4164	2.37	170	4.8557
T 8'89	1.25	0.033	3.21	824	0.006	.	.	0.67	.	.	12.48	.	.	0.31	.	.	0.260	.	.	1.04	.	.
T 8'89	3.00	0.051	8.83	1410	0.006	.	.	0.80	.	.	7.97	.	.	0.59	.	.	0.225	.	.	1.01	.	.
T 8'89	5.00	0.095	8.30	1188	0.003	1.20	5.6021	0.80	35	4.6410	.	1590	.	0.28	21	4.8751	0.159	75	5.6737	0.83	201	5.3841
T 8'89	6.50	0.322	9.33	1542	0.003	1.20	5.6021	1.06	34	4.5062	10.14	1250	5.0909	0.64	44	4.8373	0.142	92	5.8115	1.35	229	5.2295
T 8'89	8.75	0.948	12.23	1919	0.022	1.20	4.7368	1.34	33	4.3914	13.26	1430	5.0328	0.47	26	4.7429	0.101	90	5.9499	1.53	244	5.2027
T 8'89	11.00	3.615	4.04	2057	0.016	1.08	4.8293	1.50	53	4.5482	14.65	1690	5.0620	0.55	56	5.0078	0.239	191	5.9026	2.46	277	5.0515
T 8'89	13.25	5.069	10.25	1923	0.016	0.90	4.7501	1.30	38	4.4658	6.59	1480	5.3514	0.55	23	4.6214	0.059	86	6.1636	1.75	196	5.0492
T 8'89	14.00	6.955	9.79	1666	0.021	0.31	4.1691	1.10	33	4.4771	5.37	720	5.1274	0.50	35	4.8451	0.156	68	5.6394	1.46	230	5.1974
T 8'89	15.00	8.576	8.62	1357	.	0.25	.	1.19	27	4.3558	6.93	710	5.0105	0.52	33	4.8025	0.080	70	5.9420	1.75	150	4.9331
T 8'89	17.00	9.947	7.35	1483	.	0.34	.	1.15	33	4.4578	7.63	810	5.0260	0.54	31	4.7590	0.125	82	5.8169	1.56	180	5.0621
T 8'89	19.00	13.430	15.69	1725	0.022	0.10	3.6576	1.00	21	4.3222	5.03	830	5.2175	0.46	27	4.7686	0.066	58	5.9439	0.97	125	5.1101
T 8'89	20.00	16.850	20.92	1597	0.037	0.30	3.9089	1.08	37	4.5348	3.99	1110	5.4444	0.52	37	4.8522	0.045	58	6.1102	1.53	126	4.9157
T 8'89	22.00	17.080	11.66	1645	0.040	0.53	4.1222	1.14	29	4.4055	4.85	920	5.2780	0.59	24	4.6094	0.024	50	6.3188	1.11	200	5.2557
T 8'89	23.50	19.450	10.18	1243	0.034	0.61	4.2539	1.10	27	4.3900	3.73	980	5.4195	0.55	24	4.6398	0.028	54	6.2852	1.28	140	5.0389
T 8'89	26.00	19.930	6.68	1175	0.040	0.75	4.2730	1.15	21	4.2615	7.45	620	4.9202	0.55	19	4.5384	0.107	59	5.7415	1.63	159	4.9892
T 8'89	28.00	21.800	22.40	1668	0.032	0.19	3.7736	1.00	30	4.4771	4.42	810	5.2631	0.52	38	4.8638	0.139	54	5.5894	1.21	142	5.0695
T 8'89	29.50	21.690	9.22	1309	0.029	.	.	0.96	.	.	5.89	.	.	0.51	.	.	0.090	.	.	1.01	.	.
T 8'89	31.00	28.390	4.13	224	0.058	0.85	4.1660	0.75	30	4.6021	5.37	820	5.1838	0.37	26	4.8468	0.042	51	6.0843	0.83	165	5.2984
T 8'89	33.00	30.390	4.52	316	0.019	0.71	4.5725	0.48	23	4.6805	5.89	520	4.9459	0.30	16	4.7270	0.023	29	6.1007	0.42	142	5.5290
T 8'89	36.50	32.860	4.06	998	0.021	0.58	4.4412	0.63	24	4.5809	4.09	380	4.9681	0.28	17	4.7833	0.014	21	6.1761	0.10	115	6.0607
T 8'89	37.75	32.440	5.05	403	0.025	.	.	0.44	.	.	5.44	.	.	0.30	.	.	0.042	.	.	0.42	.	.
T 8'89	39.00	31.990	2.26	476	0.064	1.97	4.4883	0.61	48	4.8959	6.14	680	5.0443	0.59	28	4.6763	0.055	45	5.9128	0.62	283	5.6594
T 8'89	41.00	31.490	3.39	442	0.086	0.69	3.9044	0.61	34	4.7461	.	690	.	0.35	29	4.9183	0.087	43	5.6939	0.81	138	5.2314
T 9'89	0.00	0.027	3.65	391	0.001	.	.	0.48	.	.	2.80	.	.	0.27	.	.	0.050	.	.	1.48	.	.
T 9'89	3.00	0.014	2.90	362	0.001	.	.	0.46	.	.	2.76	.	.	0.25	.	.	0.018	.	.	1.40	.	.
T 9'89	5.00	0.011	3.29	476	.	.	.	0.55	.	.	3.70	.	.	0.31	.	.	.	.	.	1.66	.	.
T 9'89	6.50	0.011	7.49	549	.	0.41	.	0.55	30	4.7368	4.91	990	5.3046	0.32	30	4.9788	0.059	54	5.9593	1.36	170	5.0969
T 9'89	8.75	0.011	7.74	933	.	.	.	0.54	.	.	6.12	.	.	0.32	.	.	0.036	.	.	1.05	.	.
T 9'89	11.00	0.022	19.33	1420	.	.	.	0.70	.	.	0.10	.	.	.	.	.	0.051	.	.	1.01	.	.
T 9'89	15.00	0.229	33.43	3850	0.003	0.63	5.3222	0.66	39	4.7715	2.76	1470	5.7264	0.30	29	4.9882	0.051	72	6.1498	0.89	110	5.0905
T 9'89	17.00	0.591	29.08	2980	0.003	0.51	5.2304	0.90	41	4.6585	5.64	1510	5.4277	0.37	35	4.9794	0.041	78	6.2772	0.98	110	5.0506
T 9'89	19.00	2.365	59.50	5190	0.005	0.39	4.8921	0.92	41	4.6490	4.04	1500	5.5697	0.36	35	4.9914	0.057	76	6.1288	1.24	106	4.9322
T 9'89	22.00	6.286	47.92	4290	0.009	0.38	4.6255	0.77	42	4.7368	4.53	1350	5.4742	0.36	35	4.9914	0.066	74	6.0530	1.20	100	4.9208

APPENDIX 1 (cont.)

			SPM	POC	Cadmium			Copper			Manganese			Nickel			Lead			Zinc		
Survey	Stn.	Salinity	mg/l	µg/l	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd
T 9'89	23.50	7.916	14.52	2080	0.009	0.22	4.3882	0.94	24	4.4071	5.08	670	5.1202	0.38	29	4.8849	0.086	55	5.8079	1.22	106	4.9389
T 9'89	26.00	9.880	21.34	2480	0.008	.	.	0.89	.	.	4.01	.	.	0.43	.	.	0.048	.	.	1.12	.	.
T 9'89	28.10	9.951	12.72	1880	0.011	0.21	4.2808	0.96	23	4.3795	5.53	786	5.1527	0.38	22	4.7615	0.059	39	5.8180	1.24	100	4.9069
T 9'89	28.00	14.943	20.88	1730	0.009	0.20	4.3468	0.89	29	4.5130	1.17	1230	6.0217	.	23	.	0.024	61	6.4069	1.45	70	4.6837
T 9'89	31.00	19.969	7.46	693	0.009	.	.	0.60	.	.	5.01	.	.	0.34	.	.	0.032	.	.	0.89	.	.
T 9'89	33.00	26.306	9.54	463	0.011	0.87	4.8981	0.59	16	4.4333	4.49	270	4.7791	0.29	11	4.5775	0.050	33	5.8230	0.60	74	5.0925
T 9'89	37.75	27.175	2.76	389	0.013	.	.	0.48	.	.	6.47	.	.	0.33	.	.	0.024	.	.	0.98	.	.
T 9'89	39.25	26.095	4.63	420	0.010	.	.	0.53	.	.	4.94	.	.	0.32	.	.	0.024	.	.	0.60	.	.
T 9'89	41.00	27.394	3.25	409	0.017	0.86	4.7040	0.61	133	5.3385	5.19	1160	5.3493	0.35	48	5.1322	0.058	123	6.3272	1.05	366	5.5423
T 11'89	6.50	0.047	6.01	606	0.016	.	.	0.60	.	.	5.20	.	.	0.36	.	.	0.230	.	.	3.63	.	.
T 11'89	8.75	0.046	9.36	1820	0.029	0.92	4.5014	0.85	25	4.4685	8.18	430	4.7207	0.36	21	4.7659	0.379	49	5.1116	3.89	134	4.5372
T 11'89	11.00	0.053	16.40	2470	0.039	.	.	1.35	.	.	11.18	.	.	0.83	.	.	0.636	.	.	6.47	.	.
T 11'89	13.25	0.107	39.43	3070	0.022	0.11	3.6990	1.11	34	4.4862	18.72	710	4.5790	0.43	25	4.7645	0.816	62	4.8807	6.22	53	3.9305
T 11'89	15.00	0.425	49.96	2900	0.029	0.10	3.5376	1.36	35	4.4105	22.62	620	4.4379	0.51	35	4.8365	1.031	70	4.8318	7.57	64	3.9271
T 11'89	17.00	2.163	32.58	2840	0.028	0.22	3.8953	1.62	31	4.2818	17.59	670	4.5808	0.51	35	4.8365	0.909	36	4.5977	7.57	60	3.8991
T 11'89	19.00	4.927	37.31	2030	0.014	0.33	4.3724	0.60	47	4.8939	4.42	1560	5.5477	0.38	39	5.0113	.	97	.	3.47	98	4.4509
T 11'89	20.00	6.003	20.18	2790	0.017	0.15	3.9456	0.87	36	4.6168	6.76	770	5.0565	0.45	42	4.9700	0.660	69	5.0193	0.80	122	5.1833
T 11'89	22.00	7.898	10.49	1870	0.013	0.97	4.8728	0.62	30	4.6847	4.51	1090	5.3832	0.33	23	4.8432	0.067	68	6.0064	1.55	171	5.0427
T 11'89	23.50	10.234	9.93	1710	0.018	0.91	4.7038	0.66	30	4.6576	4.19	860	5.3123	0.37	24	4.8120	0.091	69	5.8798	2.10	187	4.9496
T 11'89	26.00	12.623	14.38	1850	0.015	0.32	4.3291	0.72	23	4.5044	5.79	590	5.0082	0.42	40	4.9788	0.105	68	5.8113	2.07	114	4.7409
T 11'89	28.00	16.288	12.30	1780	0.015	0.26	4.2389	0.66	26	4.5954	5.79	440	4.8808	0.40	27	4.8293	0.147	50	5.5317	1.99	72	4.5585
T 11'89	29.50	17.703	6.22	1160	0.013	0.70	4.7312	0.50	30	4.7782	4.13	930	5.3525	0.32	35	5.0389	0.084	83	5.9948	1.29	208	5.2075
T 11'89	31.00	20.254	5.02	1200	0.018	1.53	4.9294	0.60	40	4.8239	4.45	900	5.3059	0.33	18	4.7368	0.091	64	5.8471	1.26	184	5.1644
T 11'89	33.00	22.030	4.35	1120	0.016	0.83	4.7150	1.05	51	4.6864	3.67	950	5.4131	0.31	33	5.0272	0.020	69	6.5378	1.39	198	5.1537
T 11'89	34.00	24.720	3.29	1080	0.016	2.99	5.2716	0.48	38	4.8985	3.54	470	5.1231	0.35	39	5.0470	0.036	58	6.2071	1.71	210	5.0892
T 11'89	36.50	26.452	3.00	644	0.025	.	.	0.53	.	.	3.40	.	.	0.34	.	.	0.084	.	.	1.13	.	.
T 11'89	37.75	27.889	2.33	510	0.024	3.23	5.1290	0.40	48	5.0792	3.61	950	5.4202	0.30	44	5.1663	0.070	57	5.9108	1.11	248	5.3491
T 11'89	39.00	26.638	3.96	620	0.030	1.14	4.5798	0.44	31	4.8479	3.92	750	5.2818	0.32	32	5.0000	0.029	49	6.2278	1.24	140	5.0527
T 11'89	41.00	26.033	3.89	530	0.019	2.65	5.1445	0.64	33	4.7123	4.07	850	5.3198	0.36	31	4.9351	0.077	59	5.8844	1.71	172	5.0025
T 2'90	15.00	0.059	16.70	2570	0.020	0.66	4.5185	1.56	29	4.2693	6.36	709	5.0472	0.66	50	4.8794	0.059	59	6.0000	1.39	178	5.1074
T 2'90	17.00	0.112	40.10	2970	0.014	0.34	4.3854	0.94	41	4.6397	8.44	1200	5.1528	0.46	35	4.8813	0.107	65	5.7835	0.68	110	5.2089
T 2'90	20.00	1.052	75.90	4440	0.009	.	.	1.15	31	4.4307	4.91	817	5.2211	0.41	36	4.9435	0.128	49	5.5830	0.97	156	5.2064
T 2'90	22.00	1.421	60.80	4430	0.013	0.24	4.2663	0.96	40	4.6198	5.67	1060	5.2717	0.35	33	4.9744	0.114	58	5.7065	1.04	87	4.9225
T 2'90	23.50	1.830	58.00	4230	0.052	.	.	1.17	.	.	7.12	.	.	0.56	.	.	0.113	.	.	0.94	.	.

APPENDIX 1 (cont.)

			SPM	POC	Cadmium			Copper			Manganese			Nickel			Lead			Zinc		
Survey	Stn.	Salinity	mg/l	µg/l	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd
T 2'90	26.00	4.141	53.20	3590	0.023	0.30	4.1154	0.97	40	4.6153	4.00	1130	5.4510	0.58	35	4.7806	0.092	62	5.8286	0.64	98	5.1850
T 2'90	28.00	10.287	49.40	3330	0.029	0.13	3.6515	0.76	33	4.6377	6.64	1050	5.1990	0.51	31	4.7838	0.061	60	5.9928	0.76	74	4.9884
T 2'90	31.00	15.296	35.40	2910	0.069	0.16	3.3653	1.19	39	4.5155	5.88	1100	5.2720	0.40	28	4.8451	0.020	57	6.4548	0.76	63	4.9185
T 2'90	33.00	18.870	20.90	2430	0.057	0.88	4.1886	1.18	51	4.6357	5.81	790	5.1335	0.41	25	4.7852	0.102	64	5.7976	0.81	100	5.0915
T 2'90	36.50	20.751	11.50	1190	0.015	0.25	4.2218	0.44	43	4.9900	6.73	680	5.0045	0.34	47	5.1406	0.071	61	5.9341	0.66	175	5.4235
T 2'90	37.75	26.147	17.00	1080	0.020	0.24	4.0792	0.58	37	4.8048	3.89	420	5.0333	0.27	29	5.0310	0.031	47	6.1807	0.69	110	5.2025
T 2'90	39.00	24.569	11.60	1540	0.022	0.90	4.6118	0.44	57	5.1124	6.09	570	4.9713	0.40	53	5.1222	0.050	72	6.1584	2.05	470	5.3603
T 2'90	41.00	22.059	33.30	1420	0.053	0.95	4.2534	0.81	35	4.6356	6.73	560	4.9202	0.38	37	4.9884	0.045	69	6.1856	0.88	156	5.2486
T 2'90	41.75	32.284	5.00	800	0.030	.	.	1.02	42	4.6146	1.85	710	5.5841	0.28	30	5.0300	0.050	64	6.1072	0.66	228	5.5384
T 2'90	41.76	32.281	8.60	430	0.024	.	.	1.63	.	.	2.09	.	.	0.33	.	.	0.028	.	.	0.66	.	.
T 2'90	42.25	32.274	8.50	580	.	.	.	0.49	.	.	1.88	.	.	0.27	.	.	0.111	.	.	0.80	.	.
T 2'90	42.75	32.203	4.00	600	0.045	.	.	0.47	.	.	2.63	.	.	0.26	.	.	0.232	.	.	0.69	.	.
T 4'90	11.00	0.060	16.50	1790	0.007	0.54	4.8873	0.64	30	4.6709	2.70	620	5.3610	0.24	34	5.1513	0.081	65	5.9044	0.61	159	5.4161
T 4'90	13.00	0.210	22.77	2360	0.017	0.59	4.5404	0.72	42	4.7659	3.90	957	5.3898	0.28	51	5.2604	0.092	87	5.9757	0.59	270	5.6605
T 4'90	14.00	0.720	28.37	2410	0.007	0.45	4.8081	0.72	51	4.8502	6.20	760	5.0884	0.29	38	5.1174	0.068	76	6.0483	0.76	120	5.1984
T 4'90	15.00	1.570	23.35	2150	0.037	0.64	4.2380	0.80	45	4.7501	8.90	900	5.0049	0.36	41	5.0565	0.113	73	5.8102	1.02	100	4.9914
T 4'90	17.00	5.760	14.33	1990	0.080	0.66	3.9165	1.62	65	4.6034	16.00	690	4.6347	0.39	49	5.0991	0.099	90	5.9586	2.17	190	4.9423
T 4'90	19.00	6.070	17.75	1580	0.039	0.66	4.2285	0.78	40	4.7100	15.40	720	4.6698	0.40	50	5.0969	0.075	83	6.0440	1.34	185	5.1401
T 4'90	20.00	9.050	12.03	1330	0.048	0.34	3.8502	0.85	60	4.8487	17.20	440	4.4079	0.39	32	4.9141	0.071	67	5.9748	1.19	88	4.8689
T 4'90	22.00	8.450	18.60	1430	0.024	0.55	4.3602	0.70	31	4.6463	20.50	560	4.4364	0.48	47	4.9909	0.054	64	6.0738	0.89	157	5.2465
T 4'90	23.50	10.430	14.97	1250	0.027	0.50	4.2676	0.82	54	4.8186	17.20	700	4.6096	0.36	58	5.2071	0.166	81	5.6884	1.00	187	5.2718
T 4'90	26.00	14.050	39.13	1290	0.045	0.18	3.6021	0.65	29	4.6495	19.90	940	4.6743	0.50	24	4.6812	0.102	54	5.7238	1.15	66	4.7588
T 4'90	28.00	20.040	15.17	1300	0.034	0.38	4.0483	0.71	30	4.6259	21.40	440	4.3130	0.38	35	4.9643	0.068	51	5.8751	1.02	132	5.1120
T 4'90	31.00	24.920	12.40	850	0.063	0.69	4.0395	0.77	39	4.7046	16.00	510	4.5035	0.40	23	4.7597	0.075	61	5.9103	0.85	165	5.2881
T 4'90	36.50	27.390	6.10	714	0.049	.	.	1.01	.	.	15.70	.	.	0.35	.	.	0.109	.	.	0.76	.	.
T 4'90	37.75	29.490	10.43	698	0.051	0.68	4.1249	0.62	43	4.8411	8.90	490	4.7408	0.32	24	4.8751	0.054	53	5.9919	0.76	134	5.2463
T 4'90	39.25	29.360	7.77	716	0.108	.	.	0.55	.	.	8.50	.	.	0.36	.	.	0.123	.	.	0.80	.	.
T 4'90	40.75	27.000	8.17	867	.	0.98	.	0.64	34	4.7253	11.00	500	4.6576	0.40	19	4.6767	0.054	75	6.1427	2.43	193	4.9000
T 6'90	6.50	0.061	9.54	1880	0.006	0.27	4.6532	0.95	32	4.5274	2.28	700	5.4872	0.22	22	5.0000	0.097	65	5.8261	0.70	327	5.6694
T 6'90	8.75	0.171	20.88	2600	0.006	0.25	4.6198	0.82	52	4.8022	1.59	1260	5.8990	0.27	53	5.2929	0.080	72	5.9542	0.48	190	5.5975
T 6'90	11.00	0.285	24.31	2740	0.010	0.02	3.3010	1.36	32	4.3716	3.93	810	5.3141	0.32	50	5.1938	0.142	53	5.5720	0.62	123	5.2975
T 6'90	14.00	2.674	19.54	2360	0.011	0.47	4.6307	1.06	29	4.4371	3.47	1250	5.5566	0.42	39	4.9678	0.121	61	5.7025	0.79	147	5.2697
T 6'90	15.00	3.845	20.77	2400	0.017	0.18	4.0248	1.03	41	4.5999	3.19	2020	5.8016	0.32	56	5.2430	0.047	75	6.2030	0.86	204	5.3751
T 6'90	17.00	6.868	20.43	2300	0.020	0.27	4.1303	1.24	59	4.6774	2.02	2290	6.0545	0.32	56	5.2430	0.038	81	6.3287	0.77	272	5.5481

APPENDIX 1 (cont.)

			SPM	POC	Cadmium			Copper			Manganese			Nickel			Lead			Zinc		
Survey	Stn.	Salinity	mg/l	µg/l	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd	µg/l	µg/g	Log Kd
T 6'90	19.00	9.711	15.67	2080	0.023	0.43	4.2717	1.11	38	4.5345	2.67	1830	5.8359	0.36	57	5.1996	0.023	82	6.5521	1.20	169	5.1487
T 6'90	20.00	11.920	28.07	2840	0.033	0.27	3.9128	1.31	44	4.5262	1.72	1540	5.9520	0.31	29	4.9710	0.026	63	6.3844	.	80	.
T 6'90	22.00	13.119	16.67	1850	0.021	0.32	4.1829	0.97	27	4.4446	1.54	1350	5.9428	0.41	37	4.9554	0.014	56	6.6021	0.48	139	5.4618
T 6'90	23.50	14.498	19.50	2020	0.022	0.42	4.2808	1.03	56	4.7354	1.37	1470	6.0306	0.41	63	5.1866	0.005	70	7.1461	0.89	209	5.3708
T 6'90	26.00	17.718	9.87	1340	0.031	0.53	4.2329	0.95	27	4.4536	3.47	1490	5.6329	0.32	22	4.8373	0.023	56	6.3865	0.62	138	5.3475
T 6'90	28.00	22.573	7.87	1210	0.028	0.54	4.2852	0.97	29	4.4756	6.14	1070	5.2412	0.33	19	4.7602	0.043	63	6.1659	0.62	178	5.4580
T 6'90	31.00	26.024	11.13	1300	0.029	0.30	4.0147	0.67	28	4.6211	6.24	750	5.0799	0.32	20	4.7959	0.031	54	6.2410	0.48	164	5.5336
T 6'90	33.00	28.657	8.63	1070	0.021	0.49	4.3680	0.53	40	4.8778	5.10	640	5.0986	0.25	24	4.9823	0.035	66	6.2755	0.27	188	5.8428
T 6'90	36.50	32.004	7.87	1070	0.021	0.42	4.3010	0.45	37	4.9150	2.89	540	5.2715	0.24	29	5.0822	0.052	72	6.1413	0.08	165	6.3144
T 6'90	37.75	31.162	4.97	570	0.028	1.10	4.5942	0.63	71	5.0519	4.71	980	5.3182	0.29	53	5.2619	0.076	95	6.0969	0.46	333	5.8597
T 6'90	39.25	30.443	5.93	590	0.031	0.89	4.4580	0.68	41	4.7803	6.96	710	5.0086	0.28	38	5.1326	0.082	71	5.9374	0.49	147	5.4771
T 6'90	40.75	29.500	8.63	731	0.028	0.66	4.3724	0.65	32	4.6922	6.22	550	4.9466	0.31	22	4.8511	0.076	70	5.9643	0.65	144	5.3454

APPENDIX 2 SUSPENDED PARTICULATE MAJOR ELEMENT CONTENTS (TOTAL)

Survey	Stn.	Salinity	SPM (37mm) mg/l	Al203 Wt %	TiO2 Wt %	Si02 Wt %	MgO Wt %	Fe203 Wt %	CaO Wt %	K2O Wt %	Mn Wt %	P2O5 Wt %
F 6'89	-2	0.06	45.71	16.31	1.20	45.35	2.45	9.74	1.23	2.73	0.089	0.502
F 6'89	11	5.79	62.69	.	1.38	.	.	11.80	1.11	3.63	0.071	.
F 6'89	13	9.62	42.54	.	1.49	.	.	13.60	1.26	4.30	0.077	.
F 6'89	15	13.5	31.64	.	1.63	.	.	13.48	1.26	4.17	0.101	.
F 6'89	18	17.8	27.16	28.81	1.69	71.45	4.74	14.18	1.37	4.31	0.121	0.850
F 6'89	20	20.5	28.06	25.28	1.43	61.18	4.00	12.28	1.09	3.64	0.190	0.699
F 6'89	23	26.8	30.60	.	1.59	.	.	13.14	1.46	3.76	0.193	.
F 6'89	25	28.5	27.76	29.63	1.84	71.67	5.06	15.16	2.07	4.32	0.135	0.763
F 6'89	28	30.3	25.90	.	1.55	.	.	13.07	2.14	3.51	0.118	.
F 6'89	31	31	21.94	.	1.71	.	.	14.44	2.09	3.93	0.139	.
F 6'89	38	32.2	12.30	18.33	1.05	44.07	3.03	8.99	1.13	2.52	0.095	0.548
F 6'89	56	33.1	6.91	27.68	1.54	64.61	4.47	12.60	2.70	3.48	0.339	0.717
F 6'89	93	33.8	2.51	8.94	0.43	22.89	2.31	4.92	0.78	0.99	0.391	0.965
F 8'89	-2	0.04	30.86	24.43	1.78	64.82	3.70	14.41	1.79	3.99	0.156	0.669
F 8'89	3	0.277	547.00	.	1.56	.	.	13.04	1.67	3.50	0.065	.
F 8'89	6	1.516	153.00	26.00	1.61	66.75	4.01	13.08	1.46	3.84	0.072	0.662
F 8'89	8	2.585	64.29	.	1.54	.	.	12.98	1.62	3.95	0.073	.
F 8'89	11	3.277	93.14	.	1.67	.	.	14.03	1.71	4.05	0.145	.
F 8'89	13	8.05	38.86	26.85	1.65	68.24	4.39	13.60	1.31	4.01	0.225	0.809
F 8'89	15	10.013	29.40	21.14	1.71	78.73	4.78	14.60	1.85	4.49	0.105	1.086
F 8'89	18	19.785	41.64	.	1.42	.	.	11.80	1.51	3.28	0.097	.
F 8'89	20	22.246	23.28	27.02	1.60	69.74	4.42	13.21	1.86	3.90	0.125	0.884
F 8'89	23	28.034	26.27	26.89	1.73	68.67	4.53	14.13	1.74	4.14	0.124	0.701
F 8'89	25	29.832	26.27	24.13	1.61	60.76	4.05	13.25	1.75	3.73	0.223	0.607
F 8'89	28	31.517	24.39	.	1.54	.	.	12.84	2.16	3.48	0.177	.
F 8'89	31	31.778	18.92	.	1.49	.	.	12.57	1.86	3.38	0.131	.
F 8'89	38	33.047	11.22	26.96	1.69	66.32	4.53	13.41	2.50	3.89	0.137	0.616
F 8'89	59	33.785	6.20	.	1.56	.	.	12.10	3.21	3.51	0.133	.
F 11'89	6	0.035	17.43	20.20	1.33	54.55	3.70	12.89	0.69	3.06	0.102	0.619
F 11'89	13	0.102	258.00	29.43	1.78	71.45	4.83	13.84	1.43	4.29	0.073	0.584
F 11'89	15	0.393	294.00	27.60	1.57	65.25	4.43	12.78	1.23	3.87	0.058	0.543
F 11'89	18	1.249	188.00	31.86	1.60	70.38	5.15	12.81	0.79	3.99	0.257	0.619
F 11'89	20	5.765	234.00	24.69	1.53	61.18	4.04	12.13	0.99	3.51	0.221	0.513
F 11'89	23	8.706	212.00	.	1.62	.	.	13.14	1.40	3.67	0.077	.

APPENDIX 2 (cont.)

Survey	Stn.	Salinity	SPM (37mm) mg/l	Al203 Wt %	TiO2 Wt %	Si02 Wt %	MgO Wt %	Fe203 Wt %	CaO Wt %	K2O Wt %	Mn Wt %	~~P2O3 Wt %~~	P_2O_5 Wt %
F 11'89	25	16.76	100.00	.	1.50	.	.	12.51	1.50	3.59	0.072	~~.~~	
F 11'89	28	20.73	225.00	.	1.13	.	.	9.82	1.38	2.33	0.068	~~.~~	
F 11'89	31	26.16	72.29	.	1.27	.	.	10.22	1.88	2.81	0.081	~~.~~	
F 11'89	38	31.03	10.94	25.25	1.57	59.69	4.15	12.66	2.82	3.56	0.235	~~0.369~~	0·477
F 11'89	48	31.6	8.27	28.39	1.53	64.82	4.52	12.35	3.08	3.58	0.256	~~0.414~~	0·534
F 11'89	84	33.5	2.44	22.89	1.05	51.13	3.80	8.54	2.40	2.58	0.118	~~0.460~~	0·593
F 11'89	74	34.09	1.20	30.79	1.47	74.02	5.45	11.73	3.16	3.71	0.134	~~0.564~~	0·729
F 3'90	13	0.037	30.15	.	1.29	.	.	11.42	1.36	3.22	0.055	~~.~~	
F 3'90	15	0.04	20.30	25.11	1.46	66.53	3.88	12.78	1.35	3.80	0.048	~~0.410~~	0·529
F 3'90	18	0.054	17.91	26.62	1.41	64.18	4.00	12.02	1.27	3.74	0.187	~~0.426~~	0·550
F 3'90	20	1.041	44.48	.	1.54	.	.	13.91	1.77	4.06	0.101	~~.~~	
F 3'90	23	9.335	14.48	33.48	1.59	75.95	5.77	14.78	1.12	4.54	0.055	~~0.571~~	0·738
F 3'90	25	14.161	18.66	35.22	1.74	80.01	5.54	15.61	2.02	4.84	0.057	~~0.564~~	0·729
F 3'90	28	14.976	12.01	22.75	1.12	50.92	4.16	10.75	0.92	3.58	0.037	~~0.412~~	0·532
F 3'90	31	18.356	10.36	31.97	1.51	69.53	4.96	14.50	1.73	4.07	0.051	~~0.580~~	0·749
F 3'90	34	20.984	10.14	31.33	1.44	67.82	4.78	13.80	2.07	3.94	0.179	~~0.534~~	0·690
F 3'90	42	26.745	8.78	36.96	1.81	82.58	5.84	16.71	3.29	4.77	0.223	~~0.589~~	0·761
F 3'90	48	28.662	8.85	26.56	1.39	61.40	4.46	12.34	1.85	2.80	0.069	~~0.406~~	0·525
F 3'90	51	27.163	7.70	30.65	1.43	68.46	4.81	13.44	2.48	3.72	0.058	~~0.490~~	0·632
F 3'90	56	29.322	7.41	35.84	1.76	58.83	5.87	15.63	3.15	4.56	0.083	~~0.554~~	0·715
F 3'90	61	31.314	4.75	24.53	1.09	53.27	4.18	10.17	1.46	2.75	0.054	~~0.474~~	0·612
F 3'90	74	33.561	4.21	26.00	1.49	62.68	4.26	13.48	4.18	3.61	0.227	~~0.406~~	0·525
F 3'90	84	33.656	7.31	.	1.46	.	.	11.98	4.08	3.60	0.164	~~.~~	
F 3'90	93	32.399	6.78	23.62	1.40	56.05	3.42	12.80	3.92	3.27	0.080	~~0.415~~	0·536
F 5'90	0	0.066	7.71	13.30	0.72	48.99	2.82	9.95	.	2.06	0.128	~~1.123~~	1·450
F 5'90	8	0.184	215.40	.	2.03	.	.	17.16	2.49	4.97	0.066	~~.~~	
F 5'90	11	0.743	87.86	32.48	1.85	72.09	5.04	15.44	1.79	4.89	0.068	~~0.479~~	0·619
F 5'90	13	1.813	107.73	.	1.55	.	.	13.54	1.79	3.94	0.096	~~.~~	
F 5'90	15	4.107	62.33	.	1.78	.	.	15.46	2.24	4.78	0.143	~~.~~	
F 5'90	18	12.549	36.42	.	1.68	.	.	14.67	2.07	4.46	0.087	~~.~~	
F 5'90	20	18.013	36.87	.	1.63	.	.	13.97	2.20	4.32	0.088	~~.~~	
F 5'90	23	20.998	36.27	.	1.64	.	.	14.24	3.83	4.16	0.089	~~.~~	
F 5'90	25	26.153	39.40	25.55	1.52	63.32	4.06	13.41	1.79	3.91	0.104	~~0.486~~	0·628
F 5'90	28	29.622	34.63	.	1.67	.	.	14.21	2.43	4.30	0.190	~~.~~	

APPENDIX 2 (cont.)

Survey	Stn.	Salinity	SPM (37mm) mg/l	Al203 Wt %	TiO2 Wt %	Si02 Wt %	MgO Wt %	Fe203 Wt %	CaO Wt %	K2O Wt %	Mn Wt %	~~P2O3 Wt %~~	P_2O_5 wt %
T 8'89	20	16.85	34.17	.	1.00	.	.	9.48	1.76	2.85	0.109	~~.~~	
T 8'89	22	17.08	19.64	.	1.10	.	.	10.18	1.89	3.22	0.109	~~.~~	
T 8'89	23.5	19.45	20.72	.	1.00	.	.	8.92	1.96	2.96	0.094	~~.~~	
T 8'89	26	19.93	15.04	.	0.93	.	.	8.74	2.00	2.89	0.099	~~.~~	
T 8'89	28	21.8	29.28	.	0.88	.	.	8.71	2.07	2.70	0.119	~~.~~	
T 8'89	31	28.39	4.60	12.02	0.77	36.30	2.64	6.91	2.32	2.10	.	~~0.408~~	0·527
T 8'89	33	30.39	3.78	13.38	1.00	46.94	2.93	9.18	4.80	2.71	0.079	~~0.444~~	0·573
T 8'89	36.5	32.86	4.35	11.19	0.83	41.52	2.52	7.49	5.97	2.30	0.054	~~0.373~~	0·481
T 8'89	39	31.99	2.72	17.27	1.15	60.31	4.19	10.27	7.36	3.31	0.079	~~0.674~~	0·871
T 8'89	41	31.49	5.37	13.02	0.92	45.74	3.23	8.59	4.27	2.76	0.059	~~0.390~~	0·504
T 9'89	8.75	0.0102	57.43	.	1.40	.	.	13.51	1.72	3.85	0.233	~~.~~	
T 9'89	15	0.229	24.00	20.46	1.45	64.29	4.15	13.77	1.33	4.01	0.361	~~0.408~~	0·527
T 9'89	17	0.591	38.57	21.63	1.42	65.12	4.99	13.63	1.51	4.06	0.144	~~0.426~~	0·550
T 9'89	19	2.365	77.14	.	1.27	.	.	12.52	1.55	3.49	0.129	~~.~~	
T 9'89	22	6.286	63.14	.	1.30	.	.	12.94	1.62	3.70	0.134	~~.~~	
T 9'89	23.5	7.916	23.13	19.22	1.25	62.10	4.34	12.70	1.55	3.79	0.114	~~0.390~~	0·504
T 9'89	28.01	9.951	27.61	16.15	1.08	54.21	3.58	10.74	2.45	3.42	0.193	~~0.284~~	0·367
T 9'89	28	14.943	25.37	22.13	1.38	68.33	4.97	13.27	2.22	4.28	0.228	~~0.408~~	0·527
T 9'89	31	19.969	12.93	.	1.00	.	.	10.19	3.55	2.98	0.084	~~.~~	
T 9'89	33	26.31	6.08	14.72	1.03	48.99	3.20	9.77	5.37	2.99	0.074	~~0.373~~	0·481
T 9'89	40.75	27.39	4.84	16.99	1.20	55.54	4.00	10.88	6.83	3.52	0.074	~~0.390~~	0·504
T 2'90	15	0.059	28.81	21.71	1.25	55.96	4.44	12.82	1.57	3.71	0.084	~~0.390~~	0·504
T 2'90	17	0.112	88.29	.	0.98	.	.	9.81	1.27	2.96	0.124	~~.~~	
T 2'90	20	1.052	90.00	.	1.42	.	.	13.53	2.36	4.01	0.149	~~.~~	
T 2'90	22	1.421	84.86	.	1.47	.	.	14.48	1.60	4.32	0.099	~~.~~	
T 2'90	26	4.141	68.29	.	1.42	.	.	14.23	1.58	4.31	0.104	~~.~~	
T 2'90	28	10.287	70.57	.	1.27	.	.	12.40	1.94	3.71	0.084	~~.~~	
T 2'90	31	15.296	64.03	.	1.05	.	.	10.75	2.18	3.02	0.074	~~.~~	
T 2'90	33	18.87	50.30	.	1.17	.	.	11.34	2.66	3.30	0.129	~~.~~	
T 2'90	36.5	20.751	17.61	21.88	1.20	57.65	5.02	12.10	3.02	3.71	0.228	~~0.373~~	0·481
T 2'90	37.7	26.147	16.42	19.42	1.18	54.64	4.44	11.27	3.62	3.52	0.074	~~0.337~~	0·435
T 2'90	39.25	24.569	14.68	.	1.37	.	.	9.81	4.35	4.17	0.084	~~.~~	
T 2'90	40.75	22.059	23.12	.	1.32	.	.	12.71	3.85	3.79	0.084	~~.~~	
T 2'90	41.75	32.284	7.14	.	1.20	.	.	11.34	4.79	3.46	0.074	~~.~~	

APPENDIX 2 (cont.)

Survey	Stn.	Salinity	SPM (37mm) mg/l	Al203 Wt %	TiO2 Wt %	Si02 Wt %	MgO Wt %	Fe203 Wt %	CaO Wt %	K2O Wt %	Mn Wt %	~~P2O3 Wt %~~	P_2O_5 wt %
T 4'90	11	0.06	24.63	22.09	1.43	67.11	4.36	13.83	2.17	4.31	0.099	~~0.444~~	0·573
T 4'90	13	0.21	30.30	.	1.40	.	.	14.13	2.27	4.37	0.109	~~.~~	
T 4'90	14	0.72	38.06	.	1.38	.	.	13.95	2.18	4.25	0.099	~~.~~	
T 4'90	15	1.57	30.60	.	1.52	.	.	14.98	2.35	4.75	0.183	~~.~~	
T 4'90	17	5.76	26.27	22.92	1.40	68.59	4.87	13.41	2.41	4.35	0.203	~~0.373~~	0·481
T 4'90	19	6.09	23.13	22.24	1.32	68.39	4.83	13.24	1.94	4.29	0.089	~~0.426~~	0·550
T 4'90	20	9.05	24.18	21.50	1.35	65.74	4.83	13.08	2.55	4.20	0.084	~~0.373~~	0·481
T 4'90	22	8.45	21.58	.	1.32	.	.	13.00	2.71	4.18	0.084	~~.~~	
T 4'90	23.5	10.43	22.23	.	1.23	.	.	12.08	3.08	3.79	0.079	~~.~~	
T 4'90	26	14.05	47.70	.	1.18	.	.	11.94	3.16	3.36	0.099	~~.~~	
T 4'90	28	20.04	27.27	.	1.15	.	.	10.65	4.06	3.29	0.109	~~.~~	
T 4'90	31	24.92	17.42	.	0.97	.	.	9.75	4.09	2.85	0.059	~~.~~	
T 4'90	37.75	29.49	17.21	.	1.00	.	.	9.06	5.83	3.01	0.054	~~.~~	
T 4'90	40.75	27	15.27	.	1.18	.	.	11.27	6.25	3.49	0.064	~~.~~	
T 6'90	6.5	0.061	15.20	20.54	1.30	64.82	5.15	12.89	1.22	3.98	0.156	~~0.628~~	0·811
T 6'90	8.75	0.171	21.90	16.85	1.06	50.64	3.75	10.95	1.09	3.20	0.240	~~0.466~~	0·602
T 6'90	11	0.285	35.20	.	1.29	.	.	12.84	1.59	3.88	0.220	~~.~~	
T 6'90	14	2.674	21.60	21.89	1.38	66.25	5.37	13.69	1.30	4.15	0.181	~~0.503~~	0·649
T 6'90	15	3.845	26.30	.	1.35	.	.	14.05	1.63	4.02	0.206	~~.~~	
T 6'90	17	6.868	28.60	.	1.21	.	.	12.45	1.56	3.67	0.202	~~.~~	
T 6'90	19	9.711	22.40	.	1.13	.	.	11.47	1.71	3.62	0.191	~~.~~	
T 6'90	20	11.92	34.50	.	1.22	.	.	12.19	2.11	3.61	0.198	~~.~~	
T 6'90	22	13.119	22.70	.	1.02	.	.	10.01	1.76	3.25	0.200	~~.~~	
T 6'90	23.5	14.498	.	11.46	0.71	34.79	2.85	7.19	0.48	2.13	0.092	~~0.253~~	0·327
T 6'90	26	17.718	15.00	15.49	0.97	53.89	.	9.44	2.05	3.22	0.170	~~0.479~~	0·619
T 6'90	28	22.573	14.80	.	0.98	.	.	9.11	2.42	3.01	0.129	~~.~~	
T 6'90	31	26.024	13.20	.	0.95	.	.	8.73	2.85	2.84	0.103	~~.~~	
T 6'90	33	28.657	11.80	.	1.05	.	.	9.72	4.16	3.31	0.145	~~.~~	
T 6'90	36.5	32.004	7.30	.	0.95	.	.	9.76	4.35	2.80	0.169	~~.~~	
T 6'90	37.75	31.162	6.20	18.14	1.19	60.02	4.51	10.86	5.61	3.82	0.093	~~0.422~~	0·544
T 6'90	39.25	30.443	6.30	16.97	1.19	56.50	4.10	11.12	4.77	3.66	0.095	~~0.388~~	0·501
T 6'90	40.75	29.5	10.60	.	0.84	.	.	7.82	3.77	2.59	0.063	~~.~~	

APPENDIX 3 SUSPENDED PARTICULATE MAJOR ELEMENT CONTENTS (LEACHED)

			Al2O3	TiO2	SiO2	MgO	Fe2O3	CaO	K2O	Mn	~~P2O3~~	P_2O_5
Survey	Stn.	Salinity	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %	~~Wt %~~	Wt %
F 11'89	6	0.04	18.89	1.24	49.63	2.90	10.38	0.56	2.77	0.048	~~0.295~~	0·380
F 11'89	15	0.4	27.21	1.58	65.46	3.83	11.77	0.74	3.72	0.020	~~0.245~~	0·316
F 11'89	20	5.77	24.56	1.56	62.25	3.33	11.28	0.74	3.53	0.031	~~0.236~~	0·3065
F 11'89	38	31.03	24.75	1.57	60.76	3.42	11.25	0.69	3.35	0.013	~~0.204~~	0·264
F 11'89	48	31.6	28.72	1.62	68.03	3.85	11.61	0.66	3.63	0.033	~~0.197~~	0·254
F 11'89	74	34.09	30.80	1.49	73.38	4.19	10.71	0.54	3.75	0.055	~~0.351~~	0·454
T 9'89	8.75	0.01	18.30	1.36	58.47	3.55	11.95	0.90	3.48	0.044	~~0.245~~	0·316
T 9'89	17	0.59	21.12	1.39	64.68	4.17	12.63	0.92	2.14	0.052	~~0.277~~	0·358
T 9'89	23.5	7.92	18.60	1.23	61.04	3.62	11.59	0.90	3.49	0.034	~~0.259~~	0·334
T 9'89	28.1	9.95	15.55	1.04	50.97	3.04	9.60	0.75	2.91	0.027	~~0.222~~	0·286
T 9'89	28	14.94	19.85	1.29	64.01	4.00	11.46	0.82	3.69	0.028	~~0.254~~	0·328
T 9'89	33	26.31	14.51	1.02	49.01	2.75	8.98	0.80	2.83	0.027	~~0.228~~	0·294

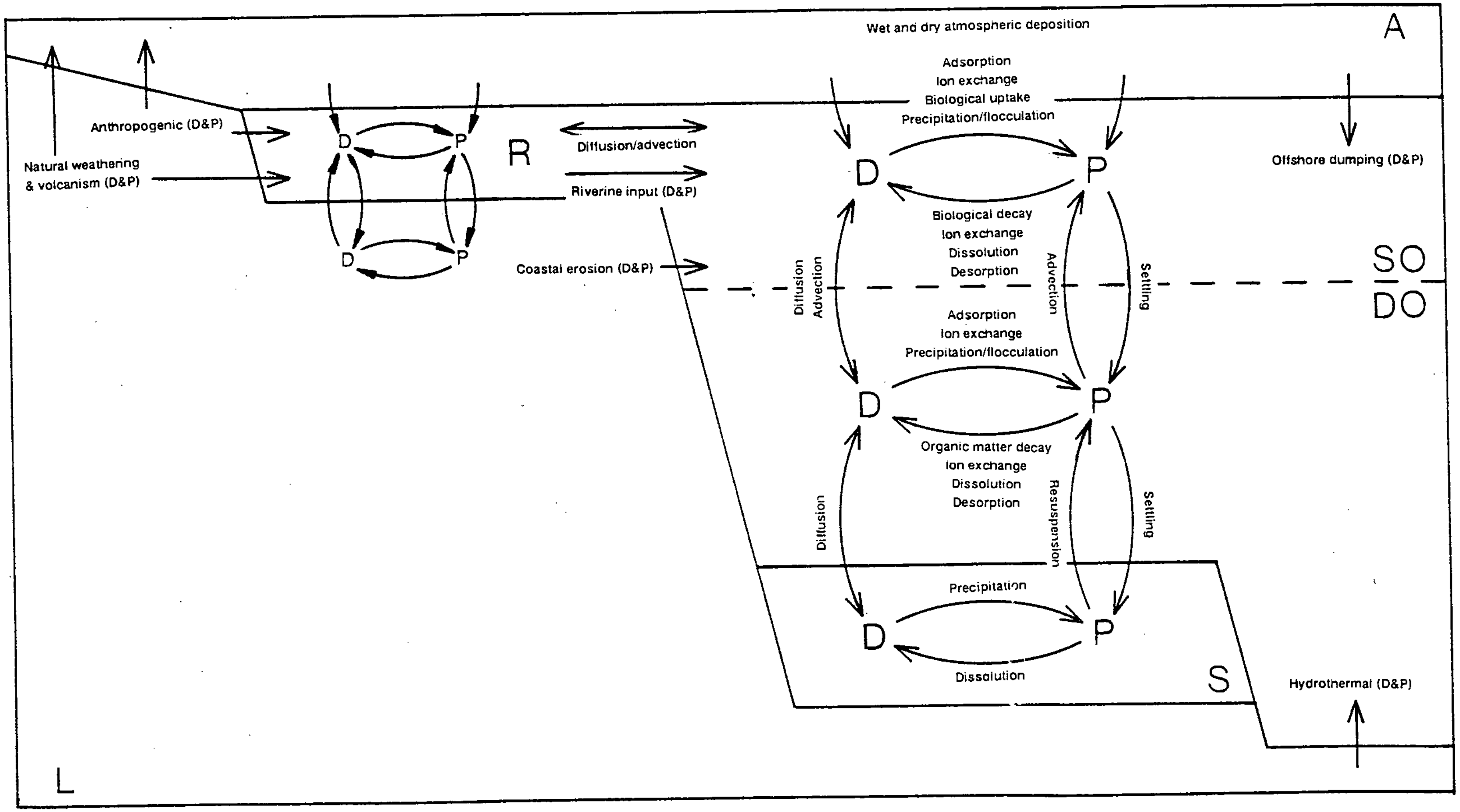

Figure 1.1. Particle-water interactions in marine environments

D = Dissolved, P = Particulate, L = Land, R = Rivers, A = Atmosphere, S.O. = Surface Ocean, D.O. = Deep Ocean, S = Oceanic Sediments.

are a measure of the total interaction between an ion and its environment, this possible relationship would explain:

(i) why metal enrichments in particulate phases correlate with ionic charge and with the reciprocal of the ionic radius (Whitfield and Turner 1983);

(ii) why the more easily-polarisable (softer) metal, for atoms of similar charge and radius, is enriched in the solid phase. (Lattice energies indicate that the bond between the softer metal and its oxide would be stronger and more stable than the bond between the harder metal and its oxide.)

Other parameters that have been linked with partition coefficients include ionisation energies, ionic potentials, hydrolysis constants, solubility products and electronegativities. Since these parameters are all linked with one another (as discussed by Li 1991), it has been proposed that metal electron binding energies be used to explain the partitioning behaviour of the elements between dissolved and particulate phases in the marine environments (Li 1991).

1.3.1: Factors affecting partition coefficients

Partition coefficients depend on many environmental variables, and it is difficult to determine what measured values actually represent. Great care must therefore be taken when applying them to environmental or experimental conditions other than those for which they were determined (Balls 1988, 1989, Bourg 1987, Cremers and Maes 1986). Some of the factors affecting partition coefficients are discussed below.