DISSOLVED TRACE METALS IN THE ESTUARINE PLUMES OF THE HUMBER, THAMES AND RHINE RIVERS

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ABSTRACT

Estuarine plumes, the coastal sea areas directly influenced by a riverine freshwater discharge, form an important transition zone in the journey of land-derived trace metals to the oceanic sink, connecting river and estuarine environments with the continental shelf and eventually the deep sea, and modifying the flux of material from the coastal margins to the world ocean.

The work described in this thesis was undertaken as part of the North Sea Project (NSP) of the Natural Research Council (NERC) of the United Kingdom. Within the wider framework of this program, five twelve-day cruises were dedicated to the survey of the estuarine plumes of the Humber, Thames and Rhine rivers at different times of the year. Dissolved and particulate trace metal samples were taken and analysed, together with salinity, turbidity, chlorophyll, nutrients and several other relevant parameters, in order to establish trace metal distributions throughout the survey areas and between the dissolved and particulate phases, and to investigate influx from estuaries and the atmosphere and exports to the central shelf sea as well as seasonal patterns and biological and sedimentary mobilisation and removal mechanisms.

Dissolved concentrations of nickel, copper, zinc and cadmium were found to be distributed in plumes around the riverine outflows, broadly reflecting the freshwater contribution to the respective areas. Effective riverine concentrations reaching the sea apparently increased from winter to summer. Extrapolations of trace metal-salinity relationships based on offshore samples frequently gave significantly different zero-salinity intercepts than those based on nearshore or estuarine samples, indicating either additional inputs or removal in the coastal zone. Dissolved concentrations of the four metals were also found to be decreased in areas of high biological activity. Effective river water concentrations estimates ranged from 90-520 nmol/l for Ni, 73-330 nmol/l for Cu, 210-1000 nmol/l for Zn and 2.3-9.3 nmol/l for Cd.

Manganese and cobalt were found to be rapidly removed from the dissolved phase in the vicinity of the outflows, but were also remobilised in estuaries, during resuspension events and in offshore areas during the summer months. Dissolved lead concentrations were generally lower in turbid nearshore areas off the Humber and Rhine rivers than offshore, resulting in positive correlations with salinity in the plumes. Iron was found to be the element strongest attached to particles. In the few cases of apparent linear mixing, especially in estuaries, the following effective riverine end member concentrations were found: 90-10000 nmol/l for Mn (including remobilisation in the low salinity zone), 350 nmol/l for Fe, 4.8-32 nmol/l for Co and 0.7-20 nmol/l for Pb.

Compared to world wide average river concentrations, the estimates show highly elevated levels for all elements except Mn and Fe: by one order of magnitude for Ni, Co and Cu, and by up to two orders of magnitude for Zn, Cd and Pb. This differentiation between the metals is consistent with a high anthropogenic contribution to the elevated levels. The river Thames was found to be a very strong source of dissolved lead (up to 20 nmol/l), whilst the Humber was shown to be a significant source of cadmium (up to 9.3 nmol/l). Point sources of cadmium were also found both in the Rhine estuary and the adjacent coastal zone.

TABLE OF CONTENTS

TABLE OF FIGURES

TABLE OF TABLES

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So Iff the Water Genie told Haroun about the Ocean of the Streams of Story, and even though he was full of a sense of hopelessness and failure the magic of the Ocean began to have an effect on Haroun. He looked into the water and saw that it was made up of a thousand thousand thousand and one different currents, each one a different colour, weaving in and out of one another like a liquid tapestry of breathtaking complexity; and Iff explained that these were the Streams of Story, that each coloured strand represented and contained a single tale. Different parts of the Ocean contained different sorts of stories, and as all the stories that had ever been told and many that were still in the process of being invented could be found here, the Ocean of the Streams of Story was in fact the biggest library in the universe. And because the stories were held here in fluid form, they retained the ability to change, to become new versions of themselves, to join up with other stories and so become yet other stories; so that unlike a library of books, the Ocean of the Streams of Story was much more than a storeroom of yarns. It was not dead but alive.

Salman Rushdie: *Haroun and the Sea of Stories.* London (1990).

CHAPTER 1: OBJECTIVES OF STUDY

Scientific papers addressing principal questions of environmental analysis frequently go to great length to emphasise the importance of a clear statement of the objectives at the outset of a research or monitoring program (e.g. American Chemical Society, ACS, 1980; Keith et al., 1983; Keith, 1990; National Research Council (of the United States), NRC, 1990). For the design and planning of environmental studies, a conceptual approach is suggested, starting with a clear-cut formulation of the questions to be addressed, followed by a decision on the type, quality and extent of the measurements required to provide a meaningful answer. The need to strengthen the link between data generation and their intended use is highlighted by Keith et al. (1983), stating that 'It cannot be assumed that the person requesting an analysis will also be able to define the objectives of the analysis properly'.

Sampling strategy and choice of the analytical method ideally should be determined by the data and data quality requirements of the chosen data interpretation tools, like graphical presentations, statistical analysis or numerical models, which in turn have to be selected depending on the questions to be answered. In NRC (1990), the need for the formulation of such a comprehensive study strategy is underlined by the quote: 'Your results will be as coherent and as comprehensible as your initial conception of the problem'.

Some of the papers referred to above are mainly concerned with environmental monitoring programs, frequently undertaken by or conducted for government authorities in order to check for compliance with statutory requirements, to establish assumed trends or to test hypotheses. Within the more experimental research framework, a strict adherence to the recommended procedures is not always possible, as scientists will try to improve and develop measurement techniques and data interpretation concepts as the study progresses, potentially leading to new methods and findings which could not be anticipated from the outset. Real-life impediments, like the unavailability of a preferred method, limited sampling opportunities or other resource restrictions, are usually common to both monitoring and research activities. Large research projects, trying to simultaneously satisfy many different interests, inadvertently represent a compromise between the optimum requirement of an individual study and what can be accommodated within the project as a whole. Although the objectives will have to be specified on a general and intermediate level, it is frequently not feasible to coordinate all the individual activities entirely from the start. Special efforts then have to be made to achieve sufficient integration and collaboration between the individual researchers as the program develops.

The work presented in this thesis forms part of the North Sea Project (NSP) and of related follow-up studies by the Natural Environment Research Council (NERC) of the United Kingdom. In NERC (1987), the ultimate objective of this project is defined as 'a prognostic water quality model to aid management of the North Sea'. Three more specific objectives are formulated:

- Generation of a transport model for conservative passive constituents
- Identification and quantification of non-conservative processes affecting the cycling and ultimate fate of constituents, with eventual incorporation of the results into models
- Definition of a seasonal cycle of the North Sea system providing a data base and reference for shelf-sea studies, and an opportunity to test models.

As part of this project, a special investigation into the physical and chemical processes in coastal plumes was undertaken. Two 12-day cruises were devoted to the estuarine plumes of the rivers Humber (December 1988) and Thames (February 1989), later followed by additional cruises outside the NSP proper, surveying the plume of the Humber at different stages during the seasonal cycle (May and July/August 1990), and an investigation of the coastal plume of the river Rhine (October 1990).

The objectives of these plume studies were also outlined in NERC, 1987: 'For eventual water quality modelling, mechanisms and parameterisations of dispersion will be sought, together with pathways for non-conservative constituents including particle-water and sediment-water interactions'. The cruise report of the first Humber cruise in December 1988 (Morris and Bayne, 1989), here taken as an example, stated the scientific objective as 'to characterise and model the processes controlling the transport of effluent species from large estuaries to the sea'. Three specific objectives of the cruise were defined, i.e. 'to define the spatial and temporal characteristics of the plume of water originating from the Humber Estuary and the Wash by repetitive sampling for selected conservative and non-conservative constituents around a grid enclosing the plume', and two more objectives relating to on-board experiments.

These objectives, although clear in their intention and eventual goal, are not yet precise enough to enable the unequivocal derivation of data and interpretational requirements. For the purpose of this thesis, however, we will try to emulate the conceptual approach referred to above. We will therefore further specify and narrow the objectives of this study, and will try to show that all data generation and interpretation efforts are their logical consequence. The objectives are thus defined as

- to define and compare, with a horizontal resolution of about 10 km, and including vertical stratification, the spatial variation of the total dissolved concentrations of several trace metals of contrasting biogeochemical behaviour and ecotoxicity in the coastal plumes of major North Sea estuaries,

- to describe and quantify the influx of these total dissolved trace metals from these estuaries into the respective coastal regions,

- to investigate the seasonal variation of these metals in coastal plumes, and the seasonal variation of the estuarine influx, and

- to investigate the correlation between dissolved trace metal distributions and other physico-chemical parameters, especially salinity, suspended particulate matter (SPM), chlorophyll and trace metals exchangeably bound to SPM, in order to

    - make qualitative statements about underlying processes, and

    - to make quantitative statements which can be incorporated into water quality models.

CHAPTER 2: TRACE METALS IN THE COASTAL ZONE

The coastal zone links estuaries to the ocean, receiving trace metal loadings discharged by rivers and modified in estuaries, together with atmospheric inputs, releases from the sediments and anthropogenic inputs from tidal water discharges, offshore activities and dumping. Trace metal behaviour in coastal waters can be interpreted as the gradual superposition of marine over ongoing estuarine processes. Therefore, in the following, aspects of trace metal behaviour in both the estuarine and open ocean environment are reviewed, before an attempt is made to describe the coastal situation as a synthesis of the two.

2.1 TRACE METALS IN OPEN OCEAN SEA WATER

The determination of trace metals in sea water has always been a formidable challenge for the analytical chemist. The combination of the frequently very low environmental concentrations and the high contamination potential of sampling crafts (stack dust and the ubiquity of corroded metal) inhibited the collection of meaningful results until very recently. Since the late 1970s, however, improved sampling devices, like the Go-flo water sampling bottle, contamination control during preparation and analysis in 'clean laboratories', rigorous cleaning of all apparatus involved and advances in the analytical instrumentation have lead to a great leap forward in sea water trace metal analysis (Bruland, 1983). The improvement of procedures and techniques has been monitored and stimulated by inter-laboratory comparisons (Bruland et al., 1985; Bewers et al., 1985). The outcome is a continuously increasing data base of 'oceanographically consistent' (i.e. compatible with known large-scale circulation patterns) values, and a revision of previously accepted values towards lower concentrations.

Within the stable open ocean environment, these recent data sets show characteristic vertical profiles for various groups of elements. Bruland (1983) distinguishes between seven different types of distribution, all the result of specific geochemical processes. Whitfield and Turner (1987) identify three major types, which will be referred to below. The main driving force behind these distributions had already been identified by Turekian (1977) as the 'great particle conspiracy', but its operation in the ocean has only subsequently been elucidated in more detail.

Biological activity in the sunlit surface layer is the main production mechanism for particles in the ocean, efficiently sequestering nutrients and also some trace metals from the dissolved phase to build living matter, with faeces and dead remains of organisms as by-products. Trace elements can either be directly involved in biochemical reactions, or become rather unspecifically adsorbed to biogenic surfaces. Particles will also enter the ocean from coastal areas or as atmospheric dust. If not consumed in the upper ocean, these particles will eventually sink through the water column, where they can be re-packaged by other organisms feeding on them. Only a small proportion, though, will immediately reach the sea bed and be incorporated into the sediment; a fraction will re-dissolve due to chemically or biologically mediated processes, releasing their elementary components into intermediate and bottom waters, where they accumulate in solution, until the water re-surfaces, e.g. in an upwelling zone, and the constituents become again available to biological uptake. Individual atoms may undergo many of these internal oceanic cycles, before they finally leave the system through the sedimentary sink. Resulting profiles, with depletion of the surface layer and enrichment at mid-depth (P, NO_3^-, Cd, As), or deeper (Si, CO_3^{2-}, Ba, Zn), depending on the dissolution of the particles in which the elements in question are predominantly incorporated, have been described as 'nutrient-type' (Bruland, 1983) or 'recycled' (Whitfield and Turner, 1987). These profiles become more pronounced, as the water mass ages during the oceanic grand tour from the North Atlantic to the North Pacific, leading to a horizontal segregation in addition to the vertical one, between young and older intermediate water. Dissolved concentrations of Ni, Zn and Cd, for example, have been found to be substantially lower in North Atlantic deep water than in the North Pacific (Bruland and Franks, 1983).

'Scavenged' elements, however, have a much higher affinity to particles. They are usually supplied to the open ocean surface layer by atmospheric sources, with contribution from land drainage at the ocean margin, are subsequently scavenged by particles and transported downwards. Although the particle population diminishes with depth, their high particle reactivity is sufficient to ensure a comparably fast incorporation into the sediment. Their concentration in the surface layer is largely controlled by external inputs, whilst being generally depleted in deeper water. Mn and Al from continental dust are the best examples for this behaviour, recently together with Pb, mainly from anthropogenic sources.

'Accumulated' elements (Whitfield and Turner, 1987), without a tendency to associate with particulate matter to an extent which significantly affects their sea water concentration ('conservative behaviour'), do not undergo any of these fractionating processes. When normalised to salinity, their distribution will be uniform throughout the water column, and in the absence of an effective removal mechanism they are relatively abundant in sea water. This group includes major sea salt components.

Direct measurements of particulate fluxes to the sea bed are being made using sediment traps, moored at the ocean floor for weeks or months (e.g. Broecker and Peng, 1982). Estimates of the associated trace metal transport, however, are rather sparse. Net removal rate estimates also would have to take into account, that not all particle-bound trace metals reaching the sea floor will necessarily become permanently buried, but can potentially re-dissolve during diagenetic processes in the sediment.

The different time scales involved in the passage of trace elements through the ocean as part of the geological grand cycle have frequently been characterised by residence times, calculated from the total amount of a substance present in a reservoir, divided by the rate of throughput (input or output), assuming a steady state system with mixing times short compared to the residence time. One formulation of this concept are the Mean Oceanic Residence Times (MORT's), defined as the total quantity of an element present in the oceans divided by its riverine input rate or sedimentary loss rate. Whitfield and Turner (1987) relate previously calculated MORT's and oceanic concentration ranges of individual trace elements to the three types of vertical profiles described above and their different trace metal removal efficiencies. Accumulated elements, with a MORT exceeding 100,000 y, usually have concentrations of 10^{-8} - 10^{-1} mol/l. Recycled elements, with a MORT of 1,000 to 100,000 y, usually are found at concentrations between 10^{-11} and 10^{-5} mol/l, whilst scavenged elements, with MORT's no longer than 1,000 y, are depleted to concentrations between 10^{-14} and 10^{-11} mol/l.

It has been pointed out, though, that MORT-values can only be rather crude estimates, because they ignore a number of potentially important input and output terms, like atmospheric deposition, hydrothermal vents, atmospheric exchange and the rock sink (Chester, 1990). For riverine inputs, world averaged values have been given (Martin and Whitfield, 1983), but only a fraction of these fluxes will actually reach the open ocean, because a significant proportion is being trapped in estuaries or the near-shore zone (Bewers and Yeats, 1977). With regard to other sources, however, especially atmospheric inputs, the available data are scarce and unreliable, as they are for global sedimentation rates. The concept of residence times also assumes a well stirred reservoir, which, as the profiles for recycled and scavenged elements show, the ocean is not. It may therefore be more appropriate to calculate residence times for surface and deep sea separately, recognising that these values, especially for the surface ocean, are variable with time, e.g. seasonality, and space, e.g. distance to continental sources or upwelling zones (Wangersky, 1986).

Attempts have been made to devise mathematical models to simulate oceanic removal of trace metals by both scavenging and recycling processes. Scavenging models frequently use nuclides in the natural radioactive decay series, especially Th-isotopes, and estimate removal rates from a comparison of the observed abundance of parent and an adsorption-prone daughter with their production rate. Recycled element behaviour has been simulated with carrier models, linking trace metals to their ratios to major ions in the biogenic carrier phases, and two-box models, calculating the particle downflux from riverine and atmospheric sources to the surface ocean box and its exchange with the deep ocean. For theoretical considerations of both types of particle-interactive behaviour, surface-complexation models (SCM's) have been used. For a recent review of the different models see Chester (1990).

2.2 TRACE METALS IN ESTUARIES

It is probably fair to say that during no other stage on their journey between mobilisation on the continental crust and permanent burial in the sediment are trace metals subject to such dramatic change within so small an area as when passing through the worlds estuaries.

These changes take place in response to strong physico-chemical gradients in a very complex and time-variable environment, created by the continuous supply of matter and energy from two so different sources as the land and the sea. Nevertheless it seems possible to reduce the multitude of processes and changing conditions to two or three basic features, i.e.

(i) the interaction of river water and associated particulate material (including biogenic particles) with sea water and associated particulate material during estuarine mixing

(ii) the interaction between particulate matter and the dissolved phase, and

(iii) the interaction of the bottom sediment with the overlying water column,

which will all be discussed in the following.

2.2.1 Estuarine mixing

Conceptually, estuarine mixing can be seen as the interaction between two end members, the river water and its associated particulate material, and the sea water and its associated material as driven by the estuarine circulation pattern. The two end members differ widely in composition and physico-chemical characteristics.

Sea water contains about 35000 mg/l salt, notably sodium and chloride ions, resulting in a high ionic strength, has a pH at around 8.1 and is generally depleted in trace metals. Although sea water is considered to be of a far more uniform character than the river end member, the properties of coastal waters can vary under the influence of other freshwater inputs, atmospheric deposition and dumping of anthropogenic wastes in the vicinity of an estuary. Suspended particulate matter of both biogenic (e.g. planktonic blooms) and lithogenic (e.g. resuspension, sea bed and cliff erosion) origins can reach estuaries from the seaward end.

River water compositions vary widely both for one individual river with time, and also between different systems. High freshwater discharges of rivers in spate contribute disproportionally to the overall sediment transport, and also bring about changes in the composition of the dissolved phase. The salt concentration of many river waters is in the range of 20 to 200 mg/l, dominated by calcium and bicarbonate (Burton, 1988). Rivers can contain substantial concentrations of organic ligands, and pH values can range from 5 to above 8, but are usually more acidic than sea water. Trace metal concentrations vary, depending on the drainage area, and can be significantly increased by anthropogenic inputs.

Mixing is driven by the prevailing longitudinal estuarine circulation pattern, resulting from the relative importance of river flow compared to tidal stirring. Without the latter, freshwater can reach the sea almost unaffected by an underlying salt wedge, with a steep salinity gradient preventing any mixing ('salt wedge estuary'). Increased current velocities at the halocline can lead to some entrainment of saline water into the overlying river water, as observed in 'highly stratified' estuaries. In the context of the southern North Sea, with usually medium to high tidal stirring, estuaries are mostly 'partially stratified', with vertical mixing between the inflowing saline bottom water and the outflowing river water due to turbulent eddy diffusion. In estuaries where the tidal flow is completely dominant, the generated turbulence may be strong enough to mix the water column completely (vertically 'well mixed' estuaries). A short summary of longitudinal estuarine circulation patterns can be found, e.g., in Chester (1990). Estuaries with a sufficiently large width to depth ratio can also develop lateral circulation systems, where, due to the Coriolis force, river water (on the northern hemisphere) leaves the estuary predominantly on the right hand side, whilst sea water enters closer to the left hand shore.

Apart from mixing the water masses and thus the dissolved constituents of the two end members, the estuarine circulation also leads to specific transport and mixing processes of the particle populations. Residual circulation alone can trap particles in a convergence between the seaward moving surface layer and the landward moving bottom layer, leading to a turbidity maximum in the low salinity region. This effect, though, is small compared to the turbidity maximum produced by 'tidal pumping', the stepwise upstream movement of resuspended particulate material during flooding, enabled by the asymmetry of the tidal velocities. Both processes concentrate suspended particulate material in the upper reaches of the estuary, where they are mixed with riverine particles. Recent reviews of riverine particle transport are given by Dyer (1986) and Dyer (1988).

In order to determine the proportional influence of the two end members on the dissolved phase of any estuarine water sample, a component with constant, but strongly different concentrations in river and sea water, and not experiencing any loss or gain within the estuary, can be used as an index of mixing. Salinity is the most commonly used, but at salinities below 3 the contribution from riverine ions, not fulfilling the conditions mentioned before, makes it necessary to use the chloride concentration instead (Morris, 1985). Because of the selective transport mechanism, the estuarine generation and modification, and variable end member concentration (Morris et al., 1987), there is no equivalent parameter to monitor the mixing of particles originating from the two opposing ends of the estuary. In special situations, however, it is possible to identify two distinctly different suspended particle populations coming from the river and the seaward end, characterised by differing mineralogy, chemical or isotopic composition (Salomons and Förstner, 1984), and explain estuarine distributions as the result of physical mixing. Nolting et al. (1989), using Ca content of the SPM as a mixing index, could show that particulate trace metal concentrations in the Rhine decreased towards the sea because of dilution with less polluted marine sediments. Schoer (1990) used kaolinite/smectite, kaolinite/chlorite and $^{16}O/^{18}O$ (in carbonates) ratios as well as hafnium concentrations in order to determine the origin of different grain size fractions of suspended and bottom sediments in the Elbe estuary. Dilution of contaminated riverine material by marine particles was shown to be effective up to 40 km above the location of the low discharge salt wedge.

For trace metals, the analysis of dissolved component-mixing index relationships has become a valuable tool to establish particle-dissolved phase interaction, so called non-conservative behaviour, and a means to investigate the existence of additional sources and sinks of dissolved species, as discussed in 3.1.

Changes in pH, pE, alkalinity and the concentrations of organic and inorganic complexing agents during estuarine mixing can also lead to re-distribution phenomena involving only dissolved trace metal species. Sea water cations start competing with riverine trace metals complexed by humic ligands, whereas sea water anions act as additional inorganic complexants, forming e.g. highly stable chloro-species (Chester, 1990). Colloidal material, containing trace metals, and previously stabilised by negative surface charges, can become neutralised by sea water cations and subsequently flocculate to form larger colloids (Eisma, 1986). Although flocculation processes can eventually lead to the generation of hydrous oxide particles, complexation by inorganic and organic ligands can also stabilise trace metals in solution. Using Cathodic Stripping Voltammetry (CSV), a technique able to distinguish between electrochemically labile and complexed dissolved trace metal species, van den Berg et al. (1987) were able to investigate the relationship between organic ligand concentrations and the extent of Cu and Zn complexation in the Scheldt Estuary. Up to 95% of total dissolved Cu and up to 66% of total dissolved Zn were found to be complexed by dissolved organic ligands. Covariation between total dissolved trace metal and corresponding ligand concentrations suggested dissolved phase transport being controlled by organic complexation. Using a similar method, Apte et al. (1990a) could show that riverine dissolved copper was transported conservatively through the Severn estuary in organically complexed form.

2.2.2 Suspended particle - dissolved phase interaction

Particle - water interactions are of such prime importance, because they mark the transition between a transport regime governed solely by the water circulation, and one governed by water circulation and gravitational settling, with far-reaching consequences for the fate of a compound in the environment, including its bioavailability and potential to be permanently buried in the sedimentary sink.

Conventionally, suspended particulate matter is defined as the part of a water sample not passing through a filter with 0.45 μm nominal pore size. However, very small particles may well be carried by the water circulation without being significantly affected by gravitational settling.

Two types of particle - water interaction are considered in the following:

(i) processes removing trace metals from the dissolved phase and incorporating them in or attaching them surficially on particles, including processes leading to the formation of particles solely from dissolved constituents, and

(ii) the desorption of trace metals from particulate matter and their addition to the dissolved phase, including the complete dissolution of particles.

Riverine trace metals can enter an estuary in colloidal form when complexed by humic substances or hydrous iron oxides. As already mentioned in 2.2.1, these colloids can form larger colloids and eventually either form particles or become adsorbed to already existing particles as coatings after particle collision. Redox-sensitive elements with a reduced dissolved form can be scavenged or precipitated in oxic conditions, either coating particles or leading to the formation of new ones. Most of these processes are particularly strong in the particle-rich upper reaches of estuaries. Ackroyd et al. (1986) report oxidative precipitation of Mn, catalysed by initial sorptive uptake on suspended particles in the low salinity zone of the Tamar Estuary, coinciding with sorptive removal of Cu and Zn. In the rather different situation of the Scheldt estuary, with an anaerobic low salinity zone, Duinker et al. (1982) suggest precipitation of Cd as an insoluble sulphide under reducing conditions as one possible explanation for decreased dissolved concentrations. Another form of trace metal removal from the dissolved phase is the biological uptake and subsequent particle production as living, dead and decaying biomass, or faeces. Removal of Cd, Cu and Pb by phytoplankton blooms has been observed, e.g. by Valenta et al. (1986), again in the Scheldt Estuary.

Desorption of trace metals from suspended particulate material can be achieved by increased competition from dissolved inorganic ligands, mainly chloride, as particles are mixed with more saline water, as has been observed, e.g., by Elbaz-Poulichet et al. (1987) or Comans and van Dijk (1988) for cadmium. Windom et al. (1983) report release of Cu from particles in the upper estuaries of the Savannah and Ogeechee rivers, and suggested the increase in pH as an explanation. The dissolution of solid oxides of redox-sensitive elements in reducing environments of the water column has been suggested as one estuarine source of dissolved manganese by Duinker et al. (1979).

Estuarine trace metal distributions are frequently controlled by a complex pattern of both sorption and desorption, as shown by the example of lead in the Gironde Estuary. Elbaz-Poulichet et al. (1984) found sorptive removal of dissolved lead by SPM in the upper estuary, followed further downwards by a mobilisation of exchangeable and carbonate lead and simultaneous coagulation of dissolved organic lead associated with hydrous iron-manganese oxides. The lead-depleted particles were subsequently transported back into the upper estuary by a residual landward bottom current. The reverse of this process has been found for manganese by Evans et al. (1977) in the Newport River, and by Duinker et al. (1979) for manganese in the Rhine and Scheldt estuaries, with removal from the dissolved phase in the lower estuary, particulate transport up-estuary and subsequent reductive remobilisation there, probably involving a sedimentary stage.

The direction and extent of trace metal particle-water interaction depends on many parameters, notably the element concerned, surface area and surface properties of the particle population, the type and concentrations of dissolved complexing agents competing with them, and the abundance of dissolved cations competing with the trace metals for complexation and adsorption sites. These parameters, in return, are frequently dependent on master variables like pH, pE and the ionic strength of the solution. Mixing experiments under controlled laboratory conditions were able to isolate the influence of coagulating salts and pH on the coagulation of trace metals with humic acids (Sholkovitz and Copland, 1981).. Attempts have been made to predict these processes from thermodynamic equilibrium data. If, under special circumstances, equilibrium distributions in the natural environment are closely approached, these models can be useful. Wollast et al. (1979), e.g., were able to predict general trends of the dissolved manganese concentrations during estuarine mixing in Rhine and Scheldt.

An empirical model describing trace metal distribution and re-distribution between the dissolved phase and suspended particles is the K_d distribution coefficient, the ratio of exchangeably bound particulate trace metals and the corresponding dissolved concentrations, explained in more detail in 3.2. K_d-values, however, do not take into account the different ways in which trace metals are present in the different phases, (e.g. dissolved complex, particulate lattice), and because of their dependance on other master variables, like compexant concentrations, salinity, pH and pE, values can vary strongly between different environments. These problems have been addressed by the development of *conceptual* adsorption models, describing adsorption a set of (complexation) reactions perceived to be relevant, especially between dissolved trace metals and solid phase adsorption sites, and possibly simulating differing complex stabilities. A critical review of both empirical and conceptual metal adsorption models is given by Bourg (1987), who simulated trace metal behaviour in the Gironde Estuary, using complex formation constants, adsorption properties, turbidity and pH profiles from previous surveys.

2.2.3 Interaction between bottom sediment and water column

These two compartments are very closely coupled by constantly ongoing erosion, suspension and deposition processes, driven by tidal motion, river flow and gravity. In the case of fluid mud, a very pronounced type of turbidity maximum, the compartmental boundary even seems to disappear altogether. Also, the interaction between the dissolved phase and surficial sediments is very similar to the interaction between the dissolved phase and suspended particulate material. Nevertheless, estuarine bottom sediments play the distinct part of the least transient estuarine compartment. They act as a temporary and permanent sink for, on average, 90% of the particulate matter and the associated trace metal loadings (Postma, 1980). However, mobilised by tidal scour and river flow, sediments can be re-suspended and thus again take part in the overall estuarine mixing as additional inputs, or be transported as bedload. Erosion takes place as a result of high bed shear stress, a function of bottom current velocity and bed roughness. Erosion of bed sediments usually requires flow velocities above those necessary to keep eroded particles in suspension, which leads to a scour lag. Once decreasing currents cannot keep particles in suspension any longer, they will still travel for some time with the prevailing current until the particles actually reach the bed, the so-called settling lag. These two effects produce a phase shift between circulation pattern and erosion/deposition (Dyer, 1988). Estuarine sediments can also inject dissolved trace metals from interstitial water back into the water column by ways of diffusion, flushing or exposure concomitant with re-suspension. This is of particular importance for redox-sensitive trace elements in anoxic sediments, shown, e.g., by Knox et al. (1981) for Mn in the mid-estuarine stretches of the Tamar.

2.3 TRACE METALS IN COASTAL WATERS

Coastal and shelf waters provide the link between estuaries and the oceans and, in a trace metal context, processes in coastal waters frequently reflect characteristic features of both environments in varying proportions. Estuarine processes, characterised by freshwater dilution, strong lateral gradients, short time scales, fast reactions and high particle populations, will continue in adjacent coastal waters, beyond the topographically defined seaward end of an estuary (Burton, 1988), although possibly decreasing in intensity. As the distance from the riverine source and possibly the depth of the water column increases, controlling processes will show a more and more oceanic element, e.g. the narrowing of the ambient salinity range, increasing time scales, predominance of biogenic particles and vertical fluxes.

Trace metal behaviour in both ocean and estuary has received significant attention by marine scientists. The importance of estuaries with regard to both global geochemistry and environmental protection, and their special characteristics have lead to the emergence of estuarine chemistry as a fairly autonomous discipline within marine chemistry, with its own methodologies and approaches. Despite the similarities between estuarine processes and their extensive homologues in the ocean, care must be taken to use the right paradigm for the right event. Elements passing conservatively through estuaries do not necessarily behave conservatively in sea water, and elements developing 'nutrient-type' profiles across several thousand meter depth after numerous internal cycles do not necessarily show a close relationship with nutrients in estuaries.

A recent report by the Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP, 1987) considering the flux of pollutants across the land-sea boundary, stresses the importance of the coastal zone and the continental shelf in modifying riverine inputs stating that, compared with estuaries, the study of the advanced stages of river-ocean mixing has so far received disproportionally little attention. Distinguishing between gross river fluxes, the material transported to the land-sea boundary before any estuarine modification, and net fluxes, the material transported across the boundary, the report tries to isolate the riverine contribution to the oceanic budget, as required for global geochemical mass balances, from the material trapped near the coast. The land-sea boundary can thus extend from the downmost riverine cross-section with unidirectional flow under all tidal and discharge conditions, the boundary for the gross flux estimates, to the continental shelf break, the most offshore of the suggested boundaries for net flux measurements. The modification of trace metal budgets in the coastal zone, beyond the seaward end of any estuary, can be significant, as has been shown by surveys conducted in this area.

Early indications of specific coastal processes came from the high manganese concentrations found by Yeats et al. (1979) in the deep water of the Gulf of St.Lawrence. Dissolved concentrations were high just above the bottom, whilst particulate concentrations showed a maximum 30 - 100 m above the sea bed. The authors concluded that dissolved manganese was being released back into the water column by diagenetic processes in the sediment and subsequently precipitated on fine suspended particles. Acting as a carrier, these particles would eventually be flushed out into the ocean, a mechanism explaining a previously observed excess of manganese in pelagic sediments. A similar process was reported by Trefry and Presley (1982) for the export of manganese, trapped in Mississippi Delta sediments, to the Gulf of Mexico.

A complex interaction of various coastal zone and open ocean processes was discovered by Schaule and Patterson (1981) on a transect from Hawaii to the Californian coast. Concentrations of Cu and Ni decreased with distance from the coast, suggesting sources nearshore, like rivers, shelf sediment release or coastal upwelling. Lead concentrations, however, were highest in the surface waters of the non-productive North Pacific Gyre, from where they decreased both vertically, and laterally towards the coast. This seemed to suggest a strong atmospheric input coupled with scavenging in the particle-rich coastal zone. Mn showed a similar behaviour in the open ocean, indicative of atmospheric inputs, but also a strong riverine signal with rapid offshore removal.

On a similar transect in the North Atlantic, stretching from the coast of New England to the Sargasso Sea, Bruland and Franks (1983) found Mn, Ni, Cu, Zn and Cd concentrations to decrease with distance from the coast, strongly correlated to the rise in salinity. Here the distribution seemed to be dominated by river-sea water mixing, and net riverine input concentrations calculated from zero-salinity intercepts broadly agreed with selected trace metal measurements in rivers.

In the North Sea, the influence of lead discharged by rivers was found to be restricted to the immediate nearshore zone, probably due to effective scavenging and sedimentation by particles. The dominance of the atmospheric pathway offshore is reflected by the increased surface concentrations in the central and northern parts of the North Sea, possibly due to the longer residence and thus exposure time of these waters (Brügmann et al., 1985).

A series of surveys around the British Isles revealed additional information about the processes controlling trace metal distributions in shelf waters. Two transects across the continental shelf edge are described by Kremling (1985), one leading from Hamburg through the English Channel and the Celtic Sea, the other from Hamburg through the central North Sea to the Atlantic waters north-west of Scotland. Both transects show a sharp rise of trace metal concentrations at the shelf edge, leading to three-to-five-fold increases in concentrations from the Atlantic towards the North Sea and the Channel. Distributions along the southern transect could largely be explained by the mixing of Atlantic water with the continental freshwater runoff, with concentrations of Mn, Ni, Cu and Cd following a conservative dilution line with salinity. In Scottish coastal waters, however, trace metal concentrations, together with P and Si, increased sharply over a very narrow salinity range near the shelf edge, forming a 'front' which could not be explained by riverine inputs. At the time, diagenetic remobilisation or advection of trace metal rich water from the Irish Sea were suggested explanations. A similar study by Balls (1985b), however, found enhanced trace metal levels only in conjunction with a salinity decrease, and no enrichment of bottom waters, pointing at freshwater mixing and advection as the dominating processes.

On a follow-up survey, Kremling and Hydes (1988) found no more evidence of the frontal structure observed three years before, although the salinity structure was similar. Ruling out advective sources from the Irish Sea as not sufficient, the authors then attributed the 'front' observed before to a sporadic coastal upwelling event.

The bulk of the data from this cruise, leading from Hamburg through the North Sea, around Scotland, through the Irish Sea and the English Channel to Le Havre, could again largely be explained by conservative mixing, and effective end member concentrations did agree well with other published values. The considerable amount of scatter, though, confirmed the existence of further modifying processes. Apart from differing freshwater source concentrations, the authors suggest biological uptake and sediment release mechanisms. Profiles taken in the North Sea on the same cruise (Kremling et al., 1987), however, showed no vertical gradients for Mn, Ni, Co, Cu or Cd despite of an existing thermocline. It was suggested that, because of the generally high background levels, inefficient deep water regeneration and the short time scales involved, biological uptake in European shelf waters could only be investigated by comparison of summer and winter conditions.

The existence of sedimentary trace metal sources was corroborated by the significant correlation of other elements with manganese and an elevated concentration of Ra^{226}, thought to be mainly of sedimentary origin (Kremling and Hydes, 1988). Special importance was attached to the strong correlation between Co and Mn concentrations, supposedly due to similar recycling mechanism in sedimentary pore waters.

Paulson et al. (1989a) compared different mixing lines from Elliot Bay (Seattle, US) and tributary rivers in order to calculate increased trace metal transport due to unmonitored anthropogenic discharges. From a comprehensive set of dissolved and particulate trace metal samples, the same group computed a trace metal mass balance for Elliot Bay, accounting for inputs, export and loss to the sediment (Paulson et al., 1989b).

There is considerable scope for mathematical models to be applied in the analysis of survey data and investigation of coastal processes, notably with models based on metal-salinity relationships, box models and hydrodynamic transport models. The former two approaches have been used by Yeats and Bewers (1988) and Bewers and Yeats (1989) to investigate particle-water interaction and sedimentary remobilisation of trace metals in the Gulf of St.Lawrence. Dissolved fluxes across any isohaline can be calculated from the zero-salinity intercept of a the tangent to the metal-salinity mixing curve. In theory, the net addition or removal in between any two salinity values could then be calculated, enabling, e.g., the separation of estuarine and coastal processes. Alternatively, box models can be devised, consisting of a single box or a sequence of boxes. Mass and salt conservation are usually assumed, and existing knowledge on freshwater, SPM and trace metal inputs, outputs and exchange between boxes can be fed in, potentially leading to the computation of the uncertain or unknown parameters. Box models are particularly suitable for semi-enclosed water bodies if there is some previous knowledge about the cross-boundary fluxes.

In a more open situation, hydrodynamic models, or series of such models, with boundary conditions for the more refined models computed by a larger model, can be coupled with a transport model for (usually passive) tracers, as described, e.g., by van Pagee et al. (1986) and van Pagee et al. (1989). So far it has proved difficult, however, to include realistic sub-models for SPM transport, particle-water interaction or bottom sediment exchange.

Summarising present knowledge on coastal processes affecting trace metal distributions, it has become clear that the controlling mechanisms show similarities with both oceanic and estuarine concepts. In the presence of salinity gradients, trace metal distributions can partly be explained by river - sea water mixing, recognising the complications if sources of different concentrations are involved. Additional sources potentially include atmospheric deposition, remobilisation from sediments, anthropogenic inputs and, under special hydrographic conditions, the coastal upwelling of deep water. Potential removal mechanisms include scavenging by particles and biological uptake, leading to predominantly lateral and seasonal gradients, in contrast to the primarily vertical signature of these processes in the open ocean.

CHAPTER 3: DATA INTERPRETATION TOOLS

3.1 MIXING MODELS

Estuarine mixing diagrams have been used as a fundamental tool in the analysis of estuarine reactivity, sources and sinks of a substance since the early development of systematic studies in estuarine chemistry. Samples are taken, synchronically or sequentially, along the estuary, ideally stretching from the freshwater end to the coastal sea. After analysis, the determined concentrations are plotted against salinity or any other appropriate mixing index. A theoretical dilution line is drawn from the concentration at the saline end of the diagram to the value thought to be an acceptable representation of the concentration at the low salinity end. If sea and river water concentrations remained constant for a period of several estuarine residence times, and in the absence of additional sources or sinks, i.e. any type of addition or removal, one would expect the observed concentrations to follow this line, discounting analytical noise. A positive deviation could be interpreted as an addition, a negative one as a removal occurring along the sampled stretch. The position of the deviation on the graph may even be indicative of the location of the zones in which removal or addition occurrs.

In a fundamental paper, Boyle et al. (1974) elucidate the mathematical foundations of this approach. For steady state, one dimensional and tidally averaged conditions, they formulate the net fluxes for salt and a riverine constituent across an isohaline surface, assume the net salt flux to be zero, rearrange and yield an expression for the change of flux of a riverine constituent

$$\frac{dQ_c}{dS} = -Q_w (S - S_r) \frac{d^2C}{dS^2}$$

with Q_c being the flux of the component, S salinity, Q_w the river discharge, S_r the salinity of the river water, and C the concentration of the component.

For conservative behaviour the flux must not change at all, i.e.

$$\frac{dQ_c}{dS}=0=\frac{d^2C}{dS^2}$$

which also implies that for non-conservative behaviour the second derivative of the metal-salinity-relation must be unequal to zero, i.e. the mixing graph must be curved.

Reviewing several data sets assumed to exhibit non-conservative behaviour, the authors show that a good fit could be achieved with two linear segments, indicative for a third end member (tributaries, coastal water of intermediate salinity) rather than a removal mechanism acting steadily over the entire mixing range. For their own dissolved iron data from the Merrimack estuary, they fitted two arbitrary functions, explaining the data equally well, but resulting in widely differing removal estimates. Monitoring the increase in standard deviation, they progressively fitted three linear segments to the data and suggested conservative mixing in the upper and lower estuary with removal processes in the middle. It was not possible to constrain the functionality of the iron-salinity-relationship any further.

Useful information can be gained by the extrapolation of a linear segment of a mixing diagram. Linear segments near the seaward end have frequently been extrapolated to obtain 'effective' river end member concentrations, i.e. the riverine contribution actually reaching the lower estuary, from the zero-salinity intercept. Using a model similar to Boyle et al., Officer (1979) showed the mathematical consistency of the approach. The steady-state assumption of the advection-diffusion model, i.e. the requirement for the end member concentrations to remain constant, came under mathematical scrutiny in a paper by Officer and Lynch (1981), who developed earlier ideas of Loder and Reichard (1980). They solved the model analytically for a conservative river end member concentration varying sinusoidally with a period of T, and also included the hydrodynamic residence time of the estuary, t, in the equation. Plotting mixing diagrams for different ratios of t and T, they could show that i) frequent source variations in a system with a long residence time are restricted to the uppermost region, ii) slow source variations have little effect on the theoretical dilution line, and iii) for systems with t and T about equal, the distortion is still limited for small amplitudes.

A far more sophisticated tidal transport model has been published by Rattray and Officer (1981), taking account of estuarine geometry and tidal phenomena when calculating estuarine losses or gains, but also requiring a far more complex input data set. A similarly complex model, accounting for time-varying river inflow, estuarine geometry and varying dispersion coefficients has recently been applied to alkalinity and nitrate distributions in San Francisco Bay and Delaware Bay (Cifuentes et al., 1990).

For most survey applications, though, data and validation requirements of the more complex models often are prohibitive, and problems with regard to the limitations of the simpler models can be avoided otherwise. Knox et al. (1981) analysed profiles of dissolved ammonia and manganese in the Tamar Estuary. They observed manganese removal in the upper estuary and mid-estuarine maxima for both constituents. They postulated identical mid-estuarine injection mechanisms from interstitial water for both substances and thus expressed the concentration of one constituent as a function of salinity, a linear term and the concentration of the other constituent. They successfully tested this hypothesis against assumed conservative mixing using an F-test, and even found that the input ratios of the two substances as calculated by the model reflected well the concentration ratios in interstitial water samples.

The use of zero-salinity extrapolations was further developed by Kaul and Froelich (1984) for nutrient profiles in a small, undisturbed estuary in Florida. They expressed the flux across any isohaline surface as the river discharge Q_w multiplied with the zero-salinity intercept of the tangent to the mixing curve at that salinity, C^*, i.e.

$$Q_C=Q_w(C-S\frac{dC}{dS})=Q_wC^*$$

Gains or losses between two isohaline surfaces can then be calculated as

$$Q_1-Q_2=R(C_1^*-C_2^*)$$

In this special case, assuming that there was nutrient uptake in the upper estuary, and remobilisation confined to the lower reaches, it was possible to deconvolute the spatially separated input and removal processes within the estuary, eventually specifying all the terms of the mass balance

$$Q_{Inflow}+Q_{Sources}+Q_{Sinks}=Q_{Outflow}.$$

Subsequently, an exponential function to simulate nutrient consumption, and a quadratic term quantifying remineralisation, were introduced into the linear mixing model, explaining most of the observed distributions successfully. The functions, however, had not been derived directly from the data set, but from assumptions about the underlying input and removal processes.

Mixing diagrams have been widely used for the analysis of dissolved trace metal distributions in both estuaries and coastal waters. Qualitative considerations in estuaries include the identification of removal near the turbidity maximum (e.g. Ackroyd et al. (1986) for Mn, Cu and Zn, or Elbaz-Poulichet et al. (1984) for Pb), but also of Cu mobilisation at low salinities (Windom et al., 1983); mid-estuarine inputs (Ackroyd et al. (1986) for Mn, Cu and Zn, or Apte et al. (1990b) for Ni, Cu, Cd, As and Cr), and desorption from particles at high salinities (Elbaz-Poulichet et al. (1984) for Pb or Elbaz-Poulichet et al. (1987) for Cd). Broadly conservative estuarine mixing has been observed for Cu (Apte et al., 1990a). Ackroyd et al. (1986) used the statistical testing method from Knox et al. (1981) to investigate relationships between the mid-estuarine sources of Cu, Zn and Mn, and reported a link between Cu and Zn distributions. Salinity has also been used as a mixing index and estuarine reference parameter for suspended sediments (e.g. Duinker et al., 1982).

In coastal waters, distinct changes in the slope of the mixing curve are more difficult to identify. Observed concentrations frequently fall along a conservative dilution line, with indications of non-conservative behaviour being of more indirect nature, like a high amount of scatter. In such cases, additional information can be gained by the correlation of trace metal concentrations with other tracers of known or assumed behaviour, like Ra^{226} or dissolved manganese for sedimentary sources, or nutrients as an index of biological uptake. Zero-salinity extrapolations have frequently been used in outer estuaries and coastal water bodies to assess the impact of river discharges and the extend of estuarine and coastal trapping, of obvious interest to both environmental management and global geochemical mass balancing. Comparison of zero salinity intercepts based on estuarine and coastal samples has been used to identify coastal modification, e.g. by Bewers and Yeats (1989).

Linear mixing models are usually fitted to a given data set by a least-squares regression. This procedure computes the straight line that minimizes the sum of the squared vertical distances between all individual points and this line. This 'best fit' line is expressed as a linear equation $y=ax+b$, with the slope a and the intercept b. The intercept gives the value of y, i.e. the trace metal concentration, at $x=0$, i.e. at zero salinity.

There are several diagnostics which indicate how well the model fits a given data set. The coefficient of determination, R^2, expresses the fraction, or percentage, of the data variability explained by the model. The correlation coefficient indicates the strength of the relationship between two independent parameters x and y, and indicates positive and negative correlation. The significance of a linear relationship is expressed as the probability p for the slope to equal nought, i.e. for y being uncorrelated to x. A linear model is thus the more significant, the smaller p is. Many statistical packages give model estimates together with a margin of error, covering 95 or 99% of all cases. In this study, model parameters are given with ± the 95% error margins, p-values, correlation coefficients and R^2 coefficients of determination. However, it has to be borne in mind that some of these parameters are based on the assumption of normally-distributed data, normally-distributed errors or constant variance (e.g. Draper and Smith, 1980; Weisberg, 1985). Since these assumptions have not been tested, the dependent statistics only give a rough indication about the extent to which the data are represented by the linear model.

The standard linear model of a trace metal-salinity relationship can also easily be influenced by the distribution of data along the salinity axis. If, as typical for many coastal surveys, a large number of high salinity offshore samples are plotted together with a few samples from the vicinity of a freshwater outflow, the pattern shown by the bulk of the data at the high salinity end can be overridden by the straight line between this cluster and a few, possibly widely scattered points at the low salinity end. There are several ways to alleviate this problem:

(i) attempting an even spread of stations along the salinity gradient during sampling

(ii) splitting the data into subsets and calculating different linear segments along the salinity axis

(iii) transformation of the data set, for example log-normally (e.g. Gilbert, 1987)

(iv) usage of more robust, non-least-squares estimation procedure (Bunke and Bunke, 1987)

In this work, the aim has been to use evenly-spread sampling strategies, and division into subsets has been widely employed. The use of non-linear transformations and of other estimation methods has not been attempted during this work, but may well merit further consideration in the future.

3.2 EMPIRICAL PARTICLE - WATER INTERACTION MODELS

Empirical particle-water interaction models try to explain and predict the distribution between particles and the dissolved phase present in natural or near-to-natural systems on a macroscopic scale, summarizing the effects rather than investigating the mechanisms of the underlying molecular processes. The observed partitioning is assumed to represent the equilibrium distribution between the fraction bound exchangeably to particles and the fraction in solution, under the existing conditions.

A most basic tool is the computation of the dimensionless distribution coefficient K_d, the ratio of the concentration of the exchangeably bound trace metal per unit mass of particulate matter, c_p, and the concentration of the dissolved trace metal per unit mass of water, c_d:

$$K_d = \frac{c_p}{c_d}$$

Frequently a dissolved concentration per unit volume is taken as the value of c_d, without introducing any significant error.

The amount of particle-bound trace metal effectively able to take part in exchange processes with the dissolved phase and thus contribute to the equilibrium, is still subject to a large uncertainty. Trace metals can be bound to particles in many ways, ranging from rather weak surface adsorption to carbonates and amorphous manganese and iron oxides, oxyhydrates and hydroxides, moderate sorption to organic substances, to the almost irreversible incorporation in authigenically formed minerals or detrital silicate structures. Sequential extraction procedures have been devised, with individual steps aiming to dissolve a specifically bound trace metal fraction, but selectivity, reproducibility and therefore comparability are still problematic. A review of sequential extraction procedures, their merits and problems is given in Salomons and Förstner (1984) and Martin et al. (1987). However, even if the differently bound fractions were clearly defined, their contribution to the 'exchangeable' fraction would still depend on the environmental conditions to be expected and the time scales involved. The K_d-value therefore will remain a conditional parameter.

Some K_d dependencies have been summarised by Duursma and Bewers (1986). K_d-values are reported to depend on the substrate, especially its clay-mineral content, specific surface area and grain size, and on temperature and redox conditions, although grain size and redox potentials are seen to be of only moderate importance. Comparing K_d-values from different areas and investigators, Balls (1989) found usually good agreement between values from one study area, but considerable regional variability. Again, particle size and composition, notably manganese and organic material content, are possible explanations, apart from analytical differences, like extraction intensity and contamination potential. Phytoplankton blooms are reported to be able to increase the K_d for cadmium considerably (see also Valenta et al., 1986). The single most important feature in this comparison, though, was the decrease of the K_d's for all the observed metals (Hg, Ni, Cu, Zn, Cd and Pb) with increasing SPM loading. This effect was attributed to particle-particle interaction, a process not yet fully understood. In a radiotracer mixing experiment of Hudson River and sea water, Li et al. (1984) report K_d's for Co, Mn, Cs, Cd, Zn and Ba to decrease with salinity, and for Fe, Sn , Bi, Ce and Hg to increase.

Whenever K_d-values seem to show a clear, quasi-linear relationship with one single parameter, attempts have been made to normalise the distribution coefficient with respect to this variable. Thus, K_d-values have been normalised for clay mineral (illite) content of the substrate, specific surface area and base-exchange capacity (Duursma and Bewers, 1986), manganese content (Balls, 1989) and organic carbon (Pavlou, 1987).

An experiment, where the sorption of zinc on a marine clay had not reached equilibrium after 200 days is used by Duursma and Bewers (1986) to demonstrate very slow sorption processes, possibly involving gradual transport into the crystal lattice. The authors therefore distinguish between fast, short-term processes (as we would expect them in the estuarine water column) and long-range partitioning, including the incorporation into minerals, and, opposed to it, the slow dissolution of detrital material in the oceans. Looking at the time-dependence of K_d-values in coastal sediments, Nyfeller et al. (1984) find the adsorption of Be, Mn, Co and Fe to increase over a period of 108 days. Using a 'kinetic approach', they re-formulate the distribution coefficient as a function of time, including an equilibrium and a lattice transport term.

The kinetics of trace element uptake by marine particles has been investigated, e.g., by Jannasch et al. (1988) and Clegg and Sarmiento (1989). A recent review on metal scavenging residence times in aquatic systems can be found in Honeyman and Santschi (1988).

K_d-values for the marine environment were first derived from laboratory experiments in controlled conditions and were thus not automatically transferable to natural processes. Radiochemical tracers have been widely used both because they facilitate analysis (Nyfeller et al., 1984; Li et al., 1984) and because of the interest in their environmental behaviour with regard to radiological risk assessment (Duursma and Bewers, 1986). During the last decade, however, quite a number of papers have been published analysing both dissolved and particulate trace metal concentrations and thus allowing the calculation of K_d-values present in the natural environment. Estuarine K_d-values have been given for the Scheldt Estuary (Valenta et al., 1986) and the Rhine - Meuse Delta (Golimowski et al., 1990). A compilation of values from North-west European coastal waters can be found in Balls (1988) and Balls (1989). K_d-values for the Mississippi coastal waters have been published by Trefry et al. (1986), using an HF-leach for the particle extraction. K_d-values could also be calculated from data presented by Church et al. (1986).

However, the successful application of observed K_d-values in predictive modelling has to date been limited to a very few special situations only. Morris (1986) uses a simple sorption equilibrium model to analyse the capacity of the turbidity maximum to remove dissolved trace metals from river water at different K_d-values and turbidities. The influence of riverine SPM and the trace metal depletion of estuarine relative to riverine particles is also investigated. Using K_d-values from Li et al. (1984) and field data from the Tamar Estuary, the author is able to show general agreement between model predictions and observed behaviour for Cu and Zn, and the necessity of a permanent up-estuarine supply of trace metal depleted particulates.

In a regulatory application, Pavlou (1987) suggests the use of K_d-values to establish sediment quality criteria. As an alternative to approaches based on observed background levels or bioassays, safe levels for particulate trace metal concentrations in sediments could be set as the concentration keeping the equilibrated dissolved metal concentrations in the interstitial waters within the limits of existing water quality criteria for the dissolved phase.

CHAPTER 4: DATA COLLECTION AND DOCUMENTATION

4.1 DATA REQUIREMENTS

The objectives of this study, as specified in chapter 1, require a sampling strategy which gives a reasonably good spatial coverage of the respective river plume, necessary for the mapping of regional differences, and a fairly even coverage of the relevant salinity range, required for the meaningful analysis of trace metal-salinity relationships. For estimates of the exchange across the estuary-plume boundary, also by correlation with salinity, fixed station measurements over the tidal cycle will be necessary, possibly supported by samples from the estuary itself. Several cruises in the same area at different times of the year are needed for the investigation of seasonal features. In stratified areas and areas of sediment resuspension, sampling of both the surface and the bottom water will be required. Samples from highly productive areas will be needed for the study of biological removal.

Well-tested trace metal sampling methods and analytical techniques are required for the determination of the generally very low total dissolved sea water background concentrations. For all sampling stations, precise salinity, turbidity and chlorophyll measurements are necessary, as well as the determination of trace metals bound exchangeably to particles, nutrient measurements, and other available water quality parameters. Sampling positions should be corrected for tidal water movements to yield a synoptic picture at a reference time in the tidal cycle.

4.2 FIELD WORK

4.2.1 Introduction

All the necessary field work was conducted within the frame work of the 'North Sea Project' of the Natural Environment Research Council (NERC) and three related follow-up cruises. During the original project, the research ship RRS 'Challenger' was committed to operate in the North Sea from August 1988 to October 1989. During 15 monthly survey cruises lasting 12 days each, a pre-defined cruise track in the southern North Sea was followed, alternating with cruises investigating specific processes and features, like sandbanks, air-sea exchange, sediment resuspension, primary production etc.. Two 12-day cruises were devoted to the riverine plumes of the Humber (December 1988) and Thames (February 1989), later followed by additional cruises looking at the plume of the River Humber at different stages during the seasonal cycle (May and July/August 1990) and the plume of the River Rhine (October 1990). All data presented in this thesis were collected on board of RRS 'Challenger' during these five cruises (CH42, CH46, CH65, CH69, CH72) between December 1988 and October 1990.

Four main sampling strategies were employed:

Underway sampling:	Quasi-continuous (one value every thirty seconds) measurement of the properties of surface sea water pumped inboard via a purpose-built, non-toxic outlet. Measurements included salinity, temperature, transmissivity, fluorescence, oxygen and nutrients.
Underway stations:	Discrete water samples collected from a second, trace metal free surface sea water supply, pumped inboard over a period of several minutes, with the ship underway ('P'-stations). The ship's position at mid-sampling was taken as the sampling location.

Station sampling:	Measurement of sea water properties along a vertical profile during a CTD-downcast, with the ship stationary (CTD-stations).
Tidal stations:	Repeated CTD-downcasts at 30 or 60 minute intervals, covering at least one tidal cycle, with the ship at anchor (CTDA-stations).

Cruise dates, survey areas and number of analysed dissolved trace metal samples are given in Table 4.1.

Cruise	Period	Survey area and samples
CH42	15/12-29/12/1988	Humber plume (67) Tidal station 1 (14) Tidal station 2 (14)
CH46	12/02-20/02/1989	Inner Thames estuary (48) Outer Thames estuary (22) Tidal station (14)
CH65	06/05-17/05/1990	Humber plume (38) Tidal station (15) Humber estuary (15)
CH69	26/07-07/08/1990	Thames plume (11) Humber plume (31) Tidal station (15)
CH72	04/10-19/10/1990	Tidal river station Nieuwe Maas (26) Tidal coastal station (26) Rhine plume (20)

Table 4.1: Plume cruises and collected samples

Data were collected by many different research groups, and were later fed into the 'North Sea Project Data Base', held centrally by the British Oceanographic Data Centre (BODC) in Birkenhead, where they could be accessed via computer links by all participants (Lowry, 1990).

4.2.2 Sampling for complementary data

Underway data collected include the continuous measurement of salinity, temperature, transmissivity, fluorescence and oxygen by electrical or electrochemical sensors, and the colorimetric continuous flow analysis of the nutrients PO_4, NO_2, NO_3 and Si in surface sea water, supplied by a purpose-build, non-toxic pumped outlet.

CTD-casts allowed the profiling of the water column with regard to temperature, salinity, turbidity, fluorescence and oxygen,as well as the collection of water samples at different depths by the remote-controlled closure of sampling bottles mounted on the CTD frame. These water samples were analysed for salinity, total and combustible suspended particulate material, chlorophyll and oxygen, necessary for the calibration of the respective continuously-working sensors both on the frame and in the non-toxic supply. The temperature sensor was calibrated using a reversing thermometer mounted on one of the sampling bottles. The CTD-frame was also used for the collection of water samples for trace metal analysis, including the measurement of dissolved inorganic and organic arsenic, total unfiltered, total dissolved and reactive dissolved mercury, particulate chromium and unfiltered and particulate aluminium, as well as dissolved and particulate Mn, Fe, Ni, Co, Cu, Zn, Cd and Pb, for which the sampling methods are described in more detail below. Water samples were also analysed on board for Cu, Cd and Pb using anodic stripping voltammetry (ASV), without UV-irradiation.

Sediment collection using a 'Day grab' sampler provided information about the type of sediment in the survey area, and samples for grain size analysis were taken. Sediment box cores were taken for pore water analysis and sub-sampling of the overlying water at appropriate intervals under controlled conditions for five days after collection, leading to cross-boundary flux estimates for metals and nutrients. In another incubation experiment, dissolved trace metal radiotracers were added to sea water samples, and subsamples for the dissolved and particulate phases were taken at appropriate intervals to determine uptake rates and equilibrium partitioning coefficients.

Further surface samples were collected using a metal-free pumping system independent of the non-toxic continuous supply. Water was taken in through a polypropylene tube mounted on the precision echo sounder 'fish', which was towed from the port bow away from the ship's hull, and pumped via a teflon pump straight into the 'clean' container laboratory. Water samples could be pumped inboard whilst the ship was underway, and are referred to as 'underway'- or 'P'-stations. Samples were taken for particulate and dissolved trace metals as described below, and also for measurement of suspended particulate matter (SPM), PO_4, NO_2, NO_3, Si, particulate Cr, unfiltered and particulate Al, and different arsenic and mercury species.

However, due to the changing composition of the scientific team, availability of instrumentation and accidental loss of data, not all the parameters mentioned have been recorded during all cruises. A more detailed description of the data on a cruise by cruise basis is given in chapters 5.2, 6.2 and 7.2.

4.2.3 Sampling protocol for Mn, Fe, Ni, Co, Cu, Zn, Cd and Pb

Samples for the analysis of dissolved and particulate Mn, Fe, Ni, Co, Cu, Zn, Cd and Pb were processed in the 'clean' container laboratory described by Morley et al. (1988). When using the CTD-frame, samples were collected in modified and specially cleaned 'Go-Flo' bottles. The bottles were sent down closed and opened by a pressure release valve, to avoid contamination from the surface microlayer. Once inboard, the sampling bottles were taken from the frame and mounted on a rack on the outside wall of the clean container, where they were connected to an air line and a discharge line, leading inside the clean laboratory. From inside, the bottles were pressurised using filtered and dried air from a compressor, and the sample was filtered in-line through a 0.4 μm acid-washed 'Nuclepore' polycarbonate filter membrane into a low-density polyethylene (LDPE) sampling bottle, that had undergone week-long soaks in detergent, HCl and HNO_3, and was protected in a self-sealing plastic bag.

Using the underway pumping system, water samples were pumped into one or more 10 l reservoirs inside the clean container, after the lines had been flushed for a few minutes. The sampling time was noted down and later used to establish the station position from the ship's log. The reservoirs could also be pressurised, and water samples were filtered as described for CTD-samples.

After filtration, the water samples were acidified in a laminar flow hood with 0.1% of subboiling-distilled HNO_3 for storage until analysis on shore, and the Nuclepore filters in the all-Nylon/Teflon filter holders were exchanged and stored in labelled Petri-slides, which were bagged and kept in a deep-freezer. Details of sampling station, time, label numbers, volume, filter, filter holder identifier and the amount of acid added to each sample were recorded in a special logging sheet. Particulate samples from the Rhine survey (CH72) were analysed by I.Hall at the University of Southampton, Department of Oceanography, and all other particulate samples were analysed by A.Turner and G.Millward from the Polytechnic South West, Plymouth.

All critical manipulation, including the handling of the Go-flo bottles, were performed wearing disposable polythene gloves. However, despite all the care taken, contamination during sampling cannot be completely ruled out. Sources of possible contamination include the metal hydrowire and the sacrificial zinc anode on the CTD-frame, but they were never found to impair the validity of the analytical results.

4.3 ON-SHORE LABORATORY ANALYSIS

4.3.1 Outline of the analytical method

There is now a broad variety of methods available for the determination of dissolved trace elements in sea water. Analytical instrumentation involved includes anodic stripping voltammetry (ASV) (e.g. Nürnberg, 1984; Bruland et al., 1985), cathodic stripping voltammetry (CSV) (e.g. van den Berg, 1986), atomic absorption spectrometry following preconcentration by liquid extraction, as discussed below, or adsorption to resins (Bäckström and Danielsson, 1990; Pai et al., 1990; van Geen and Boyle, 1990), total-reflection X-ray fluorescence spectrometry (TXRF) (e.g. Prange et al., 1990), ionised coupled plasma mass spectroscopy (ICP-MS), and instrumental neutron activation analysis (INAA) (e.g. Prange et al., 1990).

For a given application, the final choice will depend on available instrumentation and expertise, required sensitivity, selectivity, accuracy and precision, practicability and economy (Aston, 1985). For this work, analysis by graphite furnace atomic absorption spectrometry (GF-AAS) after complexation with a mixed dithiocarbamate complexant, extraction into Freon TF and back-extraction into dilute nitric acid were chosen, a technique well established in the laboratory (Statham, 1985; Tappin, 1988).

Direct analysis of sea water samples by AAS is usually impossible because of the low environmental concentrations, and interferences with the sea salt. Therefore preconcentration steps have to be introduced prior to analysis, both transferring the trace metals in question into a matrix more suitable for analysis and at the same time increasing their concentrations in the injected aliquot.

Developing earlier techniques, Danielsson et al. (1978) recommend the following procedure: Neutralisation of the sample to about pH5 with purified diammonium hydrogen citrate buffer solution; complexation of the trace metals with a 1:1 mixture of ammonium dithiocarbamate (APDC) and Diethyl-ammonium diethyl-dithiocarbamate (DDDC), immediately followed by the addition of Freon TF (1,1,2-trichloro-1,2,2-trifluoro-ethane), the organic solvent in which the trace metal complexes are subsequently extracted. The organic phase is then separated from the supernatant, the complexes are destroyed by addition of concentrated nitric acid, and the trace metals are back-extracted into diluted HNO_3 ready for AAS analysis.

The complexant was shown to efficiently extract Fe, Ni, Co, Cu, Zn, Cd and Pb, and Freon TF was chosen as the organic solvent because of its good separation characteristics and assumed low toxicity. The back-extraction step was necessary because of the poor stability of the carbamate complexes and the advantage of the dilute acid matrix in AAS analysis. The pH of the sample was found to be without influence on the extraction efficiency in the range of pH 3 to pH 7. With vigorous shaking, complete extraction was achieved within 150 seconds. Metal complexes were found to be stable in Freon TF for several hours, but nevertheless back-extraction was recommended to take place as soon as possible. The amount of acid added during back-extraction had no influence on the extraction efficiency. No change in the final aqueous analyte was found over a storage period of up to 70 days. It was recommended for instrument standard solutions to have equal acidity as the samples. In a subsequent paper, Danielsson et al. (1982) show the applicability of the described procedures for filtered estuarine water samples as well.

Encouraged by the potential of the Freon TF-dithiocarbamate system to extract other geochemically important elements as well, Statham (1985) used a radioactive isotope to optimise the extraction procedure to include manganese. His paper also describes the mechanisation of the extraction step with a polypropylene rotating table holding the extraction funnels and being driven by an electric motor. For the efficient extraction of manganese, the pH of the sample had to be above pH 6, and the amount of complexant added and the shaking times had to be increased. As a result, the back-extraction had to be repeated twice, to guarantee the dissolution of all metal complexes. These modified conditions were shown to yield good (>90%) recoveries for Fe, Mn, Ni, Co, Cu, Zn, Cd and Pb. The accuracy of the technique for Mn and Cd was demonstrated by successful participation in the ICES fifth round intercalibration exercise, documented in the ICES-report CM1983/E24 (Statham, 1985).

The described method have since then been further improved in the Southampton laboratory by Tappin (1988), including the mechanisation of the backward extraction step and the use of a rotating table for the forward extraction enabling the simultaneous processing of twelve 70 ml samples. Staff members of the Southampton laboratory continued to contribute successfully to national and international intercalibration exercises (e.g. Elbaz-Poulichet et al., 1989).

4.3.2 Analytical Protocol

4.3.2.1 Introduction

For routine analysis, a batch size of 72 samples is found to be most efficient, taking full advantage of the capacities of the rotating tables in the clean laboratory and the AAS autosampler. A batch consists of 48 sea water samples collected in the study area, two recovery calibration sets with six samples each, spiked with various amounts of the mixed trace metal standard, six samples of an inter- or intra-laboratory reference standard, and six reagent blanks. Reference standards and reagent blanks are spread systematically within the batch, so that every of the twelve extraction funnels would eventually be used once. Prior to analysis, an extraction list is compiled containing 72 extract vial numbers (No's 5 to 80, without No's 1 to 4 and No's 41 to 44, the positions for the instrument calibration standards on the AAS autosampler), sample bottle numbers, and other relevant information on the samples' origin, as well as the strength of recovery calibration spikes. An example of an extraction list is given in Appendix I.

The extraction was carried out in a Class-100 laminar flow bench in a clean laboratory. Adjacent to both sides of the bench, electric motors are situated which drive the various rotating tables and can be controlled with a timer. For the extraction of a batch of 72 samples, reagents and apparatus are required in quantities as given below.

4.3.2.2 Generation of reagents

In order to generate the high-purity reagents in quantities listed in (4.3.2.3.1), significant efforts were undertaken prior to analysis, involving the following chemicals and apparatus.

4.3.2.2.1 Apparatus

- Subboiling still for SBD H_2O generation
- Subboiling still for SBD HNO_3 generation
- Isothermal still for SBD NH_4OH generation
- 1000 ml glass separatory funnel to separate Freon TF for recycling
- Conventional glass still to re-distil Freon TF
- 500 ml Fluoro ethylene propylene (FEP) separatory funnels (2), seated in a polypropylene rotating table
- Conventional glass filtration unit with glass fibre filter
- 50 ml low-density polyethylene (LDPE) bottles (10) for storage of standard solutions
- 125 ml FEP bottles (4) for storage of reagents
- 1000 ml LDPE bottle for mixing of complexant
- 1000 ml FEP bottles (4) for storage of reagents
- 2000 ml LDPE bottles (2) for storage of SBD H_2O
- 2000 ml FEP bottle for storage of acid-cleaned Freon TF
- UV-radiation unit with several 200 ml silica vials
- Airtight perspex filtration unit and suction pump
- All-plastic Chelex-100 cation exchange column with screw-capped FEP funnel and vial housing the resin
- 100 ml glass beaker
- magnetic stirrer
- pocket-size pH meter
- 50 ml volumetric pipette and suction ball
- assorted self-sealing polythene bags

4.3.2.2.2 Reagents

- milli-Q de-ionised water ($R \geq 18\ M\Omega$)
- filtered, unacidified seawater of low trace metal content
- HNO_3, analytical grade
- NH_4OH, analytical grade
- Freon TF (1,1,2-trichloro-1,2,2-trifluoro-ethane), general purpose reagent (GPR)
- NaCl (GPR)
- Ammonium pyrrollidine dithiocarbamate (APDC), (GPR)
- Diethyl-ammonium diethyl dithiocarbamate (DDDC), (GPR)
- 'Chelex-100' resin
- H_2O_2, (GPR)
- 1000 ppm Primary Standard solutions for Mn, Fe, Ni, Co, Cu, Zn, Cd and Pb (BDH)

4.3.2.2.3 Subboiling-distilled water (SBD H_2O)

Highest purity water is generated from de-ionised water using a dedicated subboiling still. The de-ionised water in the round-bottomed still fed by a reservoir is warmed by two 275 W infra-red reflectors surrounding the still, and condenses on a water-cooled finger in the centre of the still. From there it drops into a collecting funnel and leaves the still through a tube in the bottom. By distillation below boiling point, the carry-over of contaminants via droplets created by bursting bubbles is avoided. The SBD H_2O is collected in a 2000 ml LDPE bottle, double-protected by two polyethylene bags against contamination from the non-clean laboratory environment.

4.3.2.2.4 Subboiling-distilled nitric acid (SBD HNO_3)

High-purity nitric acid is generated from analytical-grade HNO_3 using a dedicated subboiling still similar to the one used for the generation of SBD H_2O, but being installed in a fume cupboard, and is collected in a double-bagged 1000 ml FEP bottle.

4.3.2.2.5 Isothermally-distilled ammonia solution (ITD NH_4OH)

High-purity aqueous ammonia is generated from analytical-grade NH_4OH in a isothermal distillation unit installed in a fume cupboard. The unit consists of two open beakers, one holding the analytical-grade ammonia, the other SBD H_2O, in a sealed container. Over the period of several weeks, ammonia (NH_3), de-gassing from one beaker, re-dissolves in the SBD H_2O to yield ITD NH_4OH, which is then stored in a 125 ml FEP bottle.

4.3.2.2.6 Acid-washed Freon TF

Previously used ('recycled') Freon TF is separated from any aqueous phase in a separatory funnel before being distilled under gentle heating in a glass still placed in a fume cupboard outside the clean laboratory. The pre-cleaned distillate, and any factory-fresh Freon TF, are then cleaned by acid-washing in the clean room. Together with 1 ml SBD HNO_3, 300 ml of Freon TF are given in a 500 ml FEP separatory funnel. Two funnels are used simultaneously. After 6 min of mixing in a rotating table, 120 ml of SBD H_2O are added and rotation is repeated. The Freon TF is now collected in a 1000 ml FEP bottle and the aqueous phase is discarded. The Freon TF is given back into the funnels and the acid washing procedure is again repeated twice, with an additional SBD H_2O washing after the third time. To obtain the required amount of 1800 ml of Freon TF, the entire procedure has to be executed three times with two funnels. The acid-stripped Freon TF is stored in a plastic-bagged 2000 ml FEP bottle in the clean laboratory.

4.3.2.2.7 Complexant

The complexant is prepared as an 2% (w/v) APDC and 2% (w/v) DDDC aqueous NaCl-solution of sea water salinity. In a 1000 ml LDPE bottle, 24.5 g of NaCl are dissolved in 700 ml of deionised water, and 14 g of each of the two complexing agents are added. After dissolution the complexant is filtered through a paper filter into a suction bottle and transferred into the clean laboratory in a 1000 ml FEP screw-capped bottle. The complexant is now split between the two 500 ml FEP funnels, and each aliquot is washed with 30 ml of acid-stripped Freon TF during a 6 min extraction on a rotating table. The Freon TF is drawn off and collected for recycling. This cleaning step has to be repeated another three times. If the complexant is not used immediately afterwards, it should be refrigerated in a 1000 ml FEP bottle (double bagged) after three cleaning steps and washed a last time directly before use.

4.3.2.2.8 Low trace metal sea water (LTMS)

From a site assumed to exhibit low trace metal concentrations, 1000 ml of filtered, unacidified sea water is collected. Portions of 200 ml are given into appropriate silicate vials, adding 2 drops of H_2O_2, and are exposed to UV-radiation for 5 hours to break down organic compounds. In order to remove any particles formed during storage or irradiation, the water is filtered again through a 0.4 μm filter into a plastic bottle, which stands in an airtight container connected to a suction pump. The removal of trace metals is achieved by leaching the sea water through a Chelex-100 cation exchange resin. Prior to use the resin has to be conditioned by leaching with 35 ml (ten bed-volumes) of 2N HNO_3, and then a few ml's of SBD H_2O, followed by an ion exchange with 35 ml 2N NH_4OH. The bed is then rinsed with SBD H_2O and neutralised below pH 9 by leaching with 50 ml of sea water. The ion exchange unit is now ready for use.

To produce LTMS, the irradiated and filtered water sample is leached through the resin at a very low (2 to 3 drops per minute) rate, which may well take up to a few days. To avoid contamination, filtration and leaching are done in a class-100 laminar flow hood. LTMS is stored in a double-bagged 1000 ml FEP bottle.

4.3.2.2.9 Mixed trace metal spiking standard

In order to assess the extraction efficiency of the process, samples are spiked with known amounts of the trace metals in question. Spiking solutions of varying composition and concentration have been used throughout the analyses. Initially, trace metal stripped sea water samples were spiked with varying amounts of a solution containing 100 μg/l of all trace metals, leading to a suite of recovery calibration samples covering sea water concentrations from 0 to 500 ng/l. Later, spiking standards were prepared containing trace metals in adjusted ratios, enabling the full coverage of the molar range for each individual trace metal expected in a given batch of samples. For offshore samples, concentrations were anticipated to range from zero to 1 nmol/l for Co, Cd and Pb, and up to 50 nmol/l for Mn, Fe, Ni, Cu and Zn. With spikes ranging from zero to 350 μl in 70 ml samples, the spiking standards had to contain 0.2 μmol/l of the first and 10 μmol/l of the second group of metals, in a 4% HNO_3 solution.

For the preparation of this standard, a 20 μmol/l intermediate dilution for the first group of metals was made by adding from 1 g/l primary standard solutions 58.9 μl for Co, 112.4 μl for Cd and 207.2 μl for Pb to 2 ml of SBD HNO_3 in a 50 ml volumetric flask, and making it up with SBD H_2O. Of this solution, 1000 μl were then added to 1 g/l primary standard solution spikes of the remaining five metals (54.9 μl for Mn, 55.9 μl for Fe, 58.7 μl of Ni, 63.6 μl for Cu and 65.4 μl for Zn) and 4 ml of SBD HNO_3 in a 100 ml volumetric flask and topped up with SBD H_2O. Intermediate dilution and spiking standards were stored in 50 ml LDPE bottles and kept double-bagged in the fridge.

4.3.2.2.10 Instrument calibration standards

For the calibration of the AAS instrument a series of standards in 4% HNO_3 was needed, containing 0, 2, 5, 10, 30, 50, and 60 μg/l of all eight trace elements. A 1 mg/l intermediate dilution was made from 1 g/l primary standard solutions by adding 100 μl spikes to 4 ml of SBD HNO_3 in a 100 ml volumetric flask and topping it up with SBD H_2O. The standards were then prepared by adding 0, 100, 250, 500, 1500, 2500 and 3000 μl of the intermediate dilution, respectively, to 2 ml of SBD HNO_3 in a 50 ml volumetric flask and topping it up with SBD H_2O.

All dilutions were stored in 50 ml LDPE bottles. The intermediate dilution was kept double-bagged in the fridge, and the instrument standards were prepared afresh for every sample batch. At the same time, 250 ml of a 4% HNO_3 washing solution was prepared to be used for the rinsing of pipette tips.

4.3.2.2.11 Neutralisation test

Although every sample should contain exactly 0.1% SBD HNO_3 after acidification at sea, and thus predictable amounts of NH_4OH should be required to neutralise each sample to a given pH, it proves to be necessary to assess the amount of base needed for neutralisation prior to every extraction, since the added acid and especially the isothermally distilled NH_4OH solution vary considerably in strength with time and batch.

Sea water samples thought to be representative for the samples to be analysed are chosen, and ca. 200 ml subsamples are taken into a glass beaker in a laminar flow hood. 50 ml of sample are drawn out of the beaker with a volumetric pipette and transferred in another beaker standing on a magnetic stirrer. A spike from a subsample of the NH_4OH solution to be used, of a quantity expected to be adequate, is added, and the change in pH is monitored with a pH electrode. This procedure is repeated, until the quantity of base is established that reliably lifts the pH of the sample in the range between pH 4 and pH 8. From these results the amount necessary for a 70 ml sea water sample is extrapolated.

4.3.2.3 Extraction in the clean laboratory

4.3.2.3.1 Apparatus

- 125 ml Fluoro ethylene propylene (FEP) separatory funnels (12), seated in a polypropylene rotating table
- 13 ml screw-capped polyethylene vials (24) in a stand, fitting into a perspex rotating table
- 2 ml polypropylene screw-capped vials (72), labelled, in a perspex rack
- 500 ml FEP funnel in a dispensing stand
- 25 ml measuring cylinder
- 100 ml measuring cylinder
- 100, 200, 1000 and 5000 μl micropipettes and pipette tips
- 50 ml glass or plastic beakers (12)
- pH meter, pocked size

4.3.2.3.2 Reagents

- acid-cleaned Freon TF, ca. 1800 ml
- high-purity complexant, ca. 700 ml
- low trace metal sea water (LTMS), 840 ml
- SBD H_2O, ca. 200 ml
- ITD NH_4OH, several ml
- SBD HNO_3, several ml
- Mixed Trace Metal Spiking Standard

4.3.2.3.3 Extraction

Prior to the first extraction, a complete blank extraction is performed to clean all separatory funnels used for the forward extraction step. In a measuring cylinder, 7 ml of Freon TF are collected and given into each of the twelve funnels. Using a micropipette, 4 ml of complexant are added. All funnels are closed and rotated for 5 min, after which the Freon TF is drawn off and collected in a waste container for recycling. Another 4 ml of Freon TF are added to the aqueous phase, and the extraction is repeated. Finally both phases are discarded and the funnels are ready for use.

For extraction, 70 ml of sample are collected in a measuring cylinder and given in a 125 ml funnel. The measuring cylinder is rinsed with SBD H_2O in between samples and remaining drops are carefully shaken off. Acidified samples are now neutralised with NH_4OH dispensed with a 200 μl micropipette (cf. 4.3.2.2.10). Recovery calibration samples are spiked with the appropriate amounts of mixed trace metal standard solution (cf. 4.3.2.2.8). All funnels are shaken shortly to mix. Funnels designated for a reagent blank so far remain empty.

Next, 4 ml of complexant are added to every funnel, followed by 7 ml of Freon TF. The funnels are rotated for 5 min, then the Freon TF phase is drawn into 13 ml screw-capped tubes. A further 4 ml Freon TF are added to the aqueous phase, and extraction is repeated. After 5 min rotation, the Freon TF phase is united with the earlier extract, and aliquots of the aqueous phase are given into 30 ml beakers for pH measurement with a 'pocket-size' electrode. The pH values are recorded on the extraction sheet. They should lie within pH 7.0 and pH 9.2. If considerably less, neutralisation was not sufficient, possibly due to over-acidification at sea. Frequently the Freon TF can then be seen to turn yellow on acidification during the back-extraction, and during AAS analysis considerable background peaks can be observed. These samples have to be extracted again in another batch.

Prior to the extraction of another dozen sea water samples, the separatory funnels have to be cleaned. This is done by a one-step blank extraction with 7 ml of Freon TF and 4 ml of complexant, which are both discarded after 5 min of rotation.

Since the rotating table for the back extraction holds 24 screw-capped tubes, the forward extraction is usually repeated once more before proceeding to the next analytical step.

For back extraction, 26 μl concentrated SBD HNO_3 are dispensed in every 13 ml tube with a 100 μl micro-pipette, and the tubes are rotated for 5 min. After adding 650 μl SBD H_2O, the rotation is repeated. Next, the 1000 μl pipette is adjusted to 720 μl, and the aqueous bubble is drawn off the Freon TF, holding each tube at an angle. If it proves impossible to accommodate the entire aqueous phase in the pipette volume (usually because Freon TF vapour bubbles interfere), the pipette volume can be increased to up to 750 μl. The back-extracts are then transferred into labelled 2 ml vials. The back-extraction step is repeated exactly as described, with the second back-extract being added to the respective 2 ml vial. The extracted Freon TF is collected for recycling.

In order to process all 72 samples, the forward extraction has to be repeated another four, the back extraction another two times. The entire extraction may take up to 24 hours, but can be divided into three 8-hour periods with two forward- and one back-extraction each. The complexant is being refrigerated during and left to regain room temperature after each break.

4.3.2.4 Extract analysis by atomic absorption spectrometry

The extracts were analysed for Mn, Fe, Ni, Co, Cu, Zn, Cd and Pb using a Perkin-Elmer 1100B Atomic Absorption Spectrometer (AAS) fitted with a HGA-700 graphite furnace and a AS-70 autosampler. The instrument was run with deuterium background correction and two replicate measurements of the absorption peak area. The internal argon gas flow was switched off during atomisation except in the case of Zn, where it was left at 200 ml/min in order to dilute the signal. During all other stages, gas flow through the tube was set to 300 ml/min. Pyrocoated L'vov platform tubes were used for all elements, with the exception of Ni, where a traditional pyrocoated graphite tube was used. Other conditions and parameters for the instruments setup were taken from the manufacturers recommendations and adjusted and improved when appropriate, as shown in Table 4.2. These parameters were stored in the instruments memory and recalled during setup.

Aliquots of extracts and instruments standards were given into 40 sampling cups held by the autosamplers rotating tray, an operation performed in a laminar flow hood. If expected to be necessary, samples were diluted with 4% HNO_3 and the dilution factor noted on the recording sheet, a copy of the extraction list (Appendix I). The tray was then installed in its fully-enclosed holder containing a layer of SBD H_2O to prevent evaporation from the sample cups. In a typical run, the instrument would first establish the background from a 4% HNO_3 solution containing no trace metals (Auto-zero) before calibrating from three standards that had been shown to lie within a linear range. Samples were analysed in groups of six, alternating with repeated auto-zeros and reslopes of the calibration line. Output, including a plot of the absorption peak, individual results in μg/l extract, and mean and standard deviation of the replicates, was directed to both the screen and a printer. Means and relative standard deviations (RSD's) were noted on the recording sheet. In most cases, RSD's were below 5%; if individual replicates deviated more than 10% from their mean, the result was rejected and the cause for the variation investigated. Auto-zero and reslope results were checked for consistency.

	Mn	Fe	Ni	Co	Cu	Zn	Cd	Pb
Wavelength [nm]	279.5	248.3	231.9	240.7	324.7	213.8	228.7	216.9
Slit [nm]	0.2	0.2	0.2	0.2	0.7	0.7	0.7	0.7
Lamp [mA]	7	12	5	6	4	4	3	7
Integration Time [s]	3.2	3.2	2.2	5.2	5.2	1.5	2.2	3.0
Injection Volume [μl]	10	10	20	4*30	10	10	10	30
Injection Temp. [°C]	100	100	--	100	100	100	100	100
Drying I [°C]	150	150	90	150	150	150	150	150
Ramp [s]	5	5	5	5	5	5	5	5
Hold [s]	10	10	5	25	10	10	10	25
Drying II/ III [°C]	250	250	110	250/ 400	250	250	250	250
Ramp [s]	5	5	10	15/10	5	5	5	15
Hold [s]	10	10	10	10/1	10	10	10	10
Ashing [°C]	1100	1500	1000	1200	1250	600	1000	800
Ramp [s]	5	5	5	10	5	10	5	5
Hold [s]	10	10	5	1	10	5	5	10
Atomisation [°C]	2200	2500	2300	2550	2300	1800	1900	1800
Ramp [s]	0	0	0	0	0	3	0	0
Hold [s]	3	3	2	5	5	2	2	3
Cleaning [°C]	2800	2800	2700	2800	2800	2200	2700	2600
Ramp [s]	1	1	1	1	1	1	1	1
Hold [s]	3	5	3	4	3	3	3	3
Standard I [ng/l]	10	10	10	2	10	10	2	5
Standard II	30	30	30	5	30	30	5	10
Standard III	60	60	50	10	60	50	10	30

Table 4.2: AAS Instrument Parameters

4.4 DATA PROCESSING AND QUALITY ASSURANCE

4.4.1 Computation of analytical end results and quality parameters

Analytical end results and quality parameters were calculated from the results of the AAS analysis using a purpose-designed spreadsheet template, as shown in Appendix II.

The header line of this spreadsheet asks for the date of the analysis, the type of furnace (pyrocoated tube or platform), the file identifier (element symbol and extraction number), the injection volume and the molar weight of the element in question. Further general information is stored in the 'AAS-System' section, including lamp energy, calibration factor (multiplier for absorbance to yield 'μg/l', as displayed by the instrument), and the average absorbance of the reslope standard. From the latter, the characteristic mass, i.e. the amount of metal causing 1% of the net absorbance (0.0044 absorbance units) for 1 second, is calculated as the product of injection volume, reslope standard concentration and the constant 0.0044, divided by the average reslope standard absorbance. Optional fields include the instrumental Limits of Detection (LoD), mean absorbance of the auto-zero, and standard deviations of auto-zero and reslope measurements, either quantitatively or qualitatively.

In the 'Extraction' section, means and standard deviations are calculated for the blank and reference samples listed further down below. It is possible to exclude outliers from the calculation, leading to a reduced count in the 'Samples' field. The procedural blank in nmol/l is calculated from the average analytical blank in μg/l and the recovery slope (see below), converting extract concentrations into molar sea water equivalents. The limit of detection is given as the threefold standard deviation of the blank ('3σ'), again expressed in both μg/l extract and the equivalent molar sea water concentration. The 3σ detection limit has been recommeded, e.g., by Long and Winefordner (1983). Detection limits have only been used as measure of data reliability, and data sets have not been censored, following the recommendations in Porter et al. (1988). A measure of the precision is given by the relative standard deviation of replicate analyses of the reference standard ('CASS' coastal sea water in the example); a valuable indication of the accuracy of the method is given by the degree of consensus between the assumed 'true' value of the reference standard (supplied by the

National Research Council of Canada (NRCC), in the example) and the result obtained during this analysis. The error, or analytical bias, is expressed as the positive or negative deviation of the mean result from the agreed value, in percent.

Of pivotal importance in the spreadsheet is the slope of the recovery calibration, being the conversion divisor from [μg/l] extract to [nmol/l] sea water concentrations. The 'ideal slope' is calculated as the product of the extraction concentration factor (70 ml of sea water divided by 1.352 ml extract volume), the molar weight and the factor 10^{-3} ('nano' to 'micro'). 'REC1' and 'REC2' summarise the results from a regression analysis of the two recovery sample sets, including the count of accepted values, correlation coefficients, slope and y-intercept (the 'background' in the unspiked sample) with standard errors. The full regression statistics are printed out on the last page of the spreadsheet. The 'used slope' field finally contains the conversion divisor chosen and applied throughout the spreadsheet.

The 'Quality Control Samples' section lists blanks, recovery and reference samples with their vial number, content and expected or intended extract concentrations. Rejected outliers are marked by parentheses around the vial number. The results of the AAS analysis are entered into the 'diluted concentration' column, together with the dilution factor, where applicable. From these two figures, the 'undiluted extract' concentrations are calculated, less, in the case of the recovery samples, the mean analytical blank. A regression analysis is now performed, with the nominal concentration of the spiked sample in nmol/l as the independent, and the undiluted extract less blank as the dependent variable. The regression results are printed on the last page of the spreadsheet, together with a plot of ideal and observed recoveries. Dividing by the slope in the 'used slope' field and, in the case of the reference standards, subtracting the mean analytical blank, the 'Endresult's are computed. For recovery samples, the last column contains the concentrations attributed to the spike alone (without the 'background' of the sample), and for reference standards the supplier's estimate is given for comparison.

In the 'Seawater Samples' section, the analysed environmental samples are listed with extract vial number, storage bottle number and station identifier. AAS-results and dilution factors are entered in the 'diluted concentration' and 'dilution factor' columns, leading to the compilation of the undiluted extract concentrations. The 'Endresult' is obtained by subtracting the average analytical blank from the undiluted extract concentration and dividing by the 'used slope'. The last column contains the ' < ' flag, if the 'Endresult' is less than the limit of detection.

To obtain a print-out in a form similar to the one shown in Appendix II, the spreadsheet was first completed as described above, and a graph of ideal and observed recoveries was plotted. Subsequently, the spreadsheet was printed to an ASCII text file, and text file and graph were imported into a word processing package.

4.4.2 Generation of the local project data base

Although, in theory, all data related to cruise CH42 would eventually be stored in the 'ORACLE' North Sea Project Data Base at BODC and be accessible through any terminal connected to the 'Joint Academic Network' (JANET) in the UK, it was found necessary to establish a local data base, holding only selected data in a form relevant to the specific trace metal research interest at Southampton.

The data storage system eventually developed consists of a combination of a database and a spreadsheet package, both running on a personal computer. Whilst the database provides more powerful data sorting and processing capabilities, the spreadsheet served as a user-friendly display and data entry facility. The data themselves are stored in a form, which can be easily transferred in between the two programs.

Data entries, or 'records,' refer to a water sample taken at a given station and a given depth, and were sorted chronologically and by depth. Within the BODC system, every single CTD downcast has its own station number, and so a second visit to the same site has always a different station number. Within our system, underway 'P'-stations were given numbers less than 1000, avoiding clashes with the CTD numbering system. Every record was given a mnemonic code. In the data bases, all records contain this code, the station number, the type of station ('P' or 'CTD'), depth, sample bottle number, extraction number, and date, time and position of sampling. These base parameters are followed by related data, including salinity and temperature, dissolved and particulate trace metals concentrations, nutrients, chlorophyll, oxygen, suspended particle parameters and, in the Humber-Wash area, positions corrected for tidal water movement. With the exception of sample bottle and extraction numbers, our own results and the tidally corrected positions, all data had been obtained from the ORACLE North Sea Project data base at BODC. Data files were transferred to the Southampton mainframe computer and subsequently copied to micro-disks. Once in the personal computer, the data had to be carefully re-edited before being loaded into the local project data base.

A full account of the structure of the local project data base can be found in Appendix III, including field name, type, length and number of decimals, as well as the source of the data (parameter acronym for data originating from the BODC 'ORACLE' data base (Lowry, 1990), or another explanation), units and a short description of every individual parameters. It should be noted that three different types of SPM measurements have been stored: routine gravimetric determinations of the residue on GFC-filters ('GRAVIMET'), calibrated transmissivity measurements ('TOTSED') and gravimetric determination of the residue on 0.4 μm Nuclepore filters samples for particulate trace metal analysis ('SCONC'). Throughout this work, SPM distributions have been plotted using GRAVIMET, or, if unavailable, TOTSED. Particulate trace metal concentrations and derived parameters were plotted against SCONC, the concentration of suspended matter trapped on the trace metal sampling filters, e.g. in the K_d-plots.

Once the sampling bottle numbers had been entered into the local project data base, analytical results and '<'-flags for dissolved trace metals could easily be loaded from the 'Analysis Calculation' spreadsheet shown in Appendix II.

The data bases of the five different cruises referred to in this thesis, in the more explanatory spreadsheet version, are included in Appendix V for CH42, Appendix VI for CH46, Appendix VII for CH65, Appendix VIII for CH69 and Appendix IX for CH72. They consist of different 'sheets' meant to lie next to each other, including a last sheet displaying K_d distribution coefficients for the eight trace metals. Since they are merely computations from other data, K_d-values do not form part of the data base proper. Parameters which were not recorded during a particular cruise, or are not referred to within this thesis, have been omitted from the print-outs in Appendix V to IX.

4.4.3 Screening of the analytical results

The end results from the dissolved trace metal analysis were screened for outliers, which were subsequently flagged with a '?' qualifier. This procedure inadvertently bears a highly subjective element, but was found useful and necessary to mark and possibly exclude single values from data analyses or plots, that would otherwise be unreasonably biased. However, when screened (outlier excluded) data sets are used, this has to be stated explicitly.

Data were screened for outliers by plotting groups of assumedly comparable data, like all offshore or all tidal station data from one cruise, against their salinities. Single points deviating significantly from an otherwise well-correlated data set were identified as outliers, taking into account the precision and the detection limits of the analysis.

4.4.4 Data verification

In a paper on the principles of environmental analysis, Keith et al. (1983) recommend that verification and validation procedures should be made part of the overall analytical process in order to assess the accuracy and reliability of an analytical method. Chester (1990) summarises the conclusions of Boyle et al. (1977) with regard to the validation of open ocean trace metal data, recommending interlaboratory confirmation, smooth vertical variation, related to other hydrographic or chemical measurements, and compatibility of regional variations with large-scale physical or chemical circulation pattern ('oceanographic consistency') as data quality criteria. With regard to estuarine and coastal water samples, however, the naturally higher variability of these environments has to be taken into account.

Within this study, data validation and verification include the use of CASS standard reference material and an outlier rejection procedure based on trace metal-salinity relationships. In order to further assess the acceptability of the generated data set, results were compared to previous studies in the same area, and results from the same samples using Anodic Stripping Voltammetry (ASV).

Table 4.3 shows, as an example, the approximate ranges of some dissolved trace metal values reported for the Humber-Wash area, as taken from contour plots in Jones and Jefferies (1983) and Balls (1985a). The former paper compiles the results of a long-term trace metal monitoring program using solvent extraction and AAS analysis, and the latter paper is based on measurements with ASV. The data ranges from this work are in good agreement with the ranges reported by Balls (1985), and generally below the values in the older study, possibly indicative of an improvement in contamination prevention techniques. None of the two papers reports values for dissolved Fe or Co.

Figure 4.1 shows, as an example, a plot of data obtained by AAS-analysis against results from ASV-determinations on identical offshore samples from cruise CH42. The diagonal line represents exact agreement between the two measuring techniques. Whilst there is broad agreement between the two techniques with regard to Pb, Cd concentrations obtained with AAS seem typically to be significantly higher than the ASV-results. For Cu, results obtained with AAS are clearly elevated compared to the ASV-results, measured without prior UV-irradiation. This difference is attributed to the complexation of copper by organic ligands, thus rendering this fraction unavailable for voltammetric determination.

From these comparisons it has been concluded that the data generated during this work lie within the expected ranges and generally agree well with results from other measuring techniques.

[nmol/l]	Mn	Ni	Cu	Zn	Cd	Pb
Jones and Jefferies (1983)	20-270	8-68	10-16	30-110	0.5-2.0	
Balls (1985a)			3-16		0.2-1.0	0-0.35
This study	1-9	2-20	2-14	2-22	0.1-0.5	0.04-0.4

Table 4.3: Data range comparison with other studies

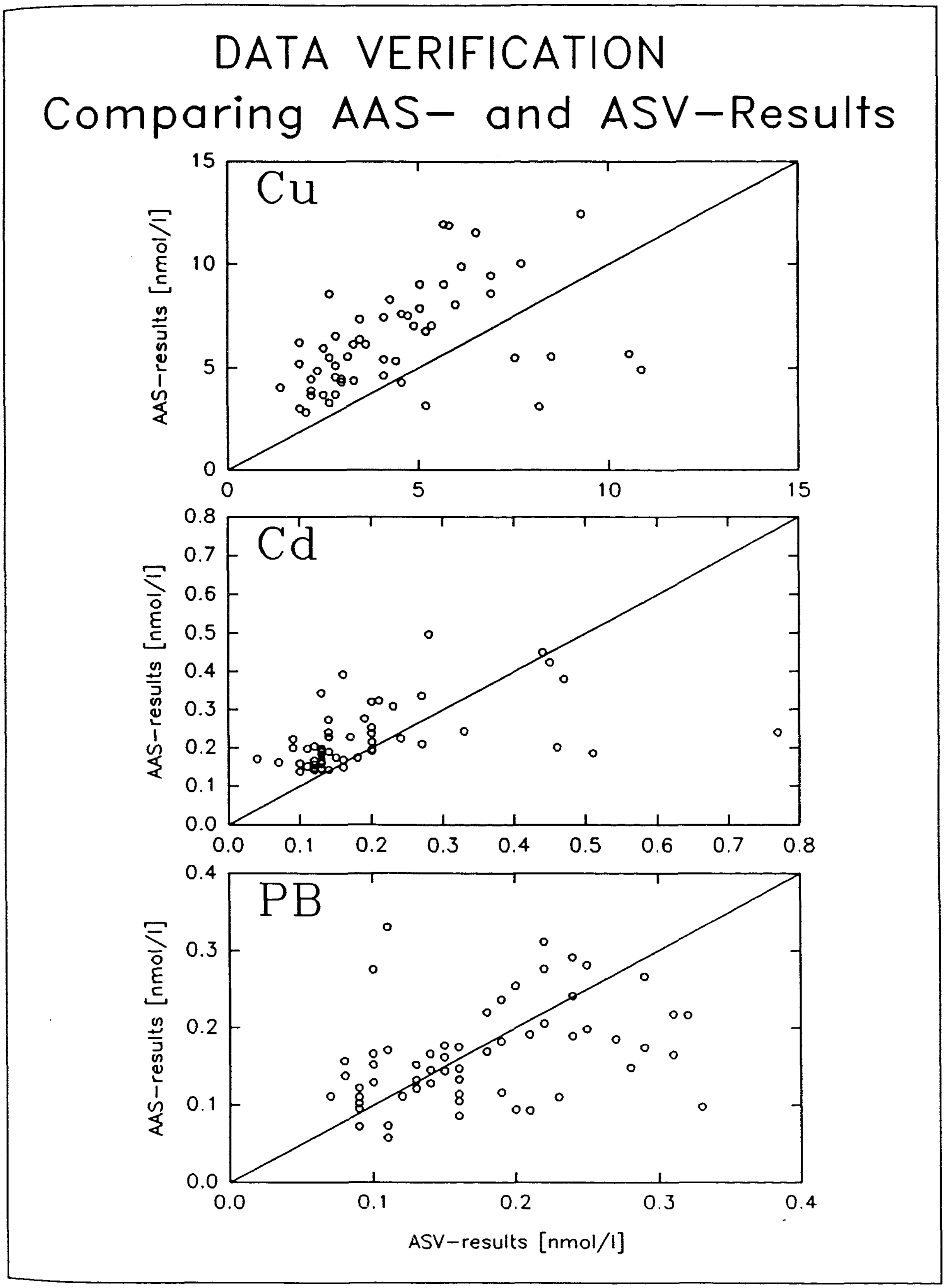

Figure 4.1: Data verification: Comparison of AAS- and ASV-results

4.4.5 Tidal Correction of sampling positions

Hydrographic measurements based on samples that have been taken in a moving water body in a time scale similar to that of the water movement, are likely to be distorted by the Doppler shift between sampling and water movement velocity. In coastal areas, surveys using ship-board measurement are prone to be affected by tidal oscillation, as shown, e.g., by Brockmann and Dippner (1987). Correction for this effect usually includes the back-tracking of sampling positions towards locations they are likely to have occupied within that water body at a chosen reference time during the tidal cycle, like high or low water. Thus a synoptic picture of the spatial distribution of the parameter in question is obtained.

A FORTRAN program for tidal corrections in the Humber-Wash area was provided by R.Wood at the Plymouth Marine Laboratory (PML). The program recalculates sampling positions using tidal amplitudes and phases from a hydrodynamic model of the survey area, times and dates of high and low water at Bull Sand Fort in the Humber mouth, and spring tide dates for Immingham. The program was run with a FORTRAN compiler on a personal computer. Tidally corrected positions were calculated for low water (LW), when freshwater influence around the outflow is most apparent, and the corrected positions were stored in the data base. Further details about the effect the tidal correction procedure will be given in section 5.2.

4.4.6 Data plotting protocol

Apart from a tabular form, results can also be presented in appropriate plots, like contour maps or time series. Data plotting, however, potentially a powerful tool to display large data sets in their spatial and temporal context, can also lead to a confusing and distorted picture, especially if underlying procedures and their implications are not clearly stated or are used inconsistently.

In chapters 5, 6 and 7, data are presented in different types of plots. Contour maps have been generated from offshore samples with a PC contouring package. The irregular spaced data, including values below the detection limit, but without data points flagged as outliers, were gridded using a kriging algorithm, and the regular spaced grid estimates were subsequently plotted with appropriate equidistant contours. Outlier data are taken account of by being printed as values onto their sampling positions. All sampling positions are indicated by asterisks. Areas without sufficient data coverage were left blank. All charts are Mercator projections to a reference latitude of 53.0, and include a coastline and a scale, expressed as the distance in km between the latitude or longitude tick marks.

Tidal station data were plotted as time series over the tidal cycle. Every page contains a salinity and SPM curve, together with four dissolved trace metal plots. Nutrient and chlorophyll concentrations have occasionally been included on a separate sheet. For the Humber and Thames surveys, all trace metal plots have a 0 nmol/l base line, and it was attempted to use identically scaled y-axes for plots from the different Humber surveys in order to facilitate comparisons. Where this proved impractical, the expansion (>1) or condensation (<1) factors of the y-scale ranges are given with the plot.

Trace metal-salinity plots were drawn in two different forms: samples from longitudinal estuarine transects were shown together with their sampling positions, and, for the Humber estuary, y-scales were again kept in line with the tidal station plots where possible; offshore samples were plotted against salinity together with an indication of the 3σ detection limit and, where appropriate, together with the parameters of the linear model.

For the graphical presentation of dissolved/particulate phase distributions, particle-bound percentages of the total concentrations have been plotted, on a probability scale, against suspended matter concentrations, on a logarithmic scale. Lines corresponding to a given K_d-value have also been plotted, as suggested by Balls (1988).

4.4.7 Data quality control

As pointed out by Taylor (1981), data quality assurance involves two related concepts: *quality control*, i.e. all measures taken in order to improve data quality, and *quality assessment*, the evaluation of the effectiveness of the quality control system. Quality control procedures have to accompany all stages of the data generation process, and are frequently implemented by the adherence to 'protocols' developed for sampling, storage, measurement, calibration, data handling and presentation.

The crucial importance of the sampling stage has been pointed out by many authors, both for environmental measurements in general (Keith, 1990) as well as for trace metals in marine samples in particular (Topping, 1986). In this study, best available precautions were taken to avoid contamination of the water samples, including rigorous choice and cleaning of all materials involved, the use of specially designed sampling equipment (acid-cleaned Go-flo bottles or teflon pump), sample handling in a clean shipboard laboratory, unequivocal recording methods and further practices described in the sampling protocol in 4.2.3, where remaining sources of contamination are also discussed.

Quality control procedures during analysis, as described in 4.3.2, include extensive pre-cleaning of apparatus and reagents, extraction in a purpose-build clean laboratory, adequate analytical equipment, clear data logging, and the support and ready advice from experienced colleagues. Checking and recording of important parameters, like extract pH, lamp energy, baseline, sensitivity and calibration of the analytical instrument, and standard deviation of replicates also help to prevent or exclude erroneous data from the data base.

Quality control during calibration and data handling is exercised by the use of electronic data transfer where appropriate, computation by a standardised and well-tested spreadsheet, and a clear and continuous documentation about the source and fate of data, as described in 4.4.1 to 4.4.5. Flagging of data below the limit of detection and the screening for outliers and suspicious data enhanced the usefulness of a data set. Finally, good scientific practice in data presentation will form the last stage of data quality control. The protocol used for this study is given in 4.4.6

4.4.8 Data quality assessment

Data quality assessment is the mechanism used to verify that the system is operating within acceptable limits (Taylor, 1981) and satisfies the data quality objectives, as outlined in 4.1. In this study, quality assessment has largely been based on quality parameters calculated by the analysis spreadsheet, which have been compiled to quality control charts for every individual metal. These charts, included in Appendix IV, allowed the monitoring of the development of the analytical performance with time. The average analytical blank and the detection limit are a measure for the effectiveness of contamination control during analysis, whilst the recovery percentage describes the extraction efficiency. The precision of the analysis is given by the relative standard deviation amongst subsamples, usually of the reference material. Accuracy can be assessed by comparing the consensus value of the reference material with the analytical result. During the early stages of this study, only an uncertified intra-laboratory reference material was used (NSP I and II), from which, due to a lack of independent results, no satisfying assessment of the analytical accuracy could be made. The use of certified standard reference materials (SRM), however, strongly recommended by Keith et al. (1983) and Topping (1986) as a means to compare the performance of an analytical system with one or more 'expert' laboratories providing the material's estimate, and to detect analytical bias, has been adopted later. Accuracy estimates from such materials (CASS I and II standard sea water) have been made and are reported in this table as the positive or negative deviation from the consensus value in percent.

The control charts in Appendix IV have been summarised in Table 4.4 as means and standard deviations of the analytical quality parameters of the eleven batches. Manganese is the element best determined, with precision and bias for the other elements broadly around 10%. The most imprecise determinations are around 15% for the contamination-prone Fe and the analytically insensitive Co.

	Mn	**Fe**	**Ni**	**Co**	**Cu**	**Zn**	**Cd**	**Pb**
Analytical Blank [nmol/l]	0.5 ± 0.3	1.0 ± 0.4	0.8 ± 0.4	0.07 ± 0.02	0.8 ± 0.5	1.1 ± 0.8	0.04 ± 0.04	0.02 ± 0.01
3σ Limit of Detection [nmol/l]	0.8 ± 0.6	1.8 ± 1.5	1.0 ± 0.6	0.16 ± 0.12	1.1 ± 0.7	1.5 ± 0.9	0.03 ± 0.03	0.04 ± 0.01
Precision	5%	15%	12%	15%	8%	8%	8%	11%
Bias	+2%	-7%	+10 %	-1%	+7%	+11%	+5%	-9%

Table 4.4: Data quality parameter (averages)

CHAPTER 5: THE HUMBER-WASH PLUME[1]

5.1 INTRODUCTION

For the purpose of this study, the survey area is defined as the coastal waters where freshwater influence is essentially dominated by discharges from the Humber estuary. Since this estuarine plume frequently extends as far as the coast of Norfolk, the outer Wash has been included in this study. Sampling stations fall between latitudes 52.6°N and 54.0°N, and longitudes 0.0° and 2.4°E, where this area is navigable by larger vessels. No data were collected in the north-eastern corner, but on one occasion additional samples were taken in the Humber estuary, west of the Greenwich meridian.

The Humber estuary provides the largest single freshwater input from England to the North Sea. It drains a catchment area of ca. 25 000 km^2, inhabited by one fifth of the UK population, and includes the heavily industrialised areas of the Midlands and South Yorkshire, with cities including Birmingham, Nottingham and Leeds.

The Humber estuary extends over 62 km from Trent Falls, the point of confluence of the two main tributaries, the Trent and the Ouse, to Spurn Head, where it enters the North Sea. The estuary is macrotidal, with an average tidal range of 5 m (2 m and 7 m at extreme neap and spring tides) at Immingham, and an average tidal excursion of 15 km (Edwards and Freestone, 1988). The flushing time of the estuary is estimated to be up to 40 days (Turner et al., 1991). As much as 1.7 x 10^9 m^3 of water are exchanged with the sea during a spring tide, leading to a flow of 110000 m^3/s at Spurn Head. The average freshwater discharge, however, is estimated to be only 246 m^3/s, with 1550 m^3/s during typical high flood conditions (Denman, 1979). Surficial sediments in the estuary are thought to originate mainly from the erosion of the Holderness coast to the North (Al-Bakri, 1986).

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[1] Throughout this thesis, figures and tables have been given the relevant chapter number, followed by a running index. Since there was only a limited number of indices available within the word processing package, figure numbers in chapter 5 run from 5.1 to 5.26 and then continue as 55.1 ff..

The Wash, the unfilled part of a large depression cut into the Jurassic clays by fluvial and glacial action (Evans and Collins, 1987), drains a much smaller catchment area, consisting of mainly agriculturally used lowlands, resulting in a freshwater discharge about an order of magnitude lower than that of the Humber. Sediments in the Wash are believed to be of both marine and fluvial origin (Dugdale et al., 1987).

Two maps of the Humber-Wash area are given in Figure 5.1. The bathymetric chart has been generated from 600 data points, which were interpolated and contoured using the standard procedures of this study. Although inaccurate in detail due to insufficient data resolution, this map shows some of the main features. Largest water depths, at one point close to 100 m, are found in the Silver Pit, a depression of glacial origin east of the Humber outflow. The 20 m contour in this area should stretch along an old river valley towards the Wash (where in fact another glacial depression, The Well, is situated, with water depths reaching 47 m in places). The 10 m contour delineates the shoals and sand flats stretching offshore from both the Lincolnshire and Norfolk coasts. A third depression, the Sand Hole, up to 40 m deep, is situated just off the Humber outflow, but again is not shown on the chart.

The second map in Figure 5.1 shows residual transport from individual grid elements, as computed by a hydrodynamic computer model. This model was developed at Plymouth Marine Laboratory as part of the larger Humber Plume research project, and its results are referred to in various parts of this study. The area is affected by the anti-clockwise North Sea gyre, leading to a longshore water movement of initially southerly, later south-westerly direction, in which the Humber discharge becomes entrained.

Several studies have investigated trace metal levels in the Humber estuary. A comparison of present-day concentrations in estuarine sediments with a 5000 year old 'base line' sample shows elevated levels for most metals, especially As, Cr, Cu, Zn and Pb, and indications for industrial sources between Grimsby and Immingham, where two titanium dioxide plants have discharged large quantities of acid waste (Grant and Middleton, 1990). An investigation of trace metal levels in *Fucus vesiculosus* (L.) on the South Bank also shows inputs of Fe, Cu and Zn in this area, while levels of Ni and Cd decrease seawards (Barnett et al., 1989).

Heavy metal levels in the < 90 μm sediment fraction have been analysed by Barr et al. (1990), who concluded that concentrations were comparable with other UK estuaries, except for Fe and Ti, where elevated values are reported between Grimsby and Immingham. Determinations of leachable trace metals in the suspended sediment, analysed by Turner et al. (1991), also reveal elevated levels of Fe, Cu and Zn, and are linked to industrial discharges in the lower estuary.

Monitoring data from water authorities have been made available in Gameson (1982) and Howard and Urquhart (1987). The effects of the dumping of industrial waste and sewage sludge off the River Humber has been assessed in a report by Murray et al. (1980), including estimates and comparisons of trace metal inputs from different sources. More recently, riverine, industrial and sewage inputs have been estimated during the PARCOM 1990 survey (National Rivers Authority, NRA, 1991). Data from these two studies have been converted into both annual load estimates and average freshwater concentrations, as shown in Table 5.1. The aggregated riverine, industrial and sewage input estimate in Murray et al. (1980) is based on data collected up to 1976 and is assumed to have a rather large margin of error. Dissolved freshwater fraction concentrations are essentially zero salinity intercepts for data collected in March 1973, 1974 and 1975, at a tidal station near the Humber mouth, as described in Jones and Jefferies (1983). Comparing inputs and exports from the Humber estuary, Murray et al. (1980) conclude that

- nickel inputs have been underestimated
- copper is transported mainly in the dissolved phase and reaches the sea
- zinc inputs may have been overestimated, or are scavenged by particles
- there must be additional cadmium inputs

The same report also states that there are major additional inputs from the disposal of dredging spoils within the estuary and the dumping of industrial waste and sewage sludge off the Humber mouth.

Trace metal inputs from rivers, industry and sewage more than a decade later, listed in the report of the National Rivers Authority (NRA) to the Paris Commission (PARCOM), suggest a significant reduction in zinc and cadmium levels, stable copper inputs and increased lead emissions (NRA, 1991). Freshwater discharges into The Wash show cadmium concentrations comparable to those in the Humber, but lower levels of Cu, Zn and Pb.

There is considerably less information available on trace metal levels and budgets in the Humber-Wash coastal zone. Dissolved and particulate trace metal data in the UK shelf seas have been compiled by Jones and Jefferies (1983). Dissolved and particulate data for Cu, Cd and Pb in UK coastal North Sea waters are given in Balls (1985a), showing high estuarine values, decreasing offshore in a south-easterly plume. Levels of superficial bed sediments, thought to consist mainly of sandy deposits, with a few mud and gravel pockets, have been analysed by Nicholson and Moore (1981), and, in the clay fraction, by Irion and Müller (1990), as part of larger, North Sea -wide surveys. Both studies indicate elevated levels in the Humber-Wash coastal zone, albeit comparable to other outflow areas.

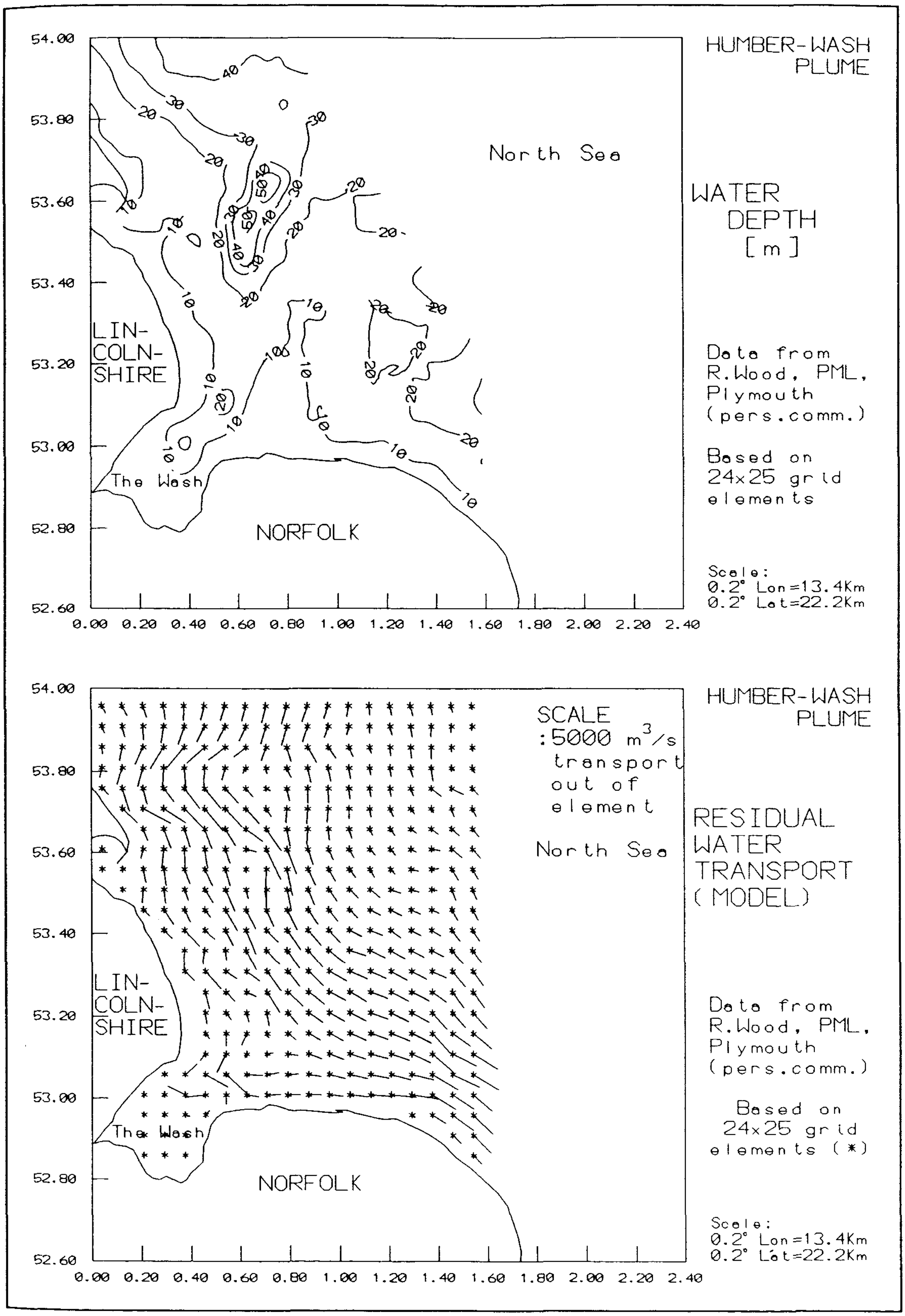

Figure 5.1: Water depth and residual transport in the Humber-Wash area

	Ni	Cu	Zn	Cd	Pb
Riverine, industrial and sewage inputs to the Humber estuary (Murray et al., 1980)					
t/year (1)	19	84	3 400	9.1	28
nmol/l (2)	56	230	9 200	14	24
Dissolved concentrations in freshwater fraction at Spurn Head (Murray et al., 1980)					
t/year (1)	220	68	400	14.0	
nmol/l (2)	650	190	1 100	22	
Riverine, industrial and sewage inputs to the Humber estuary in 1990 (NRA, 1991)					
t/year		98 to 103	780	0.8 to 3.7	72 to 85
nmol/l (3)		160 to 170	1 300	0.7 to 3.5	37 to 43
Riverine, industrial and sewage input to The Wash (NRA, 1991)					
t/year		3.4 to 3.5	8.6 to 9.4	0.11 to 0.14	2.3 to 2.5
nmol/l (4)		56 to 57	140 to 150	1.0 to 1.3	12 to 13

(1): Originally in kg/day
(2): Study assumed freshwater flow of 15.5 x 10^6 m^3/day (180 m^3/s)
(3): Assuming freshwater flow of 300 m^3/s
(4): Assuming freshwater flow of 30 m^3/s

Table 5.1: Trace metal load estimates for the Humber-Wash plume

5.2 THE DATA BASE

Three major cruises were dedicated to the underway and *in situ* measurements and collection of water samples in the Humber-Wash area under differing seasonal conditions, namely cruise CH42 (December 1988), cruise CH65 (May 1990) and cruise CH69 (July/August 1990). Plume sampling periods and tidal stations are outlined in Figure 5.5. The data bases for each cruise, compiled for this study from the much larger BODC North Sea Project Data Base, are given in Appendix V (CH42), Appendix VII (CH65) and Appendix VIII (CH69).

During CH42, sixty-seven surface water samples were collected in the Humber-Wash area either as underway stations or at CTD-positions, and coded S1 to S67. Their tidally corrected positions are shown in Figure 5.2, together with the position shift resulting from tidal correction. A considerable number of samples have been corrected to locations between 10 and 15km further north. The magnitude of this correction is attributed to sampling around a spring tide (sampling period 22-26/12/88, spring tide 25/12/88). The map also shows the approximate positions of the two tidal stations occupied at anchor at the beginning and end of the cruise in the mouth of the Humber estuary, near Spurn Head.

Samples taken during tidal station 1 are coded A101 to A114, plus an additional sample A123, taken 22 hours after the first sample. Sample A103 was not analysed for dissolved trace metals because of contamination, leaving a total of 14 samples. The samples taken consecutively from tidal station 2 were coded A201 to A214.

Together with the general sample parameters and dissolved and particulate trace metal concentrations, Appendix V also gives values for the nutrients phosphate, nitrite, nitrate and dissolved silicon ('silicate'), chlorophyll, dissolved oxygen, unfiltered aluminium and total suspended sediment (all from continuous underway measurements), for gravimetrically determined total suspended sediments, the results from the ASV- determination of dissolved Cu, Cd and Pb by scientists from MAFF, and the tidally corrected positions from the hydrodynamic model. K_d-values, calculated from dissolved and particulate concentrations, have also been included.

The structure of the database from cruise CH65 (May 1990), shown in Appendix VII, is very similar to the one for CH42. There are, however, no oxygen data available for this cruise, and no ASV measurements of trace metal concentrations were done. Thirty-five surface water samples (S1 to S35) were collected and analysed. Three corresponding bottom water samples, B16, B25 and B26 were collected at sites where sediment resuspension was suspected, with SPM concentrations increasing from 4-34 mg/l, 4.5-7 mg/l and 8-16 mg/l between the surface and the sea bed, although at the last station there was some doubt whether the sampling bottle actually fired at the right depth. The station positions are given in Figure 5.3, defining an extended sampling grid also covering the coastal waters to the north-east of Norfolk. The sites of the profiles (top and bottom samples) are indicated. Tidal correction affects a smaller proportion of samples and appears less dramatic, probably because the longer sampling period (6-15/5/90) included both a spring (11/5/90) and close-to-neap tides. Four stations in the south-western corner could not be assigned a low-water position, because this area was not covered by the hydrodynamic model.

A further 31 surface and two bottom water samples were not analysed for dissolved trace metals, but kept in the data base because they provide information on other important parameters. They were given the code-letter 'O'. Sample X1 was taken at the same position as S14, but several days later than the other samples in this area, and was therefore seen as less representative. Samples taken at the tidal station in the Humber mouth were numbered A1-A13, A18 and A24, with 13 consecutive samples and two samples taken 17 and 23 hours after A1. At the end of the cruise, eight underway stations (H1 to H8) were taken between Spurn Head and Hull, whilst steaming up the Humber estuary.

During CH69, in August 1990, thirty-one surface samples (S1 to S31) were taken in the Humber-Wash plume and later analysed. Their tidally corrected locations are shown in Figure 5.4, together with the extend of the low water relocation. About half the sampling positions have been shifted by up to 10 km in a northern and eastern direction. The sampling period (28/7-7/8/90) included both neap (1/8/90) and spring (8/8/90) tides. Again, five stations in the south-western corner of the survey area could not be adjusted for tidal water movement.

Another 13 surface samples and two deep water samples, again coded 'O', have not been analysed for dissolved trace metals, but were kept in the data base for other relevant data. Fifteen surface samples taken at the tidal station at hourly intervals are coded A1 to A15. Prior to the Humber-Wash survey, eleven samples were taken in the Thames plume (T1 to T11).

The data base for cruise CH69 is shown in Appendix VIII. Its structure is identical with the one for CH65, apart from the missing data for particle-bound trace metals, which were not analysed.

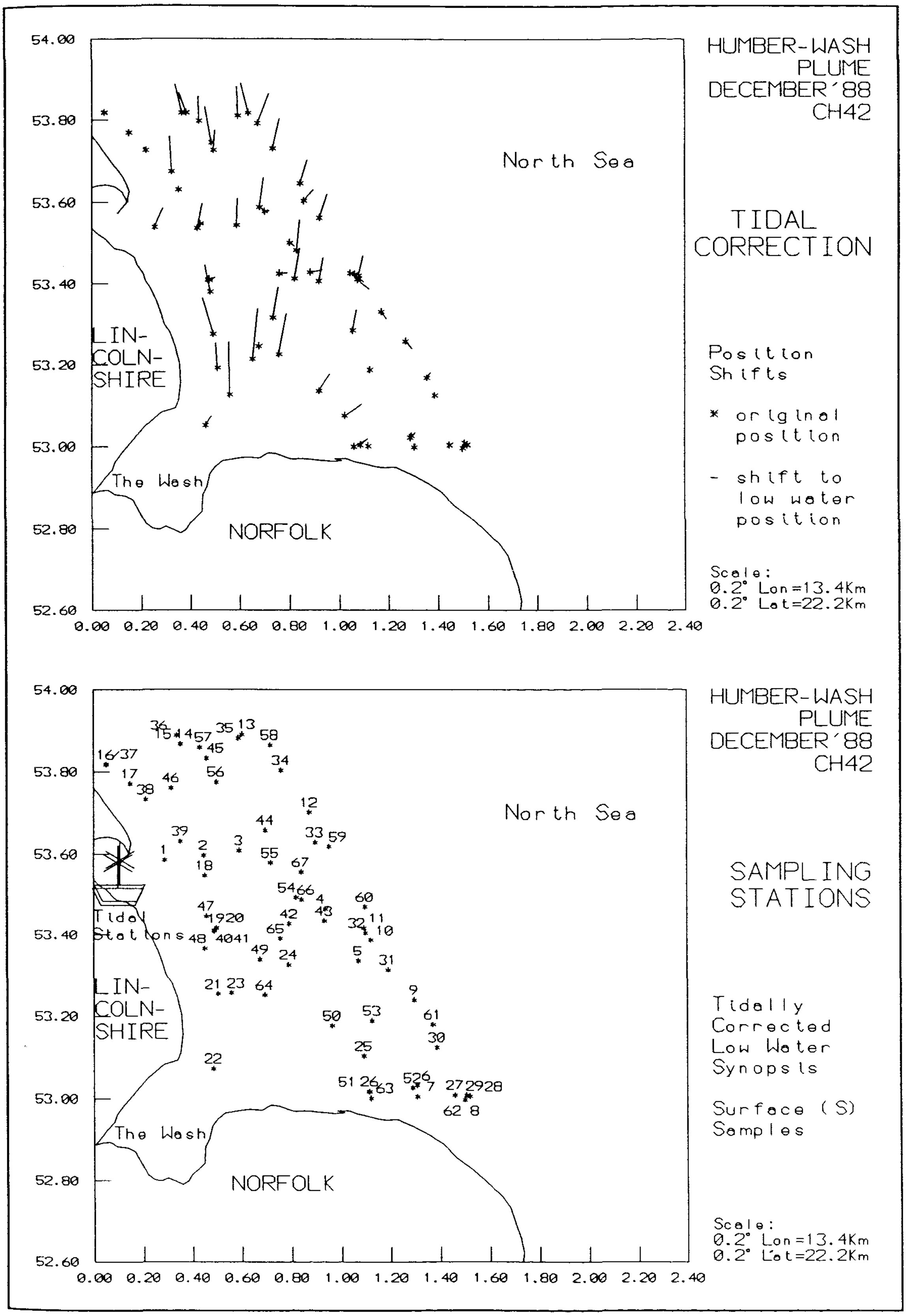

Figure 5.2: Tidal corrections and sampling positions for CH42

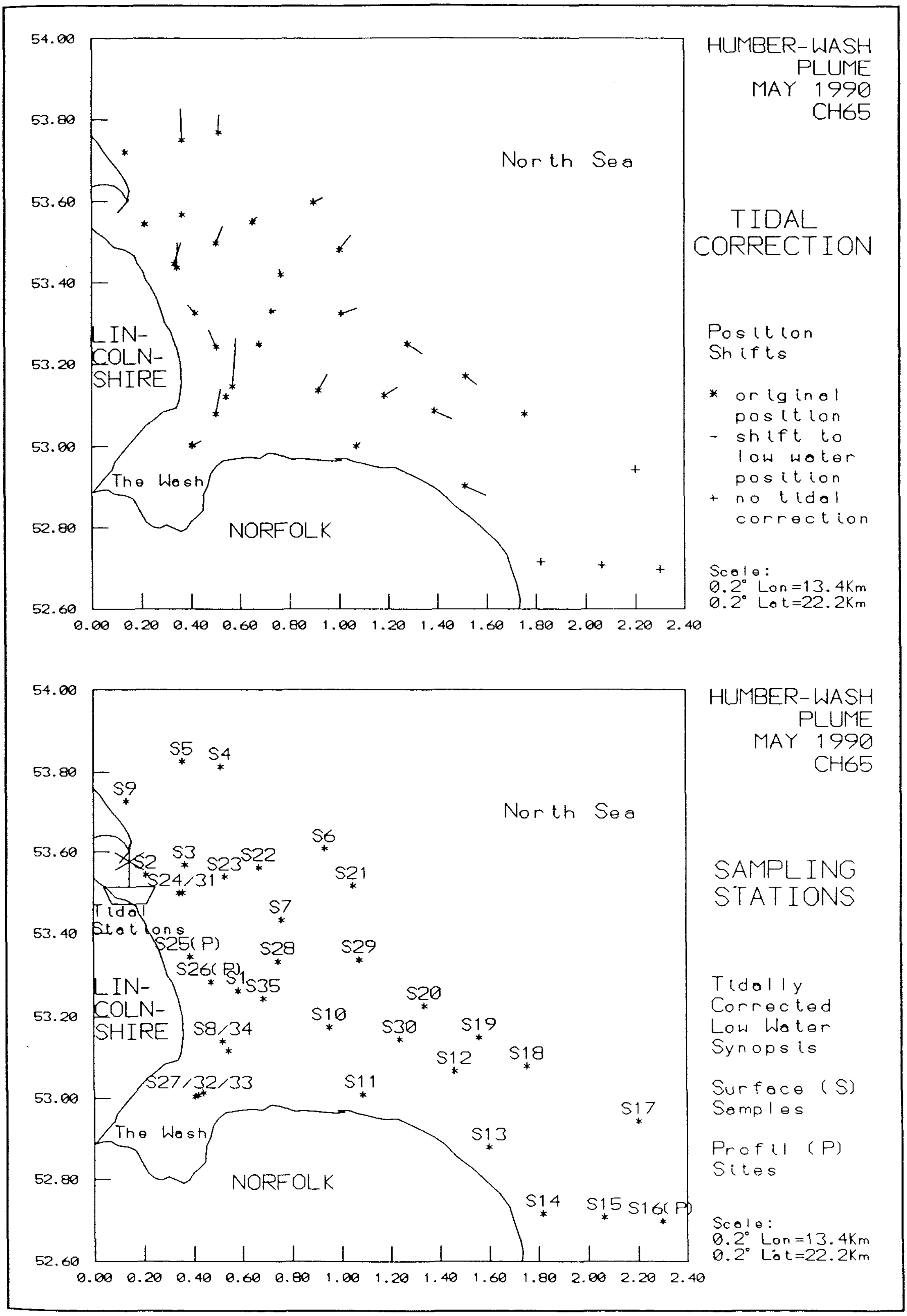

Figure 5.3: Tidal corrections and sampling positions for CH65

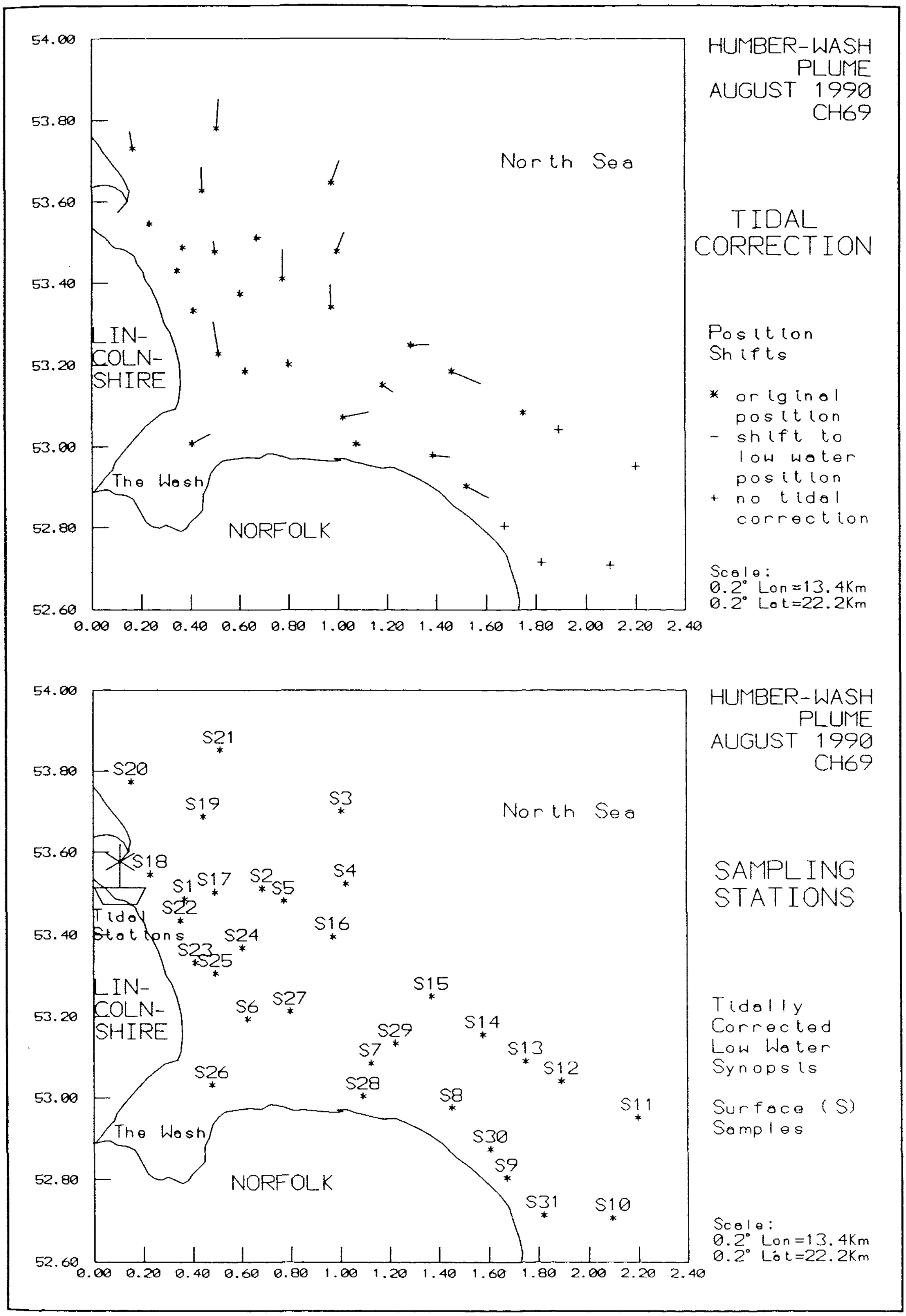

Figure 5.4: Tidal corrections and sampling stations for CH69

5.3 RESULTS AND DISCUSSION

5.3.1 The General Hydrographic Situation

5.3.1.1 Freshwater input and salinity

Figure 5.5 shows, for each cruise, daily estimates of freshwater inputs to the Humber estuary for 30 days before the last sample was taken. These data have been computed from aggregated river flow measurements and the estimated contribution from ungauged catchment areas (Institute of Hydrology, 1991). They do, however, not allow for the phase shift between the individual points of entry into the Humber or the travelling time to the outer estuary. Means, standard deviations, minima and maxima are given in Table 5.2, together with an estimate of freshwater input into the Humber-Wash coastal zone, derived from freshwater mass balance calculations by the hydrodynamic model (Woods, pers. communication). According to the river-based data, mean freshwater runoff in spring can decrease to nearly a quarter, in summer to merely a sixth of the winter discharge. The sums of the Humber and Wash estimates are generally in fair agreement with the mass balance estimates, bearing in mind the existence of a time lag to the riverine signal.

Salinity distributions found during the surveys are shown in Figure 5.6 and Figure 5.7 for the three cruises[2]. During winter and spring, the 34.0 and 34.2 isohalines run approximately on similar positions in a NW-SE direction, with the 33.8 contour dented towards the Wash, more closely following the coast. The May survey also includes 3 stations with salinities in excess of 34.6. In summer, this freshwater-influenced coastal plume has contracted, with the 34.2 contour further inshore, and the 34.0 and 33.8 isohalines restricted to the Humber mouth. These seasonal changes in salinity distribution are in broad agreement with the freshwater input estimated, although the size of the plume in May is slightly larger than expected.

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[2] In this section, the figures showing the distributions of the various parameters are printed according to the following pattern: distributions of two parameters (e.g. salinity and suspended particles) for the December cruise (CH42) are combined on one page, followed by two pages comparing the May (CH65) and August (CH69) distributions of each of these two parameters.

Freshwater Input Estimates [m^3/s] Humber-Wash Plume		River Flow (*); 30 days prior				Mass Balance (**)
		Mean	Std	Min	Max	
CH42	Humber	307	163	137	702	340
	Wash	66	34	42	164	40
CH65	Humber	85	15	64	115	175
	Wash	40	9	31	60	10
CH69	Humber	51	17	37	115	90
	Wash	16	3	13	24	5

(*): calculated from Institute of Hydrology (1991).
(**): after R.Wood, Plymouth Marine Laboratory (pers. communication).

Table 5.2: Freshwater input estimates Humber-Wash plume

5.3.1.2 Suspended particulate matter

The turbidity regime (Figure 5.6 and Figure 5.8) also shows a strong seasonality. In winter, the coastal plume shows dissolved particle concentrations well in excess of 5 mg/l, reaching 40 mg/l in places. By May, the 5 mg/l contour has moved inshore, and values in excess of 10 mg/l are only found near the Humber mouth, in the Wash and near the Norfolk coast. In summer, suspended particle concentrations have dropped below 2 mg/l for most of the area, and even nearshore values hardly exceed 3 mg/l. Seasonal effects are also seen at the tidal stations, where SPM concentrations fall from between 40-120 mg/l to 10-40 mg/l in spring and 2-7 mg/l in summer (Figure 5.17 ff.), pointing to the Humber as an important and variable source of particles. Regression of plume SPM concentrations against salinity, however, given in Table 5.4, shows that whilst salinity explains about 72% of the SPM variation in winter and 56% in spring, the summer distribution (12%) apparently is dominated by processes other than riverine advection.

5.3.1.3 Chlorophyll and oxygen

The distribution of chlorophyll (Figure 5.9 and Figure 5.10) also shows a strongly seasonal behaviour. In winter, concentrations are uniformly low across the survey area (<0.2 mg/m^3), except for a few patches along the northern boundary, in the centre and off the Norfolk coast, with the highest value (0.7 mg/m^3) in the Wash. These areas with higher chlorophyll show decreased oxygen levels, below 315 μmol/l, as opposed to over 360 μmol/l in the surrounding waters (Figure 5.9). In May, however, primary productivity has increased dramatically in the south of the survey area, with concentrations around 16 mg/m^3 in the Wash and close to the Norfolk coast, gradually decreasing offshore. In the northern half of the area, however, concentrations are uniformly around 4 mg/m^3, and the highly saline stations in the south east coincide with the lowest chlorophyll readings (<2 mg/m^3). In summer, recorded values have come down again to around 1 mg/m^3, with more elevated values around the Humber outflow and the coast of north-east Norfolk.

5.3.1.4 Nutrients

Nutrient distributions (Figure 5.11 to Figure 5.16) are dominated by riverine supply and biological uptake. The winter survey shows elevated levels of phosphate, nitrate and silicate related to the freshwater discharge of Humber and Wash. In May, a plume emanating from the Humber can still be observed, in sharp contrast to the coastal waters off Norfolk, where high biological activity, already seen in high chlorophyll levels, has consumed most of the available nutrients. The highest phosphate values have been found north of the Humber outflow, possibly a sign of other coastal sources. In summer, most of the survey area is depleted of nutrients, and riverine supply is only identifiable in the immediate vicinity of the Humber mouth, with possibly first indications of a recovery in phosphate and nitrite levels close to the Wash and the Norfolk coast. For silicate, increased levels north-east of the Norfolk coast are indeed the predominant feature of the overall distribution.

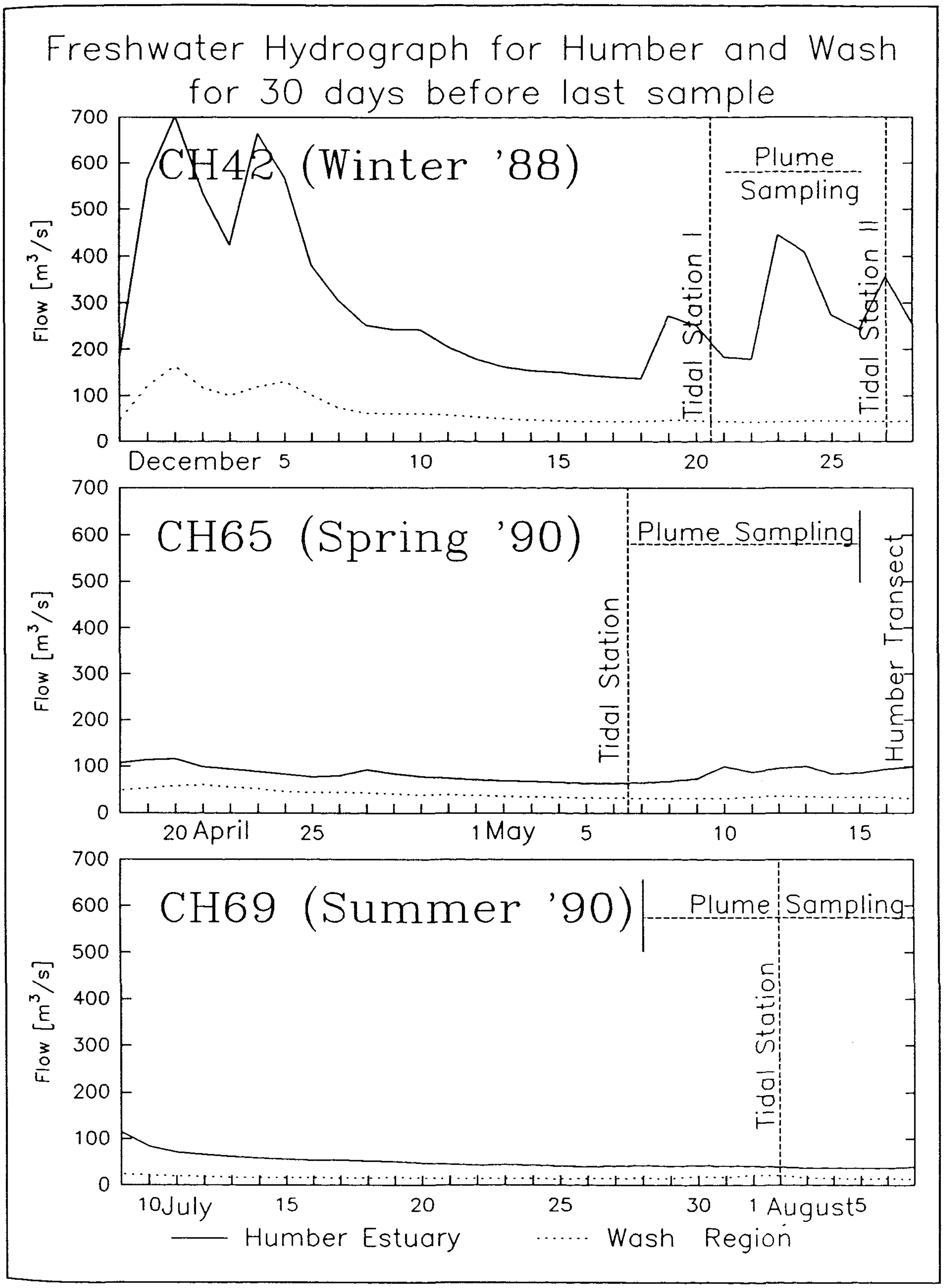

Figure 5.5: Freshwater hydrographs and sampling periods for CH42, CH65 and CH69

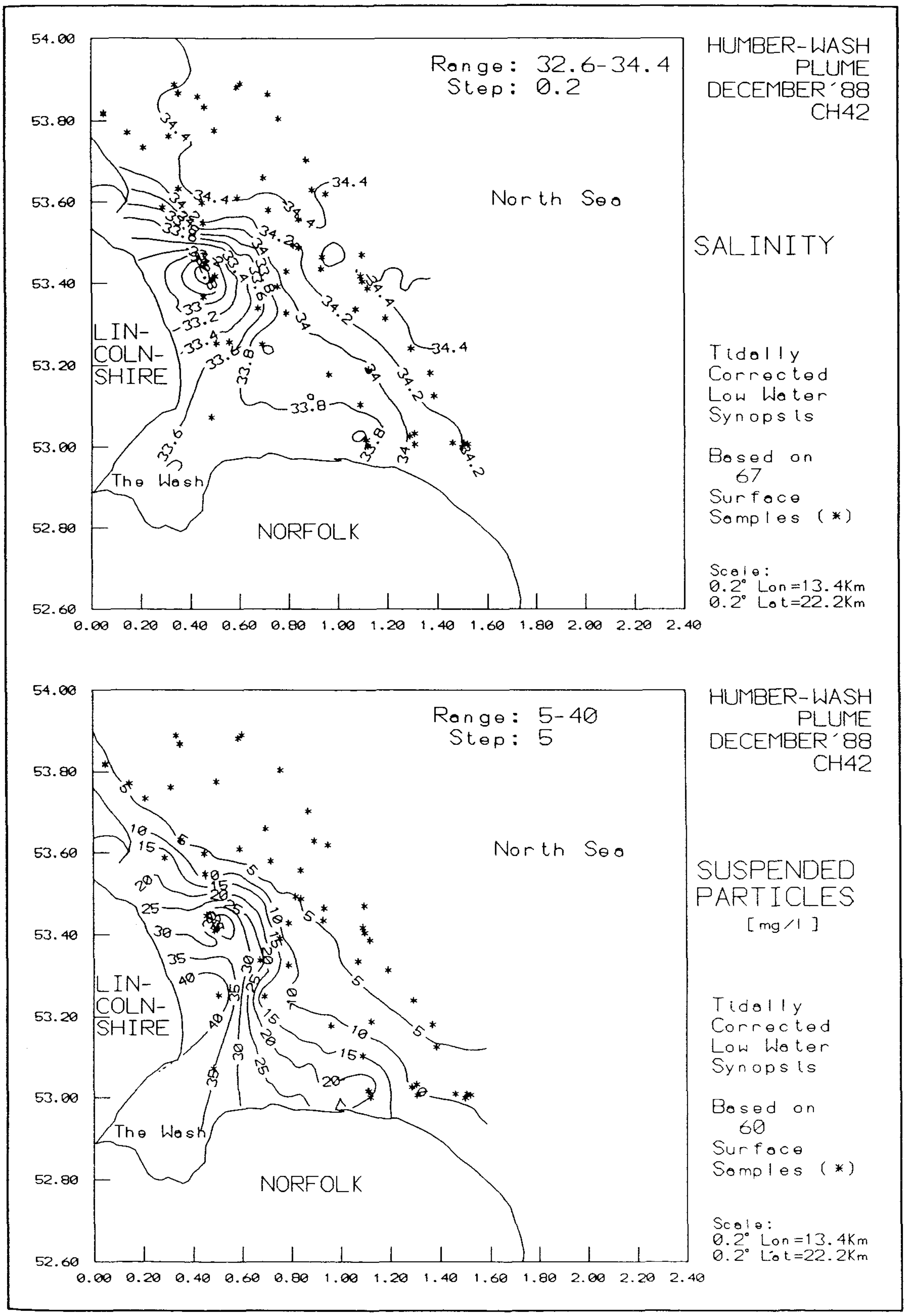

Figure 5.6: Salinity and suspended sediment concentrations in the Humber-Wash area during CH42

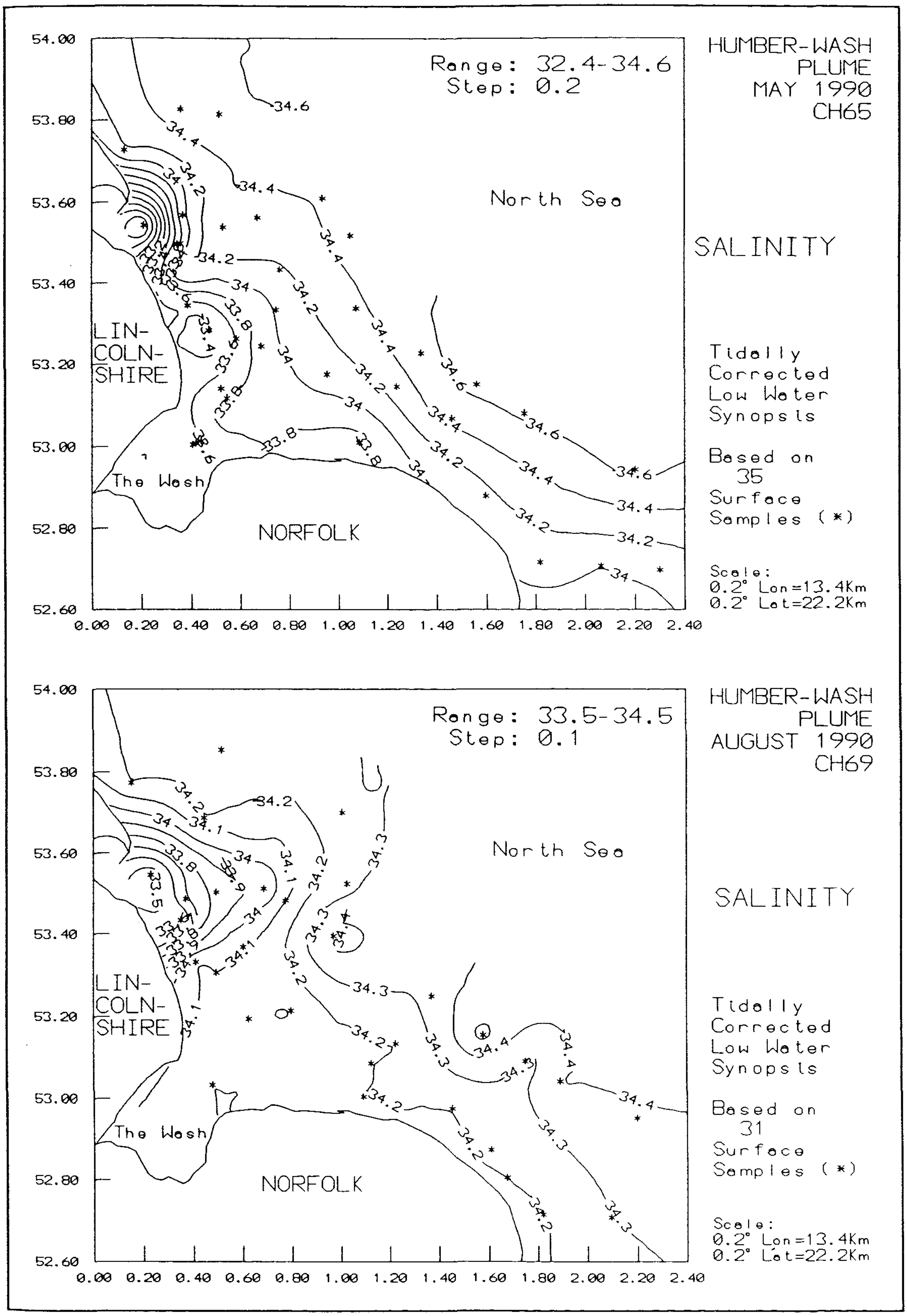

Figure 5.7: Salinity in the Humber-Wash area during CH65 and CH69

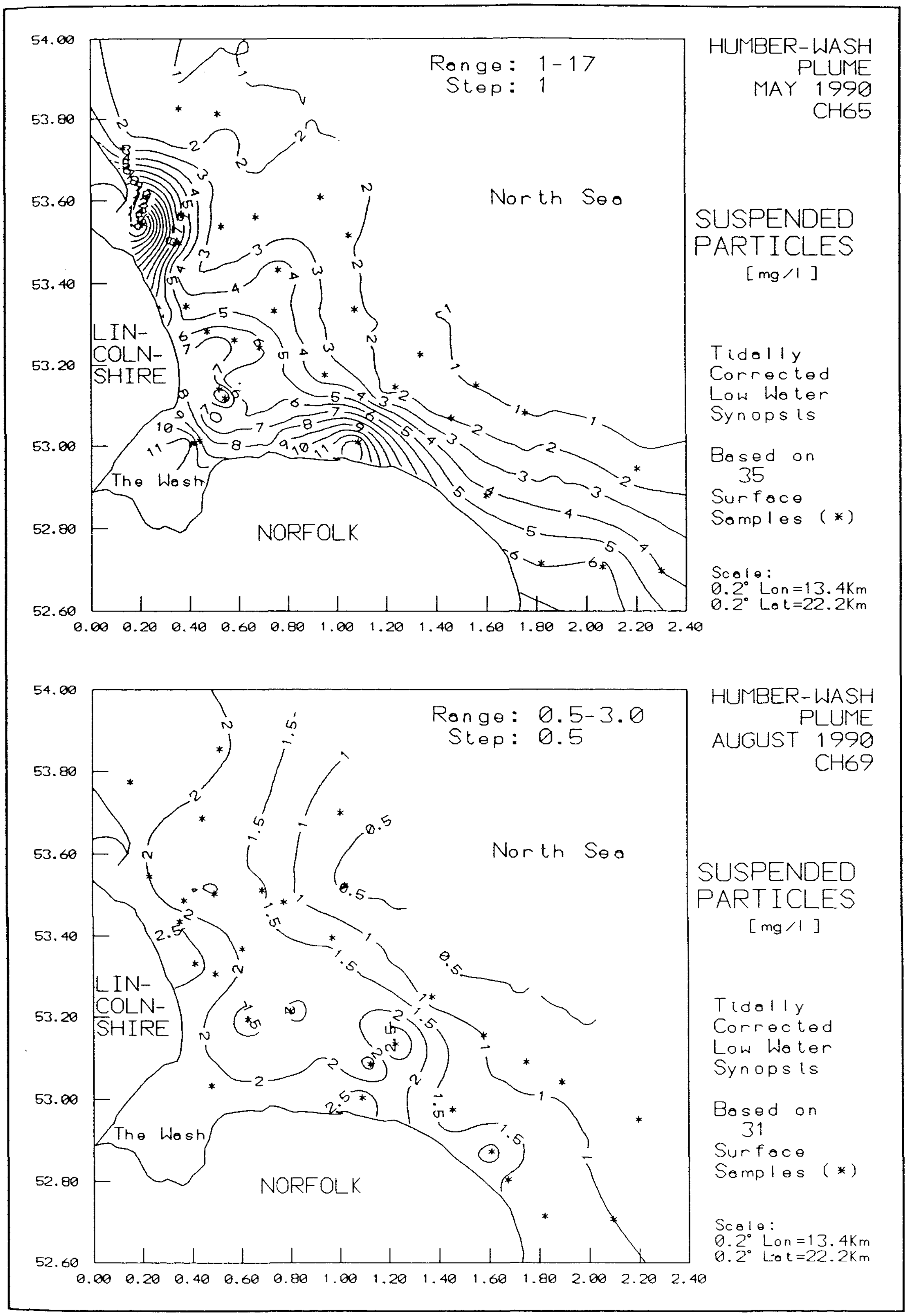

Figure 5.8: Suspended sediment concentrations in the Humber-Wash area during CH65 and CH69

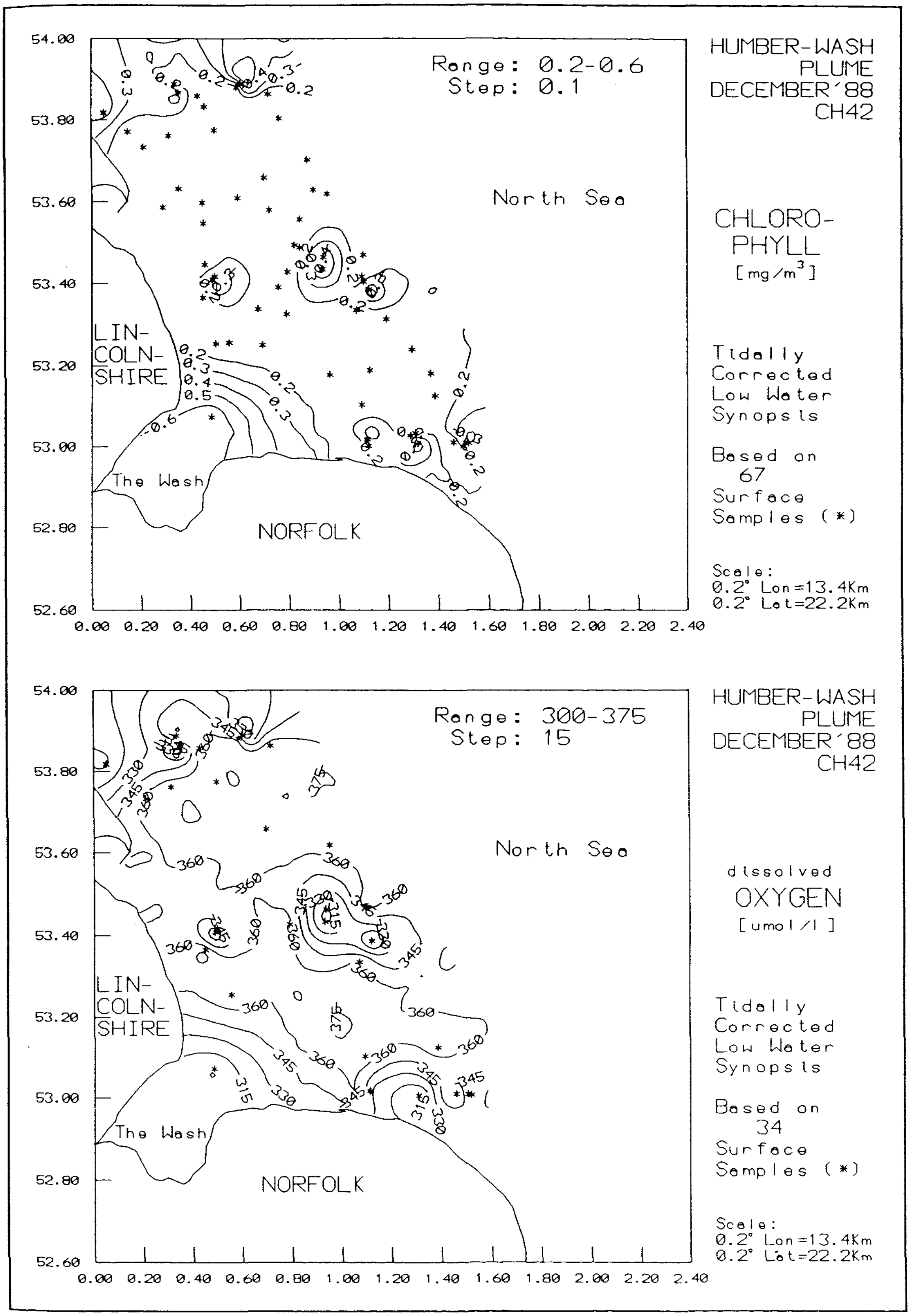

Figure 5.9: Chlorophyll and dissolved oxygen concentrations in the Humber-Wash area during CH42

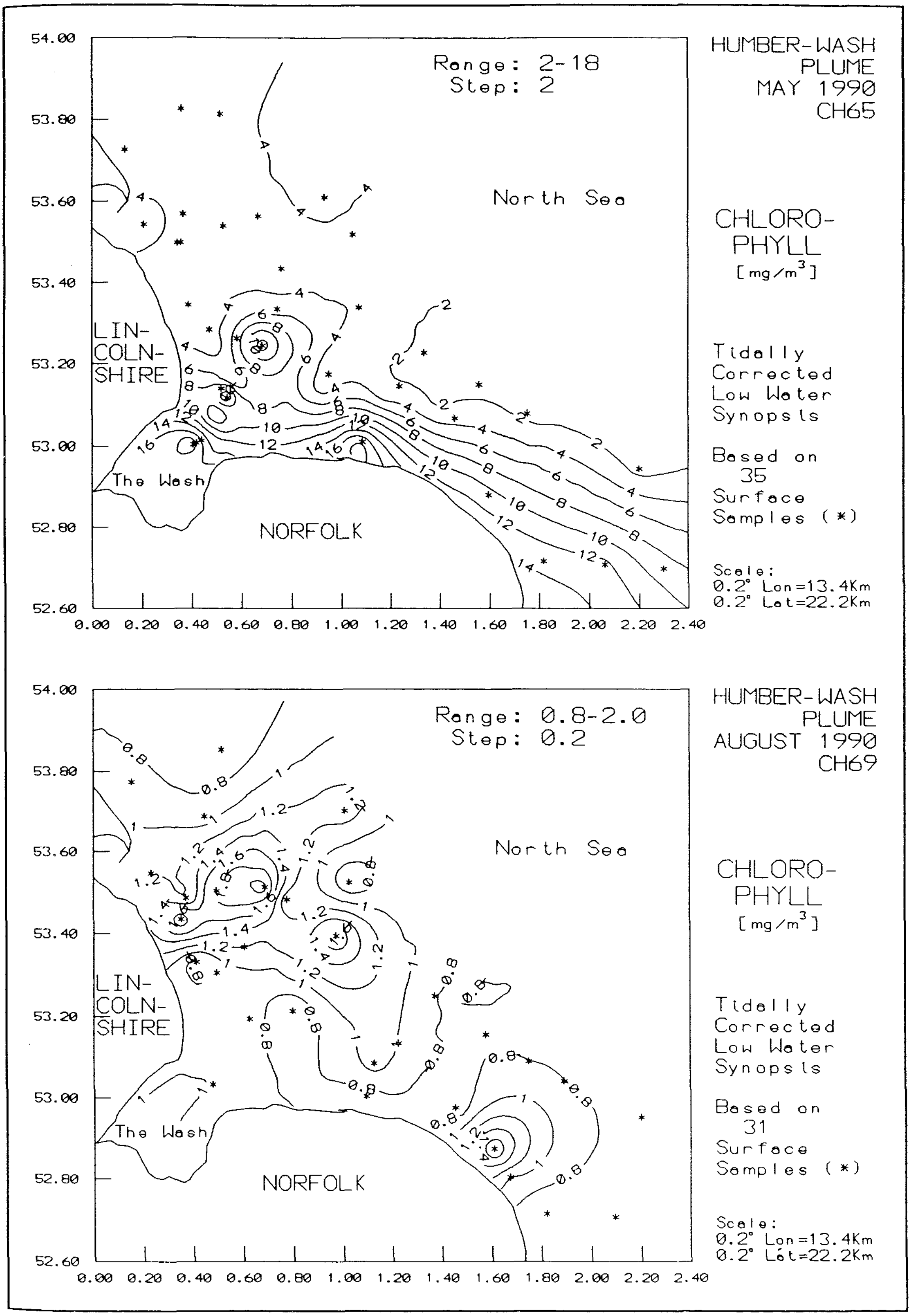

Figure 5.10: Chlorophyll concentrations in the Humber-Wash area during CH65 and CH69

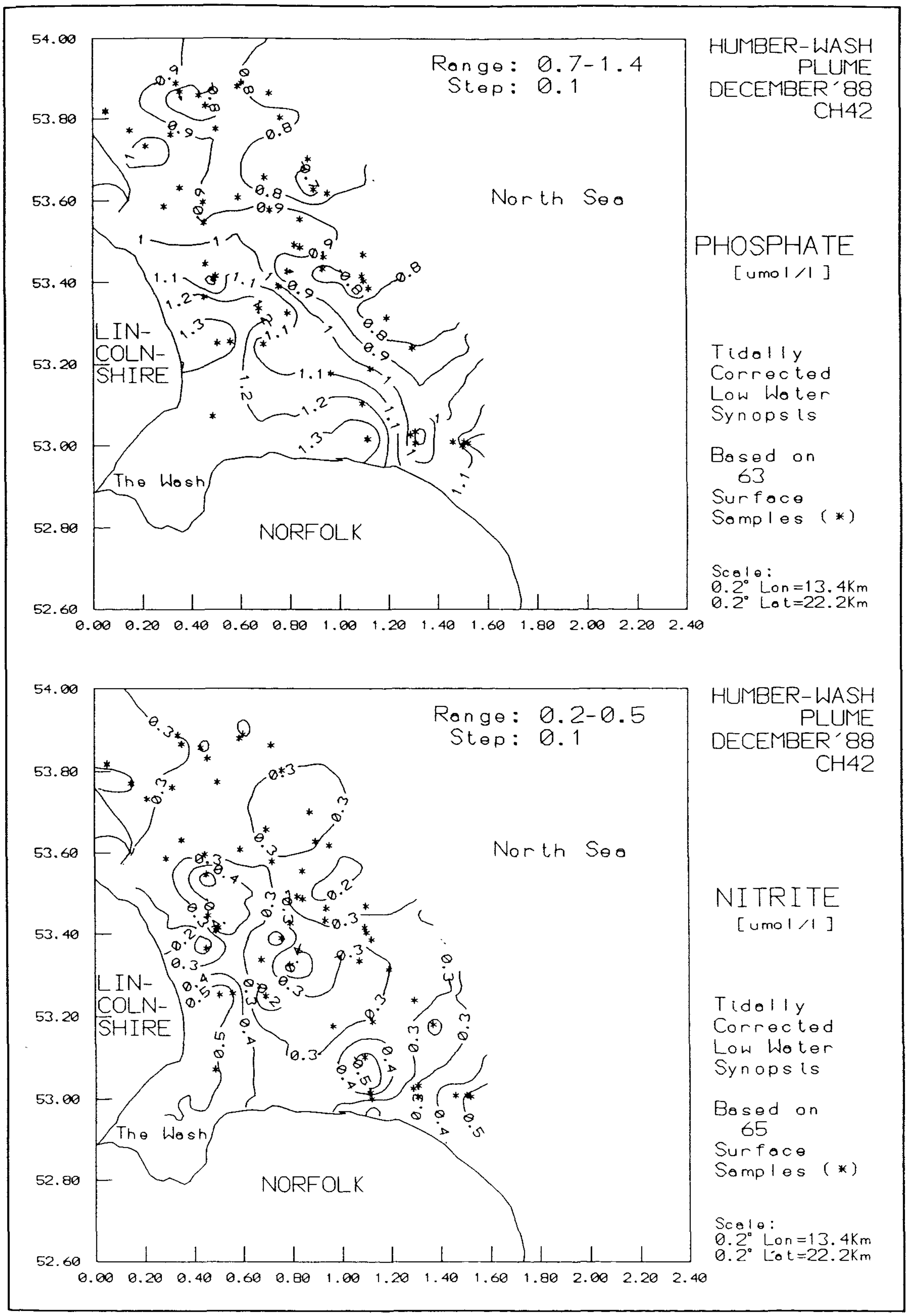

Figure 5.11: Phosphate and nitrite concentrations in the Humber-Wash area during CH42

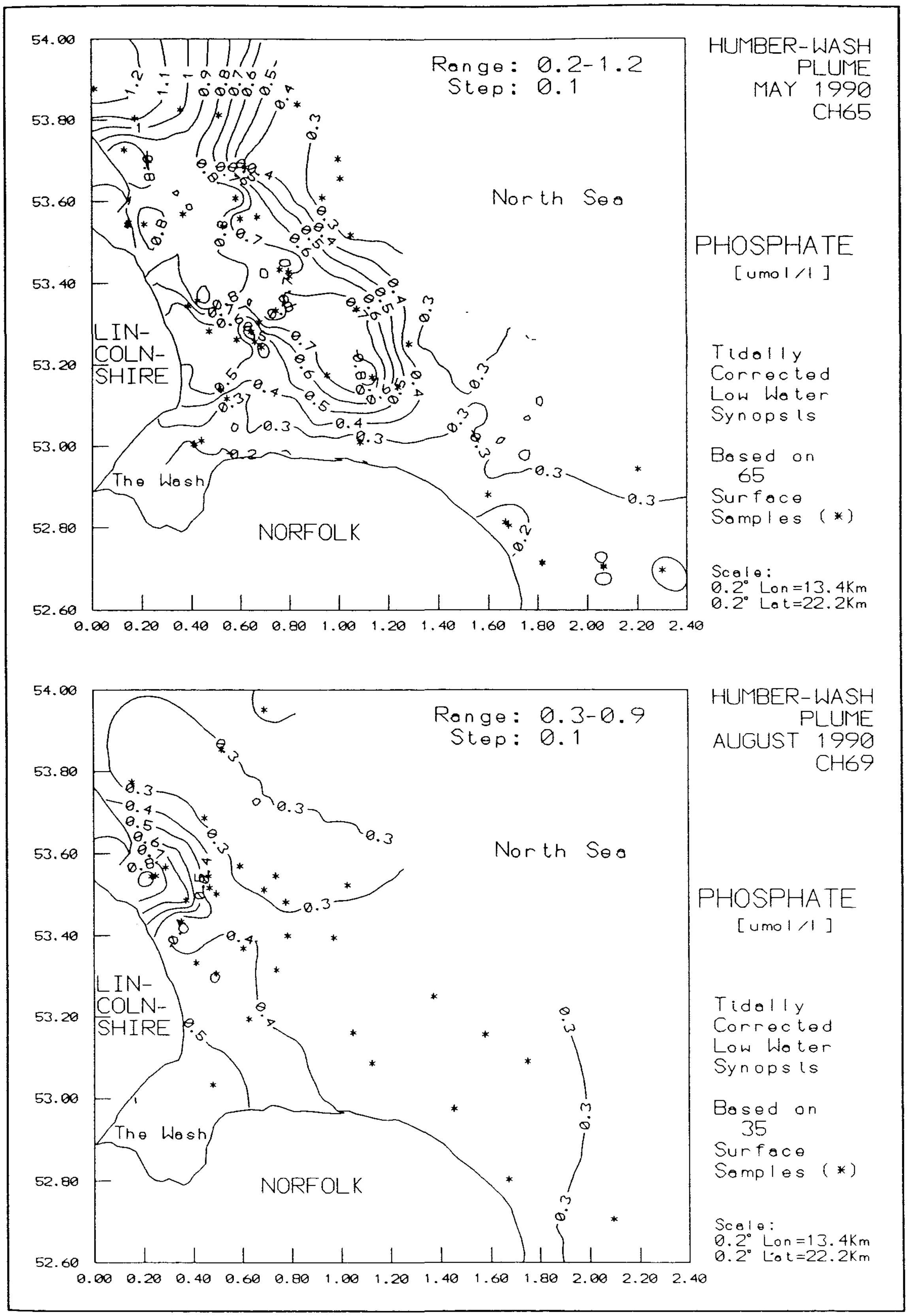

Figure 5.12: Phosphate concentrations in the Humber-Wash area during CH65 and CH69

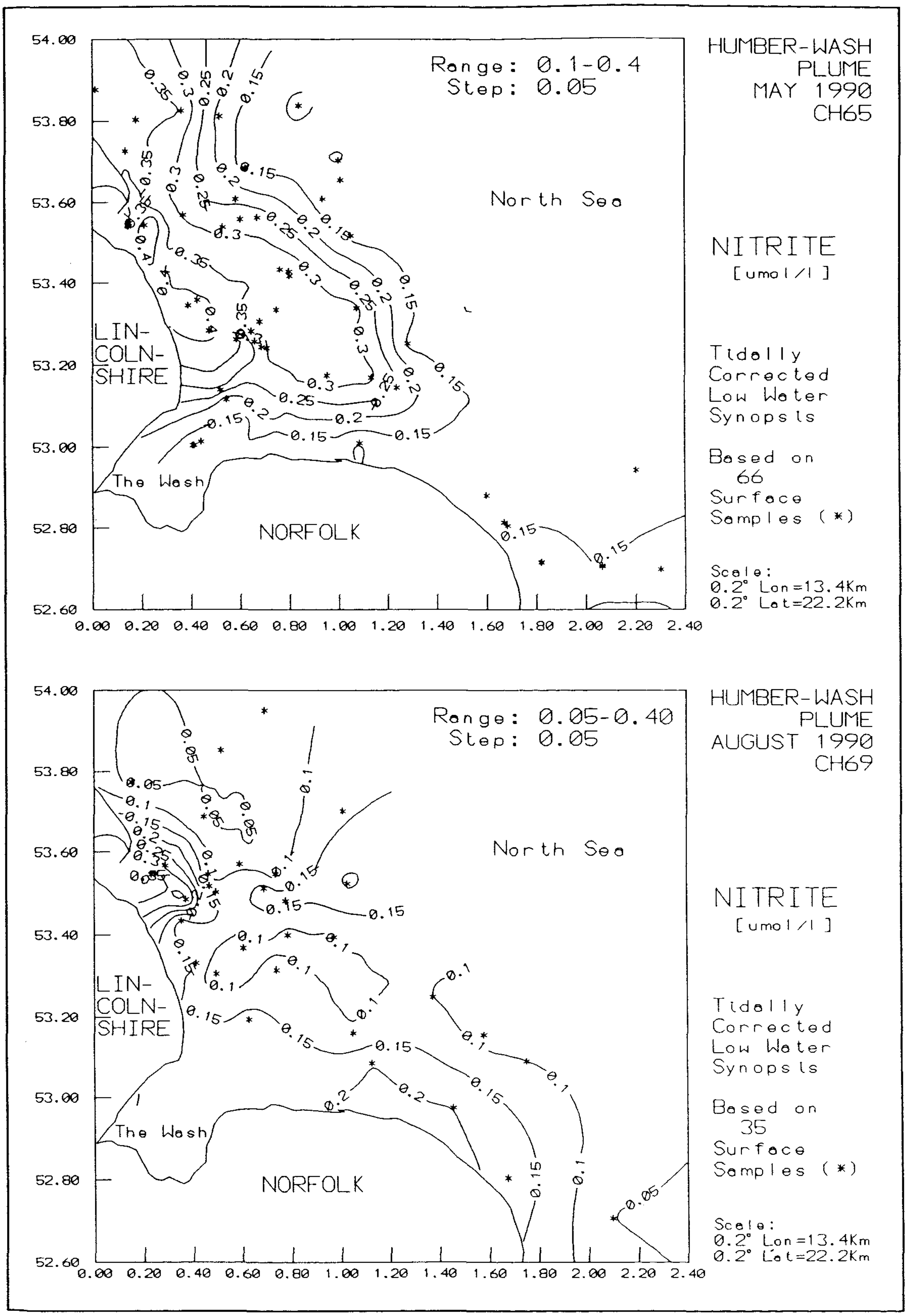

Figure 5.13: Nitrite concentrations in the Humber-Wash area during CH65 and CH69

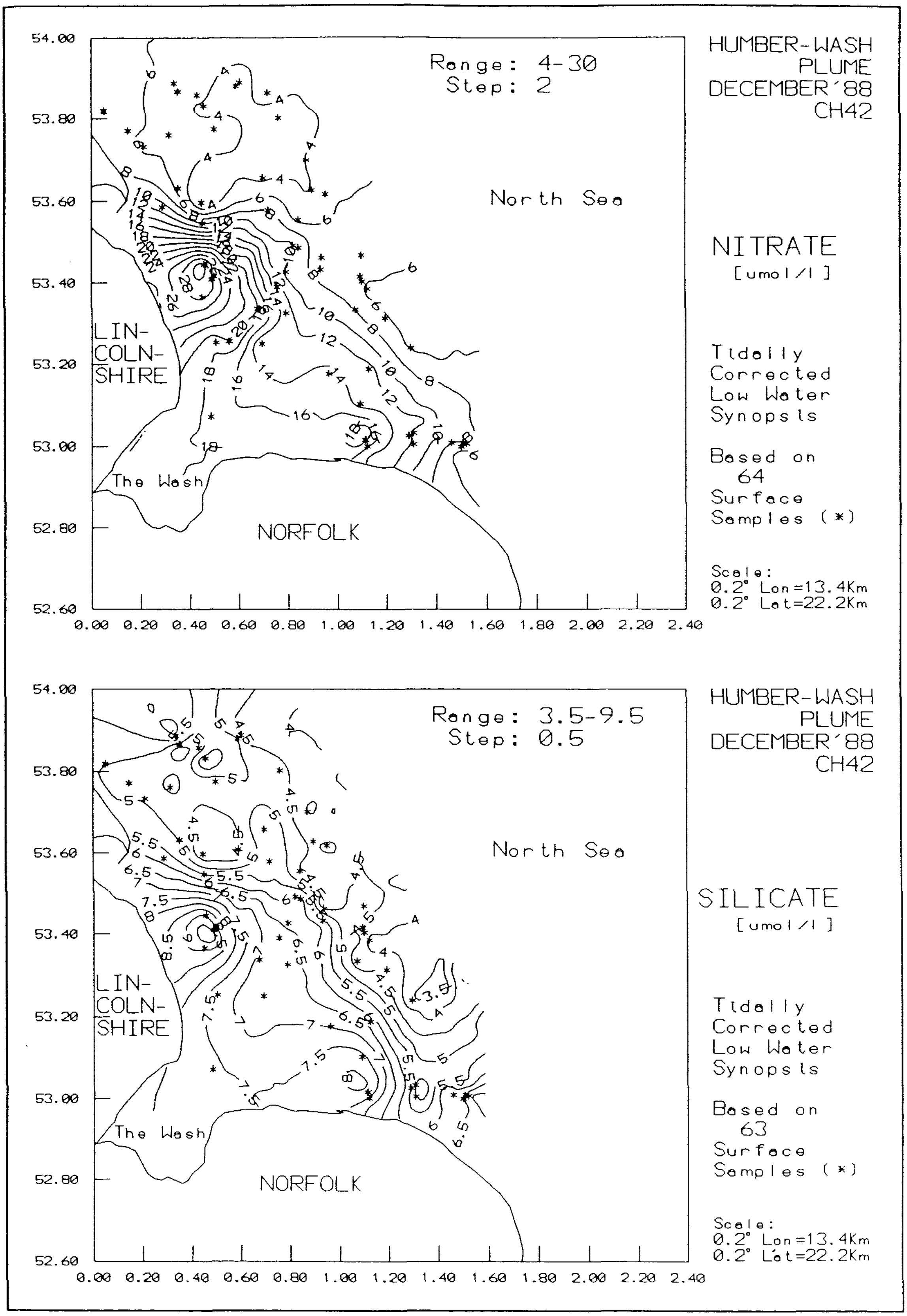

Figure 5.14: Nitrate and silicate concentrations in the Humber-Wash area during CH42

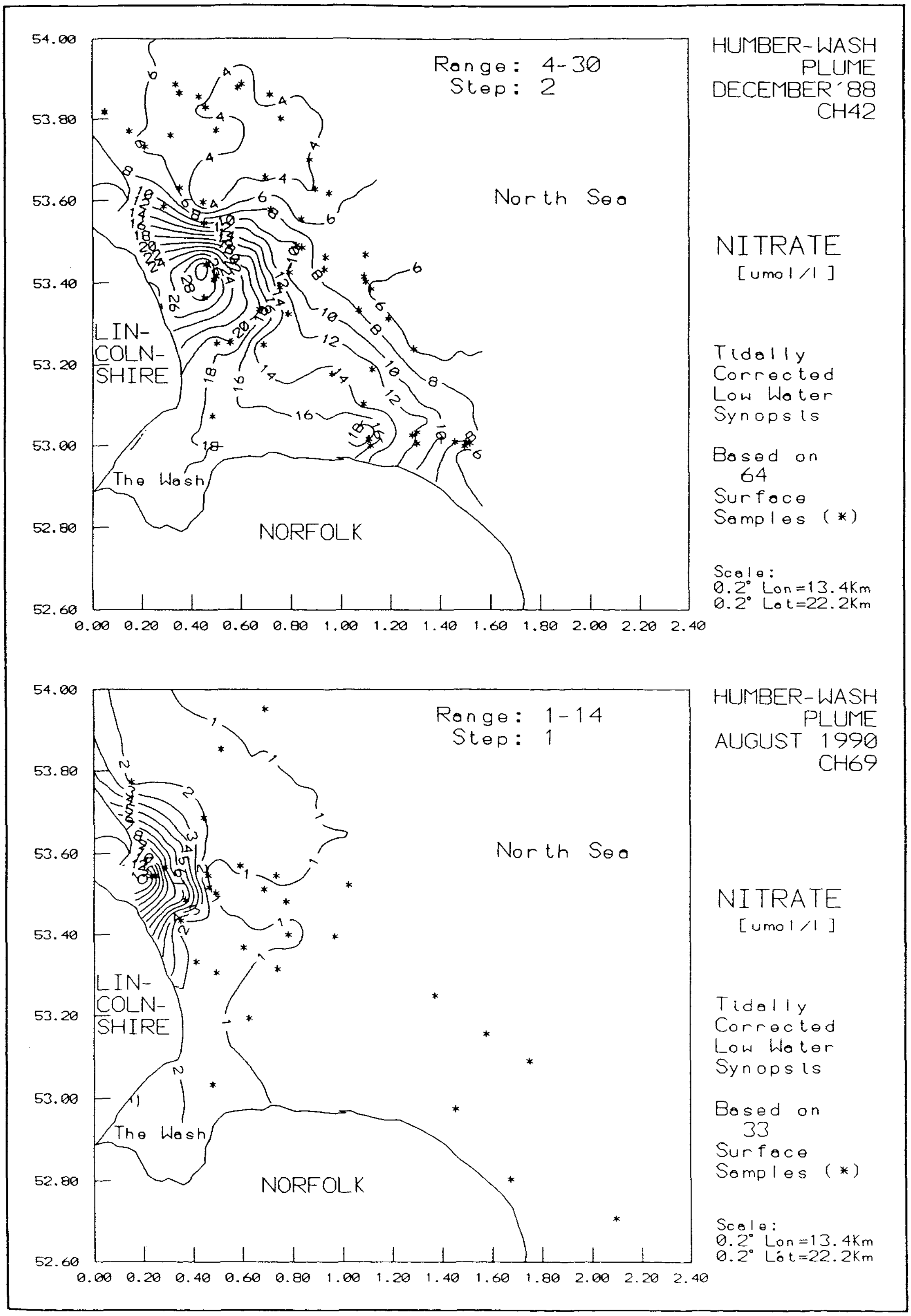

Figure 5.15: Nitrate concentrations in the Humber-Wash area during CH65 and CH69

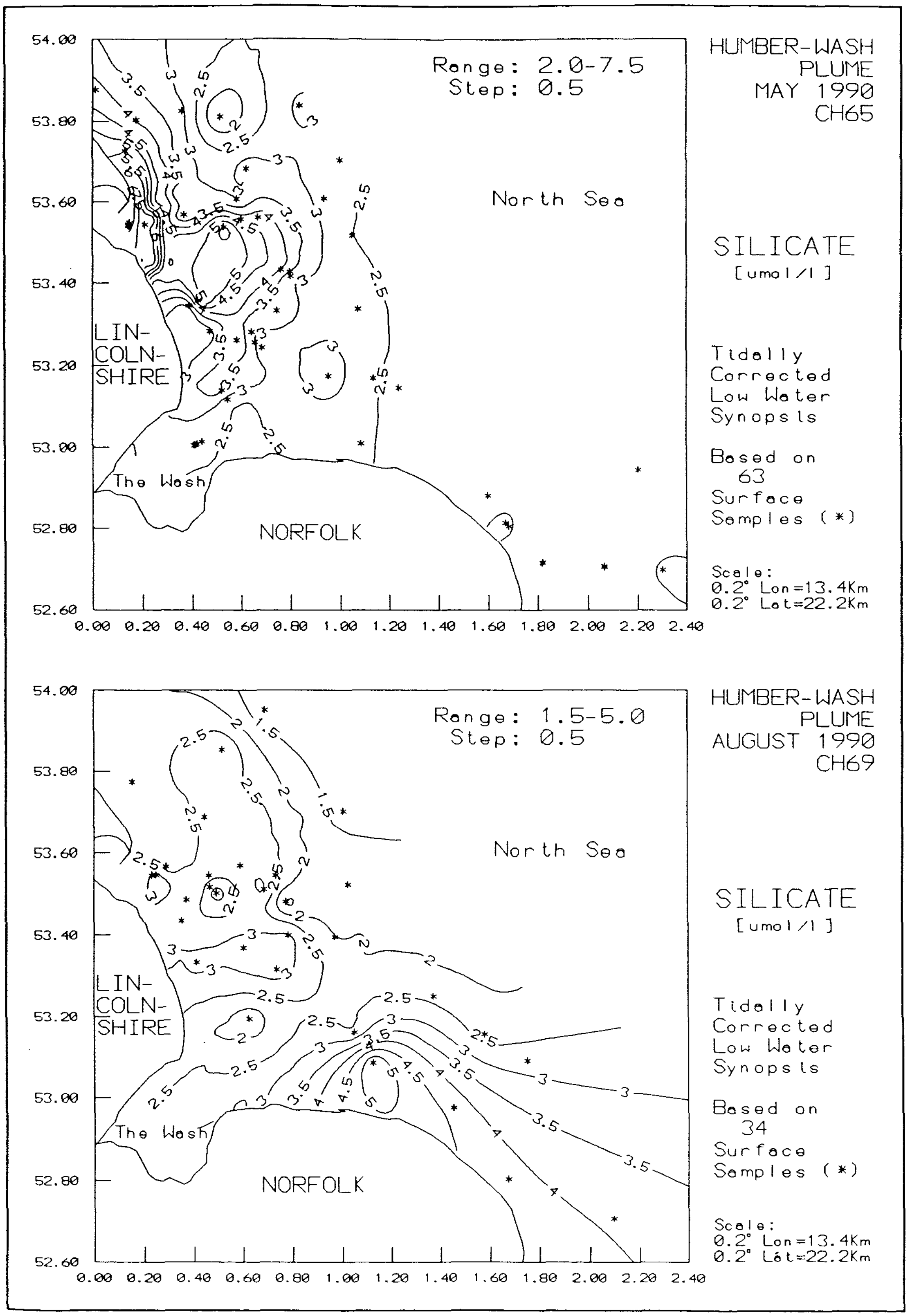

Figure 5.16: Silicate concentrations in the Humber-Wash area during CH65 and CH69

5.3.2 Dissolved Trace Metal Inputs from the Humber Estuary

In order to assess the input of trace metals from the Humber into the coastal sea across the outer estuary-plume interface, time series of trace metal concentrations at the tidal anchor stations have been plotted (Figure 5.17 to Figure 5.24). The same data have also been plotted against salinity in a series of plots in Figure 55.1 to Figure 55.8. Concentrations found during an estuarine transect further up the estuary in May 1990 are shown in Figure 5.25 and Figure 5.26 as metal-salinity plots, which will be referred to for additional information. Results from the regression of trace metal data against salinity (disregarding flagged data) are given in Table 5.4 to Table 5.6. Information concerning the tides during the anchored stations and the estuarine transect are given below in Table 5.3.

5.3.2.1 Salinity

Tidal stations were occupied at different seasons and both during a neap tide, and close to spring tides, with tidal ranges varying accordingly (3.0 to 4.9 m). Minimum salinity values in May and August, at low freshwater runoff, are 30.8 and 30.9; the higher maximum salinities encountered during the spring cruise are probably due to the wider tidal range. In winter, the two stations cover identical tidal ranges, but the range in associated salinities is significantly wider for station 1 (28.2-33.5) than for station 2 (30.0-32.7). The difference in minimum salinities between the two stations cannot easily be explained from the estimated freshwater hydrograph in Figure 5.5 because of the limitations of these data mentioned before. Assuming a travelling time of 15 days for freshwater to reach the outer estuary, the decreased salinities at station 1 could be linked to a preceding storm period. All salinity curves (Figure 5.17 ff.) are roughly sinusoidal, following the symmetric tides typical for this area.

		Time	Time	Height	Range	Spring	Salinity
		BSF	Immingham				
CH42 (station 1) 21-22/12/88 53.552°N;00.105°E	HW	16:03	16:28	6.6 m	4.9m	-4d	28.2 to 33.5
	LW	22:15	22:40	1.7 m			
CH42 (station 2) 27/12/88 53.543°N;00.098°E	LW	13:51	14:23	2.0m	4.9m	+2d	30.0 to 32.7
	HW	19:54	20:23	6.9m			
CH65 06-07/05/90 53.542°N;00.143°E	HW	04:05	04:31	6.4m	4.5m	-3d	30.8 to 33.5
	LW	10:03	10:30	1.9m			
CH65 Transect 17/05/90 Spurn Head - Hull	LW		04:04	2.5m	3.5m	+6d	20.6 to 31.6
	HW		10:17	6.0m			
CH69 02/08/90 53.542°N;00.108°E	HW	14:41	15:05	5.6m	3.0m	-7d	30.9 to 32.9
	LW	20:49	21:11	2.6m			

(from Admiralty, 1988 and 1990)
Spring: Days before (-) or after (+) nearest spring tide

Table 5.3: Tidal data for Bull Sand Fort (BSF) and Immingham

5.3.2.2 Suspended particulate matter

Suspended sediment concentrations cover similar ranges (30-140 mg/l) for the two winter stations, with high values during the mid-tide periods of high tidal velocity, and decreased values around slack water. A similar behaviour can be seen in May, but with concentrations generally being lower (10-40 mg/l) and remaining elevated until after low water. In August, during a neap tide and with very low SPM concentrations (2-7 mg/l), elevated values only exist around low water, pointing to river inputs, rather than tidal scour, as a source. During the estuarine transect in May 1990 (Figure 5.25), particle concentrations rise up-estuary towards Hull.

5.3.2.3 Manganese

During the spring tidal station, and station 2 of the winter cruise, Mn concentrations oscillate with the tides up to 250 nmol/l. The same underlying behaviour in station 1 of the winter survey and in summer is superposed by two extreme values each at low salinities, reaching up to 800 nmol/l. At station 1, these two peaks are separated by a marked decrease affecting all other metals, though to varying extents, except Ni and Cd. During the estuarine transect in May, Mn concentrations reached comparably high levels in the outer estuary, but fell again to around 200 nmol/l west of Immingham (Figure 5.25). Under these specific conditions (flooding), there seem to be strong Mn inputs to the dissolved phase, possibly from sediment mobilisation, in the outer estuary, which may well affect the outflow area when ebbing, and thus explain the peaks observed at the tidal stations.

Manganese-salinity plots in Figure 55.1 (bottom/left) show a lot of scatter, and elevated concentrations at the low salinity end. Increased values at low salinities are also found in May and August, although more than 80% of the variation of both CH65 and CH69 data can be explained by linear models (Table 5.4). The August zero-salinity intercept of 10 000 nmol/l is five times as high as the spring estimate.

5.3.2.4 Iron

Judging from the metal-salinity plots (Figure 55.2) and the regression results, iron does not appear to be related to salinity. The pattern shown in the time series at station 1 of the winter survey (Figure 5.17) however, is in perfect agreement with the pattern shown by lead (Figure 5.18), which is in essence confirmed by the albeit generally higher ASV-result, and also resembles closely the pattern of cobalt. The same 'fingerprint' agreement between Fe and Pb was found during the spring cruise, but extrema stayed well below winter levels, and occurred most pronouncedly after high tide. If this phenomenon was caused by contamination during sampling, which is unlikely for Co, other elements would also be expected to be affected, which is not the case. In summer, iron concentrations are almost three orders of magnitude less than in winter, and show no correlation with the also much decreased lead concentrations. During the estuarine transect (Figure 5.25), Fe shows signs of additional sources within the outer estuary, but, compared to manganese, more localised and less than the tidal station spikes.

5.3.2.5 Nickel

At the tidal station, nickel is one of the more conservative elements. In the time series plots (Figure 5.17 ff.), concentrations follow the inverse of the salinity curve, which leads to linear nickel-salinity plots and high coefficients of determination (Table 5.5). Effective freshwater end member concentrations increase steadily from 190 and 240 nmol/l in winter to 380 nmol/l in spring (270 nmol/l for the estuarine transect) and 520 nmol/l in summer, again possibly due to decreasing but more concentrated freshwater inputs. Although these values are less than the corresponding estimate by Murray et al. (1980) of 650 nmol/l in March (Table 5.1), they are well in excess of the estimated input to the estuary given by the same authors.

5.3.2.6 Cobalt

The similarity shown in winter at station 1 between the pattern of Co, Fe and Pb (Figure 5.17 and Figure 5.18) has already been mentioned, but there also seems to be an underlying relationship between dissolved cobalt concentrations and salinity. The same holds for station 2, where, in the absence of Fe data, Co and Pb peaks still coincide. At station 1, 61% of the variation is explained by a two end member mixing model with a freshwater concentration around 20 nmol/l, whereas data from station 2 could more appropriately be explained by a concave curve (Figure 55.4, bottom left). In spring and summer, Co concentrations in the plume closely follow the inverse of the salinity curve resulting in a linear relationship in the cobalt-salinity plot and high R^2-values. Effective end member concentrations rise from 10 nmol/l in spring to 30 nmol/l in summer (Table 5.5). Cobalt data from the estuarine transect show close similarity to manganese, with indications of additional inputs within the lower estuary (Figure 5.25).

5.3.2.7 Copper

Dissolved copper concentrations broadly follow the inverse of the salinity curve at all stations, and conservative mixing explains more than 85% of data variation, except at station 2 (CH42), where changes in S are very small. Zero salinity intercepts rise from 100 nmol/l in winter to 150 nmol/l in spring (in agreement with the equally linear estuarine transect) and 200 nmol/l in summer (Table 5.5). These results are in good agreement with the effective river concentration of 145 nmol/l given by Balls (1985a) for summer 1983, and the freshwater fraction estimate of 190 nmol/l by Murray et al. (1980), and balance the total inputs given in Table 5.1 for 1990, suggesting a dissolved phase dominated export to the sea, without major estuarine modifications.

5.3.2.8 Zinc

Dissolved zinc concentrations are also closely linked to freshwater inputs, with effective end member concentrations rising from 600 nmol/l at station 1 in winter to 850 and 890 nmol/l in spring and summer (Table 5.6), although actually measured concentrations are higher in May than in August at similar salinities (Figure 55.6). During the estuarine transect, zinc concentrations generally rise with decreasing salinity, but there are also indications for additional inputs near Immingham (Figure 5.25). Coincident with reduced inputs since the early 1970's, dissolved phase zinc exports thus seem to have dropped from 1100 nmol/l then estimated for the freshwater fraction, and now account for about half or more of the estimated total inputs to the estuary (Table 5.1).

5.3.2.9 Cadmium

Dissolved cadmium concentrations also show conservative behaviour for all tidal stations. Effective riverine end member concentrations rise from 3.0 and 4.0 nmol/l in winter to 8.1 nmol/l in spring and 9.3 nmol/l in summer, values all well below the 16.4 nmol/l estimate given by Balls (1985a) for summer 1983. The estuarine transect shows an underlying conservative behaviour, with possibly additional inputs near Immingham, similar to zinc (Figure 5.25). Comparison with the dissolved concentration given by Murray et al. (1980) indicates that cadmium export has decreased substantially since the 1970's (Table 5.1), but again a large proportion is unaccounted for by estimated inputs from rivers, industry and sewage in 1990, clearly indicating the existence of further sources.

5.3.2.10 Lead

The apparent link between elevated concentrations of Pb, Fe and Co has already been discussed. Compared to the winter station 1, lead levels are decreased at station 2 and in spring, where elevated values coincide with low SPM levels. During the estuarine transect in May, lead is strongly negatively correlated to salinity (Figure 5.25), yielding a zero salinity intercept of 0.7 nmol/l. This is only around 1% of the total inputs to the estuary in 1990 (Table 5.1), the remainder probably being bound to particles. In summer, again at much decreased concentrations and particle loadings, lead appears positively correlated with salinity, i.e. elevated levels are advected by the incoming sea water.

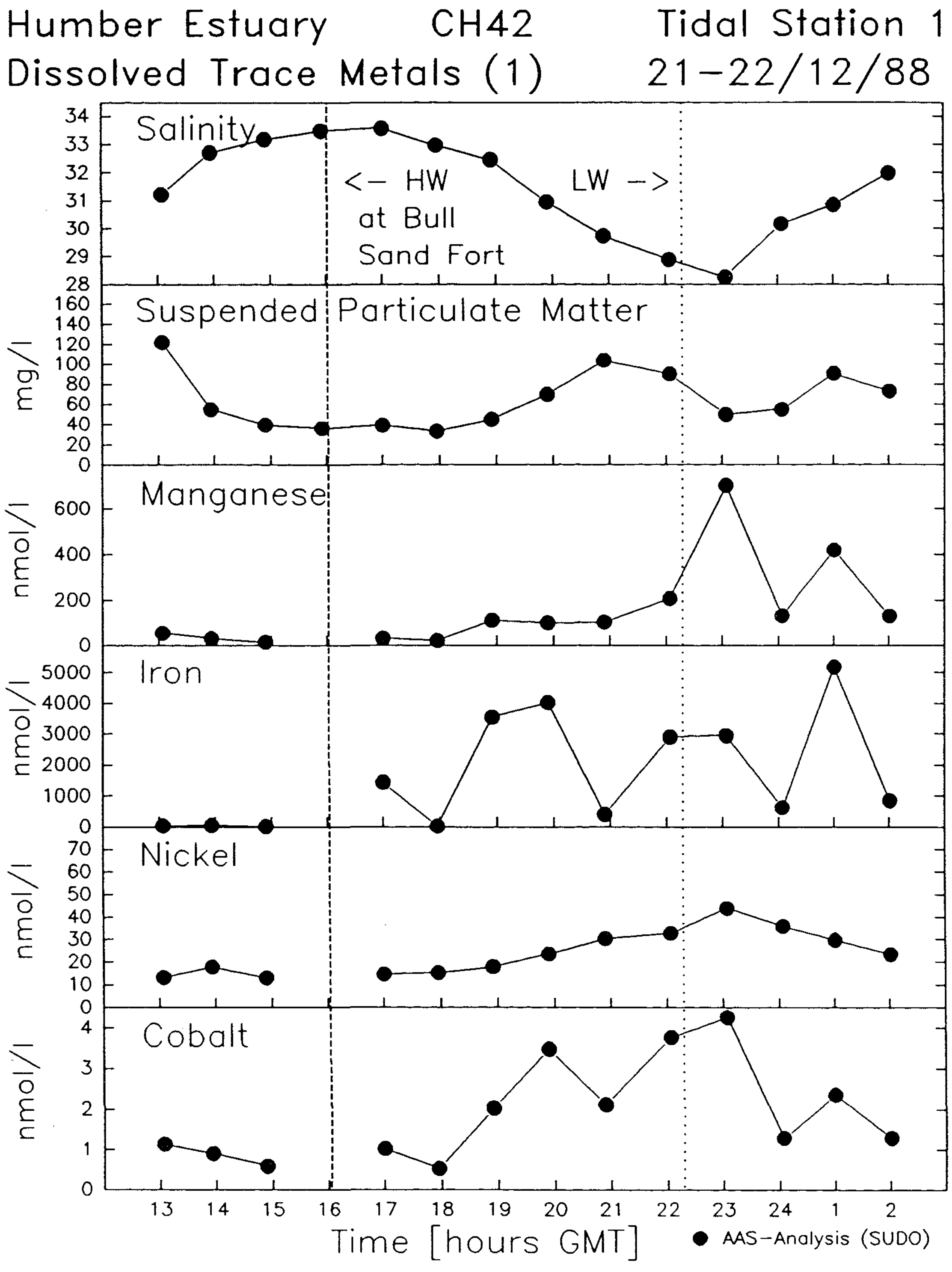

Figure 5.17: Time series of dissolved Mn, Fe, Ni and Co in the Humber mouth at tidal station 1 (CH42)

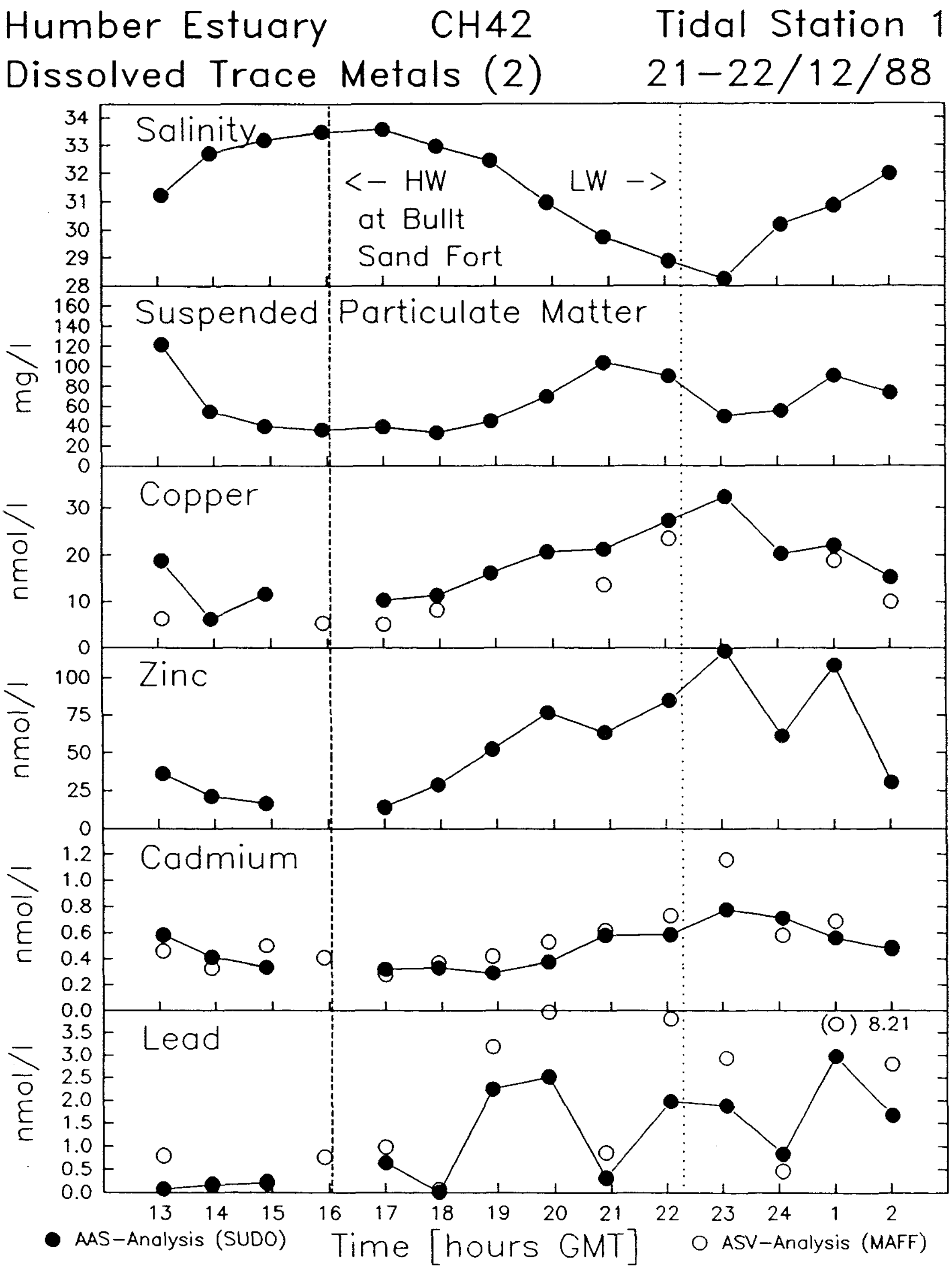

Figure 5.18: Time series of dissolved Cu, Zn, Cd and Pb in the Humber mouth at tidal station 1 (CH42)

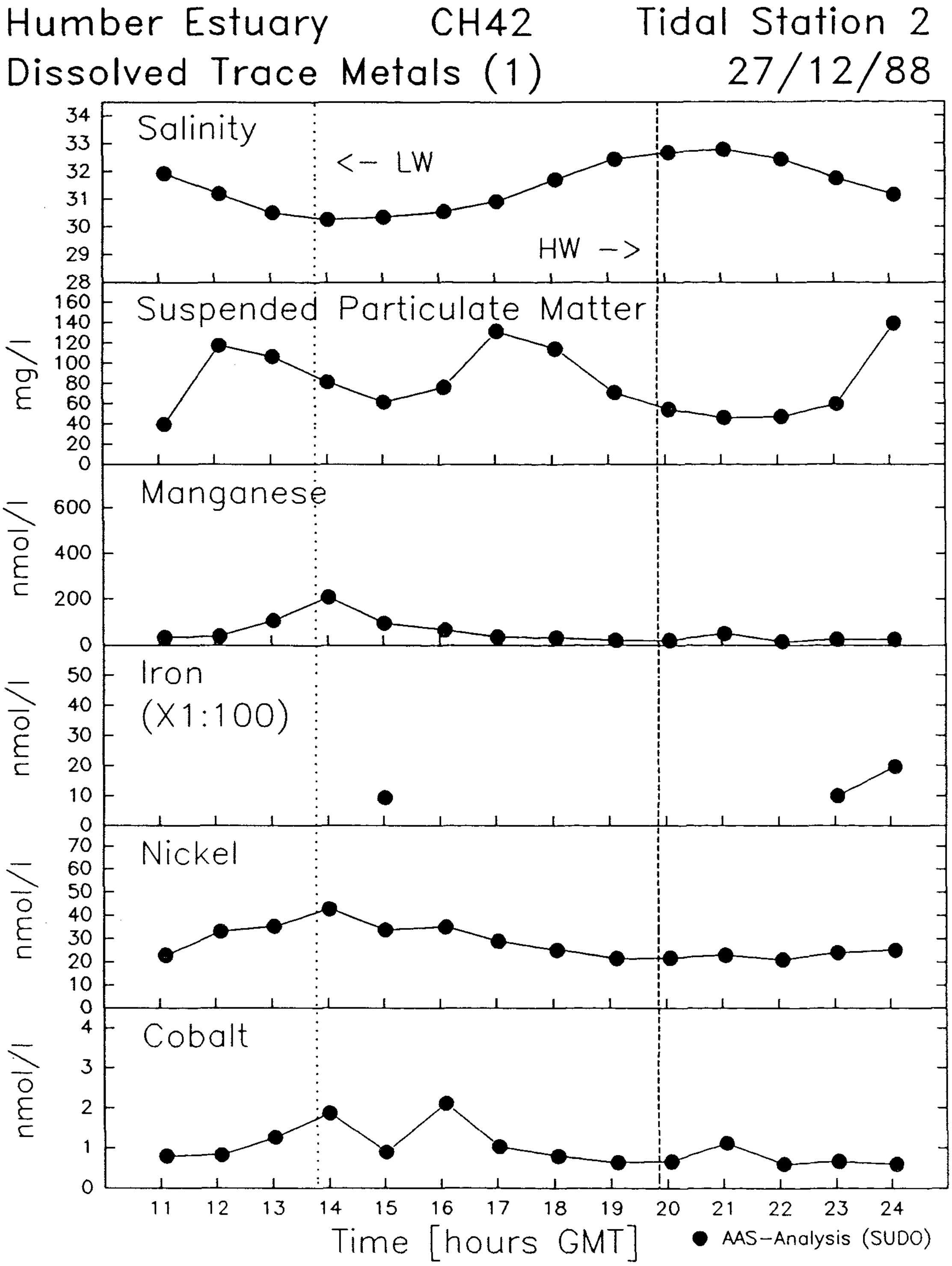

Figure 5.19: Time series of dissolved Mn, Fe, Ni and Co in the Humber mouth at tidal station 2 (CH42)

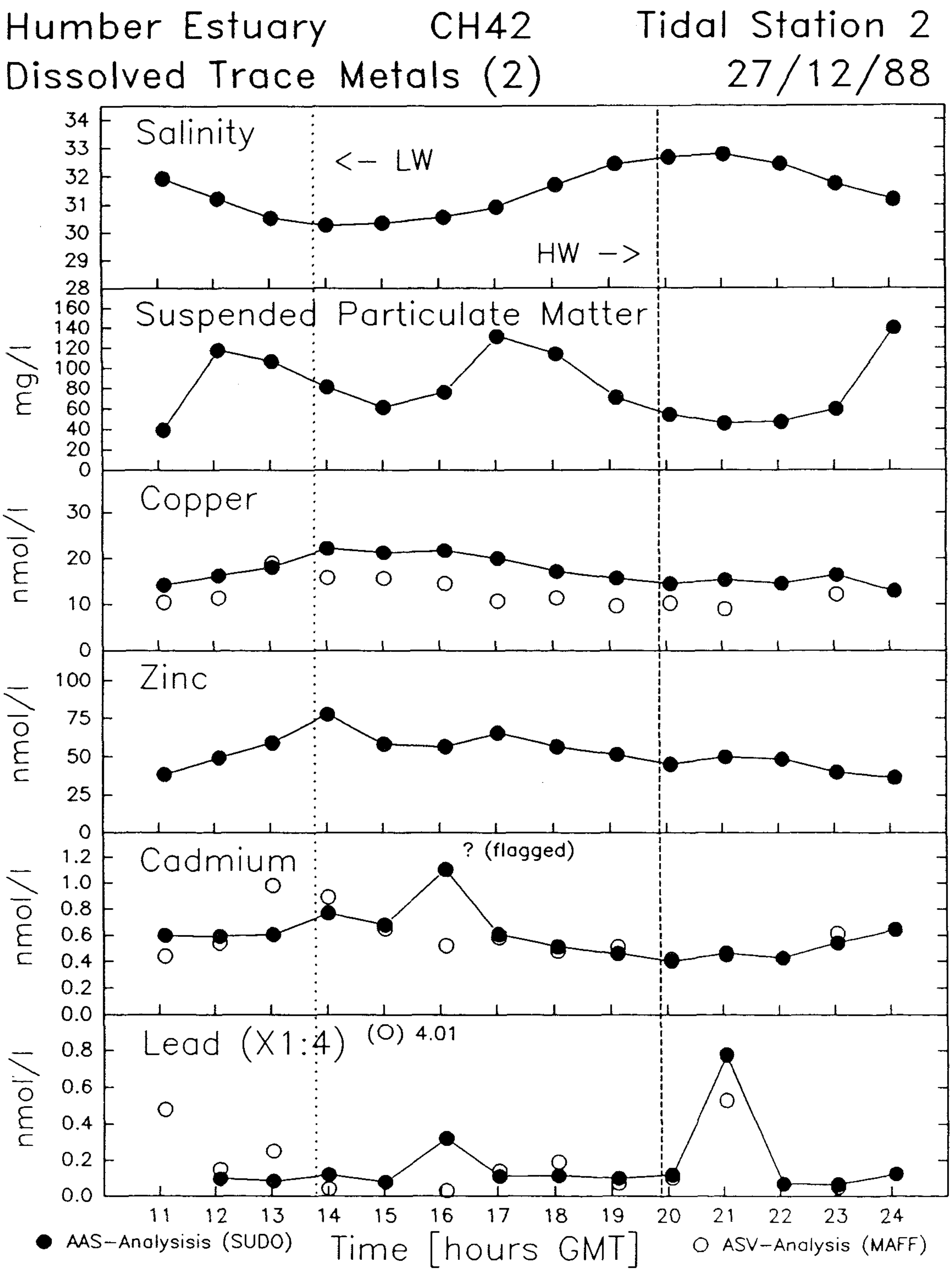

Figure 5.20: Time series of dissolved Cu, Zn, Cd and Pb in the Humber mouth at tidal station 2 (CH42)

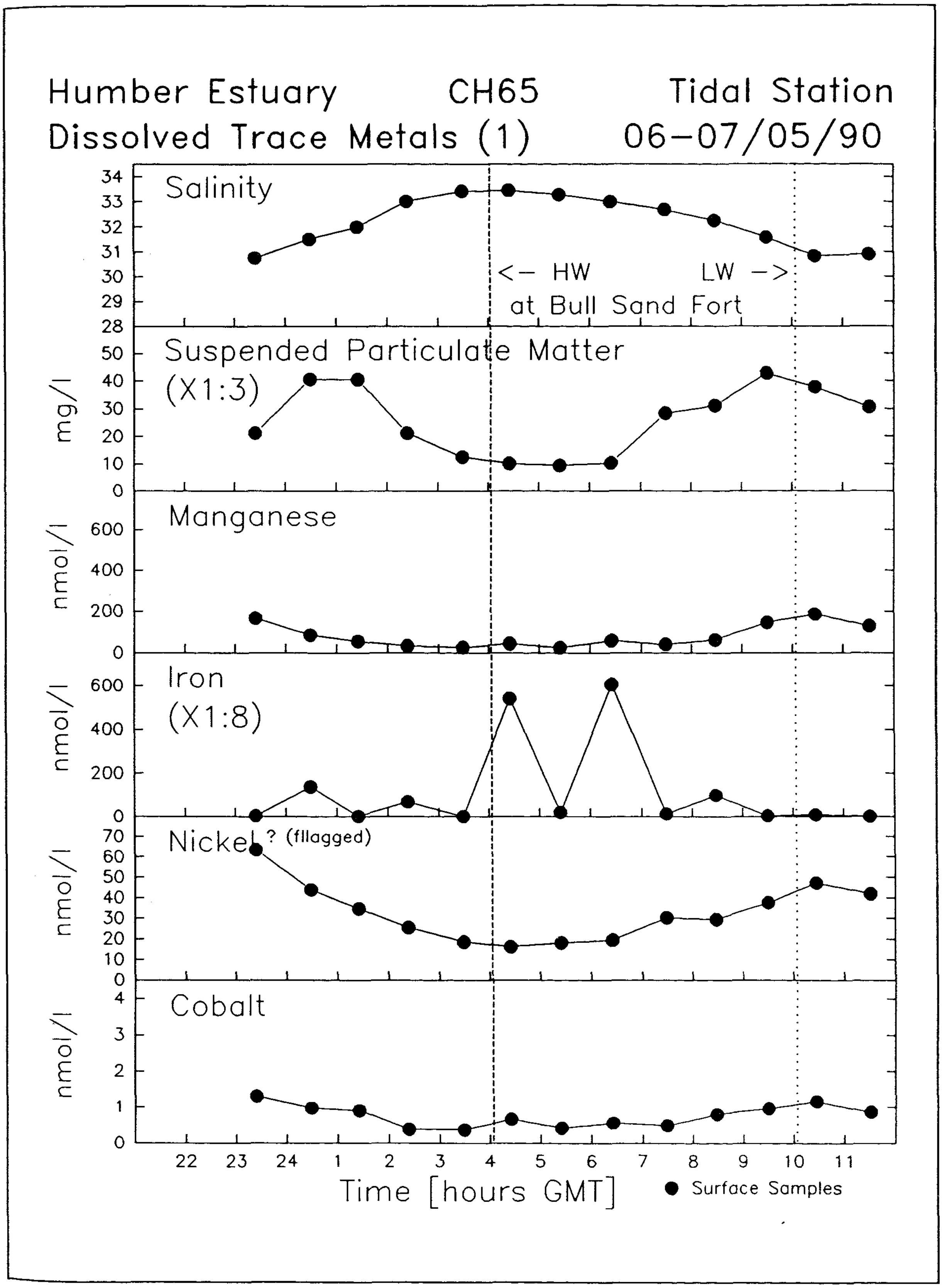

Figure 5.21: Time series of dissolved Mn, Fe, Ni and Co in the Humber mouth at the tidal station (CH65)

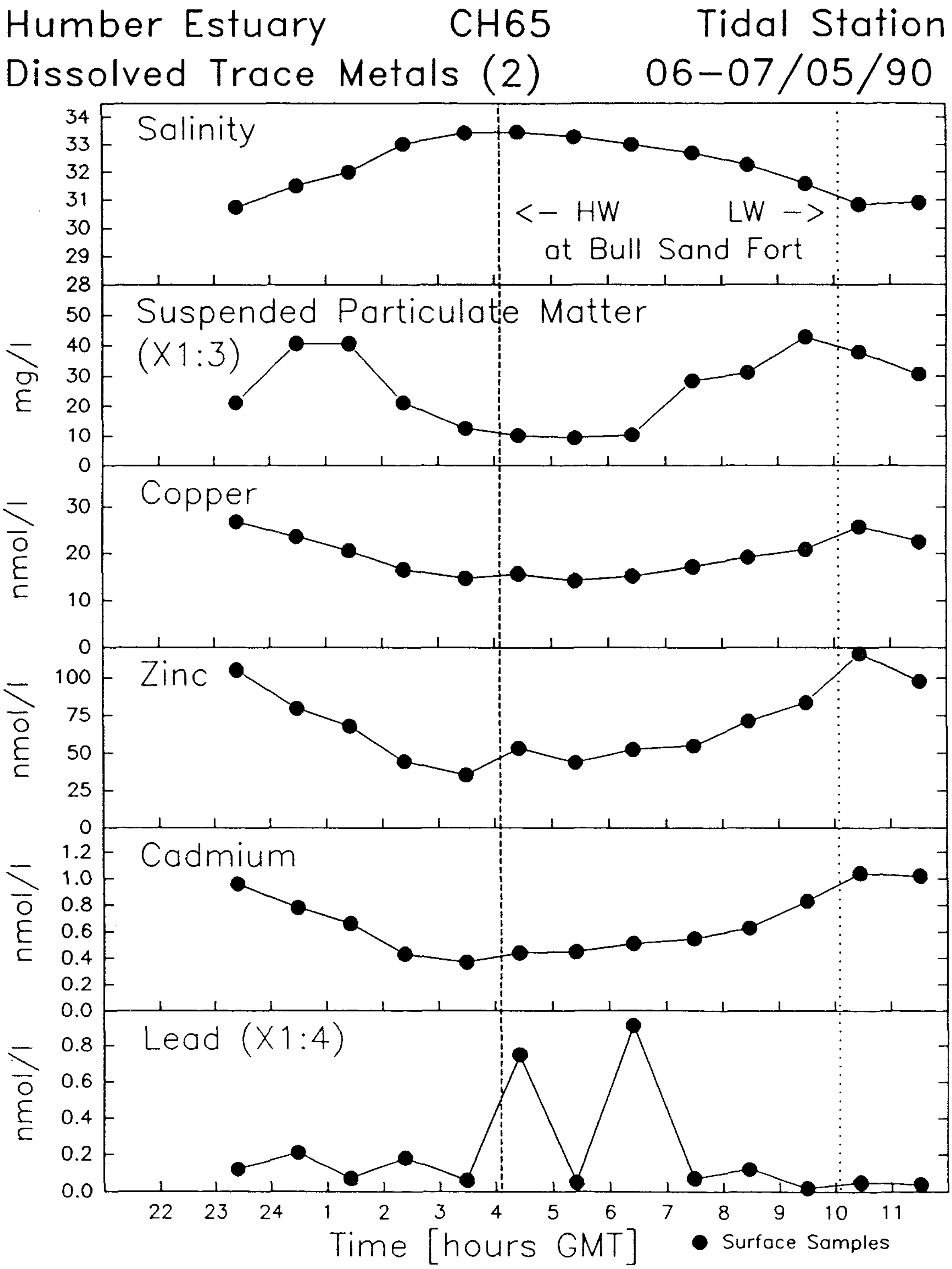

Figure 5.22: Time series of dissolved Cu, Zn, Cd and Pb in the Humber mouth at the tidal station (CH65)

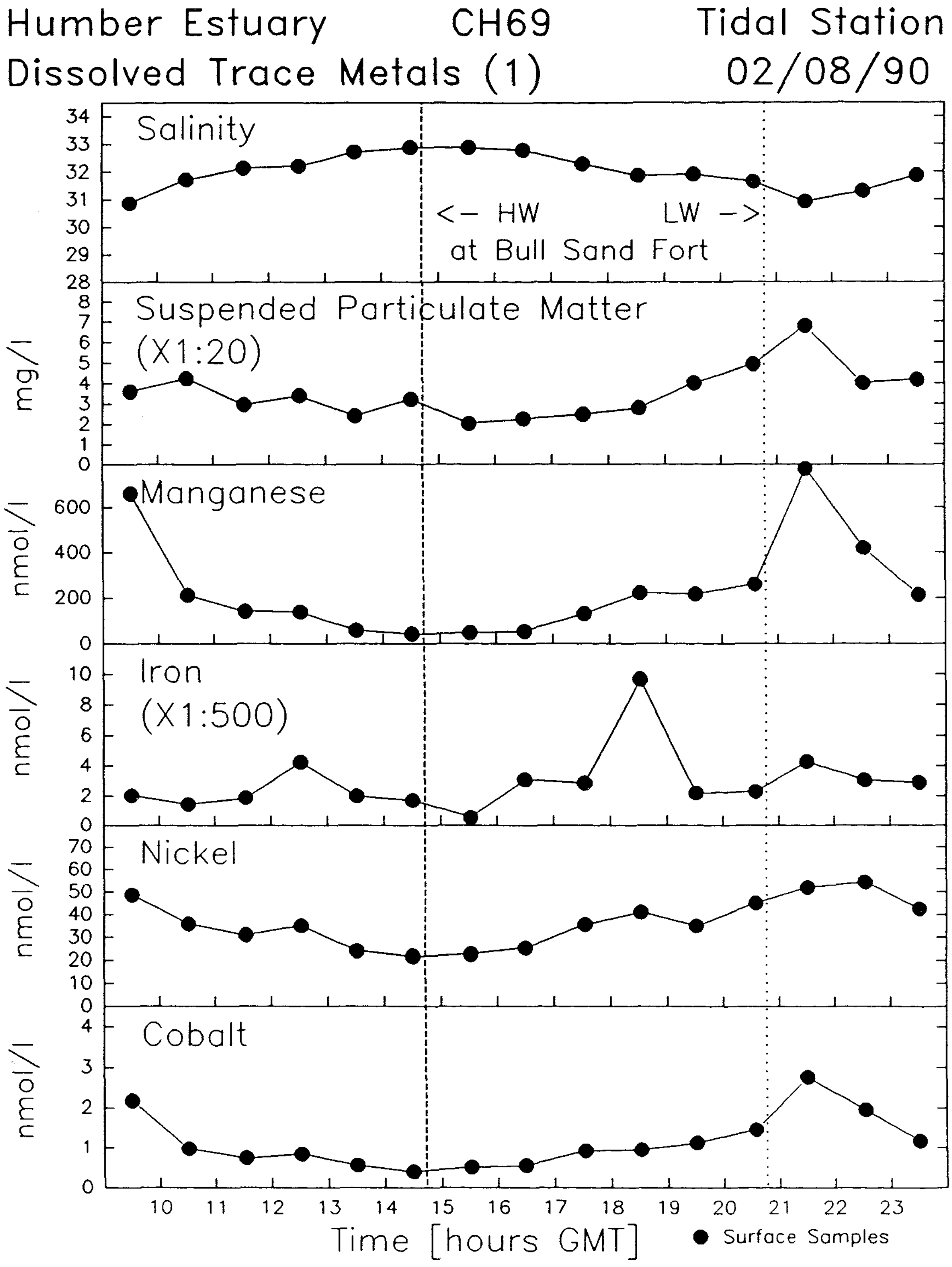

Figure 5.23: Time series of dissolved Mn, Fe, Ni and Co in the Humber mouth at the tidal station (CH69)

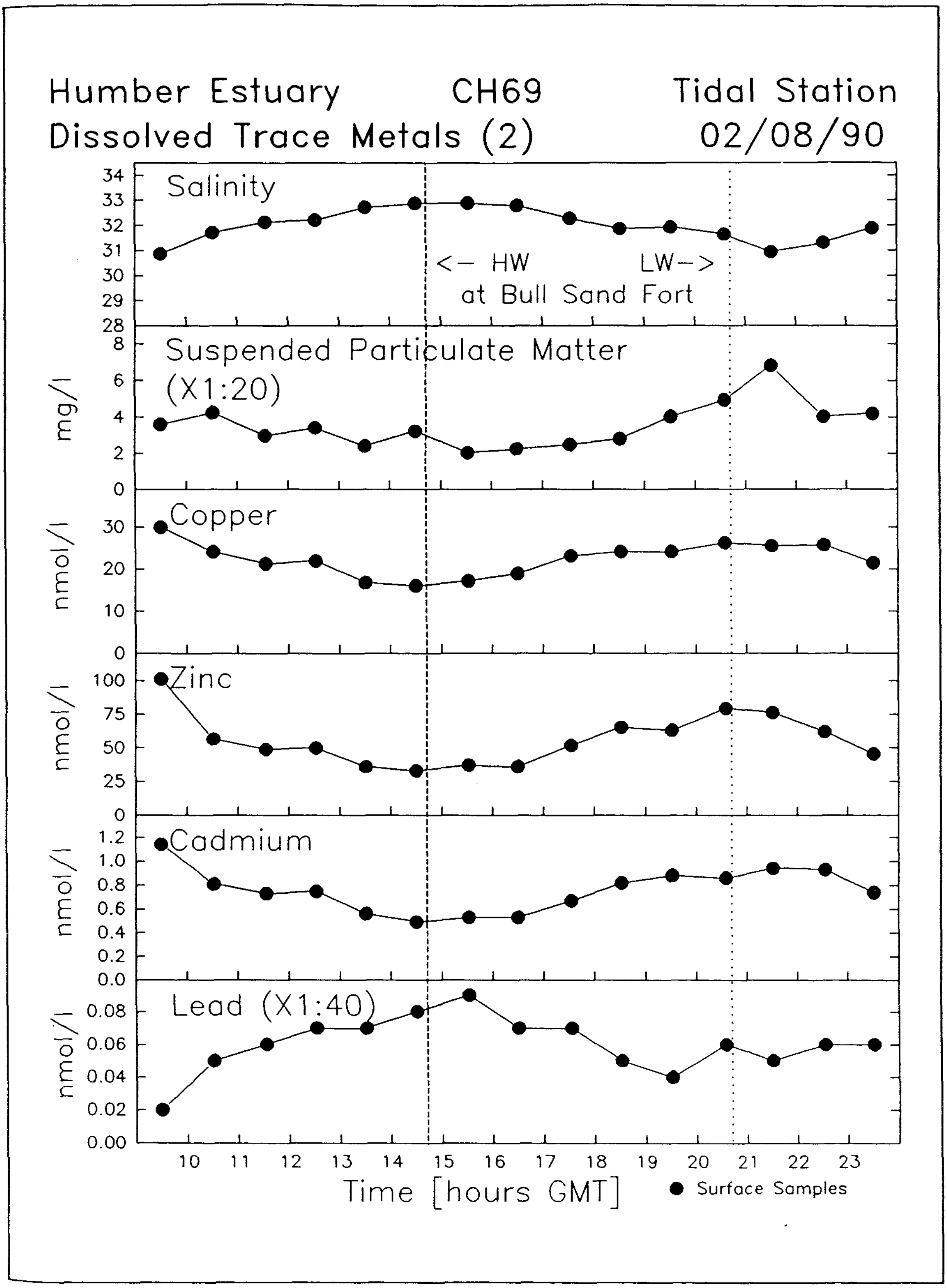

Figure 5.24: Time series of dissolved Cu, Zn, Cd and Pb in the Humber mouth at the tidal station (CH69)

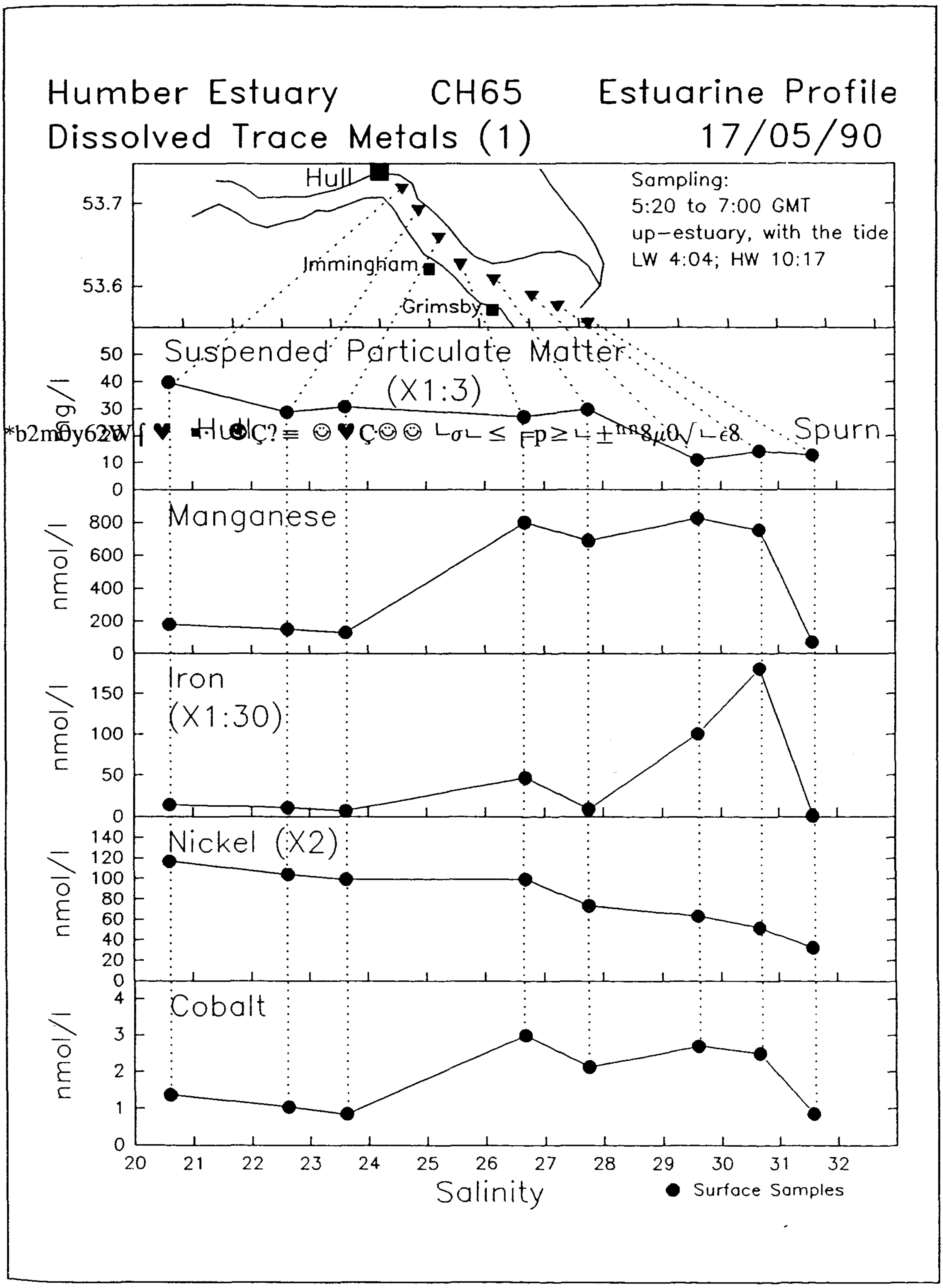

Figure 5.25: Dissolved concentrations of Mn, Fe, Ni and Co in the lower Humber estuary (CH65)

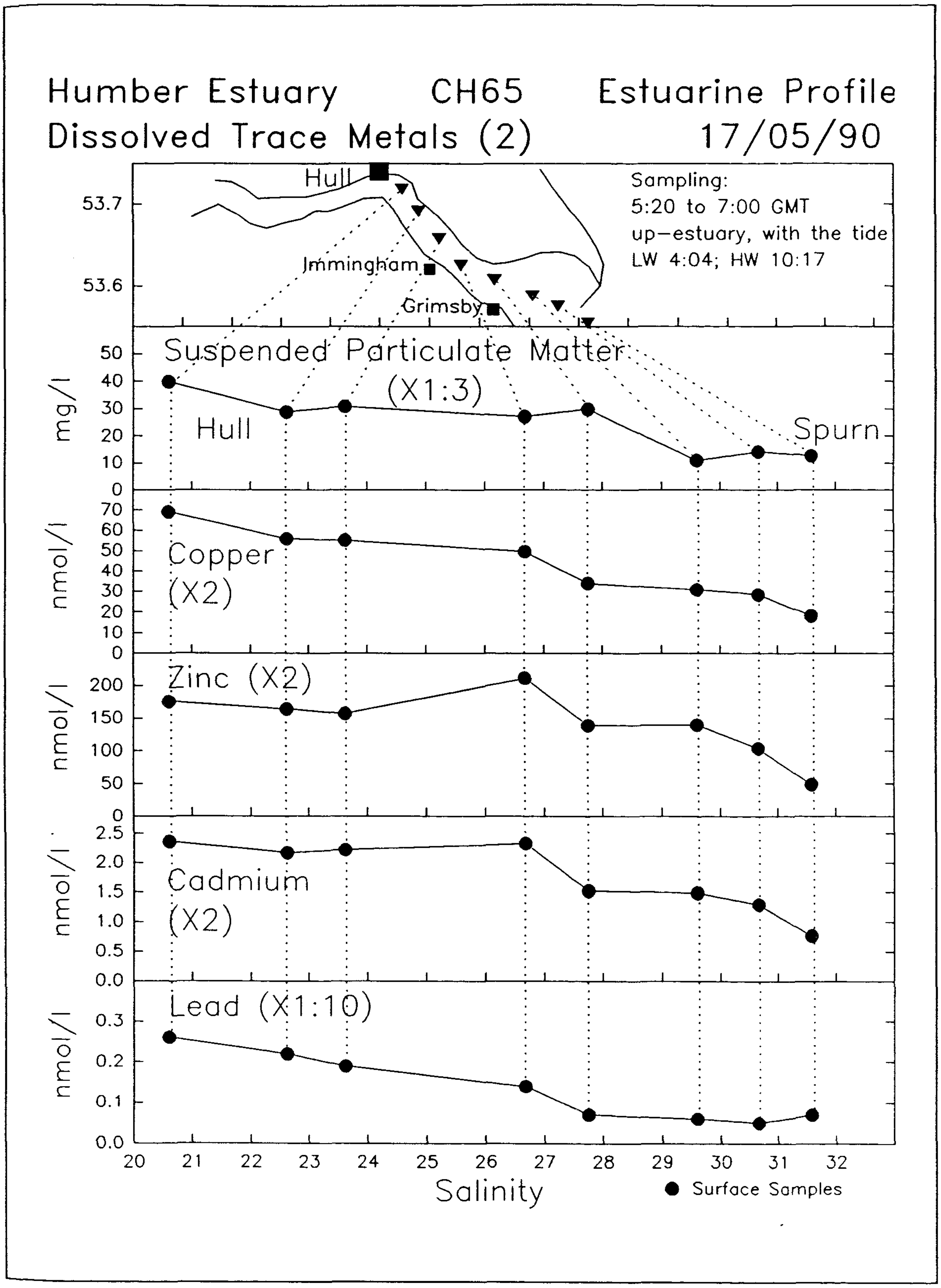

Figure 5.26: Dissolved concentrations of Cu, Zn, Cd and Pb in the lower Humber estuary (CH65)

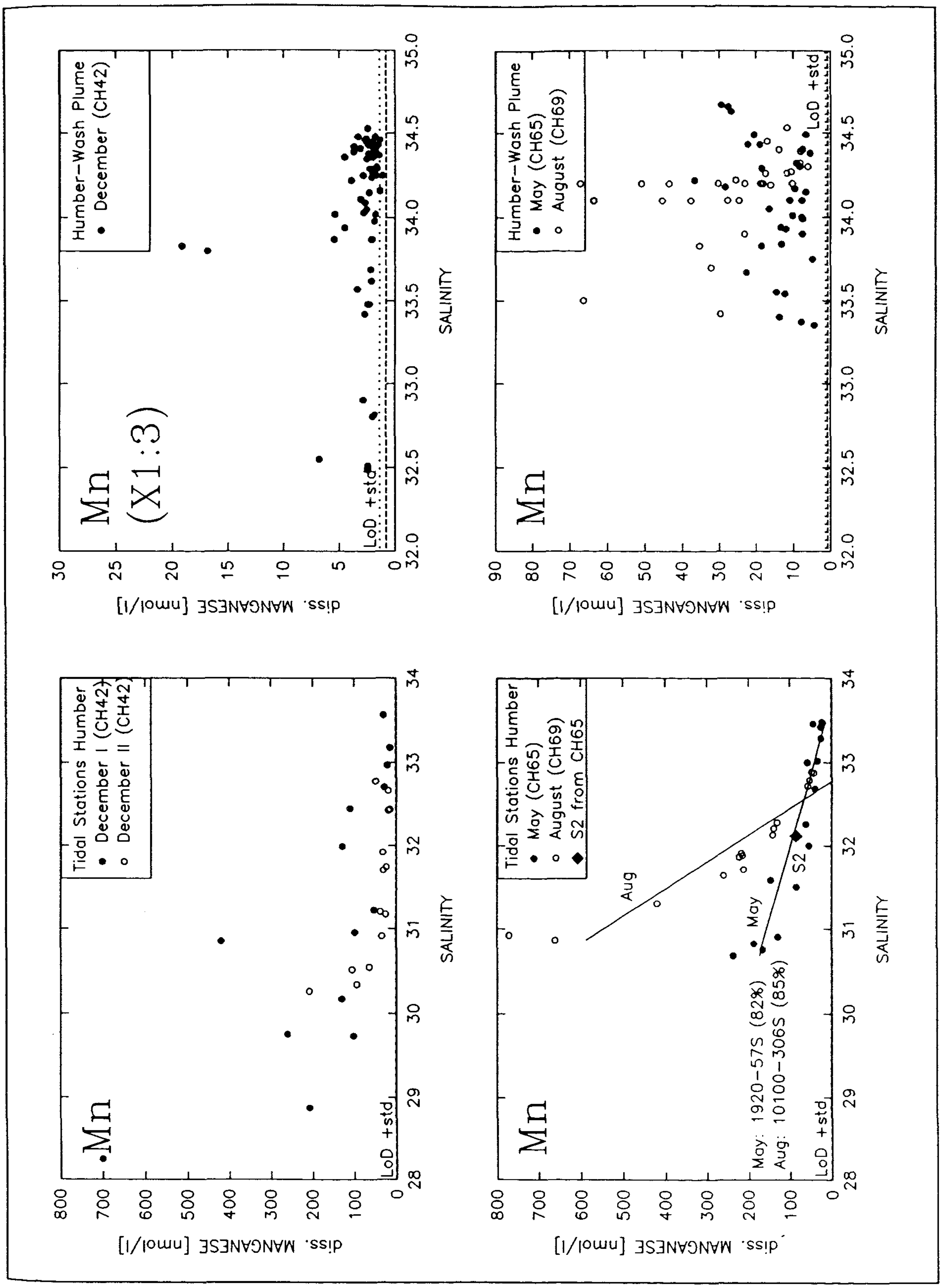

Figure 55.1: Dissolved manganese-salinity plots for the Humber-Wash area

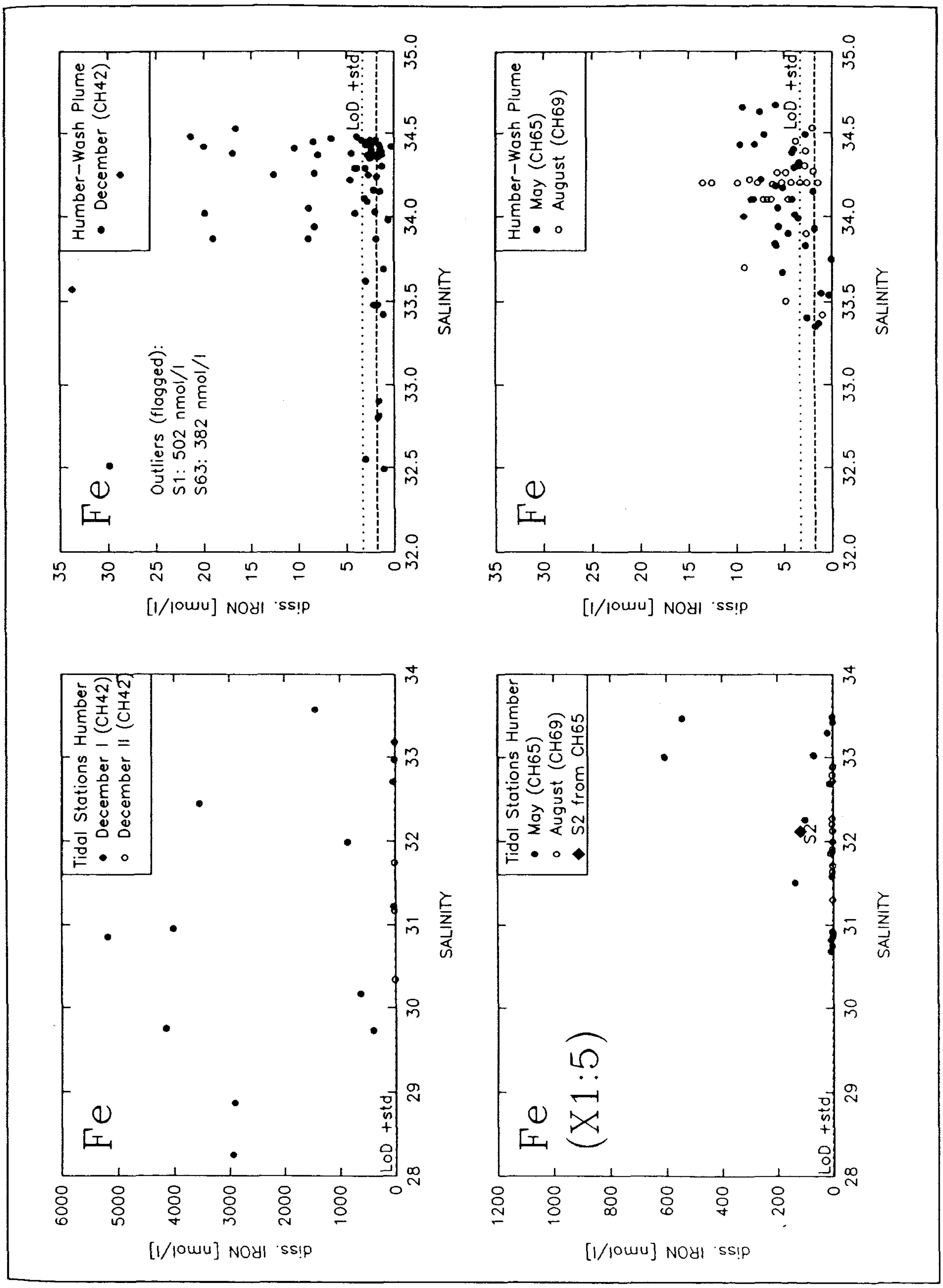

Figure 55.2: Dissolved iron-salinity plots for the Humber-Wash area

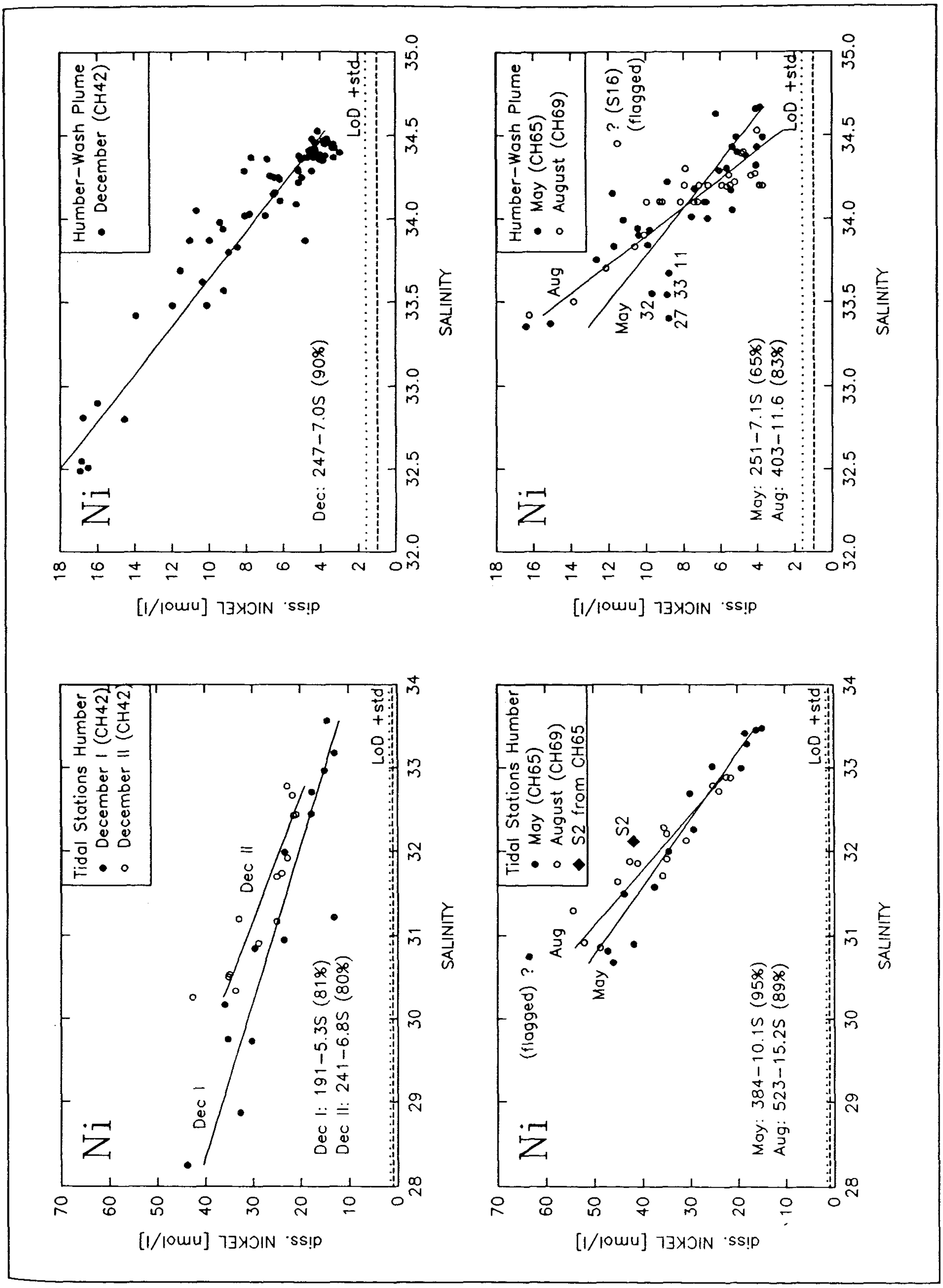

Figure 55.3: Dissolved nickel-salinity plots for the Humber-Wash area

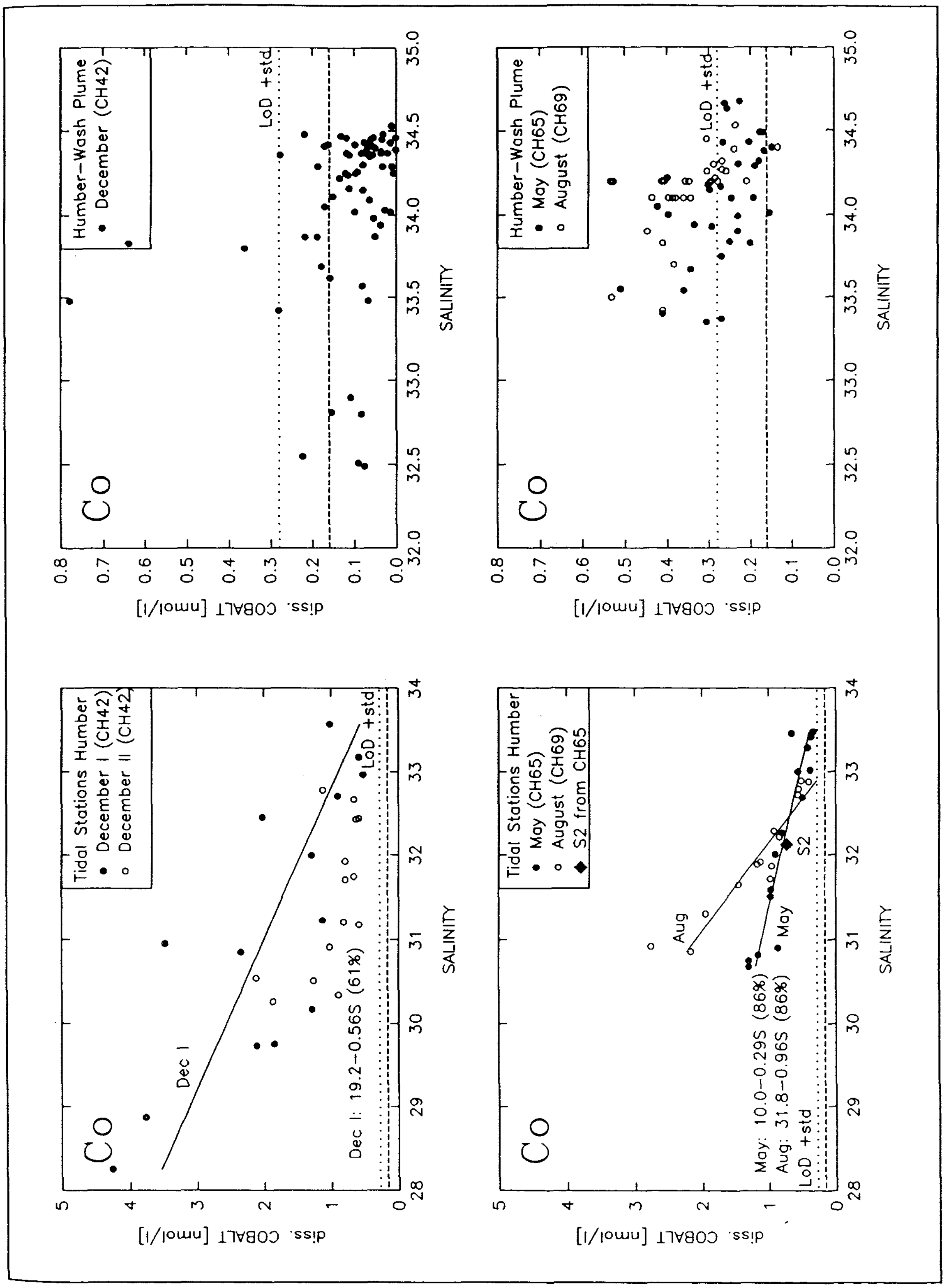

Figure 55.4: Dissolved cobalt-salinity plots for the Humber-Wash area

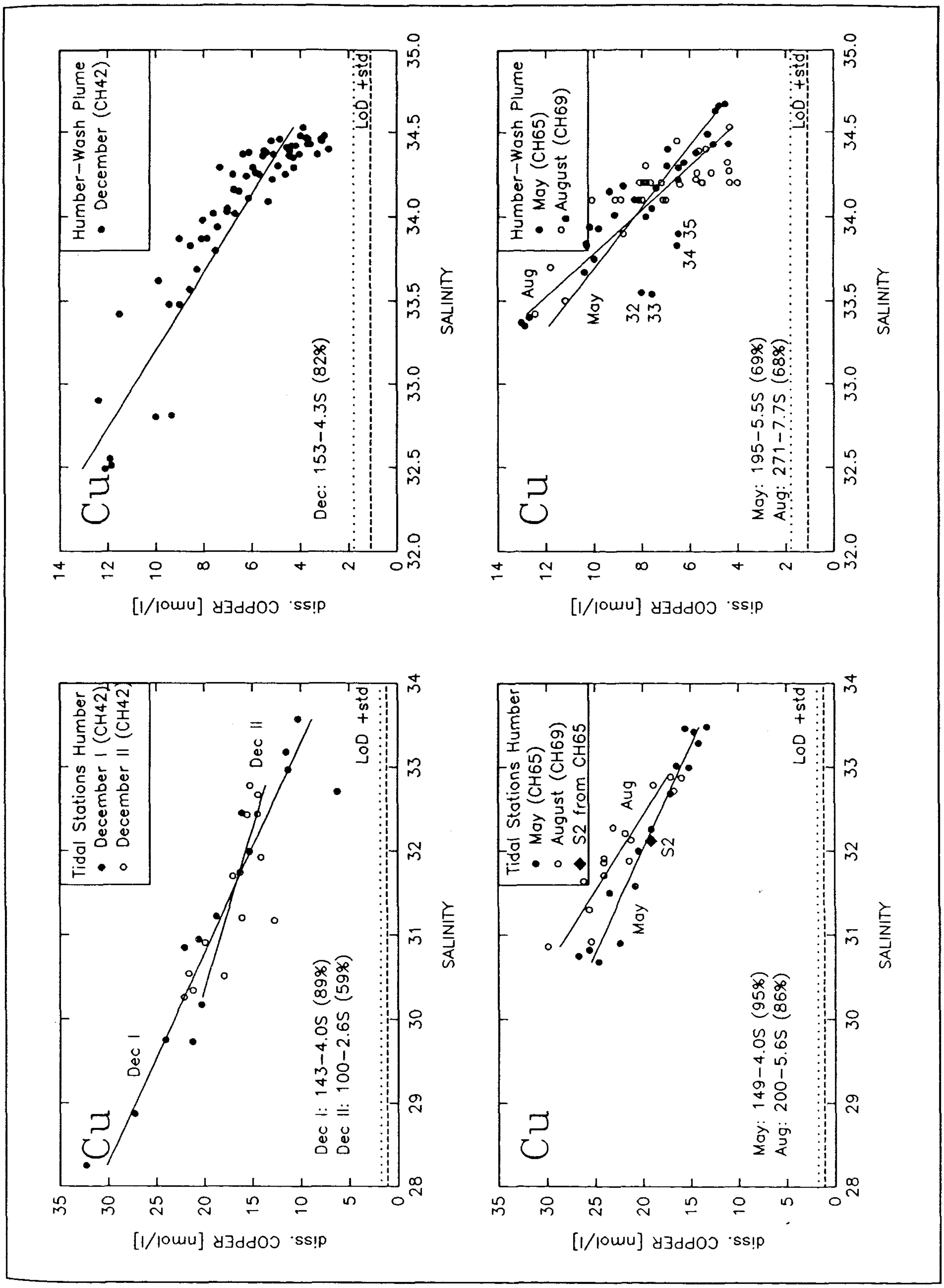

Figure 55.5: Dissolved copper-salinity plots for the Humber-Wash area

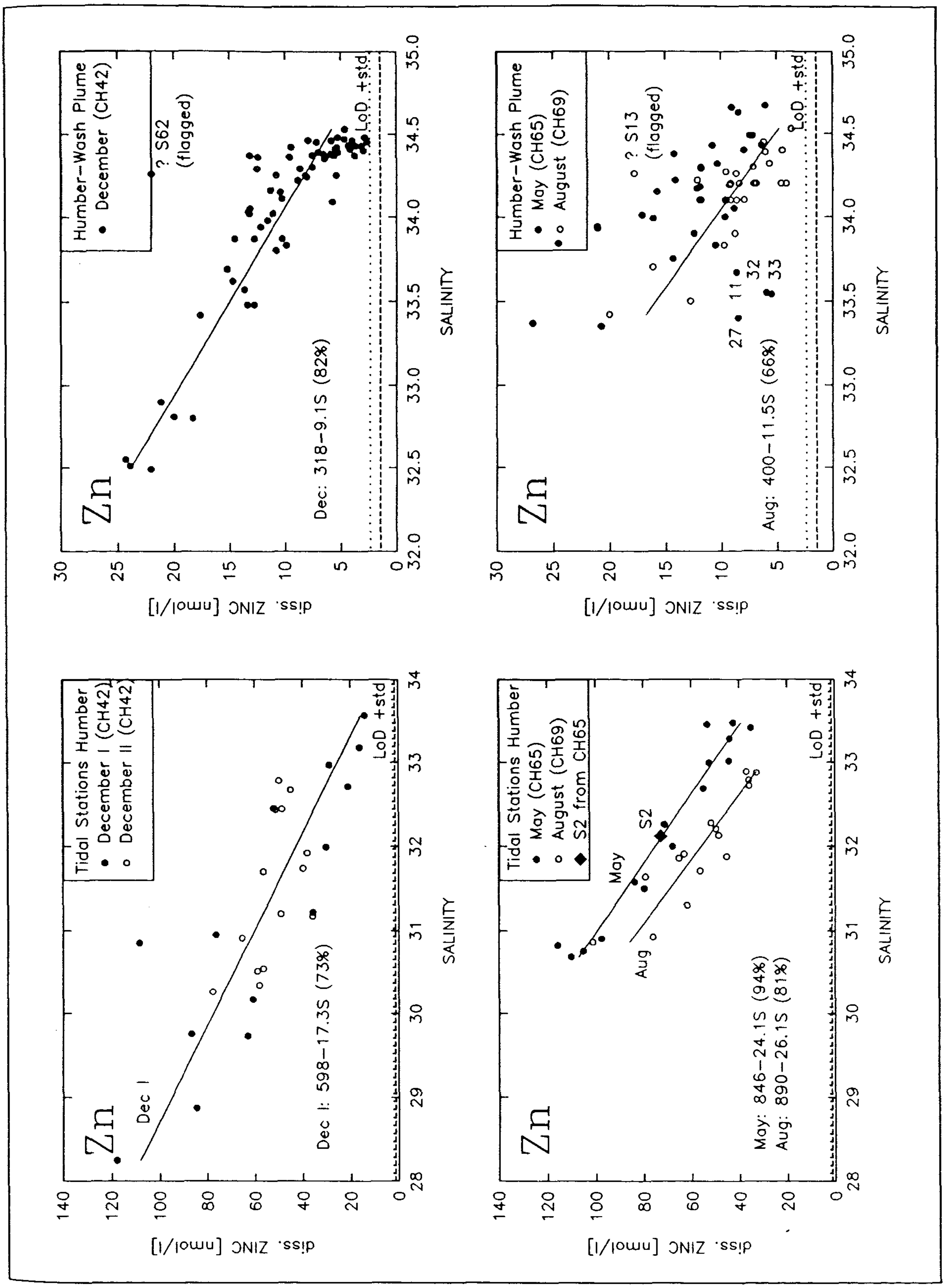

Figure 55.6: Dissolved zinc-salinity plots for the Humber-Wash area

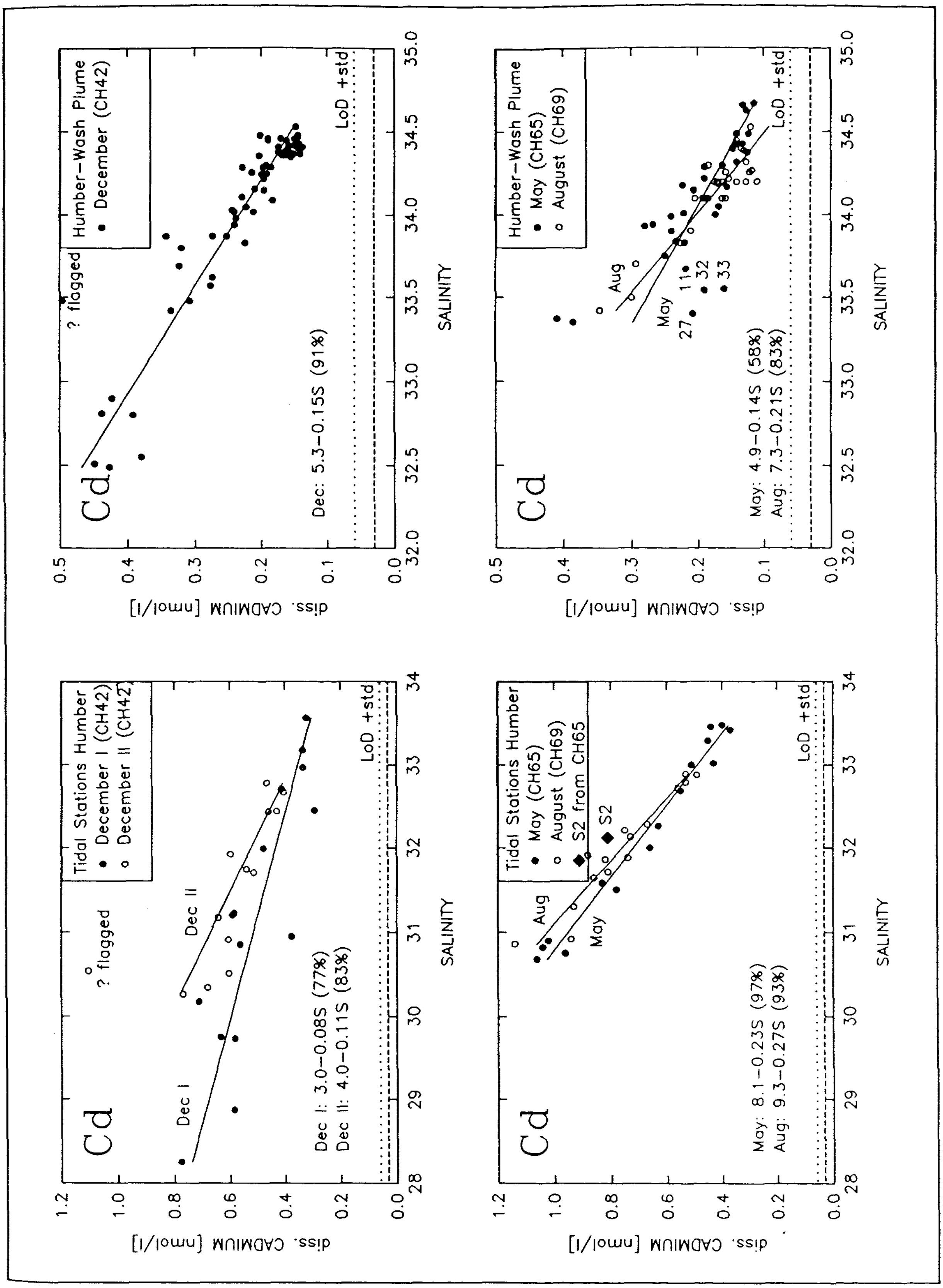

Figure 55.7: Dissolved cadmium-salinity plots for the Humber-Wash area

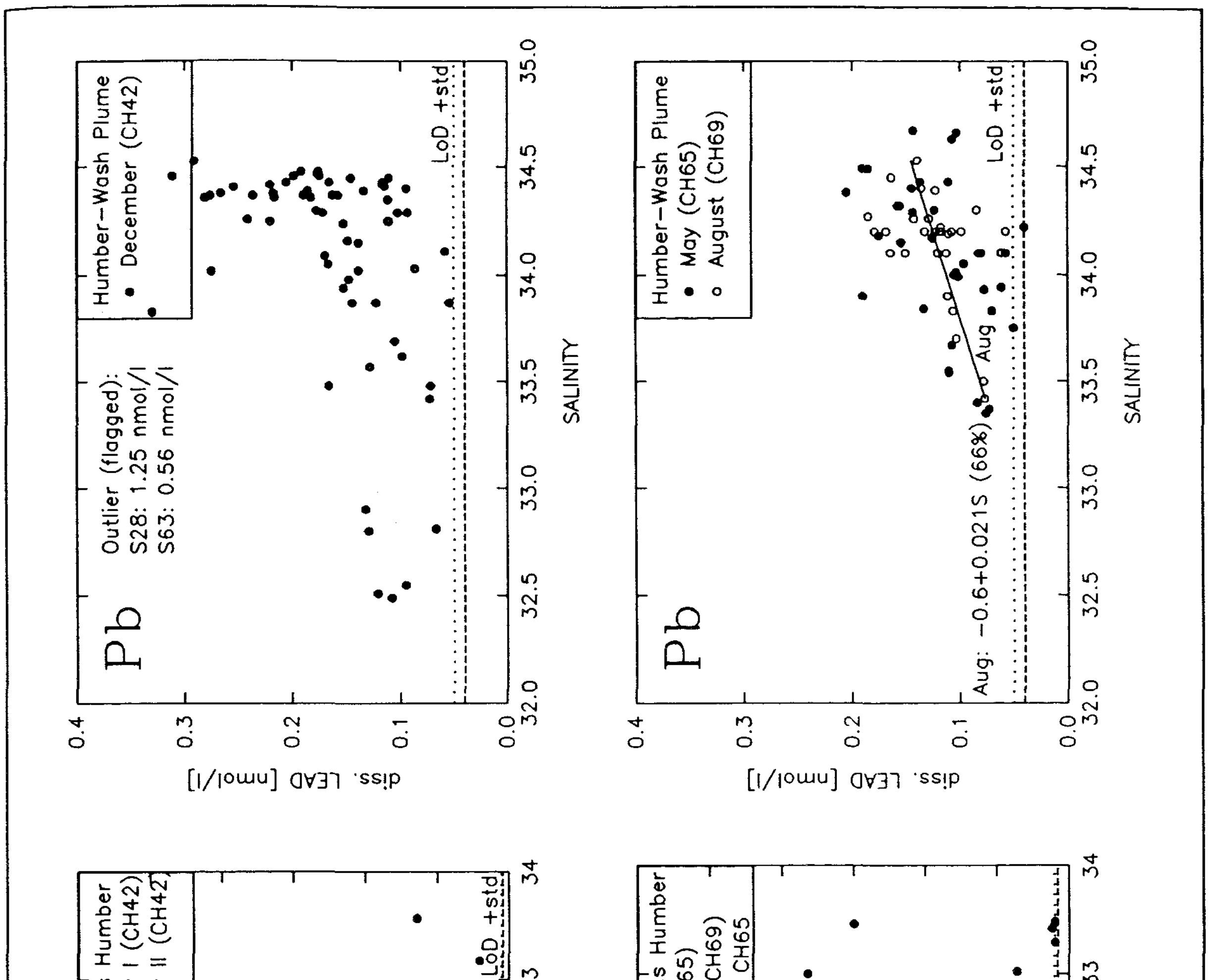

Figure 55.8: Dissolved lead-salinity plots for the Humber-Wash area

SPM	n	Intercept [nmol/l]	Slope	Significance	Corr. Coeff.	R^2
Tidal Station 1 CH42	15	305±119	-7.7±3.8	0.06224	-0.49	24%
Tidal Station 2 CH42	14	667±301	-18.6±9.6	0.07535	-0.49	24%
Plume CH42	60	713±57	-20.6±1.7	0.00000	-0.85	72%
Estuary CH65	8	86.8±12.4	-2.4±0.5	0.00222	-0.90	81%
Tidal Station CH65	15	306±69	-8.7±2.1	0.00131	-0.75	56%
Plume CH65	34	189±29	-5.4±0.8	0.00000	-0.75	56%
Tidal Station CH69	15	49±11	-1.4±0.4	0.00134	-0.75	56%
Plume CH69	31	34±16	-1.0±0.5	0.05286	-0.35	12%

Mn	n	Intercept [nmol/l]	Slope	Significance	Corr. Coeff.	R^2
Tidal Station 1 CH42	14	2660±720	-80±23	0.00462	-0.71	50%
Tidal Station 2 CH42	14	1300±390	-40±12	0.00778	-0.68	46%
Plume CH42	67	34±23	-0.9±0.7	0.17375	-0.17	3%
Estuary CH65	8	-623±826	40±31	0.23778	+0.47	22%
Tidal Station CH65	15	1920±240	-57±8	0.00000	-0.90	82%
Plume CH65	34	-282±125	8.7±3.7	0.02324	+0.39	15%
Tidal Station CH69	15	10100±1200	-306±36	0.00000	-0.92	85%
Plume CH69	31	1210±420	-35±12	0.00864	-0.46	22%

Fe	n	Intercept [nmol/l]	Slope	Significance	Corr. Coeff.	R^2
Tidal Station 1 CH42	14	16000±9000	-452±289	0.14326	-0.41	17%
Tidal Station 2 CH42	3					
Plume CH42	65	41±62	-1.0±1.8	0.57525	-0.07	1%
Estuary CH65	8	-166±151	8.0±5.6	0.20538	+0.50	25%
Tidal Station CH65	15	-2150±1500	70±47	0.15683	+0.39	15%
Plume CH65	34	-141±34	4.3±1.0	0.00015	+0.61	37%
Tidal Station CH69	15	26±28	-0.7±0.9	0.41924	-0.23	5%
Plume CH69	31	23±80	-0.5±2.3	0.83053	-0.04	0%

Table 5.4: Regression of SPM, dissolved Mn and Fe against salinity for different data sets from the Humber-Wash area

Ni	n	Intercept [nmol/l]	Slope	Signi-ficance	Corr. Coeff.	R^2
Tidal Station 1 CH42	14	191±23	-5.3±0.7	0.00001	-0.90	81%
Tidal Station 2 CH42	14	241±31	-6.8±1.0	0.00002	-0.89	80%
Plume CH42	67	247±10	-7.0±0.3	0.00000	-0.95	90%
Estuary CH65	8	265±26	-7.0±1.0	0.00036	-0.95	90%
Tidal Station CH65	14	384±24	-10.1±0.7	0.00000	-0.97	95%
Plume CH65	34	251±32	-7.1±0.9	0.00000	-0.81	65%
Tidal Station CH69	15	523±48	-15.2±1.5	0.00000	-0.94	89%
Plume CH69	30	403±34	-11.6±1.0	0.00000	-0.91	83%

Co	n	Intercept [nmol/l]	Slope	Signi-ficance	Corr. Coeff.	R^2
Tidal Station 1 CH42	14	19.2±4.0	-0.56±0.13	0.00093	-0.78	61%
Tidal Station 2 CH42	14	11.0±3.9	-0.32±0.12	0.02328	-0.60	36%
Plume CH42	67	2.4±1.0	-0.07±0.03	0.02624	-0.27	7%
Estuary CH65	8	-0.5±2.2	0.09±0.08	0.32988	+0.40	16%
Tidal Station CH65	15	10.0±1.0	-0.29±0.03	0.00000	-0.93	86%
Plume CH65	34	4.4±1.2	-0.12±0.04	0.00174	-0.52	27%
Tidal Station CH69	15	31.8±3.4	-0.96±0.11	0.00000	-0.93	86%
Plume CH69	31	8.1±2.0	-0.23±0.06	0.00049	-0.59	35%

Cu	n	Intercept [nmol/l]	Slope	Signi-ficance	Corr. Coeff.	R^2
Tidal Station 1 CH42	14	143±13	-4.0±0.4	0.00000	-0.94	89%
Tidal Station 2 CH42	14	100±20	-2.6±0.6	0.00138	-0.77	59%
Plume CH42	67	153±8	-4.3±0.3	0.00000	-0.91	82%
Estuary CH65	8	155±10	-4.2±0.4	0.00003	-0.98	95%
Tidal Station CH65	15	149±9	-4.0±0.3	0.00000	-0.97	95%
Plume CH65	34	195±22	-5.5±0.7	0.00000	-0.83	69%
Tidal Station CH69	15	200±20	-5.6±0.6	0.00000	-0.93	86%
Plume CH69	31	271±34	-7.7±1.0	0.00000	-0.82	68%

Table 5.5: Regression of dissolved Ni, Co and Cu against salinity for different data sets from the Humber-Wash area

Zn	n	Intercept [nmol/l]	Slope	Significance	Corr. Coeff.	R^2
Tidal Station 1 CH42	14	598±96	-17.3±3.1	0.00011	-0.85	73%
Tidal Station 2 CH42	14	279±93	-7.2±3.0	0.03130	-0.58	33%
Plume CH42	66	318±18	-9.1±0.5	0.00000	-0.90	82%
Estuary CH65	8	370±97	-8.5±3.6	0.05481	-0.70	49%
Tidal Station CH65	15	846±53	-24.1±1.6	0.00000	-0.97	94%
Plume CH65	34	216±80	-6.0±2.4	0.01625	-0.41	17%
Tidal Station CH69	15	890±113	-26.1±3.5	0.00001	-0.90	81%
Plume CH69	30	400±53	-11.5±1.6	0.00000	-0.81	66%
Cd	**n**	**Intercept [nmol/l]**	**Slope**	**Significance**	**Corr. Coeff.**	**R^2**
Tidal Station 1 CH42	14	3.0±0.4	-0.08±0.01	0.00004	-0.88	77%
Tidal Station 2 CH42	13	4.0±0.5	-0.11±0.02	0.00001	-0.91	83%
Plume CH42	66	5.3±0.2	-0.15±0.01	0.00000	-0.95	91%
Estuary CH65	8	5.2±0.8	-0.13±0.03	0.00356	-0.88	78%
Tidal Station CH65	15	8.1±0.3	-0.23±0.01	0.00000	-0.99	97%
Plume CH65	34	4.9±0.7	-0.14±0.02	0.00000	-0.76	58%
Tidal Station CH69	15	9.3±0.7	-0.27±0.02	0.00000	-0.96	93%
Plume CH69	31	7.3±0.6	-0.21±0.02	0.00000	-0.91	83%
Pb	**n**	**Intercept [nmol/l]**	**Slope**	**Significance**	**Corr. Coeff.**	**R^2**
Tidal Station 1 CH42	14	9.9±5.1	-0.276±0.163	0.11702	-0.44	19%
Tidal Station 2 CH42	13	-2.0±1.9	0.070±0.060	0.27322	+0.33	11%
Plume CH42	65	-1.5±0.5	0.049±0.014	0.00086	+0.40	16%
Estuary CH65	8	0.7±0.1	-0.020±0.002	0.00011	-0.97	93%
Tidal Station CH65	15	-2.8±2.1	0.094±0.064	0.16655	+0.38	14%
Plume CH65	34	-1.7±0.6	0.053±0.018	0.00612	+0.46	21%
Tidal Station CH69	15	-0.6±0.1	0.021±0.004	0.00022	+0.81	66%
Plume CH69	31	-2.0±0.8	0.062±0.022	0.00937	+0.46	21%

Table 5.6: Regression of dissolved Zn, Cd and Pb against salinity for different data sets from the Humber-Wash area

5.3.3 Trace Metals in the Humber-Wash Coastal Plume

5.3.3.1 Manganese

Dissolved manganese concentrations show a marked rise from winter to spring and again to summer (Figure 55.9 and Figure 55.10). In winter, concentrations are below 2 nmol/l in most of the survey area, apart from a nearshore strip off the Norfolk coast and the immediate vicinity of the Humber outflow, where concentrations of up to 17 and 19 nmol/l have been measured. The overall variation, however, cannot be linearly related to salinity, the coefficient of determination being as low as 3% (Table 5.4). For the spring cruise, sample S2, taken near the Humber outflow at a salinity well below that of any other sample, has been plotted together with the tidal station data rather than the plume data in the trace metal-salinity plots (Figure 55.1 ff.). For manganese, the measured value of 85 nmol/l represents the tidal station data, and thus the Humber mouth, quite well, and leads in the contour plot to a steep gradient around the outflow. This small plume, however, is surrounded by an area of very low concentrations, about covering the area of the nutrient plume mentioned before. An area of again higher concentrations, apparently located in the central North Sea, stretches into the coastal waters of north-east Norfolk, where levels decrease, with simultaneously increasing primary production, towards the coast. At the site of a strong resuspension in the very south-east corner of the survey area, Mn concentrations double to 33 nmol/l towards the bottom.

During the summer cruise, when no low salinity sample was taken near the Humber outflow, high concentrations (40-60 nmol/l) have been measured in nearshore areas around the Wash, together with tidal station values at least comparable to the May cruise. Levels decrease steadily in a north-easterly direction to less than 12 nmol/l, but without a commensurate rise in salinity, which is quite uniform in this area.

The low winter concentrations in 1988 have been confirmed by another, North Sea wide survey a fortnight later, and further surveys in August 1988 and May 1989 showed concentrations consistent with the seasonal trends found by this study (Tappin, personal communication).

5.3.3.2 Iron

A large proportion of iron concentrations from all cruises are close to or below the average limit of detection (LoD), as shown in Figure 55.2. In winter, background values are below 6 nmol/l, with several elevated patches, partly relating to features shown by manganese, or by chlorophyll and oxygen, and apparently often transient and localised, since frequently without confirmation from a nearby location or a return on a later circuit (Figure 55.11). Two values, 380 nmol/l off the Humber, and 500 nmol/l off the Norfolk coast, both coinciding with high Mn measurements, have been flagged as outliers.

In spring, distributions again show some parallels with Mn; despite a reading of 117 nmol/l in the Humber outflow, concentrations in the western half of the survey area are very low, hardly ever reaching 5 nmol/l, and there is again an area of elevated concentrations reaching in towards the Norfolk coastline from the central North Sea. There is no clear evidence for inputs of iron from sediment resuspension. In summer, the picture reverses to a clear offshore decrease from the high values measured in the Wash, with apparently little contribution from the Humber river, in agreement with the extremely low concentrations (< 10 nmol/l) measured at the tidal station (Figure 5.23).

5.3.3.3 Nickel

The dissolved nickel distribution pattern (Figure 55.12 and Figure 55.13) shows a strong correlation with freshwater influence, with a coastal plume emanating from the Humber mouth and stretching south-eastwards along the coast. Throughout the year, concentrations range between an offshore background around 4 nmol/l and about 16 nmol/l close to the outflow. The plume, however, extends furthest in winter, has contracted slightly by May, and much more by August, when values exceeding 10 nmol/l are only found close to the outflow. The close correlation with salinity results in high coefficients of determination in the two end member mixing model (Table 5.5). Examining the nickel-salinity plot for the winter cruise in Figure 55.3, however, this model appears less satisfactory: mid-salinity values lie above the mixing line, whilst the high salinity data fall below it, suggesting a convex rather than a straight mixing line. This phenomenon could be due either to additional sources in the area where the mid-salinity samples are located, i.e. between the 33.4 and 34.4 salinity contours, or result from the time lag of a decreasing source concentration in the plume. Seasonal variations of the freshwater end member, with high nickel values in summer and diluted values in winter, as observed at the tidal stations, could explain a convex mixing curve in winter, with decreased concentrations and slope at low salinities, closer to the outflow, and a steepening of the slope towards higher salinities, still reflecting the higher freshwater concentration of the preceding summer and autumn. In spring, when the freshwater end member concentration derived from the tidal station data has already increased to 380 nmol/l, the plume-derived estimate is still close to the winter estimate for the outflow. The same happens again in summer, when the plume-derived estimate of 400 nmol/l is close to the spring outflow estimate, whilst lagging behind the 520 nmol/l calculated for the summer discharge.

A third explanation for the non-linearity of the trace-metal salinity diagram of nickel, and also of copper, zinc and cadmium, questions whether the high salinity end member has been correctly identified. The data points at the high salinity end all originate from stations at the seaward boundary of the survey area and thus, with regard to the residual circulation within the area, upstream of the Humber-Wash coastal plume (cf. Figure 5.1). Although this water body may well represent the sea end member concentrations, mixing with freshwater discharged from the coastal estuaries does not take place in a laterally confined one-dimensional reactor, but by the way of entrainment, leading to the formation of a third, southward moving water body. Mixing across the residual flow lines in a SW-NE direction will only take place by means of diffusion, and thus be very slow. We may therefore expect only the highly saline samples downstream of the plume to show the full effects of mixing with the river derived inputs.

Trace metal behaviour shows further complexities in spring, where at all resuspension sites near-bed nickel values are increased, highlighting the possibility of additional inputs from sediments. At the same time, four stations with salinities around 33.5 and high primary production (S11/27/32/33), all situated in the Wash and the coastal waters to the west of it, show Ni values well below the mixing line (Figure 55.3), suggesting biological removal from the dissolved phase. If these points were discounted in the regression analysis, the freshwater end member concentration was 320 nmol/l (R^2=78%), getting closer to the tidal station estimate.

5.3.3.4 Cobalt

Dissolved cobalt measurements in the Humber-Wash area are marred by analytical difficulties. In winter, most data points fall below the 3σ LoD (Figure 55.4), leading to a distribution pattern dominated by a few elevated values near the Humber outflow and the Norfolk coast (Figure 55.12). In spring, most values have risen above the LoD, leading to a clearer picture, where elevated nearshore values, especially near the Humber and the Wash, gradually decrease offshore. A transect in the very south-eastern corner of the area, however, shows an offshore increase from 0.25 to 0.42 nmol/l. The near-seabed value for the offshore station is again higher, at 0.58 nmol/l, during what apparently was a resuspension event, with SPM concentrations increasing from 4 mg/l at the surface to 34 mg/l near the bottom. In summer, dissolved Co values have again increased, with most stations lying within the 0.28 nmol/l contour, and concentrations steadily rising inshore towards values well above 0.4 nmol/l off Norfolk and near the Humber mouth. No seasonal data set is strongly correlated with salinity (Table 5.5).

5.3.3.5 Copper

The distribution of dissolved copper in winter (Figure 55.15) relates well to the salinity distribution, and the freshwater end member estimate of 150 nmol/l is in good agreement with the intercept derived from the tidal station data. The copper-salinity plot (Figure 55.5), however, again shows data falling along a convex curve rather than a straight line, with a steeper slope at high salinities, pointing at a higher effective freshwater end member concentration, than suggested by the regression line.

In the copper-salinity plot of the spring data, again four values (S32 to 35) fall well below the mixing line. They all have been taken later during the cruise along a transect out of the Wash, after a bloom had been observed there for some time. Some earlier samples in the same area, however, do not show decreased Cu concentrations, resulting in rather convoluted contours. Sediment resuspension either has no effect on Cu levels, or even leads to decreased near-bed values (S16). The plume, apparently unchanged in size in spring compared to winter, contracts in summer around the Humber outflow, with contours widening elsewhere. Concentration ranges of the offshore samples are in good agreement with Balls (1985a). From 150 nmol/l in winter, plume-derived effective freshwater concentrations rise to 270 nmol/l in summer, which is considerably higher than any tidal station estimate.

5.3.3.6 Zinc

In winter, dissolved zinc concentrations range between 4 and 24 nmol/l, with contours broadly following the salinity pattern. The linear mixing model determines 82% of data variability, leading to effective freshwater estimates of 320 nmol/l, well below the 600 nmol/l calculated from the tidal station. This seems indicative of a rapid removal near the outflow, reducing the high estuarine input to concentrations explaining the more gentle gradient of the plume. This phenomenon has again been recorded during the spring survey, where the discrepancy between the 73 nmol/l of sample S2, well representative of concentrations measured at the tidal station, and the next closest samples, S3 and S24, both around 20 nmol/l, leads to a sharp gradient immediately around the outflow. The zinc-salinity plot in Figure 55.6 again shows samples S11,27,32 and 33 falling well below their expected values, probably due to biological uptake in the Wash and the inshore waters of Norfolk. There is no conclusive evidence for sedimentary inputs. In summer, estuarine supply of zinc only detectably influences the vicinity of the outflow, leading to very wide-spaced contours elsewhere, similar to salinity. Again, the plume-derived effective freshwater concentration of 400 nmol/l suggests removal of zinc from the dissolved phase in the vicinity of the outflow, where a zero-salinity intercept of 890 nmol/l was calculated from tidal station data.

5.3.3.7 Cadmium

Dissolved cadmium concentrations in winter broadly follow the salinity distribution, with levels around 0.40 nmol/l near the Humber outflow and 0.32 nmol/l in the Wash, decreasing north-eastwards to levels below 0.16 nmol/l. In spring, background values of 0.12 nmol/l are found at the northern boundary, and values greater than 0.24 nmol/l are restricted to inshore waters off Lincolnshire. Stations in the high productivity area in the Wash and off Norfolk have again been found to show decreased values. There are no indications of sedimentary inputs during the recorded resuspension events. In summer, the 0.16 nmol/l contour moves even closer inshore, and values above 0.24 nmol/l are only found right next to the outflow. Overall levels are slightly below those reported by Balls (1985a) for summer 1983. Freshwater end member estimates at the tidal station rise constantly from 3.0 nmol/l in winter to 9.3 nmol/l in summer (Table 5.6). In winter, the plume-derived estimate of 5.3 nmol/l is higher than the tidal station value, in summer slightly less, with 7.3 nmol/l estimated from the plume data. Discounting the stations apparently affected by biological removal, the plume derived value in spring is 7.0 nmol/l (otherwise 4.9 nmol/l), compared to 8.1 nmol/l at the tidal station.

5.3.3.8 Lead

Dissolved lead measurements are close to, but usually above the average detection limit. During the winter cruise, the highest value, 0.33 nmol/l, was measured near the Humber mouth. From there, however, values quickly decrease below 0.12 nmol/l in the area stretching from the Lincolnshire coast westwards (Figure 55.18). Elevated concentrations are, however, found along the seaward boundaries of the survey area, at high salinities (see also the lead-salinity plot in Figure 55.8). This is shown even more pronouncedly during the spring survey: elevated values in the Humber mouth decrease below 0.08 nmol/l off the Lincolnshire coast, with similar concentrations off Norfolk, but levels rise towards the central North Sea, with highest values (>0.18 nmol/l) at the northern boundary. There are indications of sedimentary inputs at station 16, where resuspension leads to a near-bed value of 0.23 nmol/l, compared with 0.10 nmol/l at the surface. In summer, two areas of decreased Pb concentrations (<0.08 nmol/l) spread out from the Humber and the Norfolk coast, again with elevated levels coming in from the northern boundary, which is in good agreement with the findings of Balls (1985a). First results from further North Sea wide surveys confirm these patterns, showing decreased values in high turbidity areas and offshore concentrations in excess of 0.2 nmol/l. No plume data set can satisfactorily be linked to salinity (Table 5.6), and the combined effects of long-range atmospheric transport of land-derived lead and its scavenging by the higher particle concentrations in nearshore areas are more likely to explain the observed pattern.

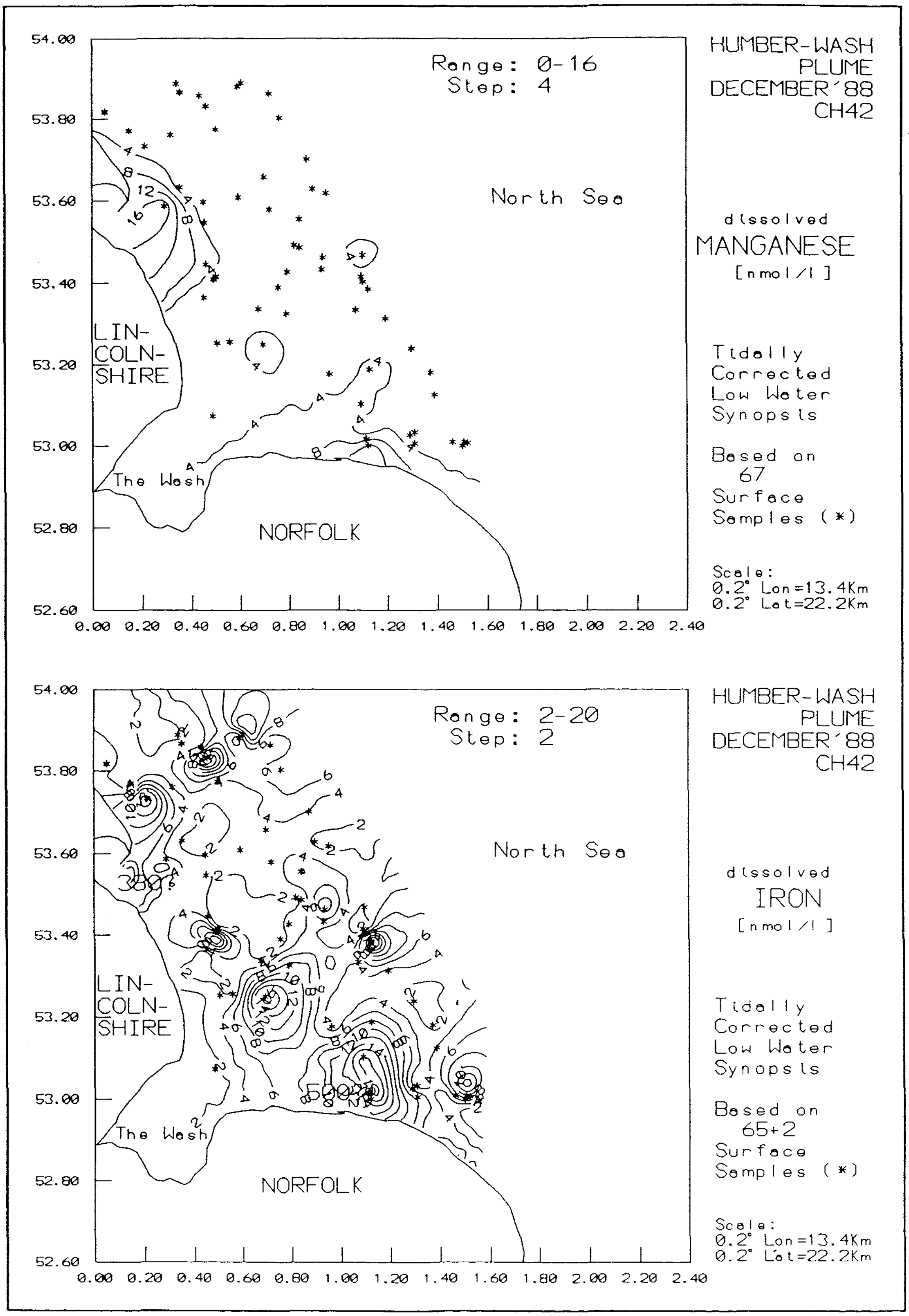

Figure 55.9: Dissolved iron and manganese distributions in the Humber-Wash area in winter (CH42)

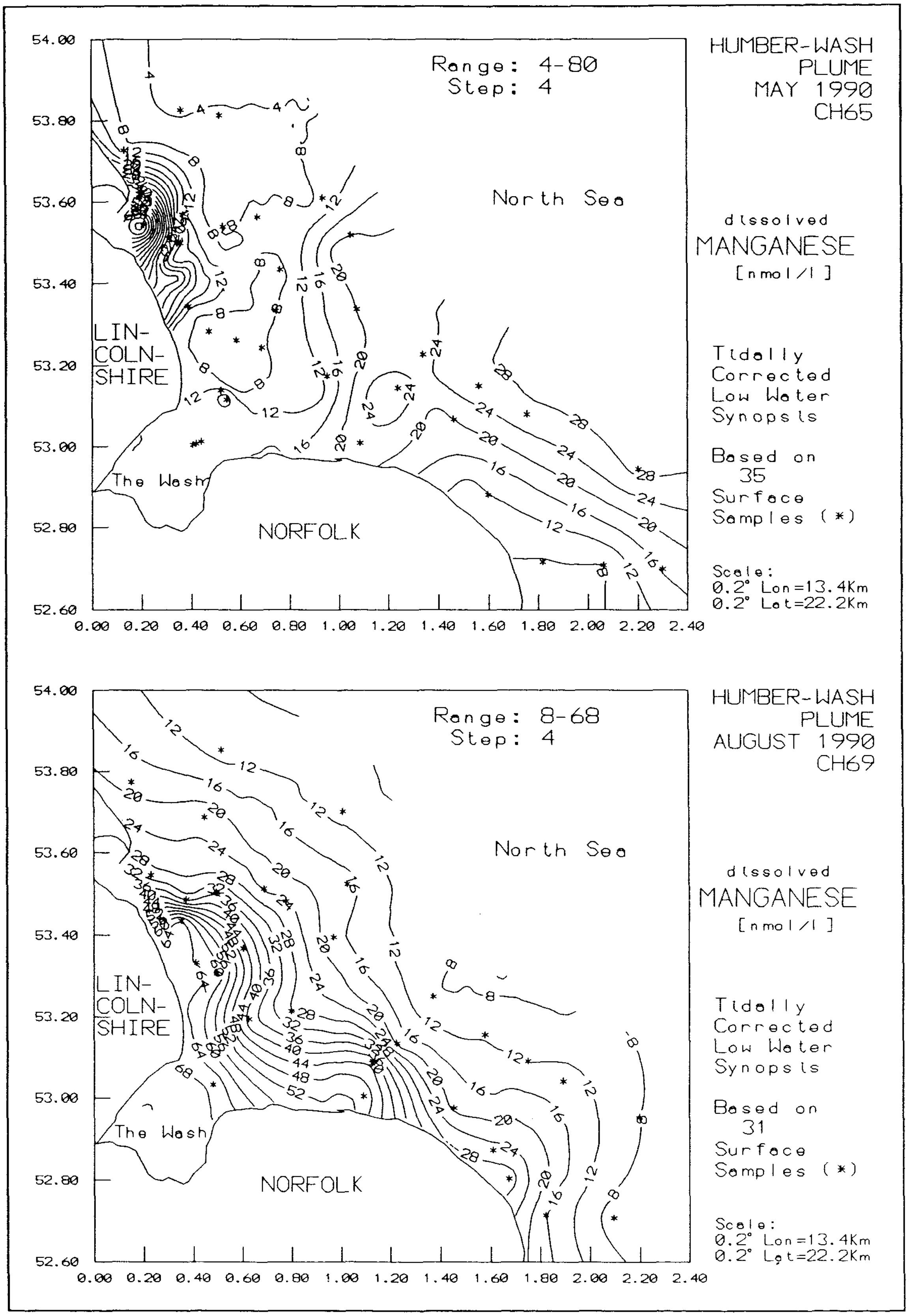

Figure 55.10: Dissolved manganese distributions in the Humber-Wash area in spring and summer (CH65 and CH69)

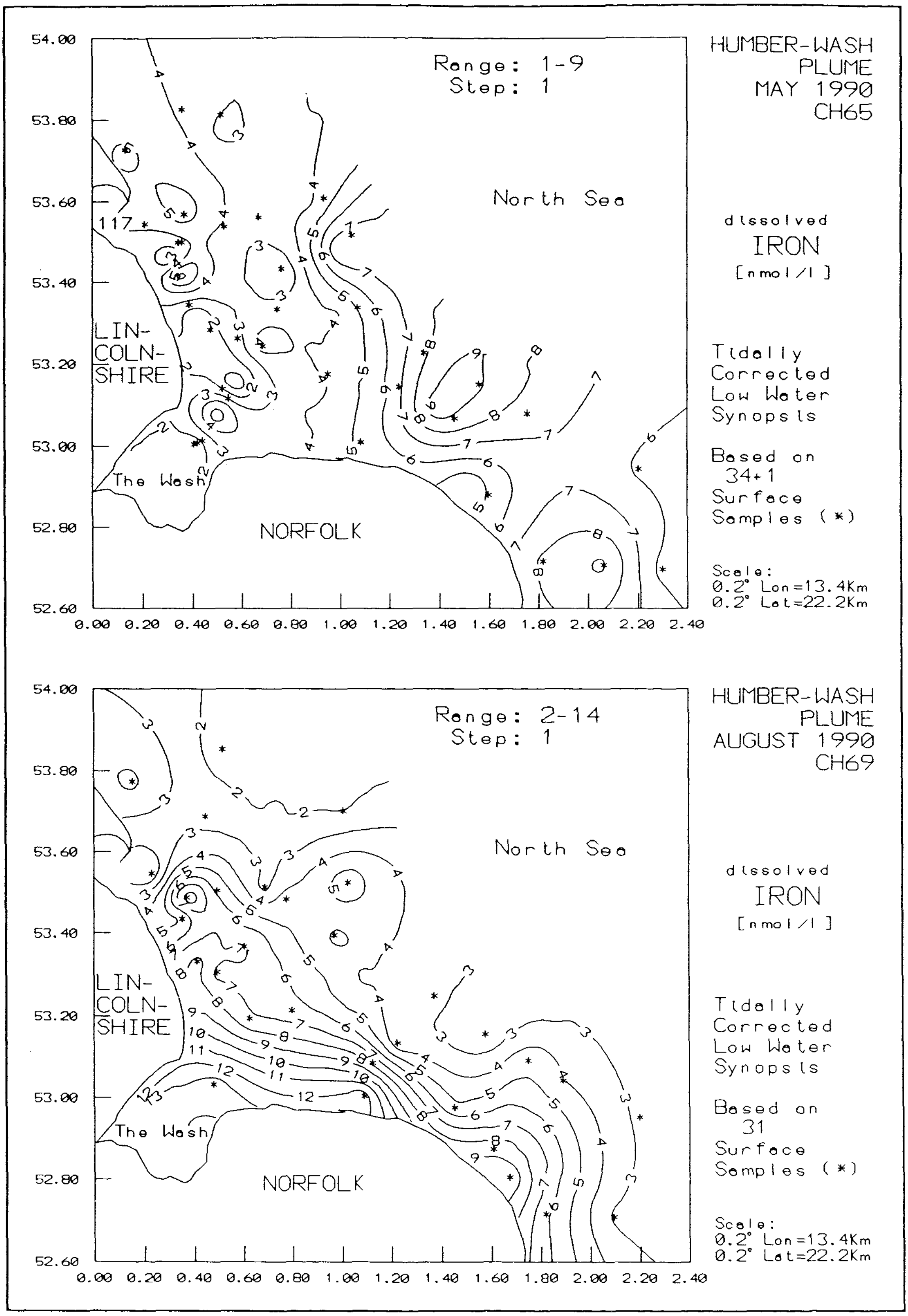

Figure 55.11: Dissolved iron distributions in the Humber-Wash area in spring and summer (CH65 and CH69)

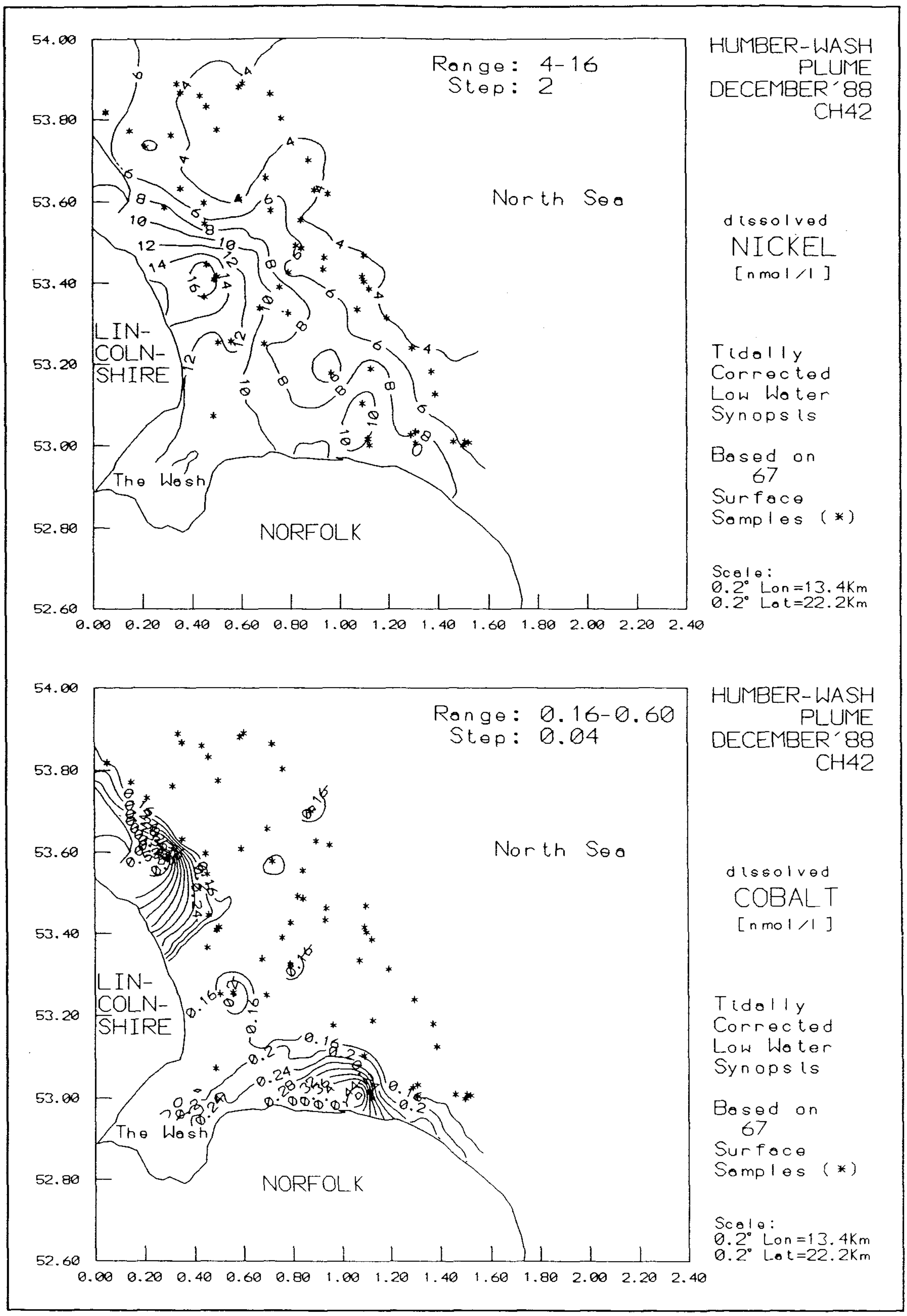

Figure 55.12: Dissolved nickel and cobalt distributions in the Humber-Wash area in winter (CH42)

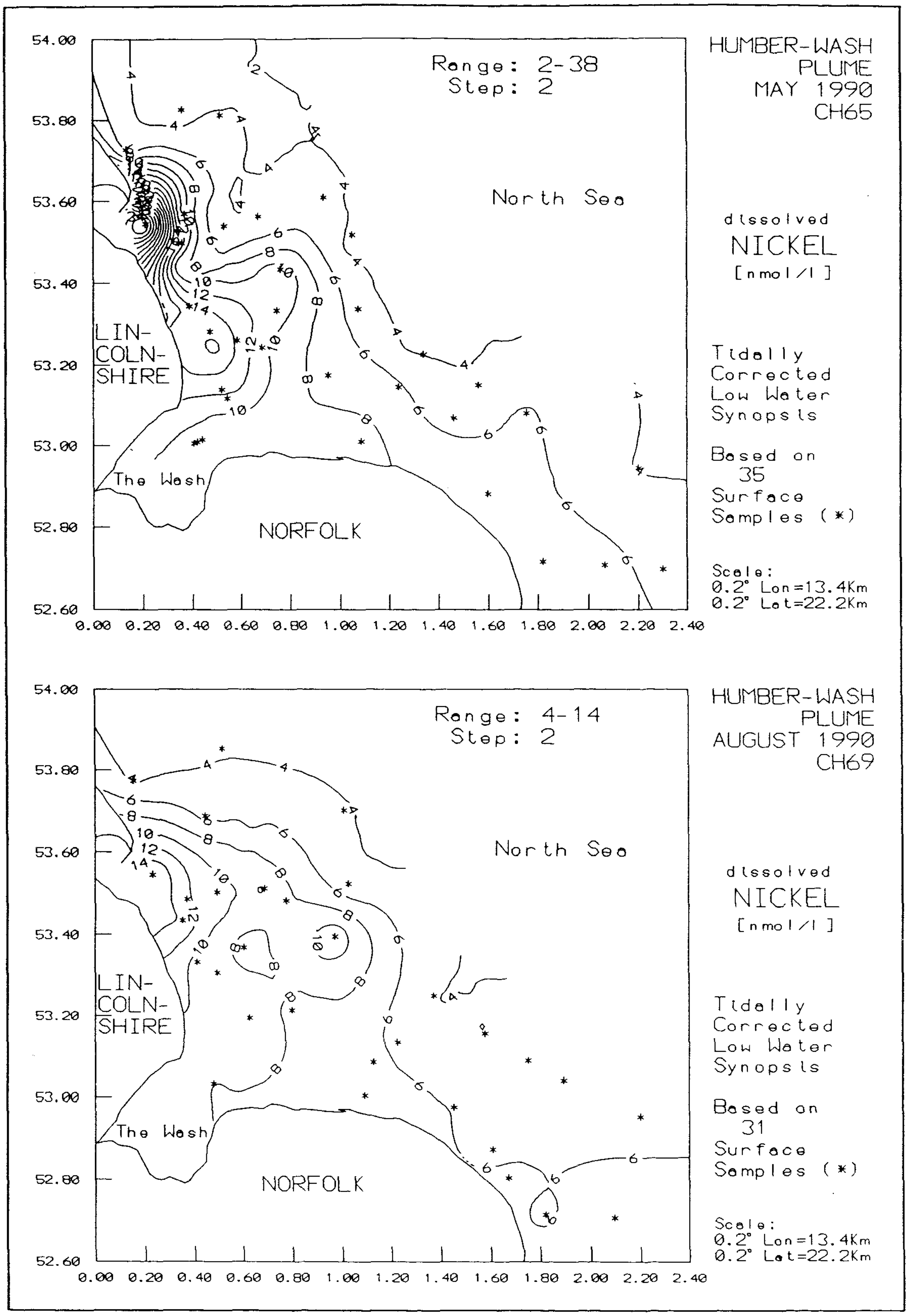

Figure 55.13: Dissolved nickel distributions in the Humber-Wash area in spring and summer (CH65 and CH69)

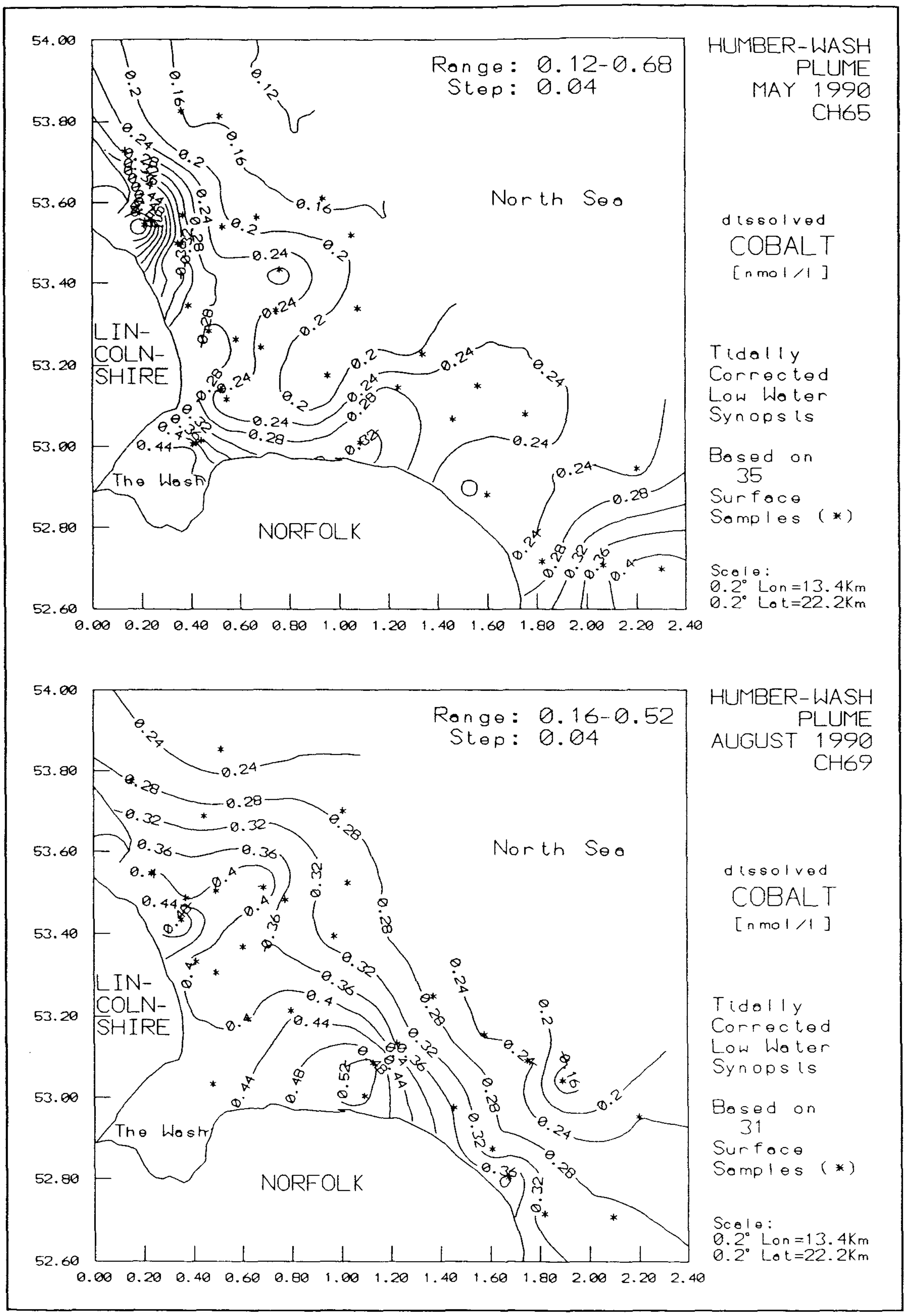

Figure 55.14: Dissolved cobalt distributions in the Humber-Wash area in spring and summer (CH65 and CH69)

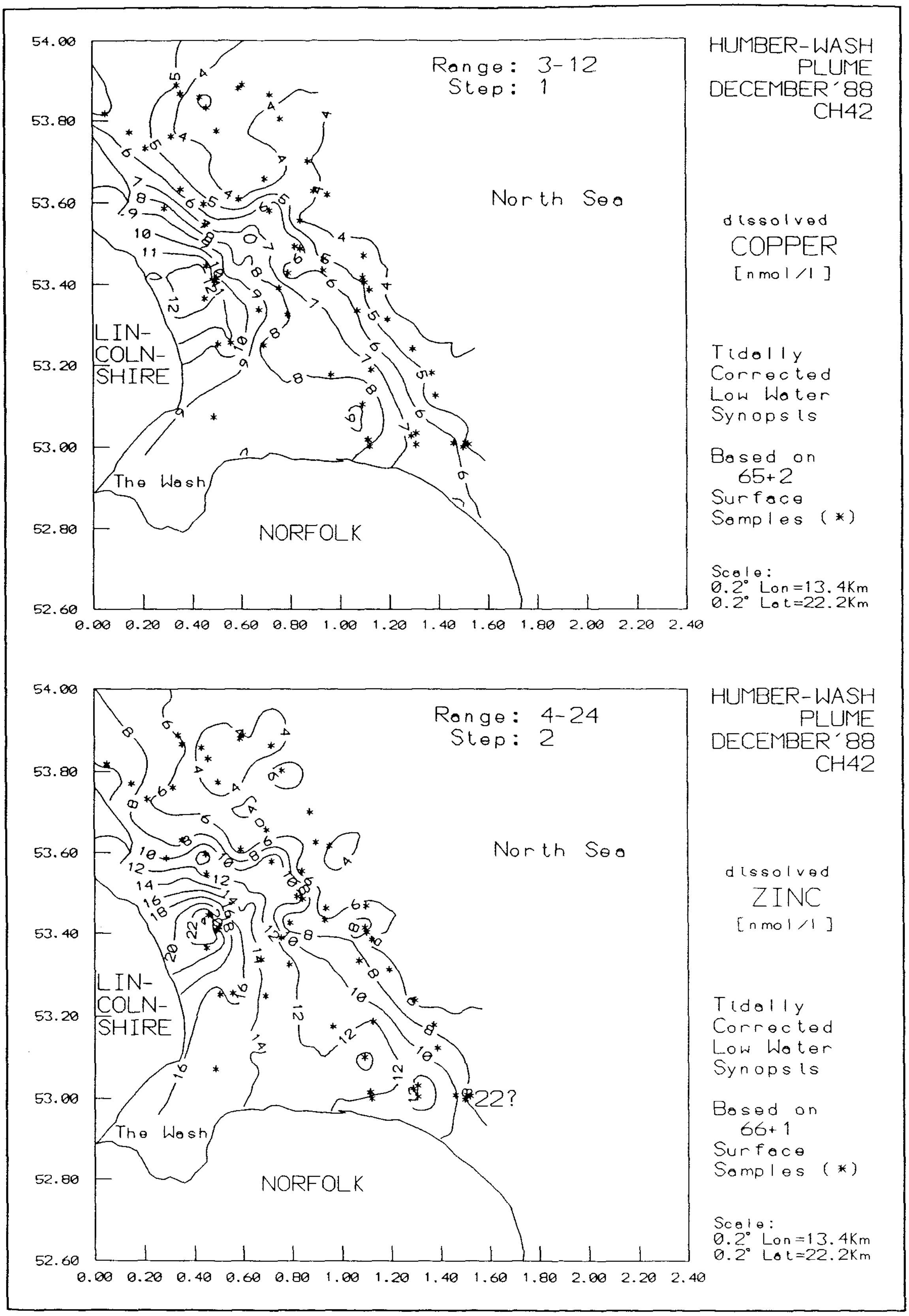

Figure 55.15: Dissolved copper and zinc distributions in the Humber-Wash area in winter (CH42)

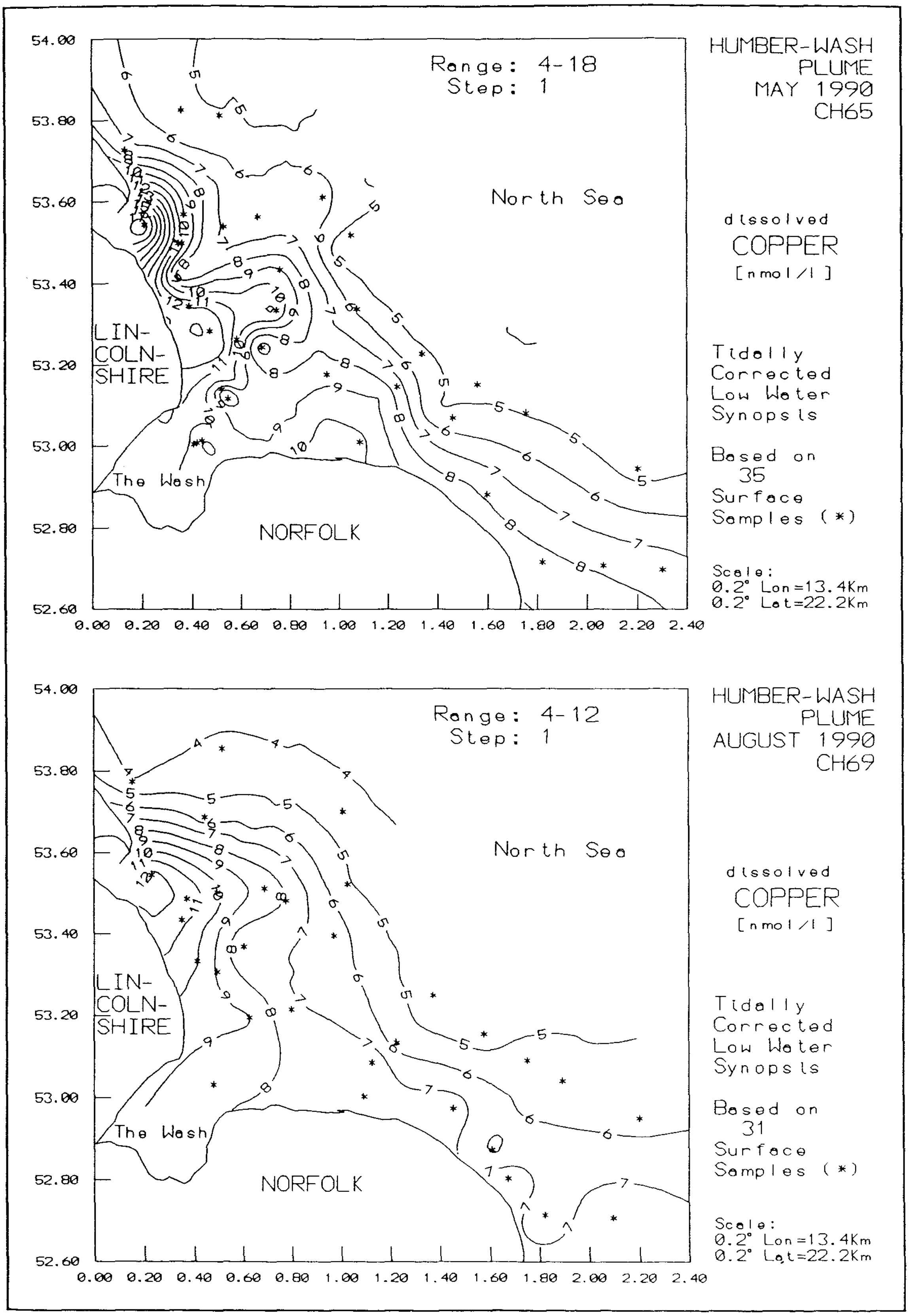

Figure 55.16: Dissolved copper distributions in the Humber-Wash area in spring and summer (CH65 and CH69)

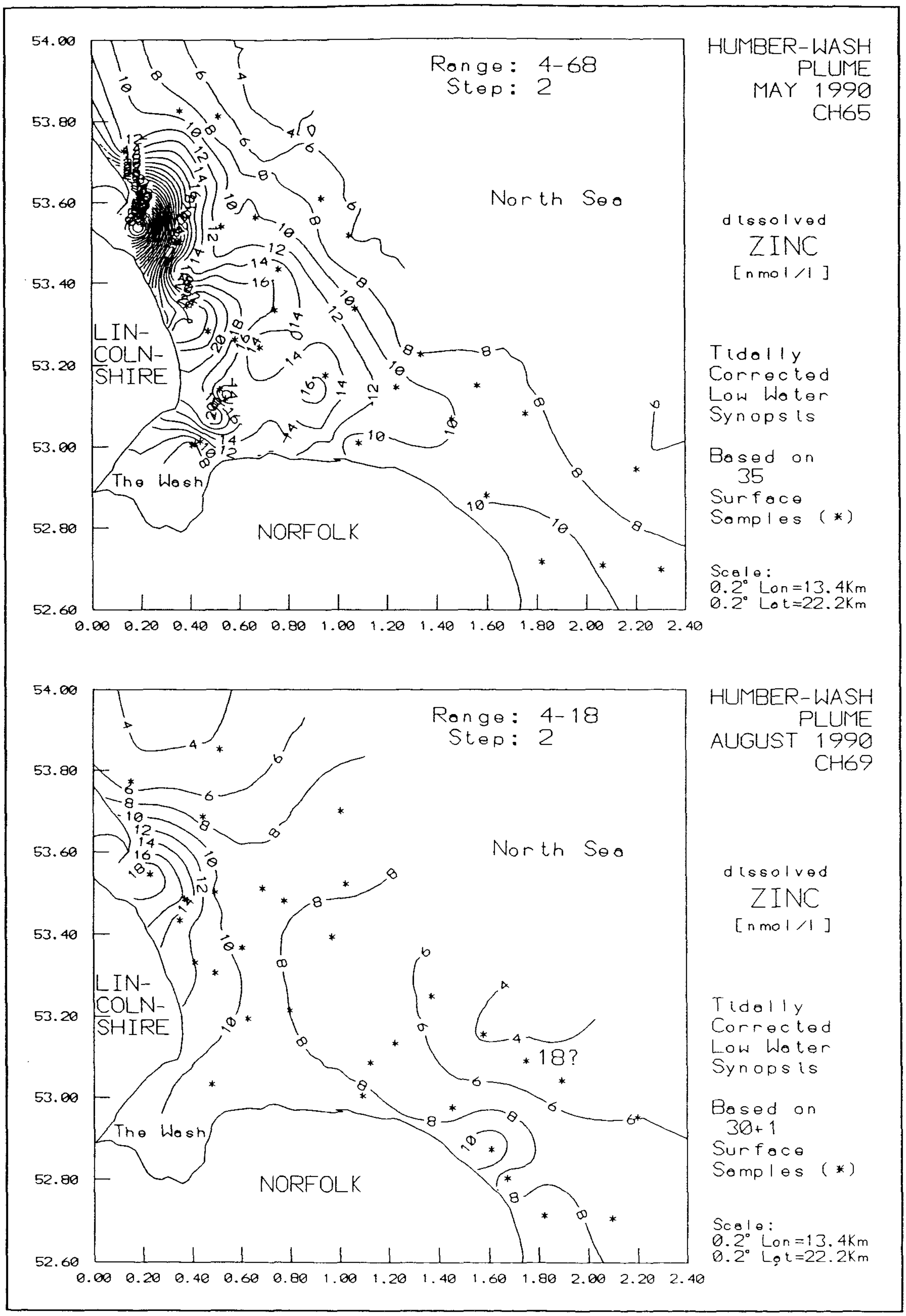

Figure 55.17: Dissolved zinc distributions in the Humber-Wash area in spring and summer (CH65 and CH69)

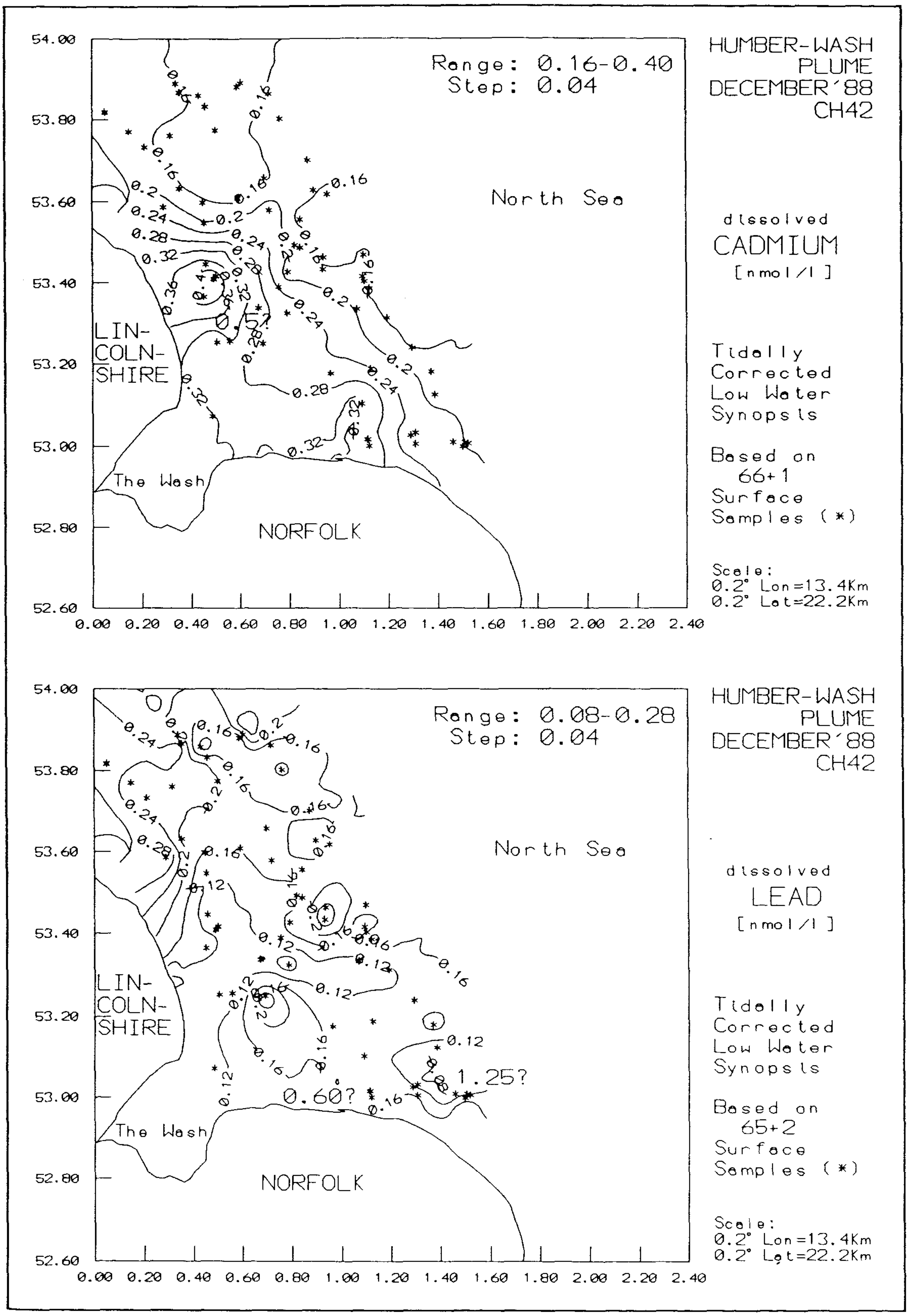

Figure 55.18: Dissolved cadmium and lead distributions in the Humber-Wash area in winter (CH42)

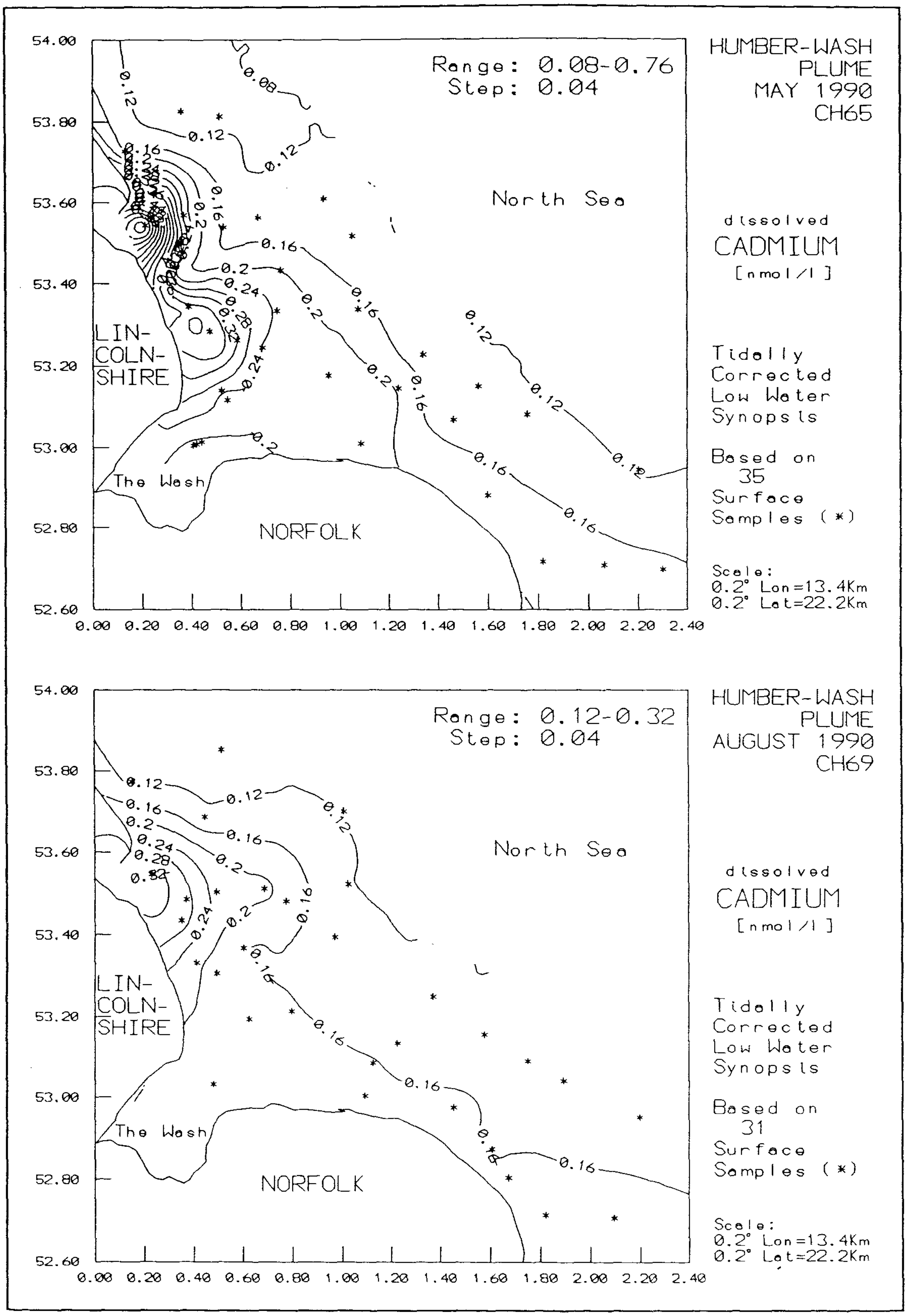

Figure 55.19: Dissolved cadmium distributions in the Humber-Wash area in spring and summer (CH65 and CH69)

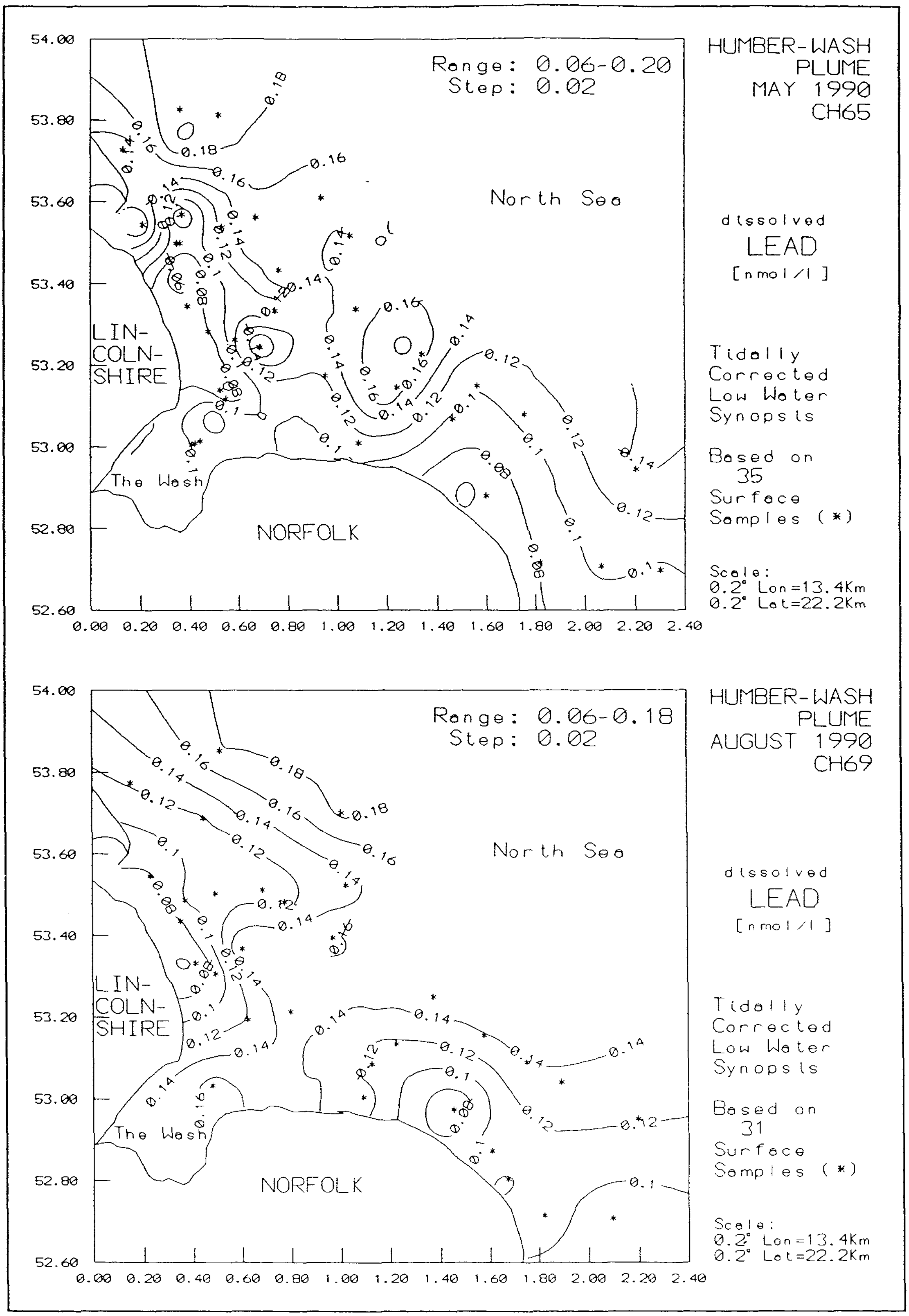

Figure 55.20: Dissolved lead distributions in the Humber-Wash area in spring and summer (CH65 and CH69)

5.3.4 Distribution between Dissolved and Particulate Phase

In Figure 55.21 ff., particle-bound percentages of the total metal concentrations have been plotted, on a probability scale, against suspended matter concentrations, on a logarithmic scale, and together with lines corresponding to a given K_d-value.

Within the Humber survey, iron shows the strongest affinity to particles; usually more than 90% is bound to SPM. For manganese and lead, followed by cobalt, association to particles also generally outweighs the dissolved phase. Zinc, copper and nickel appear to be evenly distributed between the phases, with particulate percentages rising with increasing concentrations of SPM. Cadmium, however, exist mainly in the dissolved phase. Distribution coefficients for Cu, Cd and Pb fall generally into the ranges found by Balls (1989) in the marine environment, but appear elevated for Ni and Zn.

Within individual subsets (tidal stations or coastal plume surveys, winter or spring), the particle-bound fraction of the total content increases with rising SPM-concentrations, but broadly parallel to the K_d-lines, indicating a constant relationship between concentrations in the two phases, although with a varying amount of scatter for the individual elements. Between different subsets, however, K_d-values vary considerably. For manganese, log(K_d)-values at the tidal stations range between 5 and 6 for both winter and spring. For coastal plume samples in spring, when dissolved Mn concentrations were elevated and SPM concentrations were low, log(k_d)-values are around 6. In winter, however, when a wide range of suspended sediment concentrations was recorded, log(k_d)-values lie mostly between 6.5 and 7. This phenomenon, where the winter plume data show markedly higher K_ds than the tidal station data, and thus a higher proportion of the total trace metal content bound to particles, can also be seen with Ni, Co, Zn and Cd, and, less pronouncedly, Cu. This difference may be due to a grain size effect: within the high SPM loads in the Humber mouth, we can expect a high proportion of large, but less reactive particles. Nickel is the only one of these elements to show a difference in winter and spring tidal station K_d values, with the dissolved phase being more important in spring. For Ni, Cu and Zn, K_d-values for the spring plume survey are below the winter plume values. Since absolute dissolved concentrations in spring are similar or slightly lower than in winter, this phenomenon must be due to decreased particulate concentrations in spring. For Cd, log(K_d)-values for all coastal samples vary broadly between 4 and 5.

For iron, some of the tidal station 1 data show decreased K_d-values associated with high SPM; otherwise, no clear differentiation between the subsets is apparent. In the case of lead, spring tidal station and winter station 2 values lie between log(K_d) 6 and 7, and for some of the winter station 1 samples (the same group which shows lower K_ds for Fe and coinciding dissolved peaks) between 5 and 6. Samples from the coastal zone in spring, however, show log(k_d)'s rising linearly with SPM, where the suspended particles in the more turbid nearshore waters also carry higher amounts of lead per dry weight. This suggests that inshore particle populations either include contaminated material from land-based or estuarine sources, or, possibly despite the presence of larger and less reactive particles, they have a stronger ability to scavenge dissolved lead, even at lower concentrations, than offshore particles; this could possibly reflect different surface properties, like Mn and Fe oxide coatings.

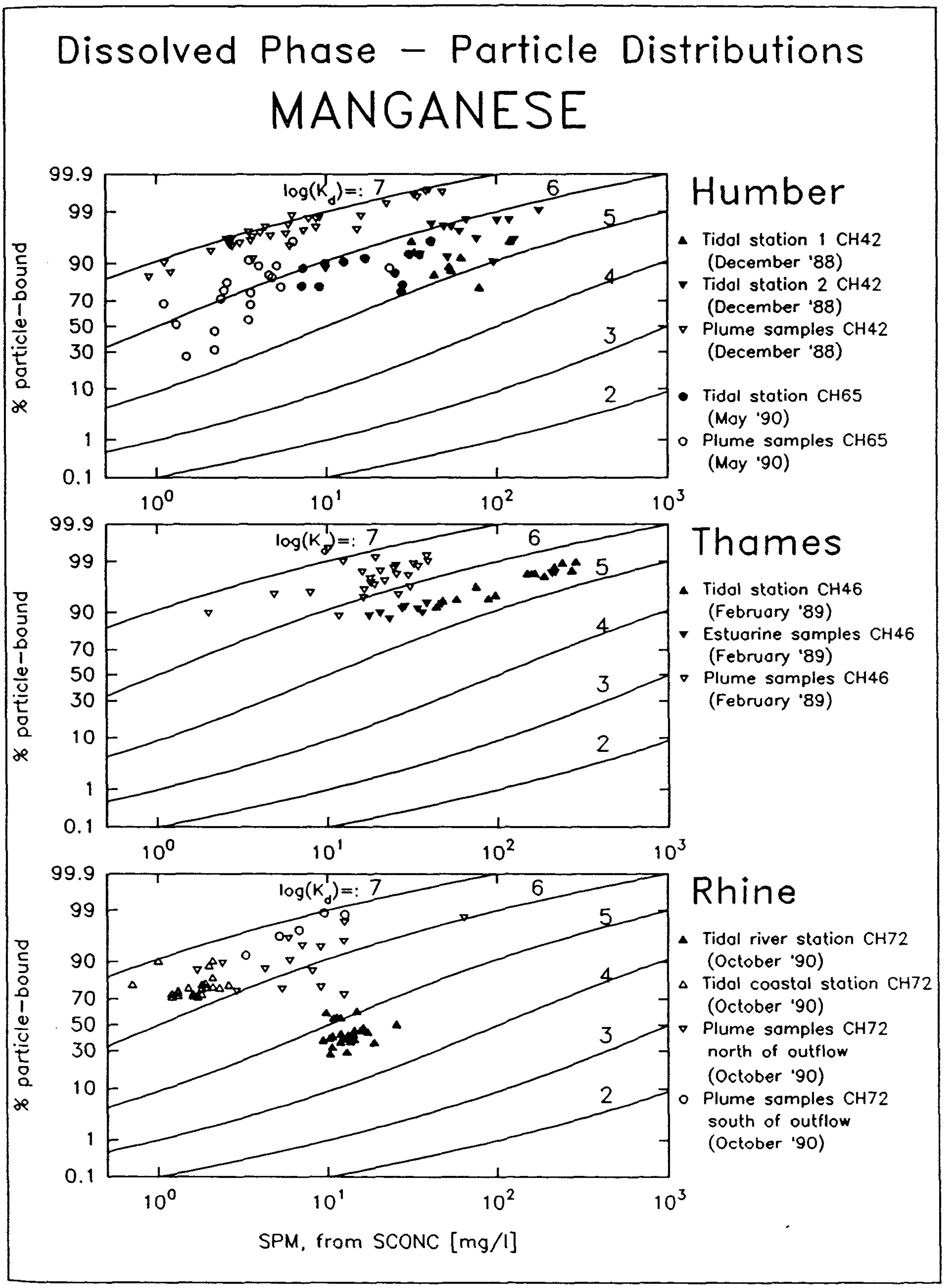

Figure 55.21: K_d distribution coefficients for manganese

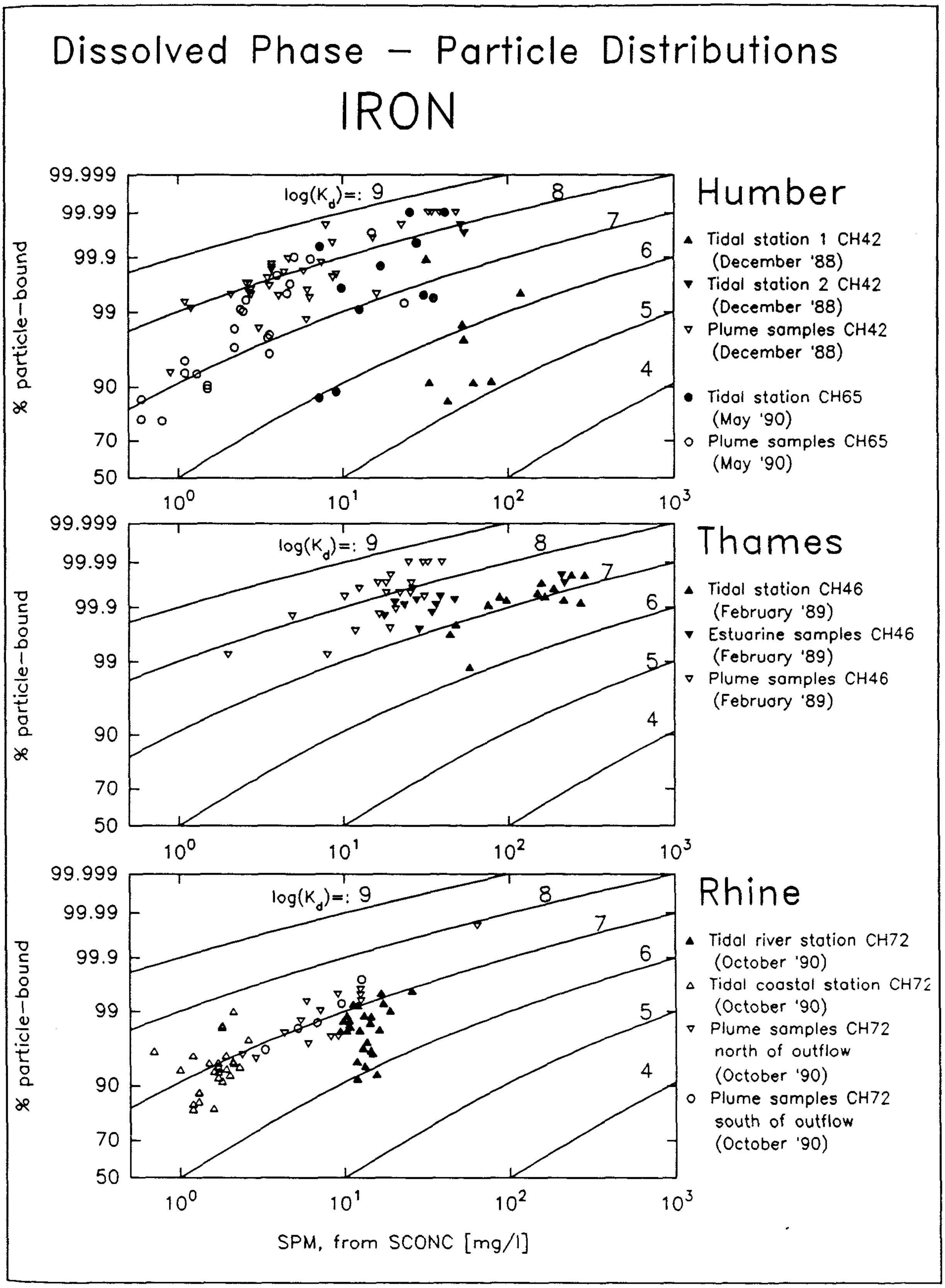

Figure 55.22: K_d distribution coefficients for iron

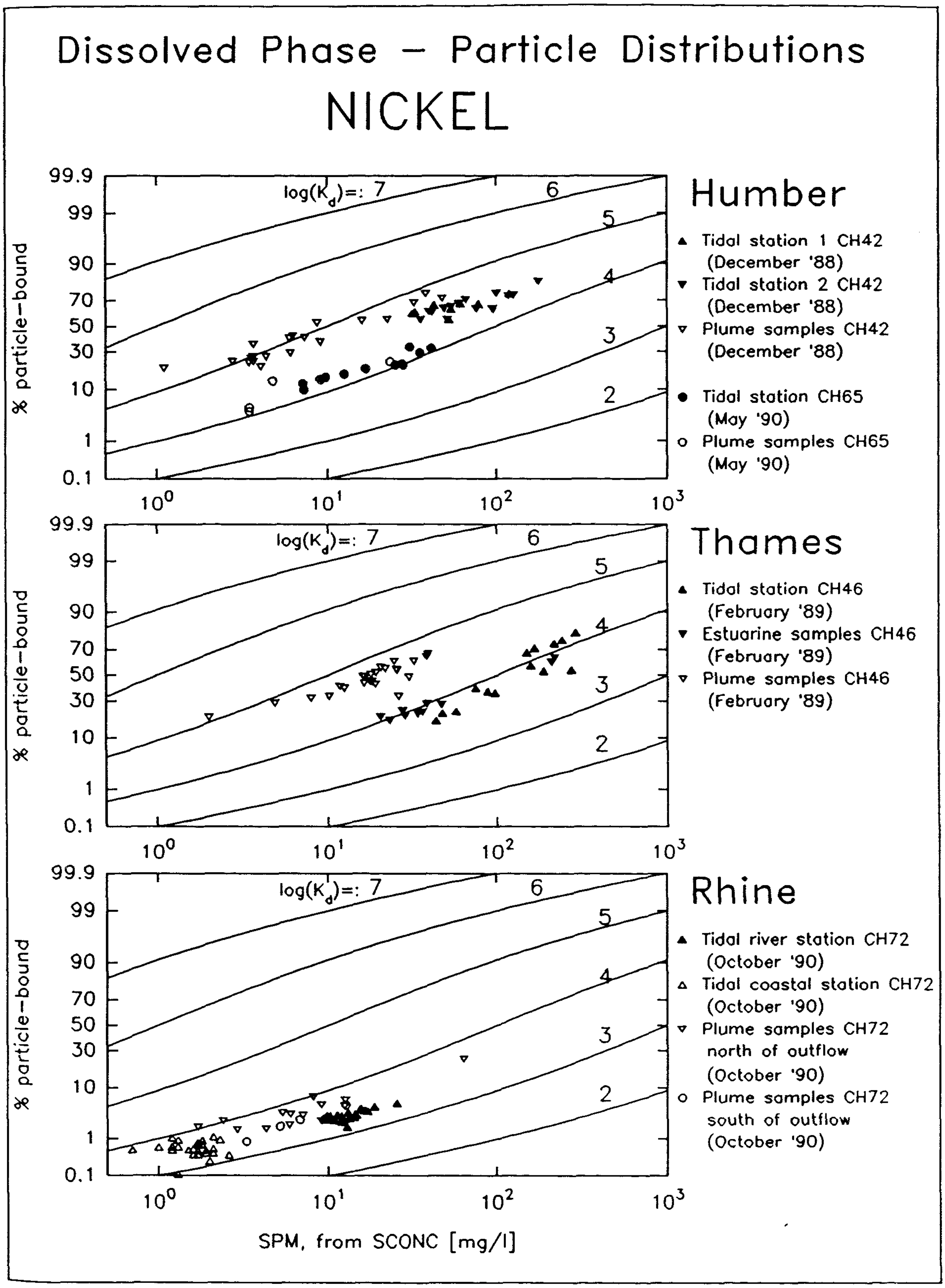

Figure 55.23: K_d distribution coefficients for nickel

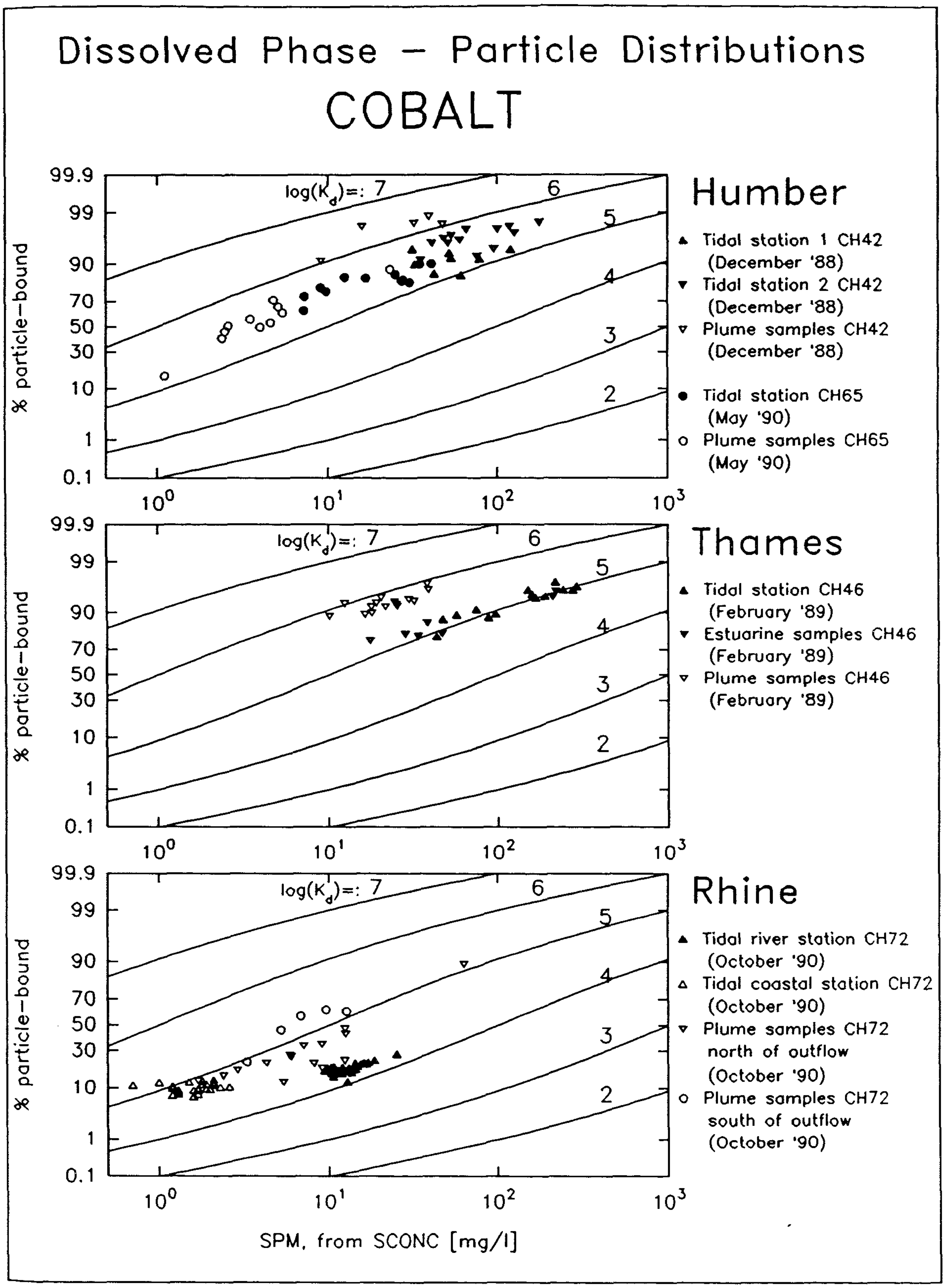

Figure 55.24: K_d distribution coefficients for cobalt

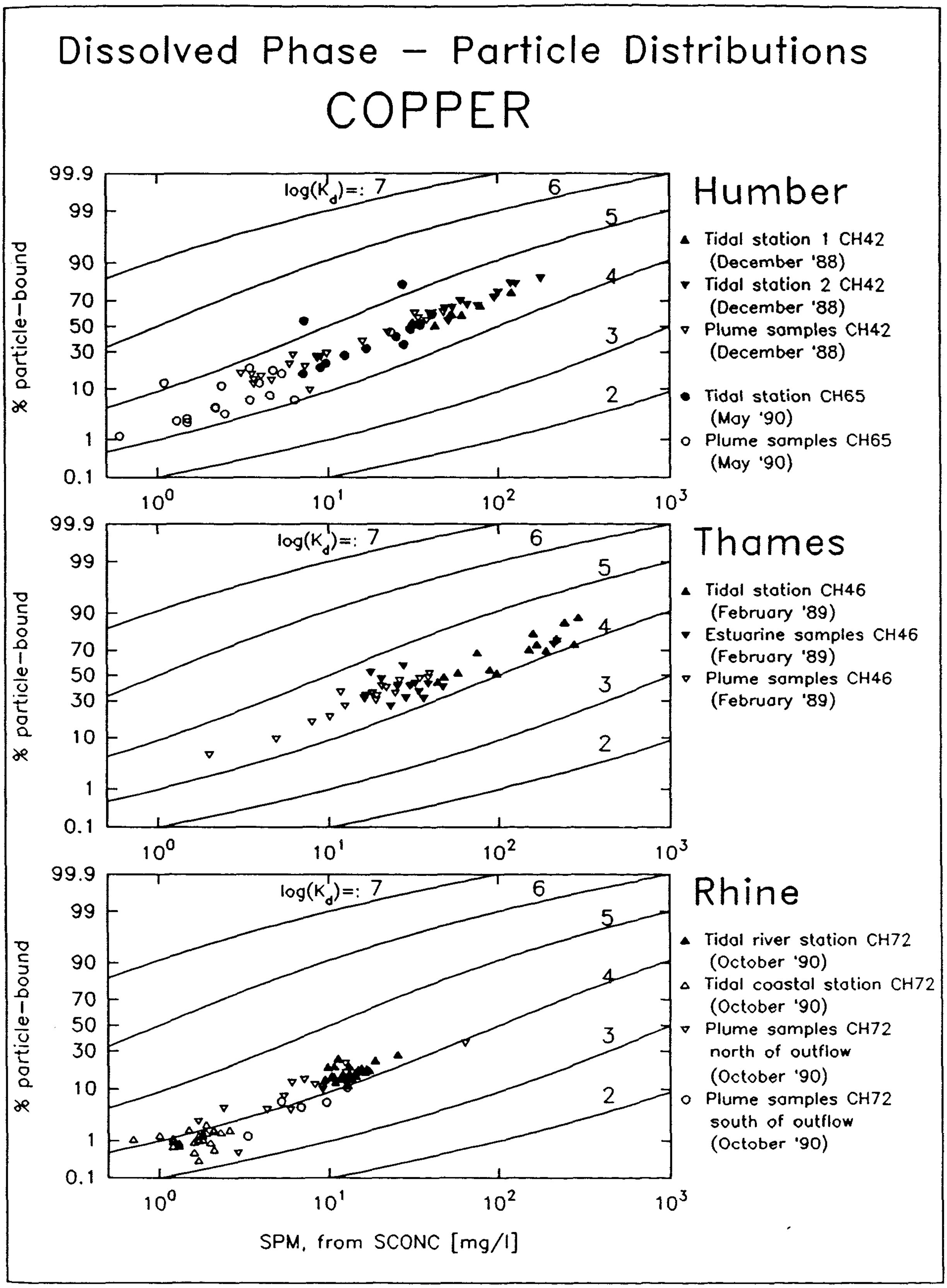

Figure 55.25: K_d distribution coefficients for copper

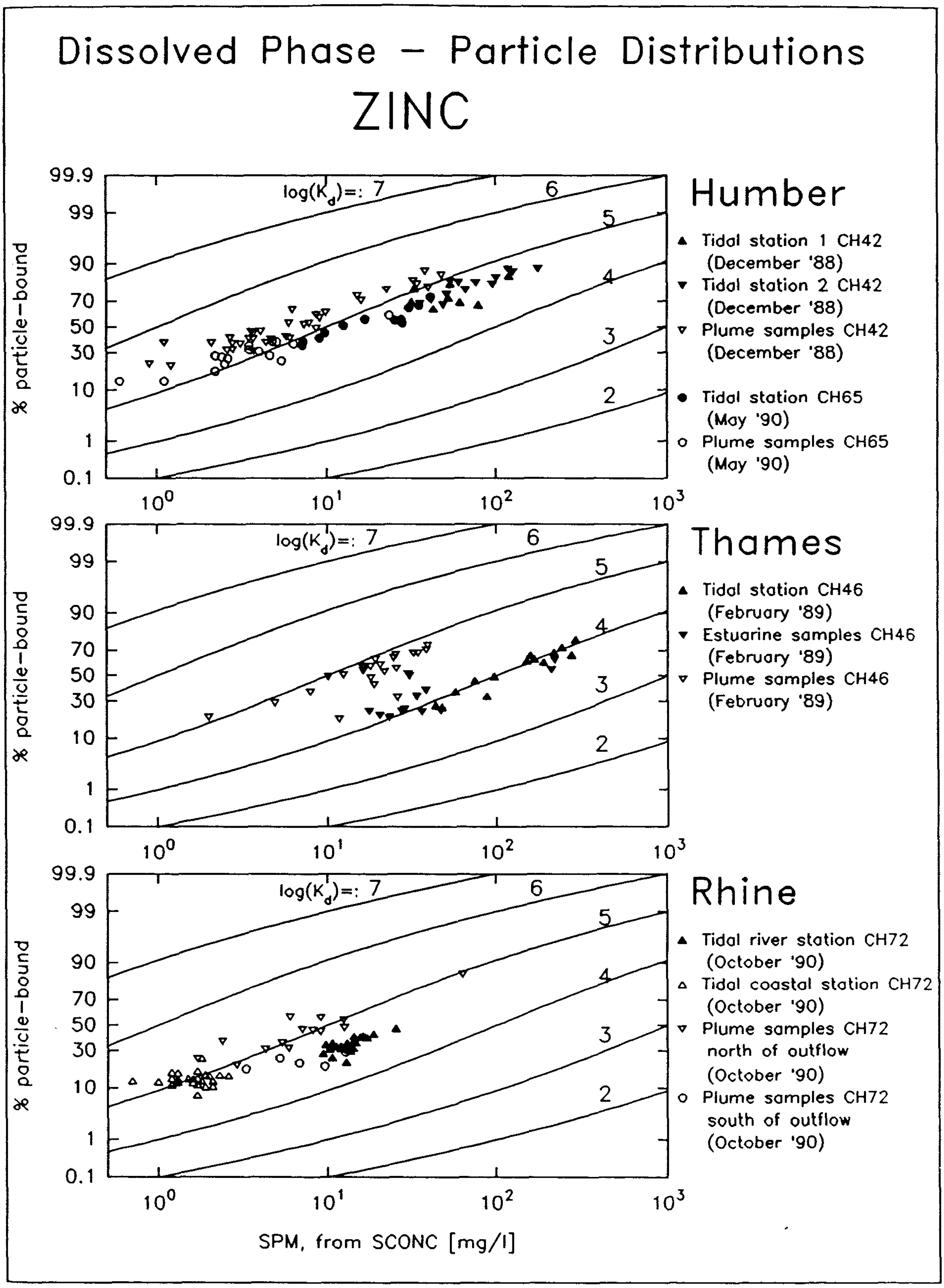

Figure 55.26: K_d distribution coefficients for zinc

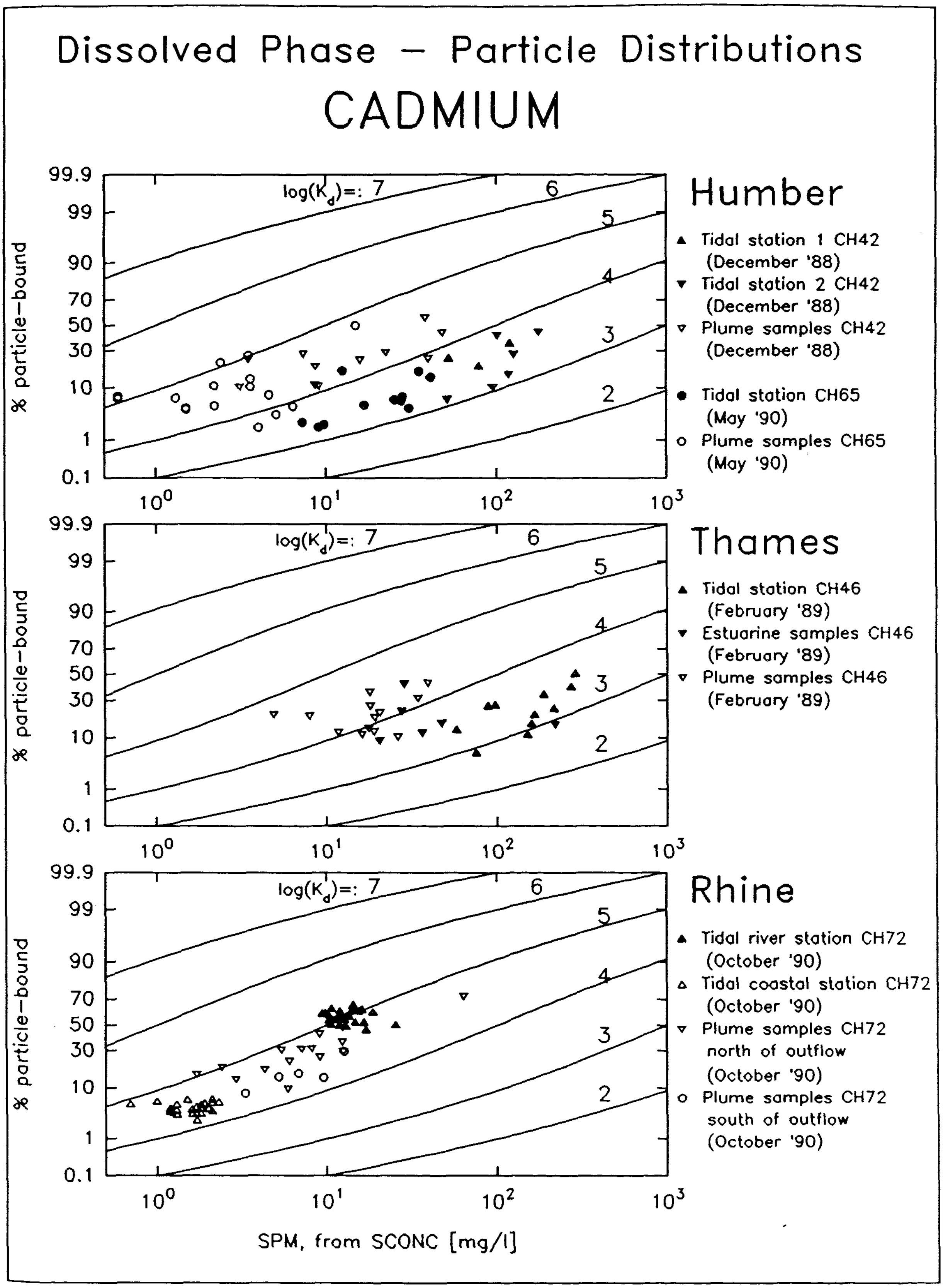

Figure 55.27: K_d distribution coefficients for cadmium

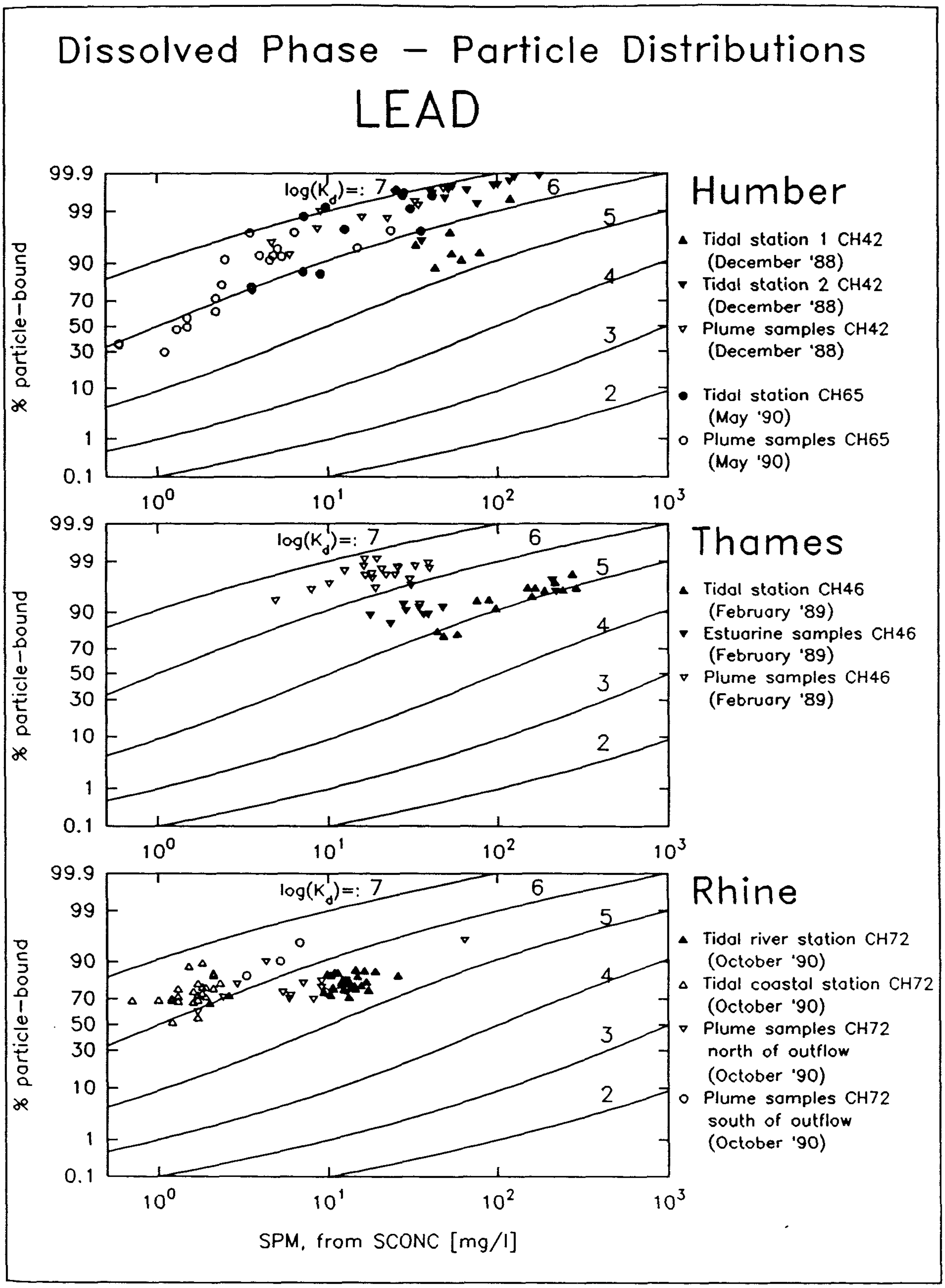

Figure 55.28: K_d distribution coefficients for lead

5.4 SUMMARY: THE HUMBER-WASH PLUME

Three surveys of the Humber-Wash area in winter, spring and summer, have yielded an extended picture of coastal trace metal behaviour, showing distribution patterns and their seasonal changes as well as indicating sources, sinks and, when compared to earlier studies, possibly also long term trends.

Seasonal changes in freshwater discharge lead, with a time lag, to changes in size and intensity of the coastal low salinity plume. Freshwater influence is strongest in winter, coinciding with the highest levels of nutrients and suspended particulate material, and lowest levels of chlorophyll. In spring, high levels of biological activity can be observed in The Wash and off the Norfolk coast, leading to sharply decreased nutrient values. In summer, however, nutrient levels start to recover again, whilst elevated chlorophyll levels are maintained only in a few patches; particle concentrations are very low, and salinity uniformly high, except for the most inshore areas.

Distributions of dissolved Ni, Cu, Zn and Cd are primarily the product of conservative river - sea water mixing, although modified by additional non-conservative processes. For all four elements, effective river end member concentrations at the Humber outflow increase with decreasing freshwater flow, suggesting a more concentrated discharge during dry seasons. For Ni and Cd, this trend seems to propagate, with about three months lag time, into the coastal plume, whilst plume-derived effective freshwater concentrations for Cu are always above, and for Zn below the outflow-based estimate, suggesting, for the dissolved phase, coastal sources for the former and a coastal sink for the latter element. All four elements show potential for biological removal, with samples from highly productive areas in The Wash and off Norfolk showing decreased dissolved concentrations, but there are hardly any indications of input via resuspension from sea bed sediments for these four elements.

Comparing total inputs into and dissolved exports from the estuary, copper is nearly balanced and seems to reach the sea in dissolved form, whilst only half the estimated total input of zinc is exported to the sea; the other, particle-bound fraction, may or may not be trapped within the estuary. Dissolved exports of nickel and cadmium are significantly higher than accounted for by the total input estimates, a strong indicator for additional sources either in the form of further direct discharges, waste dumping, atmospheric inputs, resuspension and, especially, remobilisation from dredge spoils, as suggested by data given in Murray et al. (1980).

The single estuarine transect within the present study shows, however, almost ideally conservative behaviour of Ni and Cu in the lower Humber estuary between salinities of 20.6 and 31.6, and only moderate indications for inputs of dissolved Zn and Cd between Grimsby and Immingham. In a longer-term context, there are indications that discharges of these two elements within the Humber catchment have been reduced over the last decade or so, with Cu levels remaining about stable.

Among the more particle-reactive elements Mn, Fe, Co and Pb, iron is bound strongest to suspended particulate matter, and distributions can hardly ever be related to salinity, apart from the estuarine profile, where inputs in the outer estuary have been observed. Spikes, however, can frequently be linked to similar patterns of other elements within this group.

Manganese and cobalt show even stronger similarities. During the estuarine transect, the two almost identical plots show massive inputs in the outer estuary, supported by a tendency towards concave metal-salinity plots for the tidal station data from the Humber outflow, where effective freshwater concentrations rise from spring to summer. In the coastal zone, absolute levels of both elements increase from winter to summer, where they show a strong offshore gradient independent from salinity. Both elements are also strongly increased in a near-bed sample during a suspected resuspension event. Only dissolved Mn levels, however, decrease in areas of high primary production.

Although lead appears to behave perfectly conservatively within the estuary, suggesting an effective freshwater concentration of about 1% of the total input estimate, no such correlation can be found at the Humber mouth, where in summer dissolved Pb appears to come in from the sea. This is in line with observations in the coastal zone, where low levels occur in the most turbid areas, whilst elevated readings are recorded offshore. Inshore particles also have higher concentrations per dry weight, either due to prior contamination, or stronger sorptive surface properties.

CHAPTER 6: THE THAMES ESTUARY

6.1 INTRODUCTION

The survey area of the Thames estuary and plume is shown in Figure 6.1, including the inner Thames estuary between Greenwich and Southend, the adjoining outer Thames estuary, and a part of the English Channel, with the continental coast in the very south-eastern corner. Also shown are two major dumping grounds: Barrow Deep, receiving 4.5 x 10^6 t of sewage sludge annually, and South Falls, where 50 000 t of dredged material, 55 000 t of industrial waste and 90 000 t of sewage sludge where dumped in 1985 (Harper, 1988).

The inner Thames estuary, again partly shown in more detail in Figure 6.7, stretches about 100 km from Southend to its tidal limit at Teddington weir, where it receives an average freshwater discharge of 67 m^3/s from an upstream catchment area of 9900 m^2. Down-estuary there are further inputs from tributaries, waste discharges and storm overflows, especially within the metropolitan area. Taking these into account, the mean freshwater flow to the Thames region is around 80 m^3/s (Institute of Hydrology, 1991). In winter, salt water only just penetrates up to London Bridge, 31.5 km below the tidal limit, but in summer, salinity rises to an average of 1 to 5 in this area, which is also the approximate location of the estuarine turbidity maximum. Mean tidal ranges at Southend vary between 3.3 m (neap) and 5.1 m (spring), increasing riverwards, and the estuary is thus regarded as macrotidal and, in most parts, well mixed (Department of Industrial and Scientific Research, 1964, and Morris, 1988). Within our survey area, the tidal excursion varies between 12 and 16 km (Morris, 1988), and flushing times between 20 and 75 days (Turner et al., 1991).

The outer Thames estuary is a shallow water body with water depth generally less than 20 m, and a bottom topography characterised by a series of sand banks running approximately northeast-southwest. With tidal currents of up to 100 cm/s, the water column is generally well mixed, and salinity ranges typically from 30 to 34.5 (Norton et al., 1981). Residual transport, although strongly affected by changes in the prevailing wind pattern, eventually carries the Thames discharge in a north-easterly direction due to the combined action of the North sea gyre and inflows from the Dover Straits (van Pagee et al., 1989).

For the inner Thames estuary, averaged dissolved trace metal concentrations from the late 1970s have been given in Morris (1988). Highest levels were found to coincide with the turbidity maximum in the central London area, decreasing both towards the tidal limit and the estuary mouth. Estimates of total land-based trace metal inputs to the Thames estuary (ICES-zone E12), made in response to requirements of the Paris commission, have been compiled in Table 6.1 for 1980 (Grogan, 1984) and 1990 (NRA, 1991). A comparison of the two data sets suggests a dramatic decrease of total trace metal inputs from rivers, industrial discharges and sewage outfalls within this decade, but it is not quite clear in how far this is due to improved contamination control during analysis or environmental pollution control measures. The low 1990 data, however, are corroborated by estimates of particle-bound trace metal exports from the Thames estuary, derived from low salinity end member samples taken together with the dissolved samples of this study in February/March 1989, and a general prediction equation for riverine sediment transport (Turner et al., 1991). Total inputs of lead appear to be well balanced by particle-bound exports, whilst less than half the total Zn and only a small fraction of total Cu inputs leave the estuary in particulate form, as one would expect from the differing affinity to the two phases.

	Ni	Cu	Zn	Cd	Pb
Riverine, industrial and sewage inputs to the Thames estuary 1980 (computed from Grogan, 1984) (1)					
tonnes/year	63 to 88	55 to 72	270	16 to 17	44 to 81
Riverine, industrial and sewage inputs to the Thames estuary 1990 (NRA, 1991)					
tonnes/year		7 to 22	120	0.31 to 0.75	4.0 to 8.1
Leachable particulate trace metal export from the Thames estuary to the North sea (Turner et al., 1991)					
tonnes/year	3	3	50		6

(1): Report assumed mean annual freshwater flow of 4028 x 10^6 m^3/year (128 m^3/s)

Table 6.1: Trace metal input estimates for the Thames estuary

Trace metal levels in the outer Thames estuary have been measured in 1976/77 in the Barrow Deep as part of a study investigating the effects of sewage dumping in this area (Norton et al., 1981). In the affected sediments, levels of Ni, Cu, Zn and Pb were five-to-eight fold their background concentrations, together with high organic carbon contents, whilst cadmium appeared to have been lost to the dissolved phase. Suspended sediments also showed strongly elevated values in the dumping area for all elements measured (Ni, Cu, Zn, Cd), and metal-salinity diagrams showed inputs to the dissolved phase, increasing in intensity from Cu via Ni and Zn to Cd. More recent levels of Cd and Pb in the outer Thames estuary have been reported by Harper (1988). There appeared to be inputs of both metals from the inner estuary and the two dumping grounds, with cadmium showing a stronger source in the South Falls area, where a mixture of materials, including dredge-spoil, are being dumped, whilst the sewage-sludge dumping ground in the Barrow Deep appeared to be the more important source of dissolved lead. Another Cd hot spot was found off the River Medway.

6.2 THE DATA BASE

The inner and outer Thames estuary were surveyed in February 1989 during 'Challenger' cruise CH46, and the outer estuary was again sampled for one day at the beginning of cruise CH69 in July 1990. Sampling stations are shown in Figure 6.1, and the data bases for these cruises are given in Appendix VI (CH46) and Appendix VIII (CH69). No tidal correction model was available for this area.

During CH46, a total of 84 samples were taken, which all have been analysed for dissolved, and, to a large proportion, also for particulate trace metals. An anchored tidal station was occupied in the inner Thames estuary, near Gravesend/Tilbury, on 13-14/02/89. Fourteen consecutive samples were taken at hourly intervals, labelled A1 to A14 in the data base. Another twenty-two samples were taken along the inner estuary, with salinity values below 32, coded 'T'. A further fourty-eight samples, with salinities above 32, were taken at 44 'S'-stations in the outer estuary. At one station, S43, four additional 'P'-samples were taken as part of a vertical profile. Nutrient data for this cruise have only recently become available and are not yet included in the data base in Appendix VI.

During CH69, eleven samples were taken on a short leg preceding a Humber plume survey, in order to compare summer and winter distributions. Stations are labelled 'T' and have been included in the CH69 data base in Appendix VIII. All samples have been analysed for dissolved, but not for particulate trace metals.

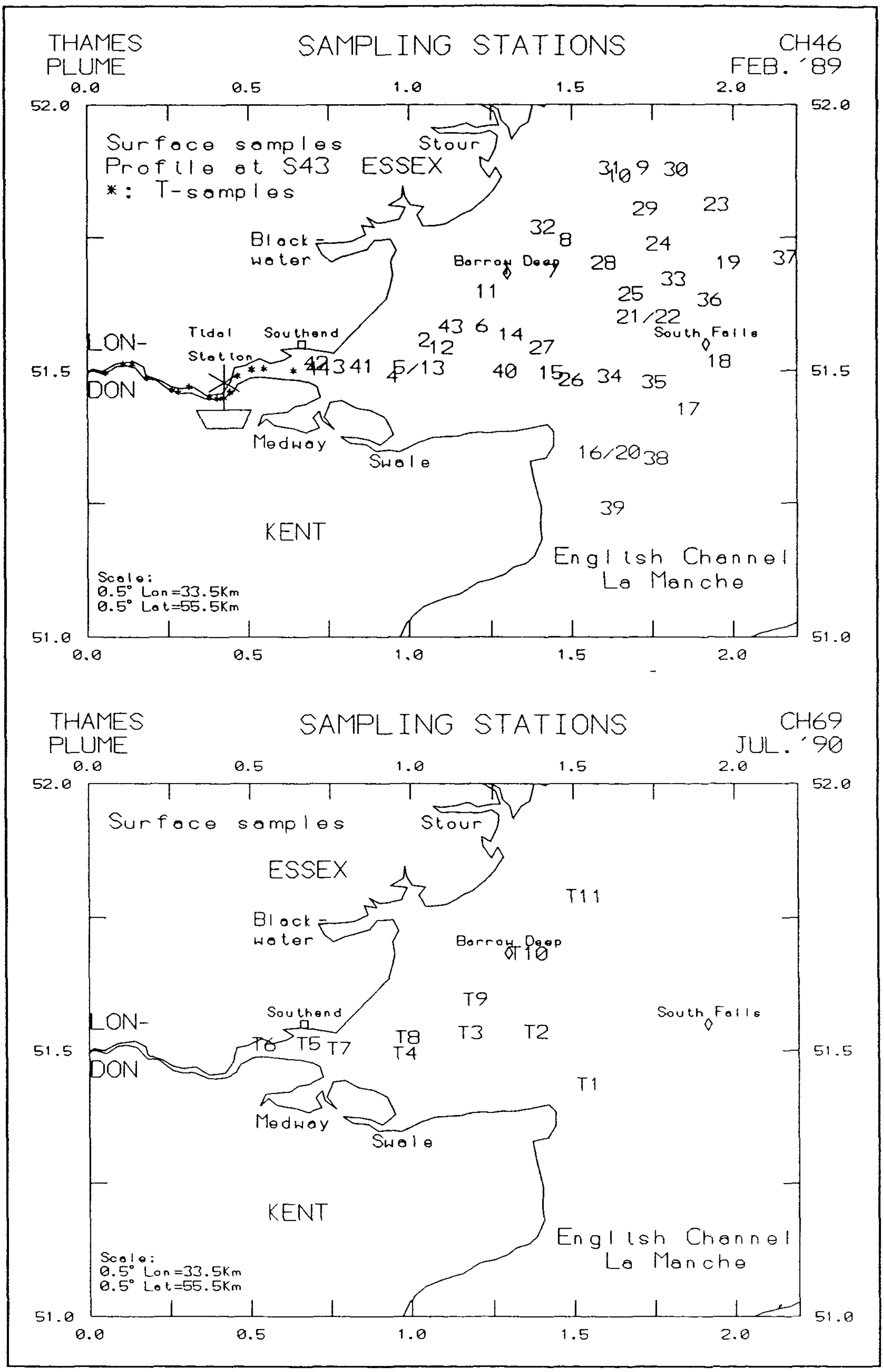

Figure 6.1: Sampling positions within the Thames estuary (CH46 and CH69)

6.3 RESULTS AND DISCUSSION

6.3.1 The General Hydrographic Situation

6.3.1.1 Freshwater input and salinity

Salinity distributions in the outer Thames estuary are shown in Figure 6.2 for both the winter and the summer survey. The 30 days preceding the last sample of the winter cruise had been very dry, with an average freshwater flow of only 31 m^3/s. In summer, the same period was even drier, with a mean freshwater discharge of only 27 m^3/s (Institute of Hydrology, 1991). As the inner estuary widens, salinity increases sharply in a seaward direction. In winter, a large part of the outer estuary shows uniform salinity values between 34.4 and 34.6, with more saline water coming in at the south-eastern flank through the Dover Straits. A group of samples off the Stour estuary again shows decreased salinity values. In the inner estuary, (in more detail in Figure 6.7), salinity decreases up-estuary down to a value of 5 near the Thames Flood Barrier, the sampling location furthest away from the sea. Due to tidal water movement, however, salinity and down-estuarine position do not always correspond. At the tidal station near Tilbury, recorded salinities range from 19.2 just after low water to 25.8 about 90 min after high water (see Figure 6.5), at intermediate tides (range 5.3 m at London Bridge).

In summer, highest salinities are around 35 in the north of the outer estuary, including the Barrow Deep area. Towards the inner estuary, salinities of 29 and 25 have been recorded, but otherwise values appear only slightly increased compared to winter, possibly due to the low freshwater flow preceding both cruises.

6.3.1.2 Suspended particulate matter

Contour plots of SPM concentrations in the outer Thames estuary are given in Figure 6.3 for winter and summer conditions. In winter, highest concentrations were encountered along the Essex coast, including the Barrow Deep dumping ground, and towards the inner estuary. In the southern part of the estuary, concentrations were sometimes lower, but never below 20 mg/l. The apparently convoluted pattern in the area could also be influenced by the sampling, which was at different stages of the tide, and at different depths. SPM concentrations decrease again dramatically towards the North Sea, where levels below 4 mg/l have been found in the high salinity water coming in from the Dover Straits. In the inner estuary, highest particle concentrations (300 mg/l) have been recorded mid-tide at the anchored station near Tilbury, with values decreasing at slack water (Figure 6.5). The estuarine profile also shows elevated levels in the Tilbury area, along with otherwise uniformly low levels around 50 mg/l, except for another smaller peak further up-estuary (Figure 6.7). The cause for this second 'turbidity maximum' at Tilbury (additional to the one reported in the low-salinity region around London Bridge, outside the scope of this study) is not clear.

In summer, SPM concentrations also reach high levels, around 40 mg/l, towards the inner estuary, but not in the Barrow Deep area. Concentrations in the outer estuary decrease seawards, but do not fall below 10 mg/l within the small number of samples.

6.3.1.3 Chlorophyll

Winter and summer chlorophyll concentrations in the outer estuary can be compared in Figure 6.4. In winter highest concentrations are found towards the inner estuary and off the northern coast of Kent. Towards the Essex coast, chlorophyll appears to decrease, coinciding with an increase in turbidity. Towards the North Sea, levels fall below 0.4 mg/m^3. In summer, chlorophyll levels are much higher everywhere, increasing from 1.3 mg/m^3 offshore to around 2 mg/m^3 in the outer estuary and 4.4 mg/m^3 in the least saline sample.

6.3.1.4 Nutrients

Nutrient concentrations have only been shown for the summer cruise CH69, in Figure 6.19 (PO_4, Si) and Figure 6.20 (NO_2, NO_3), plotted against salinity. The outer estuary appears virtually depleted of phosphate and nitrate, despite inputs from the river, but silicate and nitrite are still detectable offshore. Within the estuary, the few available data points suggest almost conservative mixing for phosphate and silicate, and inputs of nitrite and possibly nitrate.

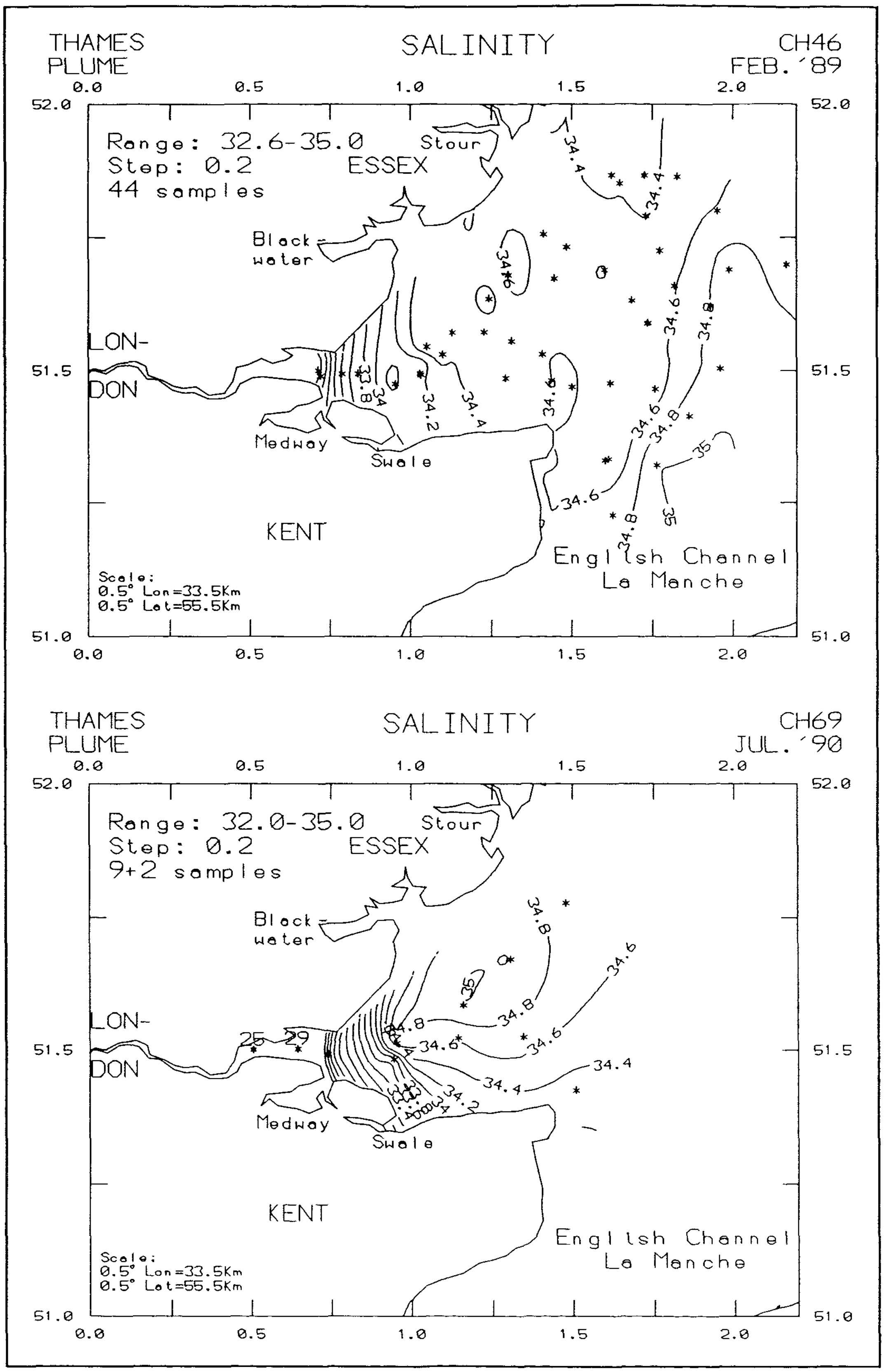

Figure 6.2: Salinity in the outer Thames estuary during CH46 and CH69

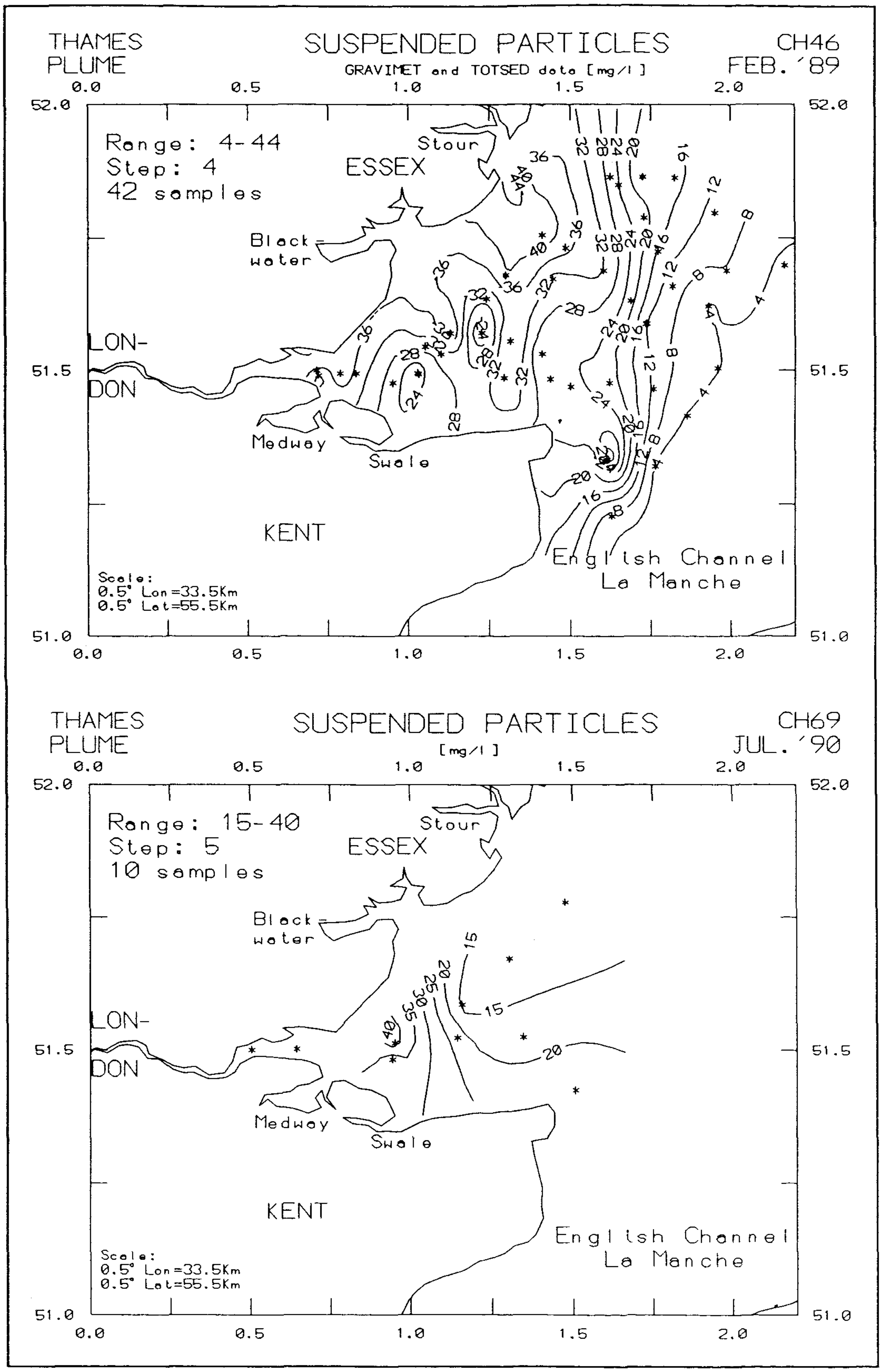

Figure 6.3: Suspended sediment concentrations in the outer Thames estuary during CH46 and CH69

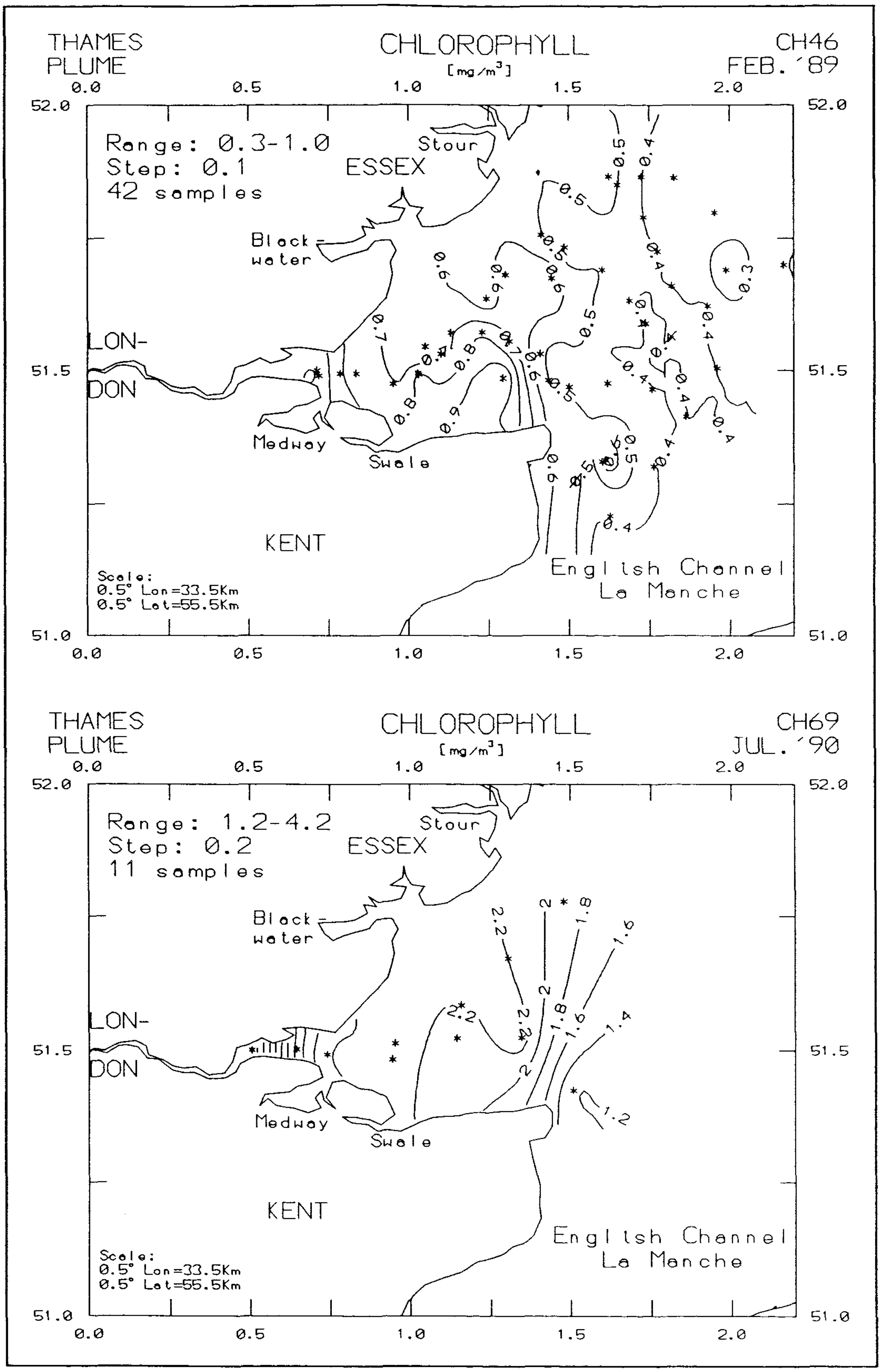

Figure 6.4: Chlorophyll concentrations in the outer Thames estuary during CH46 and CH69

6.3.2 Dissolved Trace Metal Inputs from the Inner Thames Estuary

Dissolved trace metal behaviour in and exports from the inner Thames estuary have been investigated over a whole tidal cycle at the anchored station near Tilbury, covering a salinity range from 20 to 26, and during an estuarine survey, covering the inner estuary between Southend and the Thames Flood Barrier, and salinities from 5 to 32. The time series for the tidal station have been plotted in Figure 6.5 and Figure 6.6. All samples from the inner estuary have been plotted against salinity in Figure 6.7 and Figure 6.8, together with a regression line through the estuarine survey data. Zero-salinity intercepts, an estimate for the effective riverine end member concentration, and other parameters from the linear model fitting procedure are reported in Table 6.2 as 'Inner Estuary' estimates. These models, however, do not take account of processes further up the estuary, e.g. within an assumed turbidity maximum near the freshwater boundary.

6.3.2.1 Manganese

At the tidal station, an increase in salinity by 6 units is reflected only in a very slow decrease in dissolved manganese concentrations; the following ebb, however, leads to a substantial increase in manganese well above the starting level (Figure 6.5). From the given information it does not become clear whether this discrepancy between two consecutive low waters is due to diurnal and possibly anthropogenic effects, linked to an irregular event or just part of the natural variability of the estuarine system. Plotted against salinity in Figure 6.7, most values are well in line with other estuarine samples, although there is a distinct steepening of slope towards the lowest salinities, suggesting additional inputs around low water slack. Between salinities of 7 and 32, the distribution of dissolved manganese along the estuary could be interpreted as the conservative mixing of sea water with estuarine low salinity water of an effective freshwater concentration of 100 nmol/l (Table 6.2), subject to localised inputs west of Tilbury. Including the lower value at the salinity of 5, though, the overall picture looks like a typical benthic input distribution, as described, e.g., by Evans et al. (1977) for the Newport River.

6.3.2.2 Iron

At the tidal station, no clear relationship exists between dissolved iron and salinity, although two minor spikes coincide with the two turbidity peaks at mid-tide. Looking at the inner estuary as a whole, however, iron seems to behave fairly conservatively, indicating an effective river end member concentration of 350 nmol/l. Compared to this mixing line, values at the turbid tidal station appear to be rather low, and there are further indications of a negative correlation between dissolved Fe and SPM concentrations in the high turbidity area around Tilbury, apparently in contrast with the observed minor releases at mid-tide.

6.3.2.3 Nickel

At the tidal station, changes in dissolved nickel concentrations can only partly be explained by changes in salinity, since there appear to be additional reductions around mid-tide. However, the highest concentration coincides with the highest turbidity value for the ebbing tide. Data from the entire inner estuary suggest conservative mixing seawards of a salinity of 12, possibly following additional inputs between Greenwich and Tilbury, and an effective freshwater concentration of about 260 nmol/l.

6.3.2.4 Cobalt

Over the tidal cycle, Co levels develop similarly to those of manganese: there is no strong decline before the minimum reached at peak salinity, but levels increase substantially towards the second LW. Concentrations are in fairly good agreement with the conservative mixing line based on values from sites along the entire inner estuary. The effective riverine end member concentration is 7.2 nmol/l

6.3.2.5 Copper

At the tidal station, dissolved Cu concentrations broadly follow the inverse of the salinity curve, but again reach higher concentrations during the second LW (Figure 6.6). Like nickel, the maximum reading coincides with the turbidity maximum of the ebb stream. The analytical results conducted as part of this study have been confirmed by ASV-measurements. Results from this method, measuring only electroactive dissolved copper, fall generally below the AAS determinations. This difference becomes more apparent in the later part of the tidal cycle, suggesting that a high proportion of the increased levels around the second low water is complexed dissolved copper. Looking at the entire estuarine profile (Figure 6.8), copper concentrations seem to conform to an almost conservative mixing line with a zero-salinity intercept of 120 nmol/l (Table 6.2).

6.3.2.6 Zinc

Zinc concentrations at the tidal station are mainly controlled by changes in salinity, again with higher levels being attained around the second LW. Throughout the inner estuary, dissolved Zn more or less follows a linear relationship with salinity, with deviations centred in the Tilbury area. The effective freshwater end member concentrations is 650 nmol/l.

6.3.2.7 Cadmium

Throughout the tidal cycle at Tilbury, Cd concentrations show no clear pattern relating to salinity or SPM, in agreement with the results from the ASV measurements. Within the inner estuary, mixing seems to be conservative seawards of a salinity of 15, with an intercept of 2.3 nmol/l (Table 6.2), but the mixing line apparently levels out towards the upper reaches.

6.3.2.8 Lead

At the tidal station, lead concentrations are highest after the first low water. Levels the decrease as more saline water comes in, and rise again slightly towards the second LW. Throughout the inner estuary, dissolved lead levels rise fairly conservatively towards the central London area, indicating at a freshwater-associated concentration of as much as 20 nmol/l (Table 6.2).

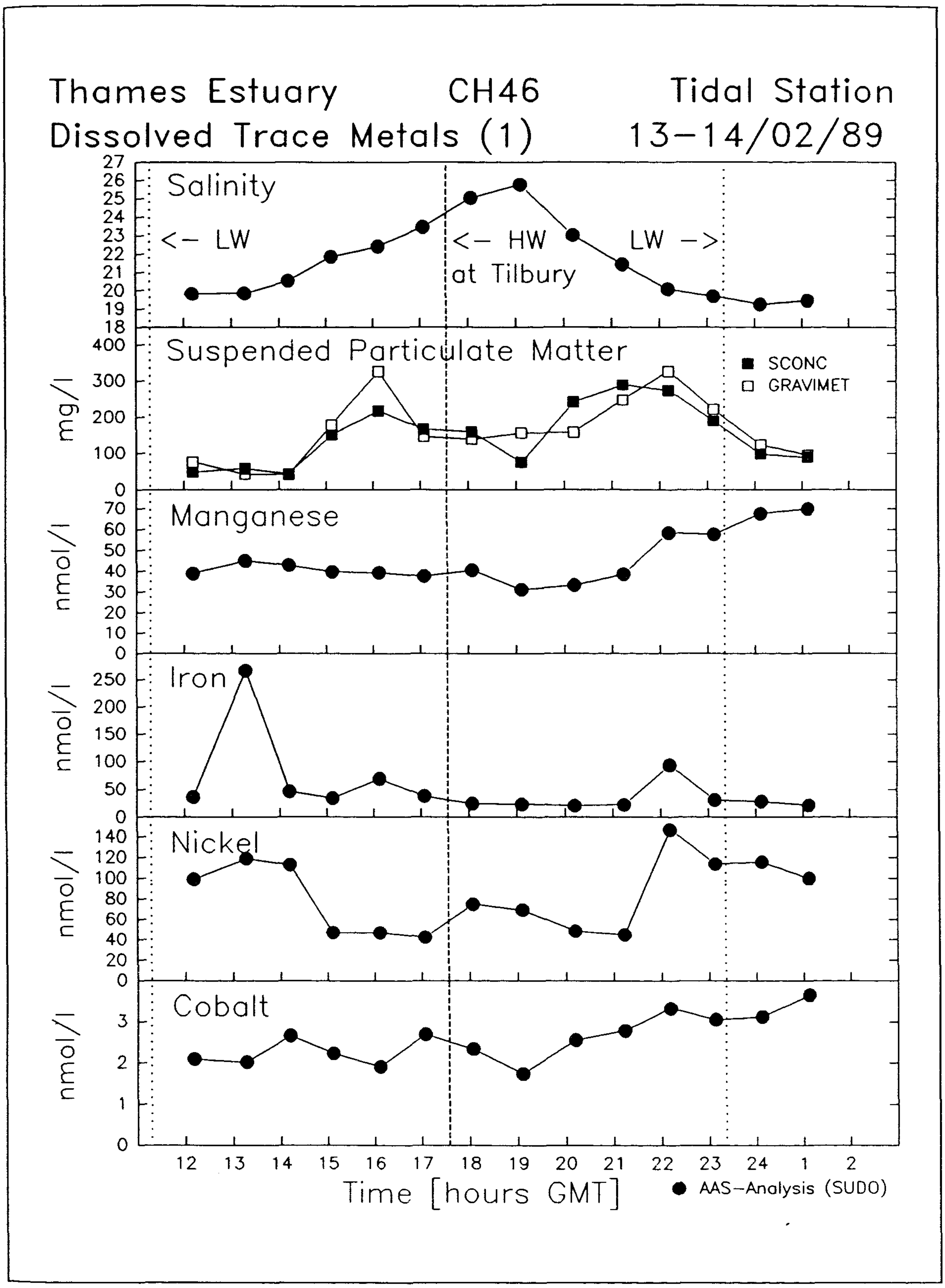

Figure 6.5: Time series of dissolved Mn, Fe, Ni and Co in the Thames estuary (CH46)

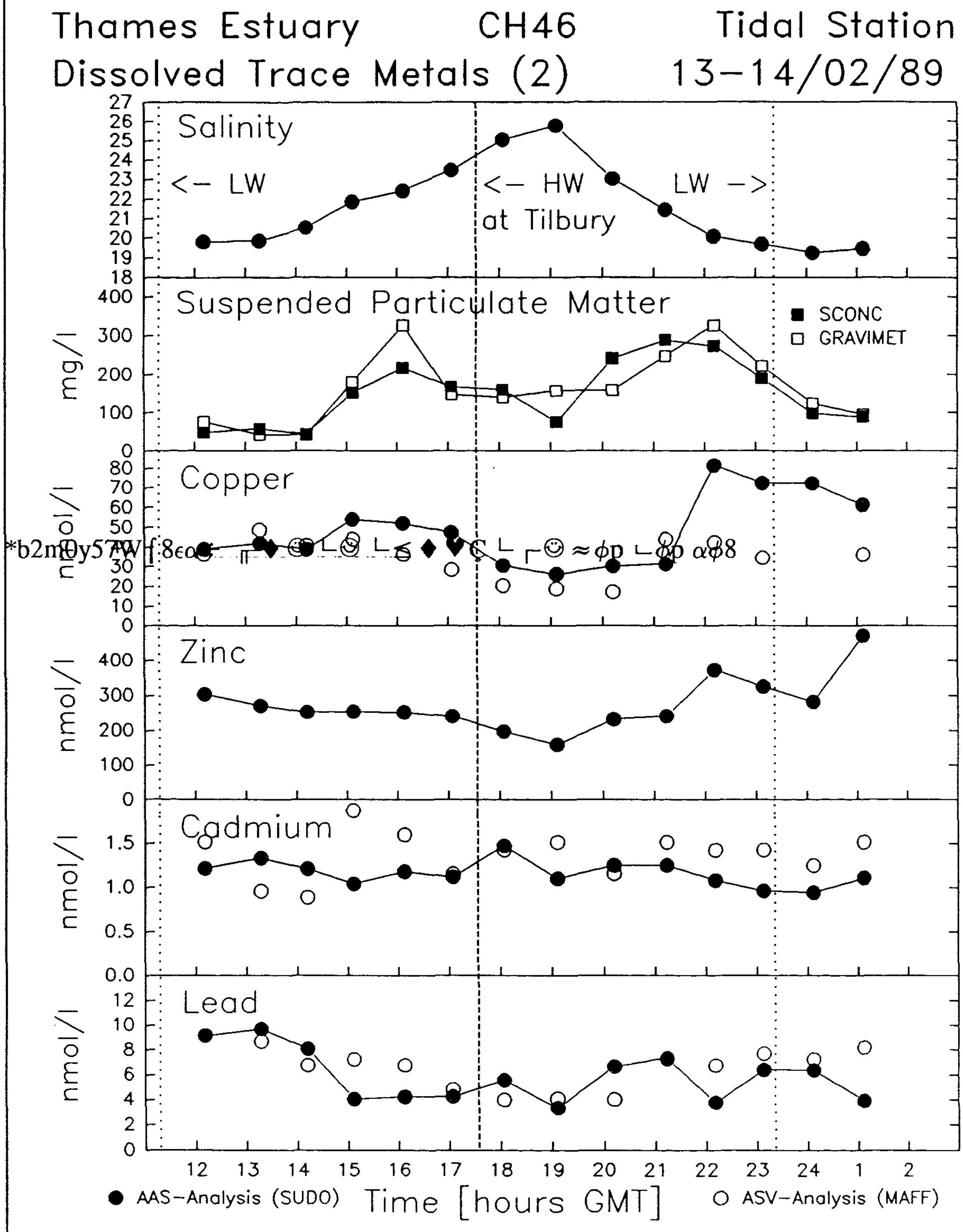

Figure 6.6: Time series of dissolved Cu, Zn, Cd and Pb in the Thames estuary (CH46)

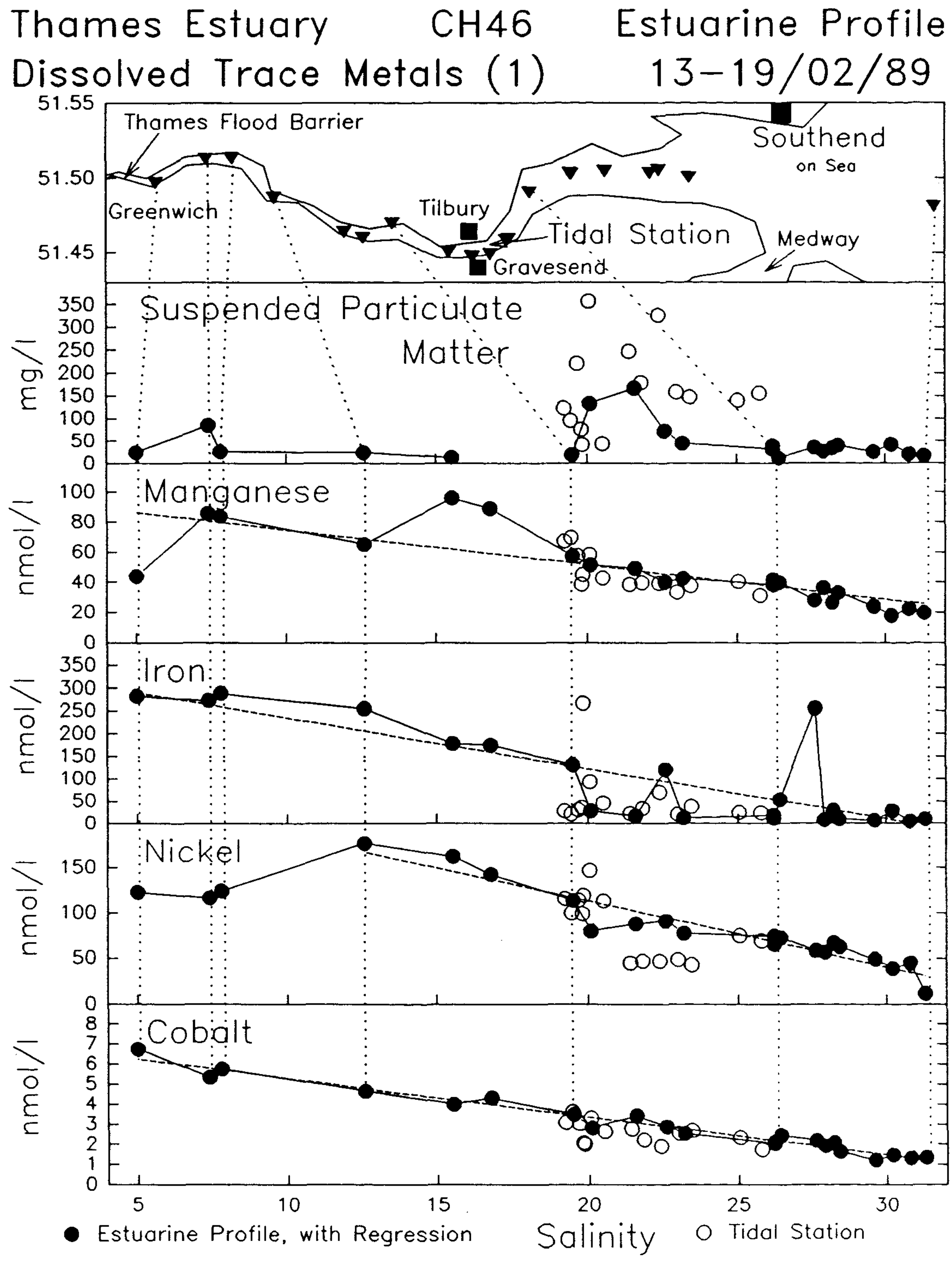

Figure 6.7: Dissolved conentrations of Mn, Fe, Ni and Co in the inner Thames estuary (CH46)

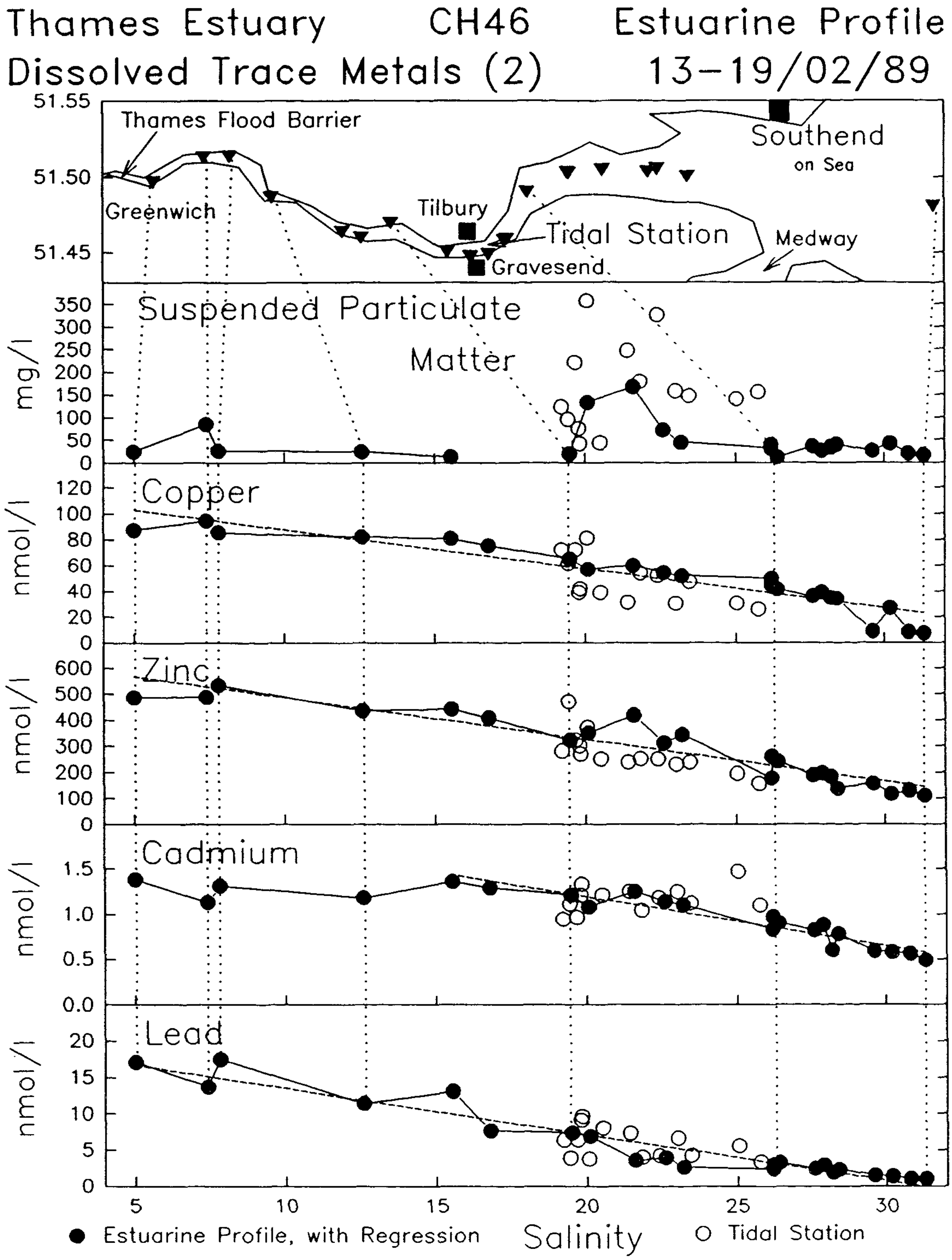

Figure 6.8: Dissolved concentrations of Cu, Zn, Cd and Pb in the inner Thames estuary

	Thames	n	Intercept [nmol/l]	Slope	Significance	Corr. Coeff.	R^2
Mn	Inner Estuary Feb '89	22	100±9	-2.3±0.4	0.00001	-0.79	63%
	Outer Estuary Feb '89	44	150±51	-4.3±0.6	0.00000	-0.74	54%
	Mid-Estuary July '90	11	90±14	-2.4±0.4	0.00039	-0.88	77%
Fe	Inner Estuary Feb '89	22	350±40	-11±2	0.00000	-0.82	68%
	Outer Estuary Feb '89	42	100±51	-2.7±1.5	0.07357	-0.28	8%
	Mid-Estuary July '90	10	83±69	-2.1±2.1	0.35148	-0.33	11%
Ni	Inner Estuary Feb '89	19	260±14	-7.3±0.6	0.00000	-0.96	91%
	Outer Estuary Feb '89	43	300±20	-8.3±0.6	0.00000	-0.91	83%
	Mid-Estuary July '90	11	270±16	-7.4±0.5	0.00000	-0.98	97%
Co	Inner Estuary Feb '89	22	7.2±0.2	-0.19±0.01	0.00000	-0.99	97%
	Outer Estuary Feb '89	43	11±2	-0.32±0.05	0.00000	-0.73	53%
	Mid-Estuary July '90	10	8.8±0.8	-0.23±0.02	0.00001	-0.96	93%
Cu	Inner Estuary Feb '89	22	120±6	-3.0±0.3	0.00000	-0.94	88%
	Outer Estuary Feb '89	39	330±46	-9.2±1.3	0.00000	-0.75	56%
	Mid-Estuary July '90	11	200±13	-5.5±0.4	0.00000	-0.98	96%
Zn	Inner Estuary Feb '89	22	650±30	-16±1	0.00000	-0.94	89%
	Outer Estuary Feb '89	43	1000±70	-30±2	0.00000	-0.92	85%
	Mid-Estuary July '90	11	870±31	-25±1	0.00000	-0.99	99%
Cd	Inner Estuary Feb '89	18	2.3±0.1	-.055±.004	0.00000	-0.95	90%
	Outer Estuary Feb '89	44	3.4±0.5	0.09±0.01	0.00000	-0.73	53%
	Mid-Estuary July '90	11	4.7±0.1	-.130±.004	0.00000	-0.996	99%
Pb	Inner Estuary Feb '89	22	20±1	-0.64±0.04	0.00000	-0.97	93%
	Outer Estuary Feb '89	44	8.2±0.7	-0.23±0.02	0.00000	-0.88	77%
	Mid-Estuary July '90	11	6.1±0.3	-0.17±0.01	0.00000	-0.99	98%

Table 6.2: Regression of dissolved trace metal concentrations against salinity for different data sets from the Thames estuary

6.3.3 Trace Metals in the Outer Thames Estuary

Contour plots of trace metal distributions in the outer Thames estuary are given in Figure 6.9 to Figure 6.16 for both winter (based on 44 samples) and summer (based on a restricted grid of only 11 samples). Trace metal concentrations have been plotted against salinity in Figure 6.17 and Figure 6.18 for the winter and in Figure 6.19 and Figure 6.20 for the summer cruises. Parameters for the linear regression model, including the zero salinity intercept, are given in Table 6.2. Samples from the winter cruise cover a salinity range from 32 to 35 and originate mainly from the outer estuary; the model is therefore labelled 'Outer Estuary'. Regression of the summer data, however, is dominated by two samples with salinities of 25 and 29, respectively, and the linear model is therefore primarily a reflection of mixing at the low salinity end of the outer estuary, near Southend, and labelled here 'Mid-Estuary'.

6.3.3.1 Manganese

Apart from a patch of lower salinity water in the north of the survey area, dissolved manganese concentrations in winter are below 3 nmol/l in the eastern outer estuary, but rise fairly steadily towards the inner estuary (Figure 6.9). Effective riverine end member concentrations, estimated to be around 150 nmol/l freshwater (Table 6.2), with a large margin of error, thus certainly dominate the distribution around the river mouth, but offshore other processes lead to a lot of scatter in the metal-salinity plot (Figure 6.17). In summer, highest concentrations are again found in the inner estuary, but offshore concentrations are higher than in winter, never falling below 5 nmol/l, and with more than 14 nmol/l in the Barrow Deep area. This seasonal feature has been confirmed by further, North Sea-wide surveys, showing winter levels below 3 nmol/l and summer levels above 10 nmol/l for offshore samples from the Thames plume (Tappin, pers. comm.). The mixing line in Figure 6.19 suggests an export from the inner estuary of 90 nmol/l freshwater, in fairly good agreement with the inner estuary estimate in winter.

6.3.3.2 Iron

In winter, elevated concentrations (> 10 nmol/l) are found off the estuaries of the Medway and the Swale, in the Barrow Deep dumping ground and within a series of stations stretching NE from the tip of the Kent coast, with iron-depleted highly saline Channel water coming in at its flank. In summer, elevated concentrations are associated with the inner estuary and one station off the Blackwater estuary. There is one outlier above 100 nmol/l in each data set, and concentrations did not correlate significantly with salinity in either winter or summer.

6.3.3.3 Nickel

The distribution of nickel in the outer Thames estuary is clearly dominated by the riverine source. In winter, background concentrations in the saline Channel water are around 4 nmol/l, and levels rise quite conservatively towards levels around 30 nmol/l in the river mouth. A single high value of 31 nmol/l has been recorded for the Barrow Deep sewage dumping ground. In summer, the much smaller sampling grid more or less reconfirms the winter distribution. The mid-estuarine mixing model suggest an effective river end member concentration of 270 nmol/l, comparable to the 260 nmol/l from the inner estuary and only just below the estimated 300 nmol/l for the outer estuary, indicating, if at all, only minor inputs to the dissolved phase, as the water moves offshore.

6.3.3.4 Cobalt

Dissolved cobalt distributions in the outer Thames estuary, similarly to manganese, are essentially the result of a river-sea water mixing process subject to offshore modifications. In winter, concentrations decrease from 0.8 nmol/l near the inner estuary to 0.2 nmol/l, already below the detection limit, in the highly saline waters in the Channel. A patch of elevated concentrations in the North is again related to freshwater concentrations influence, and a single high value of 1.0 nmol/l has been found in the Barrow Deep dumping area. In summer, concentrations in the central outer plume have risen from 0.5 to 0.8 nmol/l, a seasonal feature confirmed by other, North Sea-wide surveys (Tappin, pers. comm.), and the effective riverine end member concentration of 8.8 nmol/l lies between the winter estimates for the inner (7.2 nmol/l) and outer estuary (11 nmol/l), indicating steady inputs to the dissolved phase as the water is discharged into the North Sea (which is not the case for manganese).

6.3.3.5 Copper

Copper distributions in both summer and winter are dominated by conservative mixing. In winter, concentrations decrease from 15 to around 11 nmol/l in the central outer estuary, an area separated from the more saline Channel water, where levels are as low as 5 nmol/l, by a strong gradient almost amounting to a frontal feature. Levels in the Barrow Deep are slightly elevated (13 nmol/l) above neighbouring stations. The two samples closest to the river mouth, however, were unexpectedly low, although, as is known from the survey of the inner estuary, levels there rise normally with decreasing salinity. The linear model has therefore been fitted only to the samples with a salinity above 34, indicating an effective freshwater concentration estimate of 330 nmol/l, nearly three times as much as the estimate for the inner estuary, and a strong indication of additional inputs to the dissolved phase within the outer estuary. Data from the summer survey more or less confirm the winter distribution in the outer estuary, and the zero-salinity intercept of 200 nmol/l for the mid-estuary is well in line with the two winter estimates (Table 6.2).

6.3.3.6 Zinc

Dissolved zinc concentrations follow the salinity distribution, with levels rising from background concentrations of 12 nmol/l in the Channel to 80 nmol/l in the inner estuary. The freshwater estimate of 1000 nmol/l is well above the 650 nmol/l calculated for the inner estuary, indicating the existence of further sources of dissolved zinc in the area. A single elevated value of 49 nmol/l was found off the Essex coast. In summer, concentrations in the outer estuary seem to be only about half their winter levels, possibly due to biological uptake, and the mid-estuarine export estimate of 870 nmol/l freshwater falls well between the inner and outer estuary figures. Decreased summer levels have also been found by other surveys off the Thames estuary (Tappin, pers. comm.).

6.3.3.7 Cadmium

Dissolved cadmium distributions are also dominated by riverine inputs, with levels in winter rising from background concentrations of 0.16 nmol/l in the Channel to 0.4 nmol/l near the inner estuary. Two elevated values are reported offshore, and there is a considerable amount of scatter around the conservative mixing line. The linear model assumes a freshwater end member concentration of 3.4 nmol/l, well above the inner estuary estimate of 2.3, suggesting further dissolved inputs, and this is even not fully representative of the apparently steeper slope at the high salinity end. Although dissolved concentrations in the central outer plume appear to be decreased in summer, from 0.24 to 0.16 nmol/l, possibly due to biological uptake, the mid-estuarine end member estimate of 4.7 nmol/l is markedly higher than the winter estimate for the outer estuary.

With regard to background levels and the rising concentrations towards the river, there is good agreement with the findings by Harper (1988). However, this study did not encounter exceptionally high concentrations off the River Medway, nor in the Barrow Deep or South Falls dumping grounds.

6.3.3.8 Lead

Dissolved lead concentrations rise from background levels of below 0.12 nmol/l to concentrations above 0.6 nmol/l towards the inner estuary. The linear mixing model assumes a freshwater concentration of 8.2 nmol/l, less than half the 20 nmol/l derived from the conservative mixing within the inner estuary; an indication for substantial estuarine losses of lead from the dissolved phase. In the Barrow Deep, a concentration of 1.0 nmol/l was recorded. The summer data show a distribution very similar to the winter survey, with one outlier off Kent, and an effective freshwater concentration of 6.1 nmol/l.

With respect to background levels, the rise in concentrations towards the river mouth and also the high concentration found in the Barrow Deep sewage dumping ground, this study is in good agreement with the earlier findings by Harper (1988).

6.3.3.9 Vertical distribution

A single vertical profile was sampled during the winter cruise CH46 at station S43 in the inner Barrow Deep, about 17 km south-west of the sewage dumping ground. Samples were taken on 17/02/89 at 21:00 h in 5, 8, 12, 15 and 17 m water depth (see Appendix VI) on a flooding tide, two days after neaps. Although the water column shows a uniform salinity of 34.5, there is a sudden rise in SPM from 26 mg/l in the uppermost to above 40 mg/l in all underlying samples, together with a steady, but minor increase in chlorophyll, from 0.5 mg/m^3 in the top to 0.9 mg/m^3 in the bottom sample, both possibly due to the tidal resuspension of sediments. The 8 m sample was chosen to represent the station in contour plots, in line with other CTD-samples. Dissolved trace metal values from this water depth were generally in good agreement with those from neighbouring sites. There was, however, considerable variation within the water column for all metals except Co. Concentrations in the 5 m sample were elevated in Cu, Zn and Pb. Highest concentrations, however, were found in the 12 m sample: compared to the 8 m sample, Cu was elevated by 25%, Ni by 30% and Cd by 50%, and Pb showed a six-fold and Zn an eight-fold increase. In the two bottom samples, however, most metals were again found in their expected concentrations, although SPM concentrations remained high, and there is thus some doubt about whether the elevated levels are a result of sedimentary release, or whether they are an artifact. The vertical profile certainly shows, however, that the estuarine water body is not necessarily well mixed with regard to SPM or dissolved trace metal concentrations.

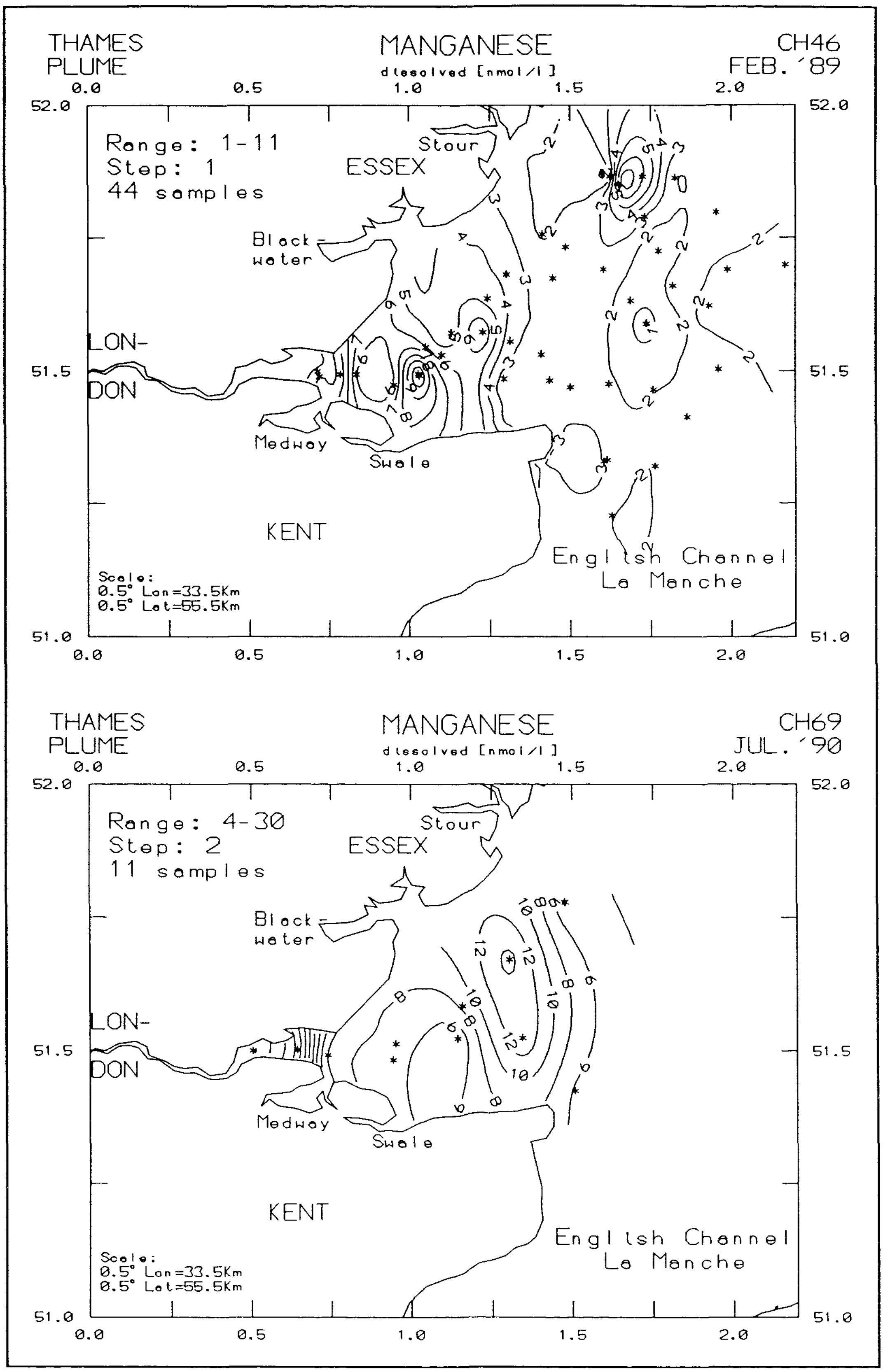

Figure 6.9: Dissolved manganese distributions in the Thames estuary in winter and summer (CH46 and CH69)

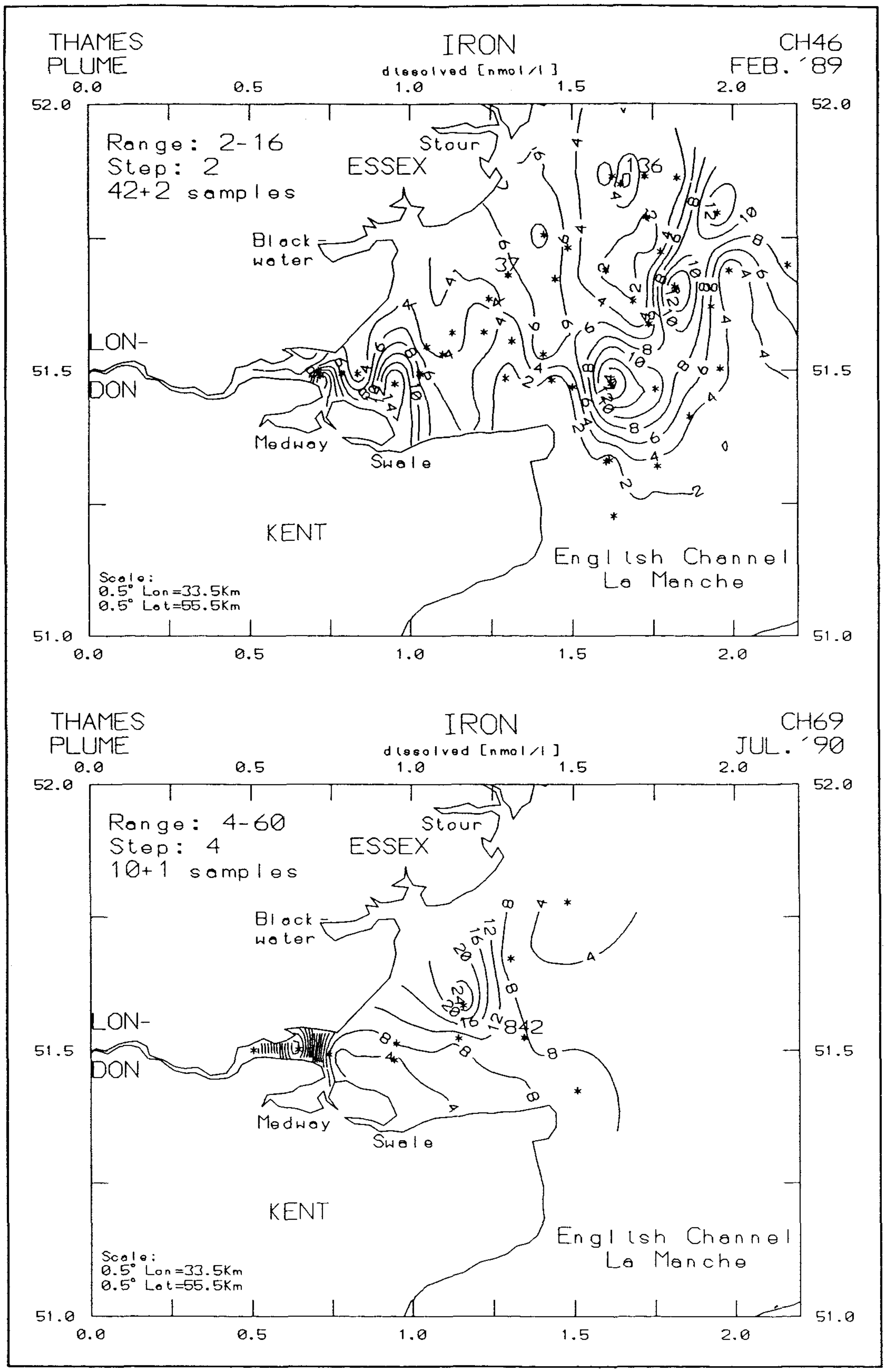

Figure 6.10: Dissolved iron distributions in the Thames estuary in winter and summer (CH46 and CH69)

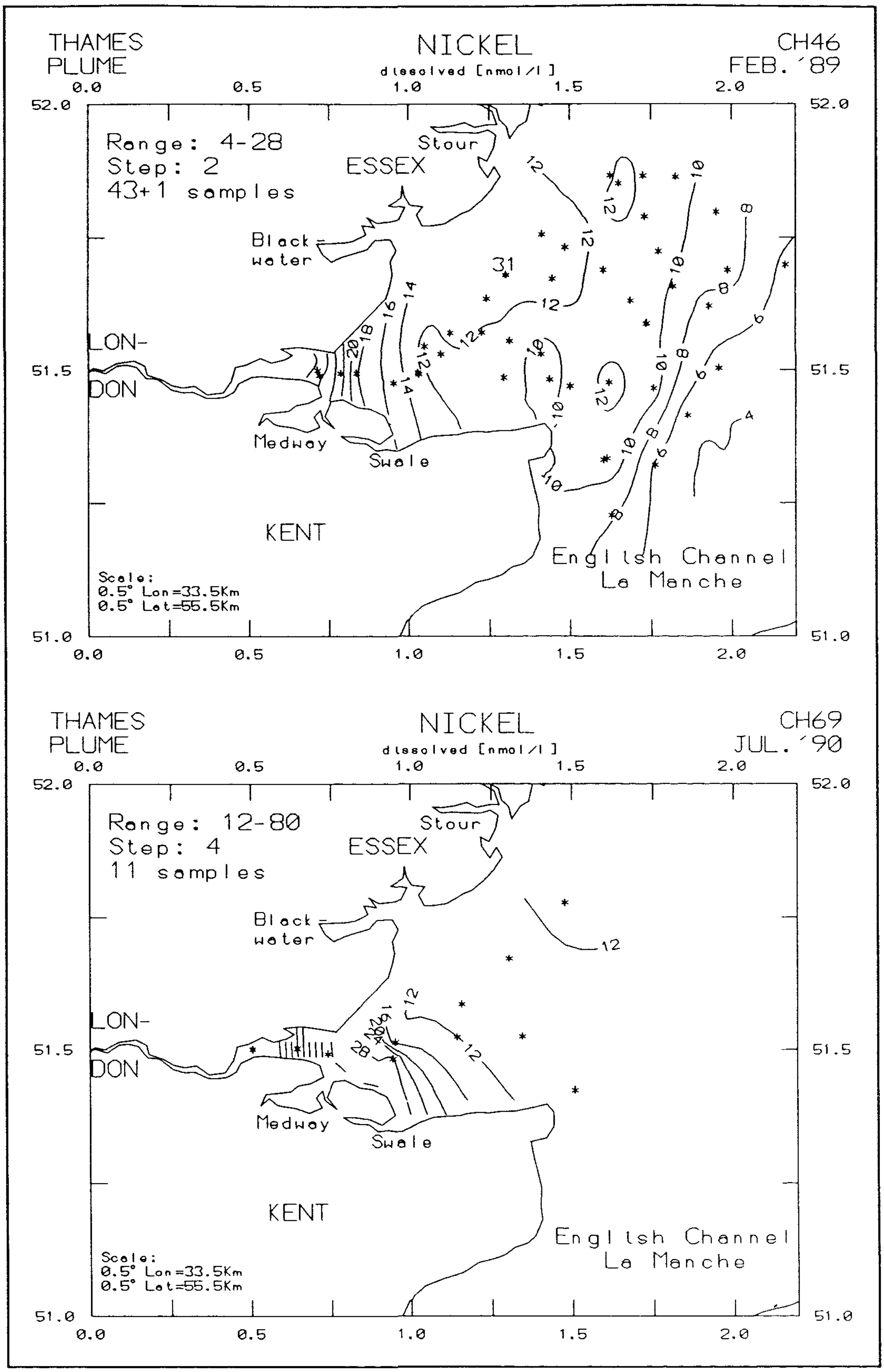

Figure 6.11: Dissolved nickel distributions in the Thames estuary in winter and summer (CH46 and CH69)

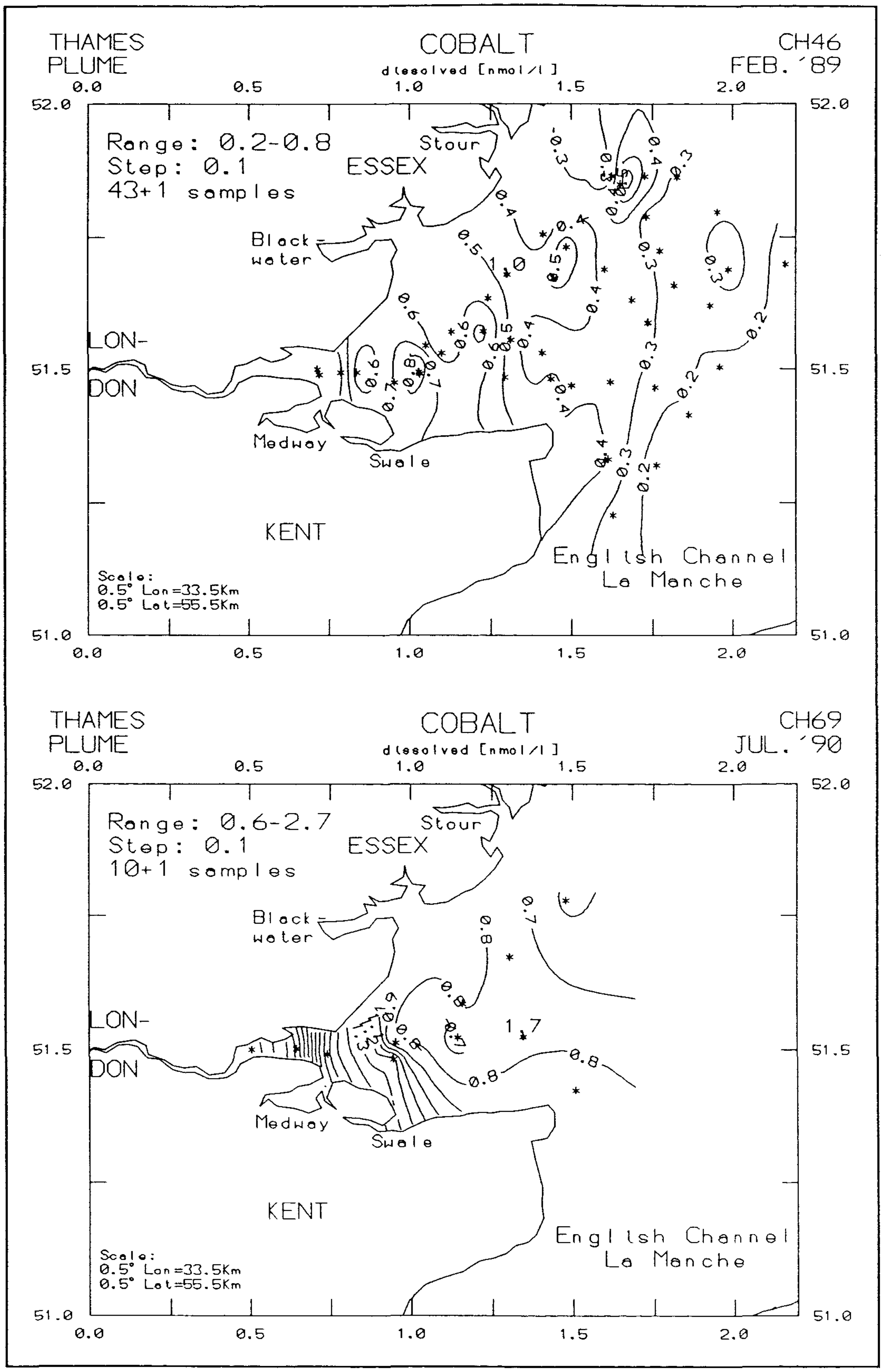

Figure 6.12: Dissolved cobalt distributions in the Thames estuary in winter and summer (CH46 and CH69)

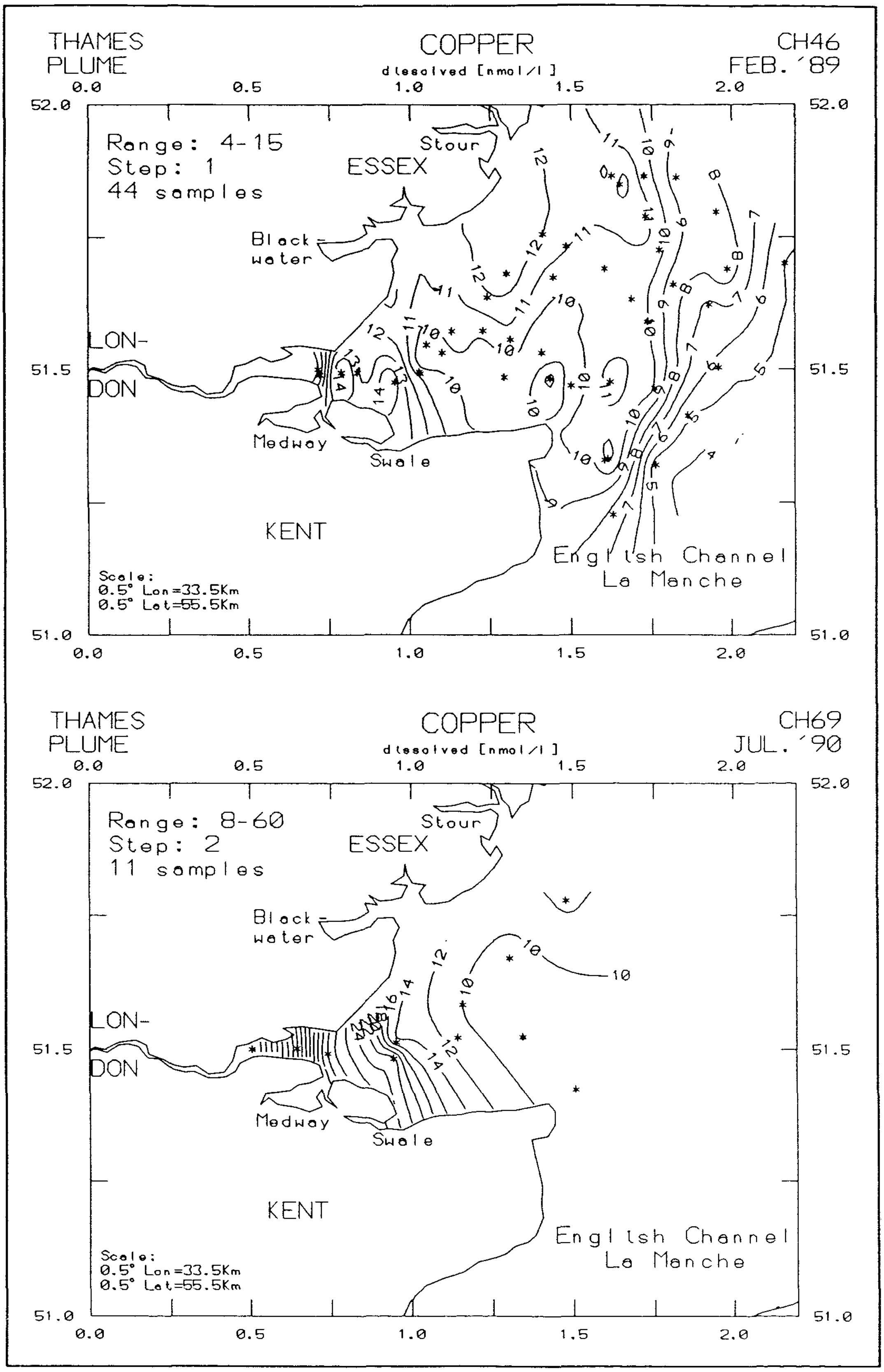

Figure 6.13: Dissolved copper distributions in the Thames estuary in winter and summer (CH46 and CH69)

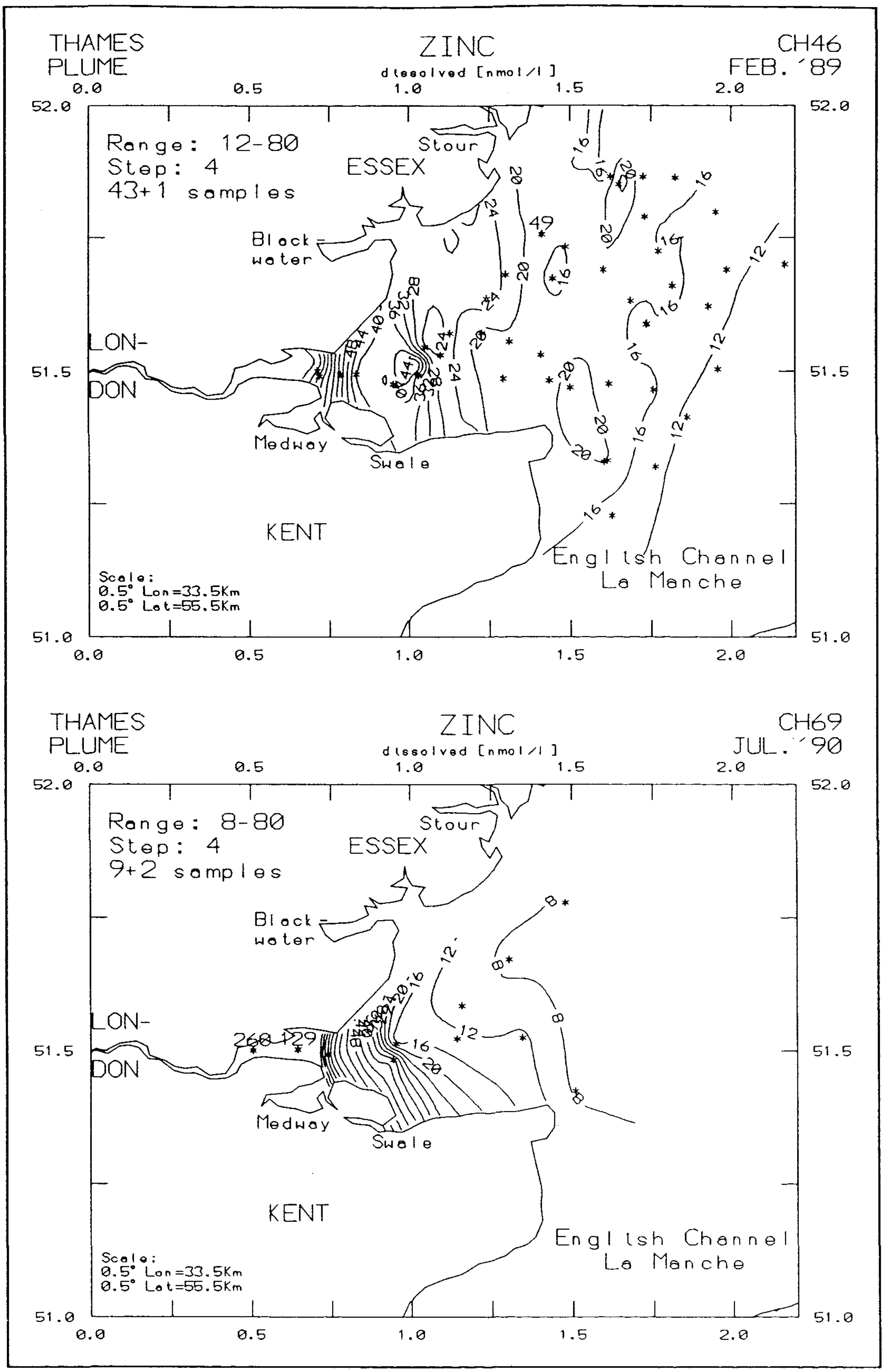

Figure 6.14: Dissolved zinc distributions in the Thames estuary in winter and summer (CH46 and CH69)

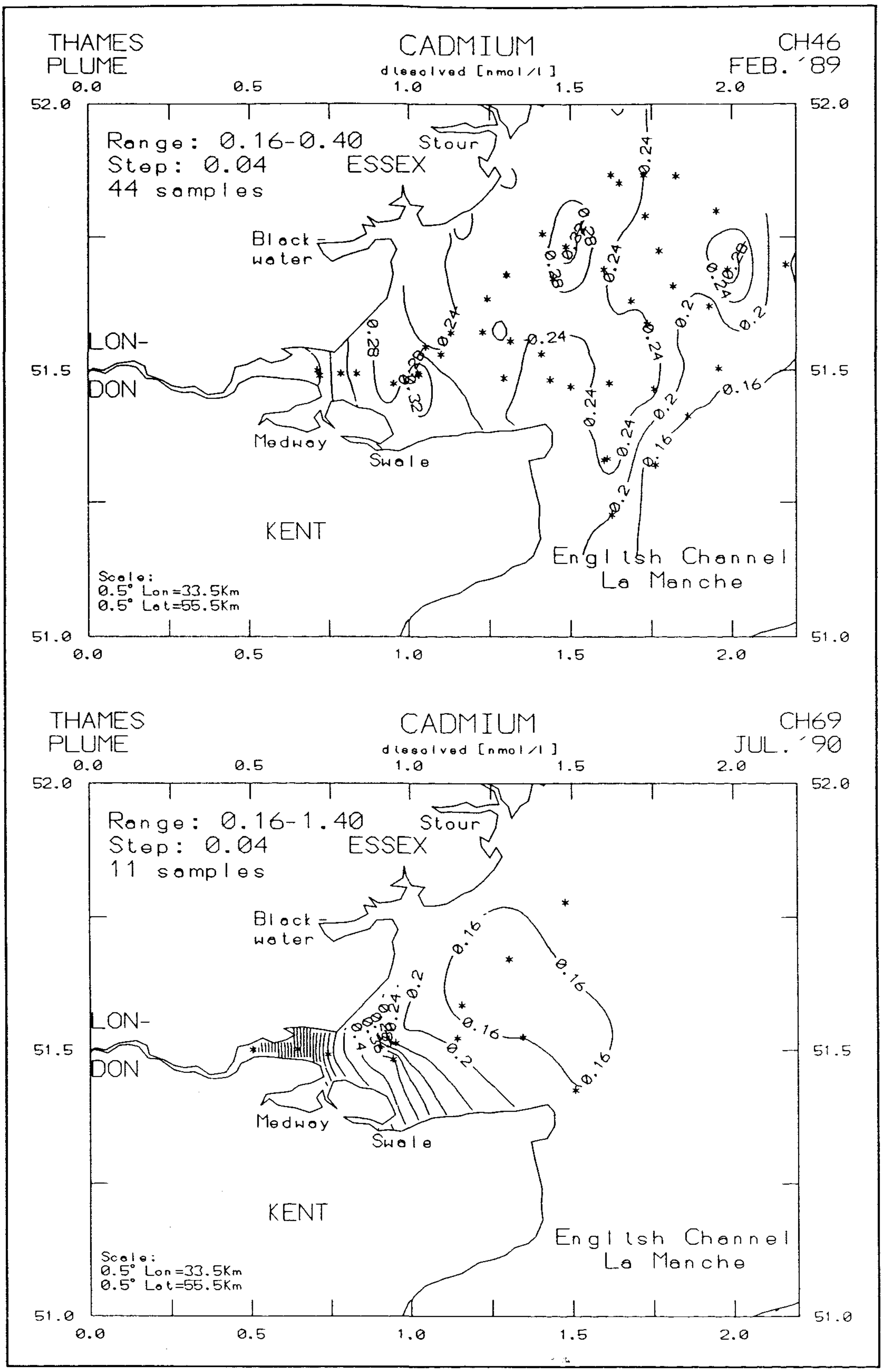

Figure 6.15: Dissolved cadmium distributions in the Thames estuary in winter and summer (CH46 and CH69)

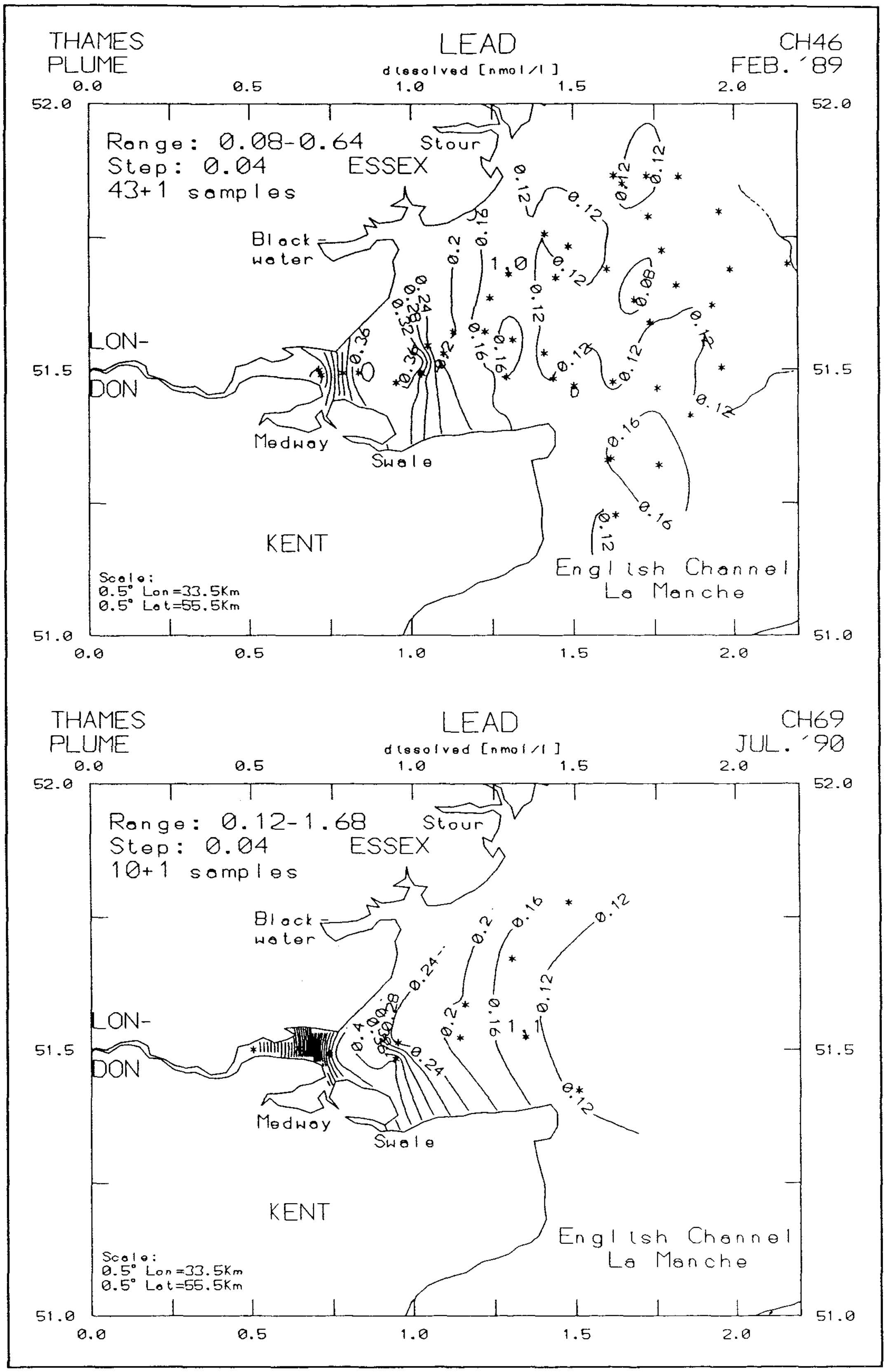

Figure 6.16: Dissolved lead distributions in the Thames estuary in winter and summer (CH46 and CH69)

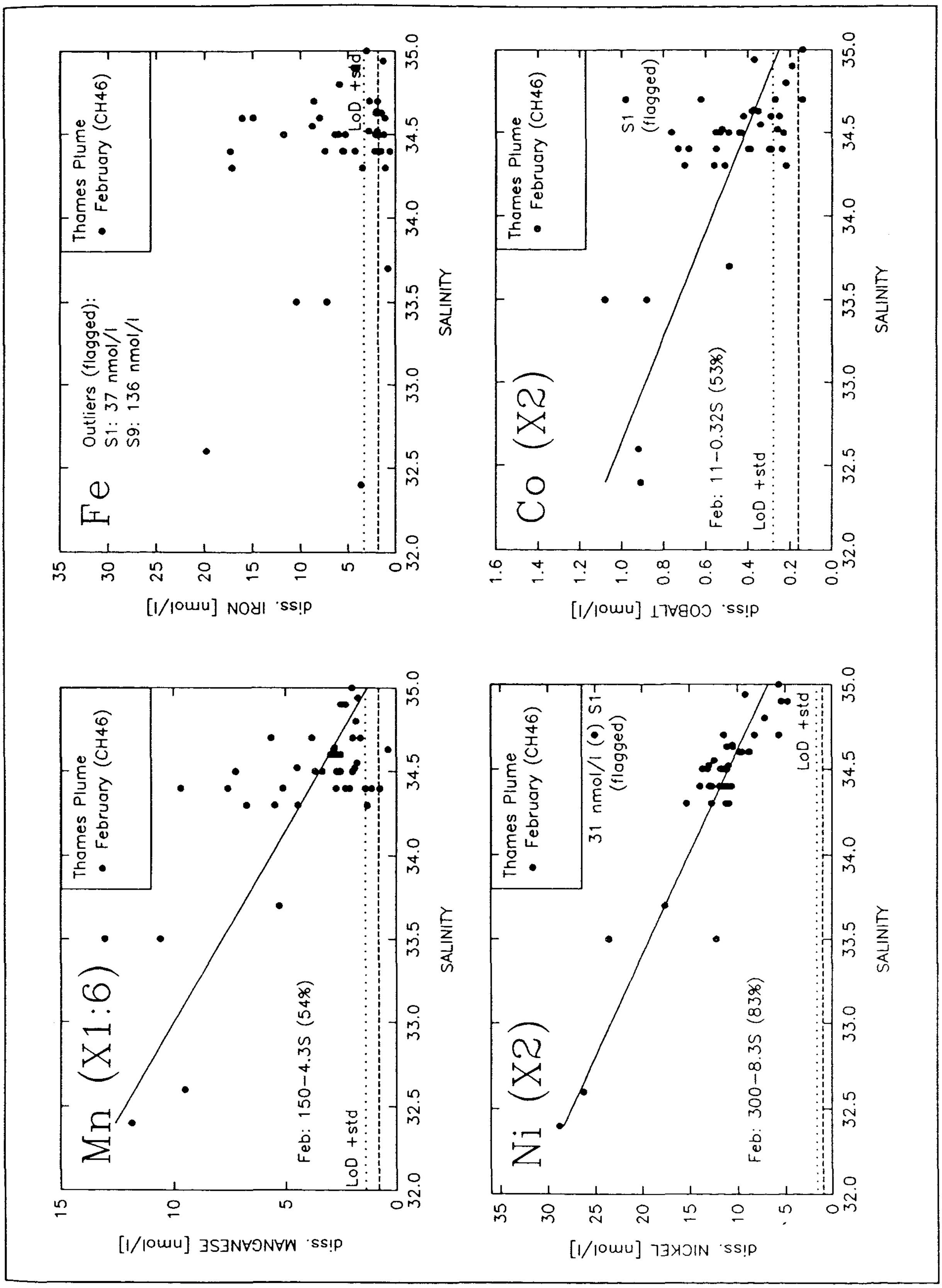

Figure 6.17: Dissolved trace metal-salinity plots for Mn, Fe, Ni and Co in the Thames plume (CH46)

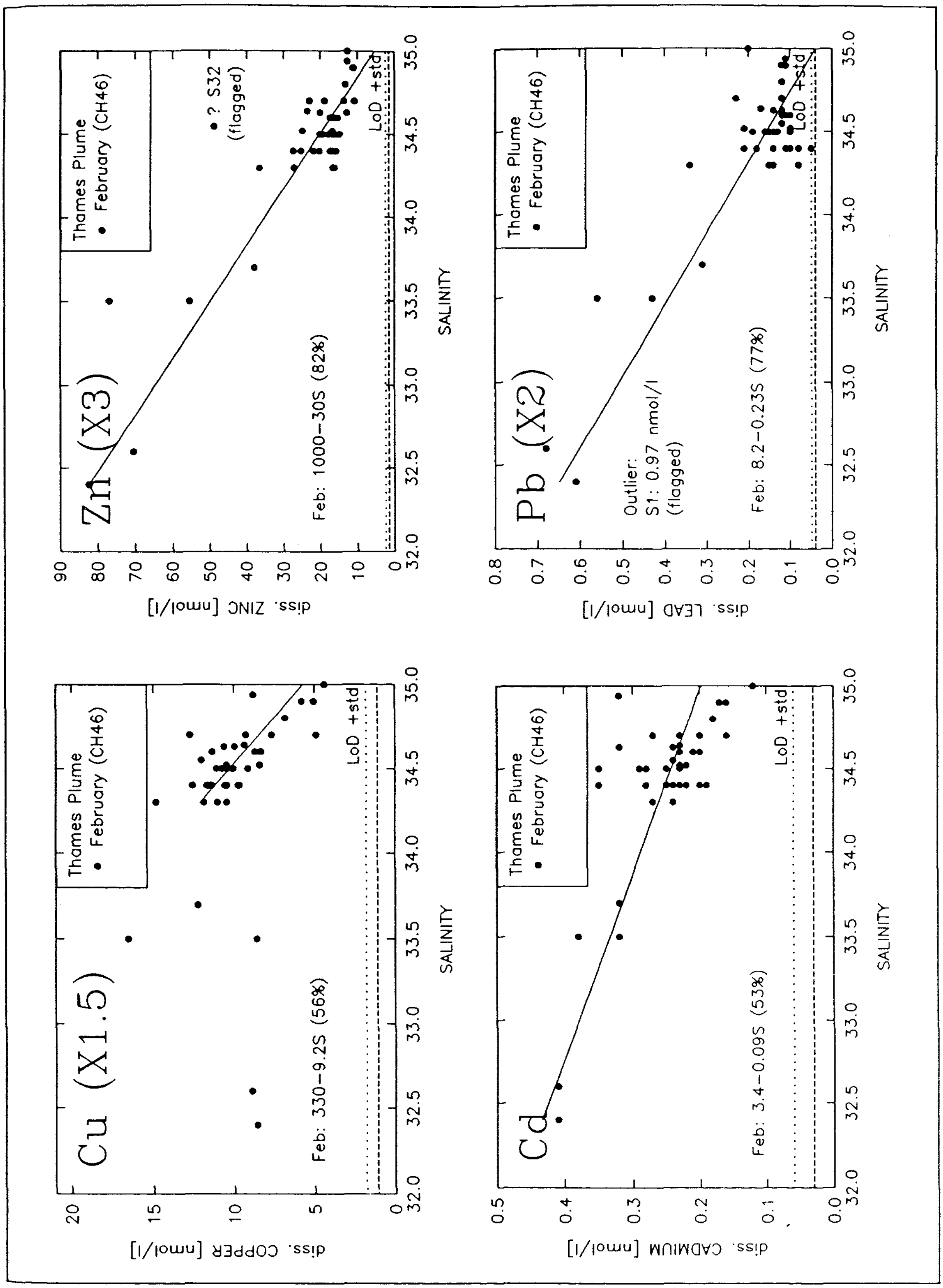

Figure 6.18: Dissolved trace metal-salinity plots for Cu, Zn, Cd and Pb in the Thames plume (CH46)

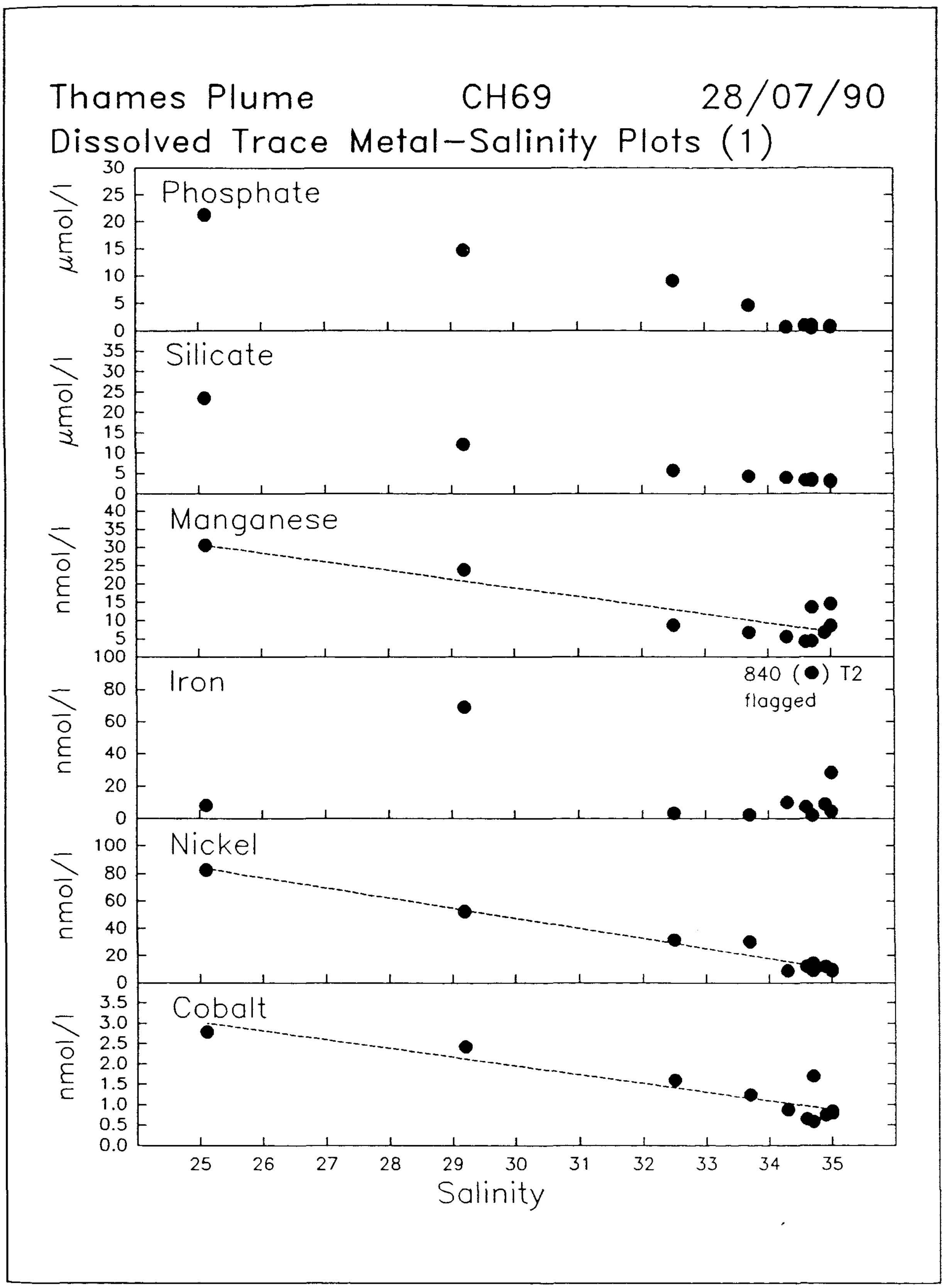

Figure 6.19: Plots of PO_4, Si and dissolved Mn, Fe, Ni and Co concentrations in the Thames plume against salinity (CH69)

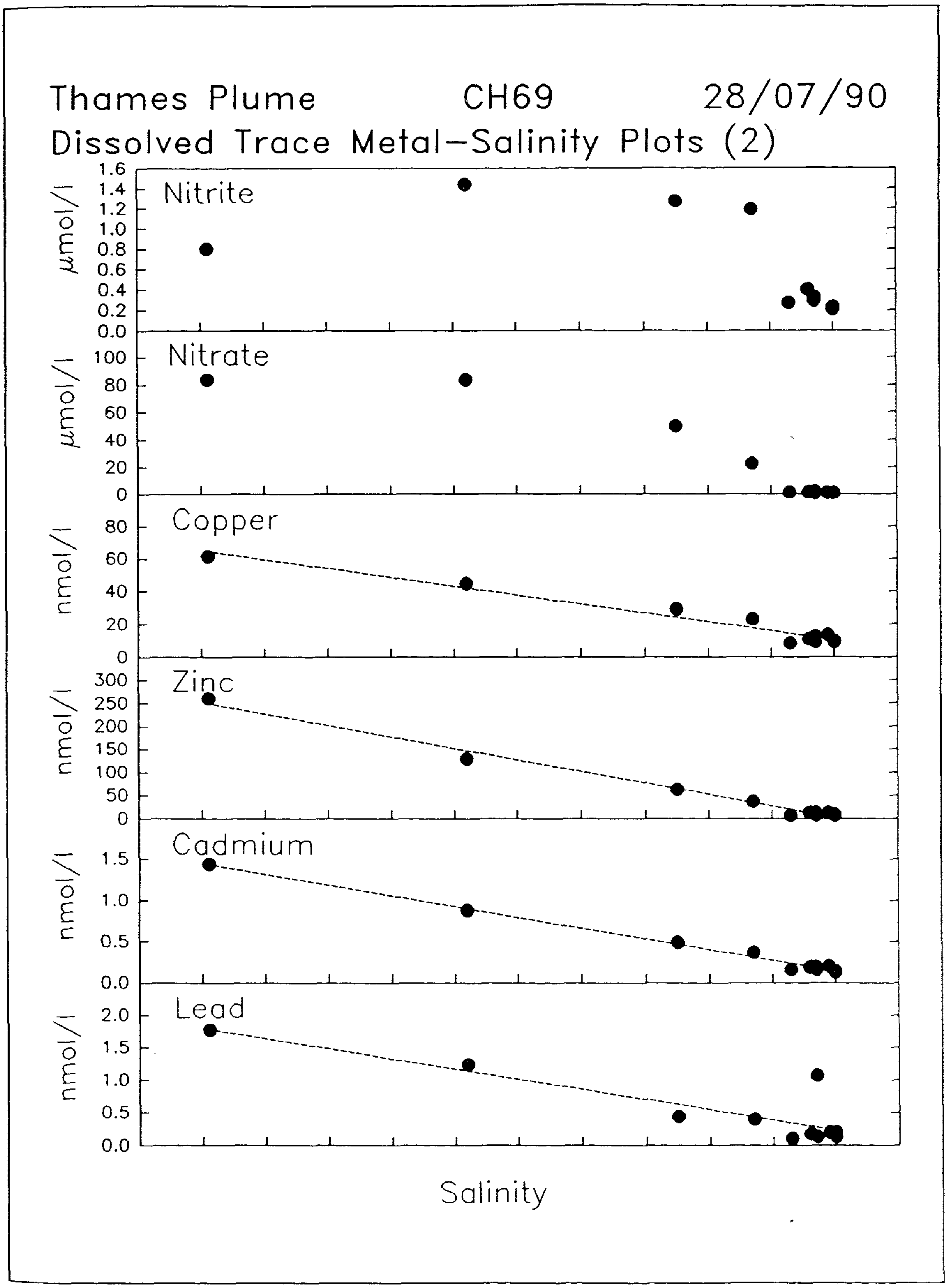

Figure 6.20: Plots of NO_2, NO_3 and dissolved Cu, Zn, Cd and Pb concentrations in the Thames plume against salinity (CH69)

6.3.4 Distribution between Dissolved and Particulate Phase

In Figure 55.21 ff., particle-bound percentages of the total load have been plotted, on a probability scale, against suspended matter concentrations, on a logarithmic scale, and lines corresponding to a given K_d-value.

Within the Thames survey, iron shows the strongest affinity to particles: more than 99% is bound to SPM. For manganese and lead, followed by cobalt, association to particles also generally outweighs the dissolved phase. Nickel, copper and zinc appear to be evenly distributed between the phases, and cadmium exists mainly in dissolved form.

For all elements except Cu, there is a clear distinction between samples from the inner ('tidal station' and 'estuarine' samples) and outer estuary, with K_d-values from the inner estuary being about an order of magnitude below K_d-values from the outer estuary. At the same time, K_d-values within the two groups are fairly constant, leading to a distribution of data points parallel to the K_d-lines for most metals. The ratio between concentrations in the dissolved phase and concentrations on particles is therefore about ten times higher in the inner than in the outer estuary, which could be due either to high absolute dissolved levels in the inner estuary, to high absolute particulate concentrations in the outer estuary, or a combination of both.

In Table 6.3 some summary statistics for dissolved and particulate phase concentrations in both environments are given. Dissolved trace metal concentrations show a much higher variability, with relative standard deviations from the mean (RSD's) of 40% or more, compared to only up to 15% for concentrations on particles. Exceptions are Cu, with higher particulate RSD's and a low dissolved phase variability in the outer estuary; Cd, with low dissolved and high particulate RSD's, the latter being due to limited detectability and many missing values; and particulate Pb, with an RSD of 30% in the outer estuary.

There is also a marked difference between the two phases with regard to the ratio of means from the inner and outer estuaries. Compared to the outer estuary, dissolved concentrations in the inner estuary are increased by a factor of 4 to 7 for Cd, Cu, Co and Ni, by a factor of 13 to 15 for the more particle-reactive elements Mn, Zn and Fe, and by a factor of 33 for Pb. Concentrations on particles, however, are fairly uniform throughout the estuary; only Cu, Zn and Pb are significantly increased in the inner estuary, by a factor of about two.

For Mn, Fe, Ni, Co, Zn and Pb, the observed difference in K_d between samples from the inner and the outer estuary is therefore mainly due to high dissolved concentrations in the inner estuary, which do not immediately translate into equally elevated concentrations in the particulate matter. Given the limited validity of the cadmium data set, copper is the only element for which estuarine inputs seem to affect both phases fairly equally, which is reflected in a constant K_d-value around 4.5 throughout the estuary.

The available data, however, do not give any information about the type, grain size distribution or origin of the suspended particles. Differing proportions of mineral and organic or coarse and fine material within the total SPM can also affect particulate trace metal concentrations, as observed, e.g., by Nolting and Eisma (1988). Within the Thames estuary, our observations leave room for two extreme scenarios:

- the suspended particle population is uniform throughout the estuary with regard to composition and trace metal concentrations (per dry weight); seaward decreases in particle-bound trace metal concentrations are due to decreasing turbidity. Dissolved and particulate phase are virtually de-coupled, and riverine inputs leave the estuary via the dissolved phase.

- suspended sediments in the outer estuary contain much finer material than in the inner estuary, and therefore offshore particles should contain higher trace metal concentrations than inshore material. Concentrations on coarser material in the inner Thames estuary only reach, and partly exceed the levels on offshore material in response to the high dissolved concentrations in the inner estuary. Sorption onto particles in the inner estuary occurs together with desorption in the outer estuary.

Turner et al. (1991), who analysed the particulate trace metal samples, concluded that there was a general trend to a seaward decrease in particulate trace metal concentrations, but explained this by the mixing of river-borne with cleaner marine material, and thus a physical rather than chemical process. This has also been the conclusion of Nolting et al. (1989) in the Rhine estuary.

For further conclusions about dissolved phase - particle interaction and trace metal budgets in the estuarine environment, more information about the type and transport of the suspended particulate matter is needed.

THAMES CH46		Mn	Fe	Ni	Co	Cu	Zn	Cd	Pb
Dissolved Phase Concentrations [nmol/l]									
Inner estuary	Mean	47	82	85	2.8	50	286	1.1	5.9
	Range	18-96	5-289	12-177	1.2-6.7	7-95	111-535	0.5-1.5	1-18
	RSD	42%	117%	45%	45%	46%	41%	24%	74%
Outer Estuary	Mean	4	5.6	12	0.5	10	24	0.25	0.18
	Range	0.4-13	0.6-20	5-29	0.1-1.1	4-17	11-82	0.12-0.41	0.05-0.7
	RSD	77%	91%	40%	51%	24%	71%	25%	76%
$\text{Mean}_{\text{Inner}}/\text{Mean}_{\text{Outer}}$		12	15	7	6	5	12	4	33
Particulate Phase Concentrations [μg/g]									
Inner Estuary	Mean	651	22000	36	16	46	154	0.4	138
	Range	480-780	16600-26000	31-40	13-21	22-56	110-182	0.1-1.7	95-166
	RSD	12%	12%	8%	13%	21%	15%	88%	11%
Outer Estuary	Mean	457	19400	35	16	18	87	0.5	83
	Range	370-550	13400-22400	30-42	13-19	10-26	73-115	0.2-1.2	48-180
	RSD	9%	14%	9%	10%	21%	11%	61%	30%
$\text{Mean}_{\text{Inner}}/\text{Mean}_{\text{Outer}}$		1.4	1.2	1.0	1.0	2.6	1.8	0.8	1.7

N.B.: Flagged data are not included.

Table 6.3: Summary statistics of dissolved and particulate concentrations from CH46

6.4 SUMMARY: THE THAMES ESTUARY

Samples taken during a winter survey of the inner Thames estuary between the Thames Flood Barrier and Southend suggest an essentially conservative mixing line for all analysed dissolved trace metals over large sections of the sampled salinity range, although there are strong indications of natural and anthropogenic sources further upstream. The resulting effective freshwater end member concentrations have been converted into annual fluxes and are shown in Table 6.4, together with the corresponding particulate estimates from Turner et al. (1991), yielding total annual loads. Because of the low freshwater runoff prior to the survey, dissolved freshwater end member concentrations may be rather high, leading to equally high annual load estimates. However, total annual load estimates for Cu and Cd are in good agreement with the higher PARCOM estimates given in Table 6.1, but the Zn estimate is exceeded by 30%, and the Pb estimate by 100%, the latter being due to very high levels of dissolved lead found in the inner Thames estuary by this survey. Manganese and iron are predominantly exported from the inner estuary in particulate form, whilst Ni, Co, Cu, Zn, Pb and presumably Cd are mainly discharged via the dissolved phase.

Annual Trace Metal Discharges from the Inner Thames Estuary

tonnes/a	Mn	Fe	Ni	Co	Cu	Zn	Cd	Pb
dissolved (1)	14	49	39	1.1	19	107	0.7	10
particulate (2)	70	400	3	<1	3	50	--	6
Total	84	449	42	1-2	22	157	>0.7	16

(1): Based on 80 m^3/s freshwater discharge.
(2): Turner et al. (1991).

Table 6.4: Annual discharge estimates for the inner Thames estuary

Results from a tidal station at Tilbury did not show a similarly close relationship with salinity, and turbidity was higher than anywhere else in the estuary. Most values, however, did broadly agree with the linear mixing model.

In the outer estuary, a general trend for a seaward decrease was observed for all metals, although additional processes lead to substantial scatter around the conservative mixing line for Mn, Co, Cu and Cd, and the linear model explained only 8% of the variation in Fe concentrations as related to salinity. A single sample taken during the winter cruise in the Barrow Deep sewage sludge dumping area showed slightly elevated concentrations of Cu, and strongly elevated values for Fe, Ni, Co and Pb. No comparable increases were found in the single sample from the South Falls dumping site. A vertical profile showed increased turbidity beneath the surface layer and increased trace metal concentrations at mid-depth. The extensive survey in February 1989 was contrasted with 11 samples taken in the middle and outer estuary in July 1990. In the surveyed area, summer distributions of Ni, Cu and Pb apparently were unchanged compared to the winter cruise, whilst levels of Zn and Cd were slightly decreased, and of Mn and Co were elevated, in agreement with the seasonal trends made by other, North Sea-wide surveys.

Because of the limited summer data set, and the almost equally dry periods prior to both cruises, it is not possible to investigate seasonal changes in the effective freshwater end member concentrations. Rather, the linear model for the summer data, including three samples taken up-estuary from Southend, has been interpreted as reflecting the two dissolved end member concentrations in the middle estuary. For Co, Cu, Zn and, to a lesser extent, Ni, zero-salinity intercepts increase steadily from the inner via the middle to the outer estuary, indicating concomitant gains to the dissolved phase. The same is probably true for Cd, although the summer mid-estuarine estimate is higher than the winter estimate for the outer plume. For lead, however, a sharp drop in the effective freshwater end member concentration between the inner and outer plume indicate substantial losses from the dissolved phase within the estuarine system. In summer, less than a third of dissolved estuarine lead load encountered in winter reaches the mid-estuary in dissolved form.

Comparing dissolved and particulate concentrations in both the inner and outer estuary, it was found that the dissolved phase shows a much higher spatial variability. Whilst particulate concentrations decline only slowly towards the sea, possibly due to mixing with less polluted marine material, dissolved concentrations in the inner estuary were several times their offshore values, leading to a clear differentiation of the two environments by the K_d distribution coefficients for Mn, Fe, Ni, Co, Zn and Pb. Further conclusions about trace metal transport and behaviour within the estuarine-coastal system, however, will require further knowledge of properties and movement of the suspendable particulate material.

CHAPTER 7: THE RHINE PLUME

7.1 INTRODUCTION

The river Rhine rises in Switzerland, and is joined by many tributaries in that country, France and Germany, before entering the Netherlands at Lobith. Then the river Rhine branches out into the rivers Lek, Waal and IJssel, with the Waal carrying the bulk of the discharge, and the IJssel providing a link to the IJsselmeer, a now enclosed former part of the North Sea. The rivers Lek and Waal are joined by the river Maas (Meuse), before debouching into the North Sea (Figure 7.1).

The long-term average discharge of the Rhine at Lobith is 2200 m^3/s, varying between 575 m^3/s and 13000 m^3/s. Discharge is usually lowest in early autumn and highest in mid-winter, but mostly fairly constant over the seasons (van Alphen et al., 1988). Freshwater discharge from the Maas is about one order of magnitude lower. Since the completion of the Delta Plan, a complex network of dams, sluices and barriers connecting the main islands of the Rhine/Maas/Scheldt delta and controlling all major water channels, most of the freshwater enters the North Sea at Hoek van Holland (south-west of Den Haag) via the Nieuwe Waterweg (New Waterway), the main shipping lane to Rotterdam Harbour, where a constant discharge of 1500 m^3/s is maintained as long as possible. Excess water is discharged primarily through the Haringvliet sluice complex (van Alphen et al., 1988). In the north-eastern quadrant of Figure 7.1, the Noordzeekanaal is shown, providing a link between the Ijsselmeer, Amsterdam, and the North Sea.

The Nieuwe Waterweg is quite an extreme case of an estuary due to the combination of high freshwater discharge and low volume, leading to a residence time of only one or two days, compared with about two months for the neighbouring Scheldt (Duinker et al., 1979). Tidal ranges at Hoek van Holland vary from 1.9 m at spring to 1.5 m at neap tides. There usually is a salt wedge, with salinity in the inflowing bottom layer between 28 and 30, and in the outflowing surface layer between 17 and 20, but also as low as 7 during periods of high freshwater discharge, when there is continuous outflow of upper layer water throughout the tidal cycle (van Alphen et al., 1988).

In the receiving waters, the Rhine forms a buoyant plume. Van Alphen et al. (1988) distinguish between buoyant spreading within a 10 km near field zone, and a gradually weakening stratification in the far field stratified zone, extending longshore, in a northeasterly direction, between 20 and 100 km from the outflow. The receiving coastal waters are also characterised by longshore tidal currents, with northeastward flowing flood currents of 0.8 to 1.1 m/s, and southeastward flowing ebb currents of 0.7 to 0.9 m/s, at neaps and springs, respectively. The resulting tidal excursions range from 8 to 12 km. Residual currents depend on wind forcing, but generally point northeastwards and reach velocities between 3 and 8 cm/s (van Alphen et al., 1988).

Mathematical models have been able to simulate the water transport in the area and confirmed the north-east-bound longshore plume feature (van Pagee et al., 1986). A mean travelling time of around 40 days has been calculated for Rhine water to reach the northern boundary of the survey area in Figure 7.1. High-resolution 3-D modelling of sedimentary transport in the outflow area revealed a strong residual eddy north of Hoek van Holland (de Kok, pers.comm.). On a larger scale, sedimentary budgets in the coastal zone have been investigated by van Alphen (1990), who showed that the Rhine was the source of between 14 and 30% of the suspended matter transported longshore. Whilst the completion of the Delta Plan had led to an anthropogenic reduction in coastal SPM, significant amounts of mud are mobilised by dredging in the Europoort harbour area and subsequent dumping at sea.

In the 1970s, several studies were investigating trace metal levels and behaviour in both the Rhine estuary and the receiving coastal zone. Analysing leachable Mn, Fe, Cu and Zn in suspended matter, Duinker and Nolting (1976) concluded that the Rhine estuary was acting as a sink for 20 to 60% of the particulate trace metals, and that riverborne dissolved Mn and Fe were precipitated in the estuary during the early stages of mixing. No indications for estuarine mobilisation were found. In a second study, the same authors also analysed dissolved concentrations of Cu, Zn, Cd and Pb, showing elevated concentration in coastal areas and estuarine removal for all but lead (Duinker and Nolting, 1977). In a more detailed study of trace metal behaviour in the Rhine estuary, Duinker and Nolting (1978) concluded that particulate trace metal concentrations were mainly determined by the mixing of fluviatile and marine derived particles in almost the same proportions as the waters in which they were suspended, and that there was estuarine removal of Fe, Zn, Cu and Cd. Manganese, however, was found to undergo continuous estuarine cycling, although also resulting in a net removal. This behaviour was again investigated by Duinker et al. (1979), showing manganese removal from the dissolved phase in the lower estuary, followed by either export to the marine environment in particulate form, or up-estuarine transport by the residual bottom current and subsequent re-dissolution owing to lower pH and Eh. Analysing a wide range of major and minor elements in the suspended matter of the Rhine river and estuary, sampled during a survey in 1976, Nolting et al. (1989) could show that seaward reductions in particulate trace metal concentrations were indeed due to mixing of riverine and marine material and not the result of estuarine desorption.

Comparing results from two more recent surveys of dissolved and particulate levels of Cr, Cu, Zn, Cd and Pb in the Rhine and Maas rivers and estuary, Golimowski et al. (1990) found a reduction in dissolved Cd and particulate Cu, Cd and Pb between August 1978 and August 1984, possibly due to environmental pollution control measures. For cadmium, biological uptake was observed in summer.

Rising nutrient concentrations in the Southern Bight of the North Sea have been attributed to increased discharges from the river Rhine between 1961 and 1978 (van Bennekom and Wetsteijn, 1990). The extrapolation of nitrate-salinity relationships in coastal waters did agree with riverine concentrations, but for phosphate, the disposal of phosphogypsum provided an additional estuarine source. The annual discharge of about 2 million tonnes of phosphogypsum slurry into the Nieuwe Waterweg also introduces 12 tonnes concomitant cadmium into the estuarine environment (van der Heijde et al., 1990).

Atmospheric deposition of trace metals to the southern survey area has been investigated by Nguyen et al. (1990), who found values common to rural central European areas at a station in the Rhine Delta. In the urban areas around Rotterdam and Den Haag, however, increased values are to be expected.

Further riverine trace metal data have been generated as part of the 'Project Onderzoek Rijn', commissioned by the City of Rotterdam as part of their efforts to reach agreement with upstream sources on pollution control measures in order to be able to dump harbour dredge spoils offshore rather than on expensive special dump sites (International Centre of Water Studies, ICWS, 1986). Since the 1970s, substantial reductions in heavy metal loadings have been achieved, a trend also observed by van der Weijden and Middelburg (1989) in a paper discussing long-term and seasonal variation in the composition of Rhine water. Some estimates from these two papers are given in Table 7.1, including weighted mean dissolved trace metal concentrations at Lobith, based on data from 1975 to 1984, together with three annual load estimates: one based on 1975-84 weighted mean total concentrations, and two yearly estimates for 1984 and 1985, respectively. A comparison of the mid-1980s data with the means from the preceding decade suggest dramatic reductions for Cu, Zn, Cd and Pb. Time series plots in van der Weijden and Middelburg (1989) indeed show substantial longterm decreases over the 1975-84 period for total Cu, Zn, Cd and Pb, a less pronounced downward trend for Co and Ni, and hardly any trend at all for Mn and Fe, in line with assumed anthropogenic mobilisation rates in the aquatic environment.

	Mn	Fe	Ni	Co	Cu	Zn	Cd	Pb
Weighted mean dissolved concentrations at Lobith 1975-84 (1)								
dissolved [nmol/l]	940	900	87	13	68	590	5.0	4.5
Total annual discharge at Lobith								
1975-84 (2) [t/a]	7900	130000	620	140	900	6600	110	1100
1984 (3) [t/a]					682	4506	17.2	547
1985 (3) [t/a]					350	2835	8.5	243

(1): Converted into nmol/l from van der Weijden and Middelburg (1989)
(2): Calculated from van der Weijden and Middelburg (1989), using 2200 m^3/s as mean annual discharge
(3): From ICWS (1986)

Table 7.1: Dissolved concentration and total annual discharge estimates for the River Rhine at Lobith

7.2 THE DATA BASE

Field work was undertaken during leg 3 of Challenger Cruise CH72 (7-18 October 1990). The riverine and the offshore anchored stations, and the 20 stations of the plume survey, are shown in a map of the survey area in Figure 7.1. The data base is included in Appendix IX. No tidal correction model was available for this area.

Trace metal sampling started on 7 October with the riverine tidal station in the Nieuwe Waterweg, taking both surface and bottom samples every hour for 13 hours, in order to estimate trace metal fluxes at the river mouth. Initially it was planned to occupy a station at Hoek van Holland, but adverse weather conditions lead to the choice of a location further upstream. Samples were eventually taken from the Nieuwe Maas (New Meuse), whilst the ship was moored to the 'Phosphate Jetty' in Vlaardingen (54°54'N; 4°22'E), up-estuary of the confluence with the Oude Maas (Old Meuse), and just down-estuary of Rotterdam Harbour. Samples were coded A01 to A13 in the data base, with the additional letter 'T' or 'B' indicating top or bottom samples. This riverine tidal station is abbreviated as 'CTDA' in some plots.

On 8 October, a first regional survey was undertaken by sampling along six transects off the North Sea coast, labelled with the starting letter of nearby towns and islands (S=Schouwen, G=Goeree, T=Terheijde, N=Noordwijk, Y=IJmuiden, and E=Egmont). For trace metal analysis, 20 water samples were collected at positions indicated in Figure 7.1. Samples were taken close to the surface except in the case of N3, collected at 8m albeit in a water column well mixed between the surface and this depth.

On 11 October, an offshore anchored tidal station was occupied at 52°13'N; 4°09'E. Again, 13 samples each were taken near the surface and the sea bed at hourly intervals, labelled 'B01T' to 'B13B'. This offshore tidal station is abbreviated 'CTDE' in some plots.

7.3 RESULTS AND DISCUSSION

7.3.1 The General Hydrographic Situation

Changes in salinity, suspended matter concentration and nutrients over the tidal cycle at the riverine station in the Nieuwe Maas can be seen in Figure 7.4 and Figure 7.6. Coastal distributions of salinity, SPM, chlorophyll, phosphate and nitrate are shown in a series of contour plots in Figure 7.1 to Figure 7.3, and time series of salinity, SPM, chlorophyll and nutrients at the offshore tidal station are shown in Figure 7.13 and Figure 7.15.

7.3.1.1 Freshwater input and salinity

Although the actual freshwater discharge of the Rhine in autumn 1990 is not available, it is likely to have been below the annual mean due to seasonal dryness. At the riverine tidal station, sampling commenced just after low water, with salinity below 3 in both surface and near-bottom samples. The incoming tide then leads to the formation of a weak salt wedge, with bottom water salinity reaching a maximum of 8 about 90 minutes after high water (Figure 7.4). At that point, surface water salinity has already started to fall again from a maximum of 7.7 to 4.8. During the shortened ebb tide, salinities throughout the water column decrease again to between 3 and 4.

The coastal salinity contour plot in Figure 7.1 shows a set of isohalines, virtually parallel to the coast north of Hoek van Holland, increasing from values below 31.5 inshore to above 34.5 offshore. Salinity south of the main outflow is quite uniformly between 34 and 34.5. The lowest salinities were measured at T1 and N2, two nearshore stations just north of the outflow, with 30.2 and 31.2. This picture is in good agreement with the pattern shown by van Alphen et al. (1988) for October 1977.

Surface salinity at the offshore tidal station (Figure 7.13), between the 32.5 and 33 contours in the contour plots, was found to fluctuate between 32.2 and 34.2 over the tidal cycle. There was evidence of a transient freshwater plume, with bottom salinity varying only between 32.8 and 34.2, and a maximum salinity difference between surface and more saline bottom water of 0.8. This is also in good agreement with the prediction given by van Alphen et al. (1988) about the extent of the stratified area under varying hydrodynamic conditions; the tidal station is just at the margin of the area expected to be stratified under average conditions. Salinity values also clearly follow a tidal pattern, with a salinity minimum 2 hours before, and a maximum 4 hours after high water at Scheveningen, probably due to the advection of freshwater from the Rhine outflow by longshore, northeast-bound flood currents, and the transport of more saline water to the station by the southwest-bound ebbing tide (van Alphen et al., 1988).

7.3.1.2 Suspended particulate matter

In the river, suspended particulate matter concentrations stayed below 30 mg/l for several hours in both surface and bottom waters, before reaching a maximum of 33 mg/l near the surface and 50 mg/l near the sea bed just before high tide, probably in connection with maximum in tidal velocity. Three hours later, values have converged again around 25 mg/l.

Coastal distributions exceed 30 mg/l at T2 and N2, stations both close to the shore and the Rhine outflow, although at T1, even closer to Hoek van Holland, a value of only 23 mg/l has been recorded, possibly due to different tidal conditions. No transmissivity or gravimetric measurement was recorded at the nearshore station Y2, but more than 60 mg/l of SPM have been found in the particulate trace metal sample, indicating very high turbidity. Throughout the plume, suspended particle concentrations decrease from high nearshore levels to values below 5 mg/l offshore. South of the outflow, in front of the old delta, SPM shows elevated levels between 9 and 17 mg/l. This pattern agrees well with a similar plot given in van Alphen (1990).

At the coastal tidal station, on the contour map close to the 10 and 15 mg/l isolines, actually measured values are amongst the lowest of the entire data set, never exceeding 4 mg/l (Figure 7.13). Turbidity reflects the transient salinity stratification, with increased surface values coinciding with the influx of low-salinity water during the flood tide. After high water, SPM concentrations are uniform throughout the water column and decrease with increasing salinity.

7.3.1.3 Chlorophyll

The distribution of chlorophyll, also shown in Figure 7.2, follows very closely the inverted image of the SPM-pattern. Within the narrowing longshore band stretching to the north east, but also the area south of the outflow, chlorophyll concentrations hardly ever exceed 3 mg/m^3. North-west of this plume there is a steep rise to 7, 8, and nearly 10 mg/m^3 at the north-westernmost points of the sampling grid. However, whether this low productivity plume emanating from the Rhine outflow is actually due to shading by high turbidity, or whether the relationship between the two features is more complex, or mere coincidence, cannot be decided based on the data available here.

At the offshore tidal station, situated near the 2 mg/m^3 contour on the plot, recorded chlorophyll concentrations range between 1.5 and 2.2 mg/m^3 (Figure 7.15). During the more saline ebb tide, concentrations are higher in surface than in bottom waters; the maximum difference (0.5 mg/m^3) coincides with the highest surface salinity and chlorophyll values (at 10:00 hrs GMT). During the advection of particle-rich, chlorophyll-depleted low salinity water to the surface layer, before and around high water, bottom chlorophyll concentrations are higher than those at the surface.

7.3.1.4 Nutrients

There are two distinctly different patterns in the nutrient time series at the riverine station (Figure 7.6): nitrate and silicate inversely reflect the salinity pattern, including the formation of an enriched surface layer during the stratified part of the cycle, and are thus probably supplied by the river. Phosphate, aluminium, and ammonia, however, appear positively linked to salinity and turbidity, with near-riverbed phosphate and aluminium concentrations exceeding surface concentrations during the high water period, indicative of further down-estuarine, possibly sedimentary sources.

In the coastal zone, the distribution of both phosphate and nitrate shows a nutrient-rich plume emanating from the Rhine outflow and stretching along the coastline to the north. Phosphate concentrations range from 2.8 μmol/l near the outflow to 0.6 μmol/l south of the plume, and to below 0.2 μmol/l in the biologically active offshore strip in the north-west of the survey area. Nitrate concentrations range from 54 μmol/l near the outflow to almost total depletion offshore. At the coastal tidal station (Figure 7.15), phosphate, nitrate, silicate and aluminium are all highly positively correlated with salinity, including a surface layer enrichment during the stratified parts of the cycle.

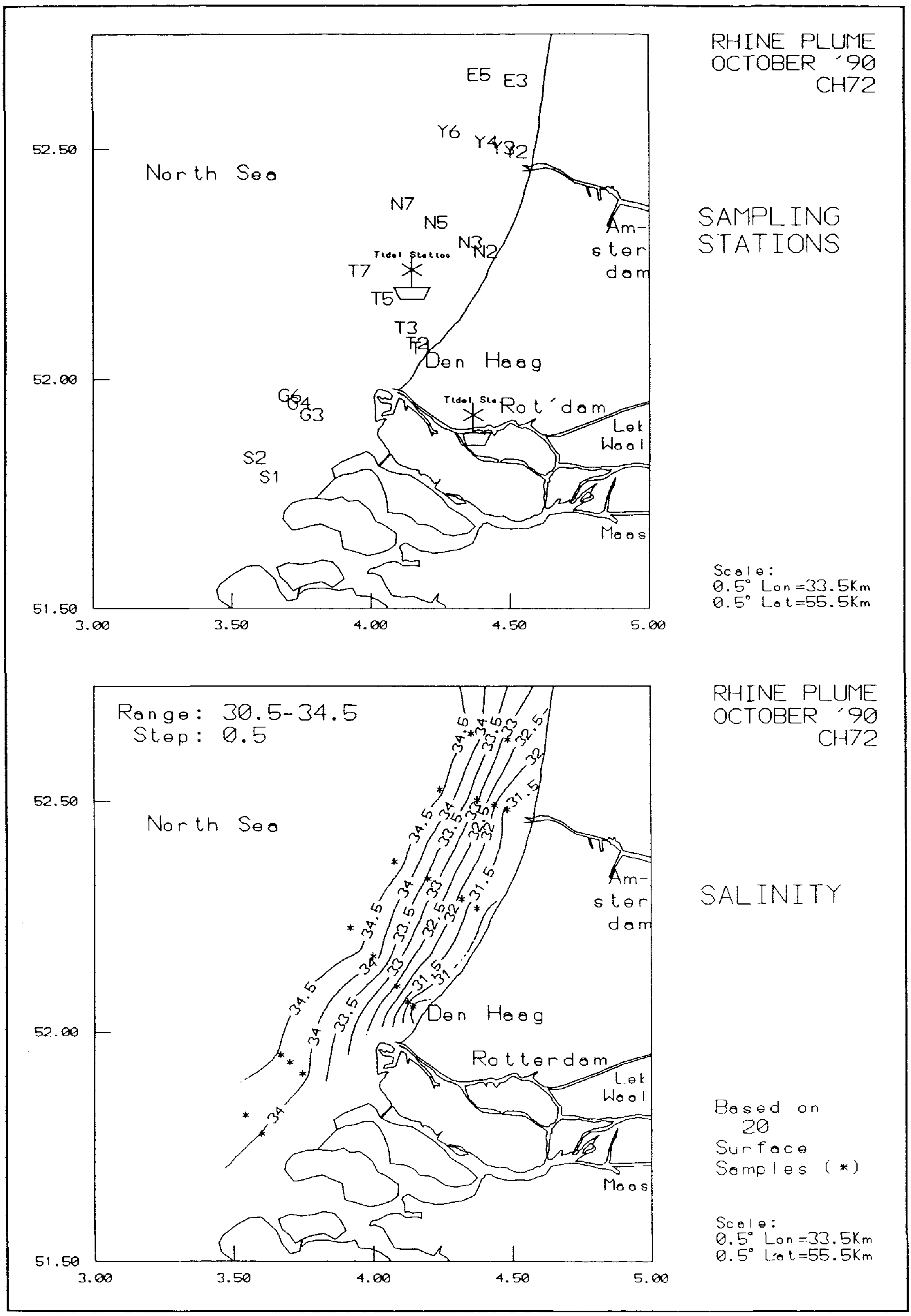

Figure 7.1: Sampling stations and salinity distribution in the Rhine plume (CH72)

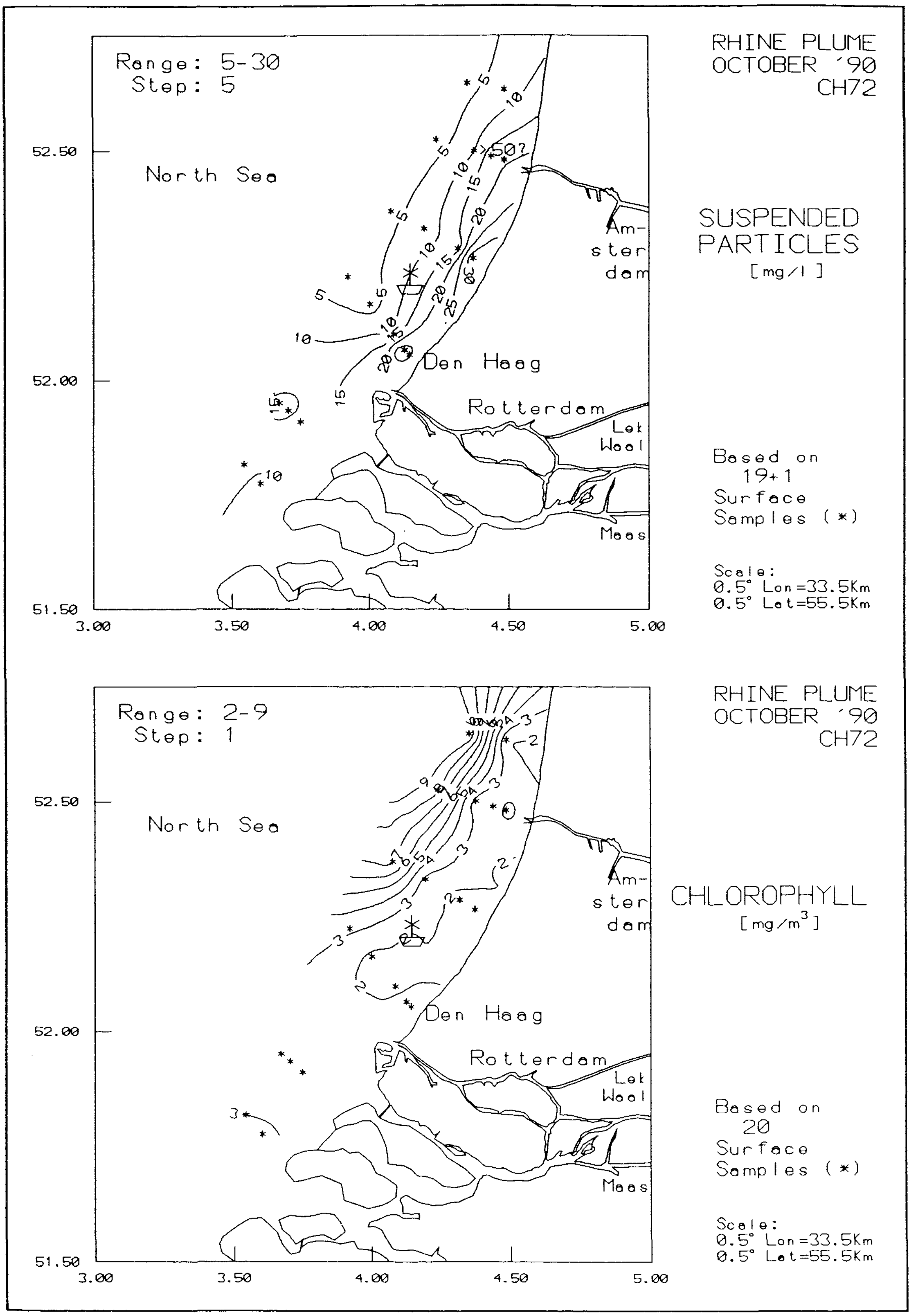

Figure 7.2: Suspended particulate matter and chlorophyll distributions in the Rhine plume (CH72)

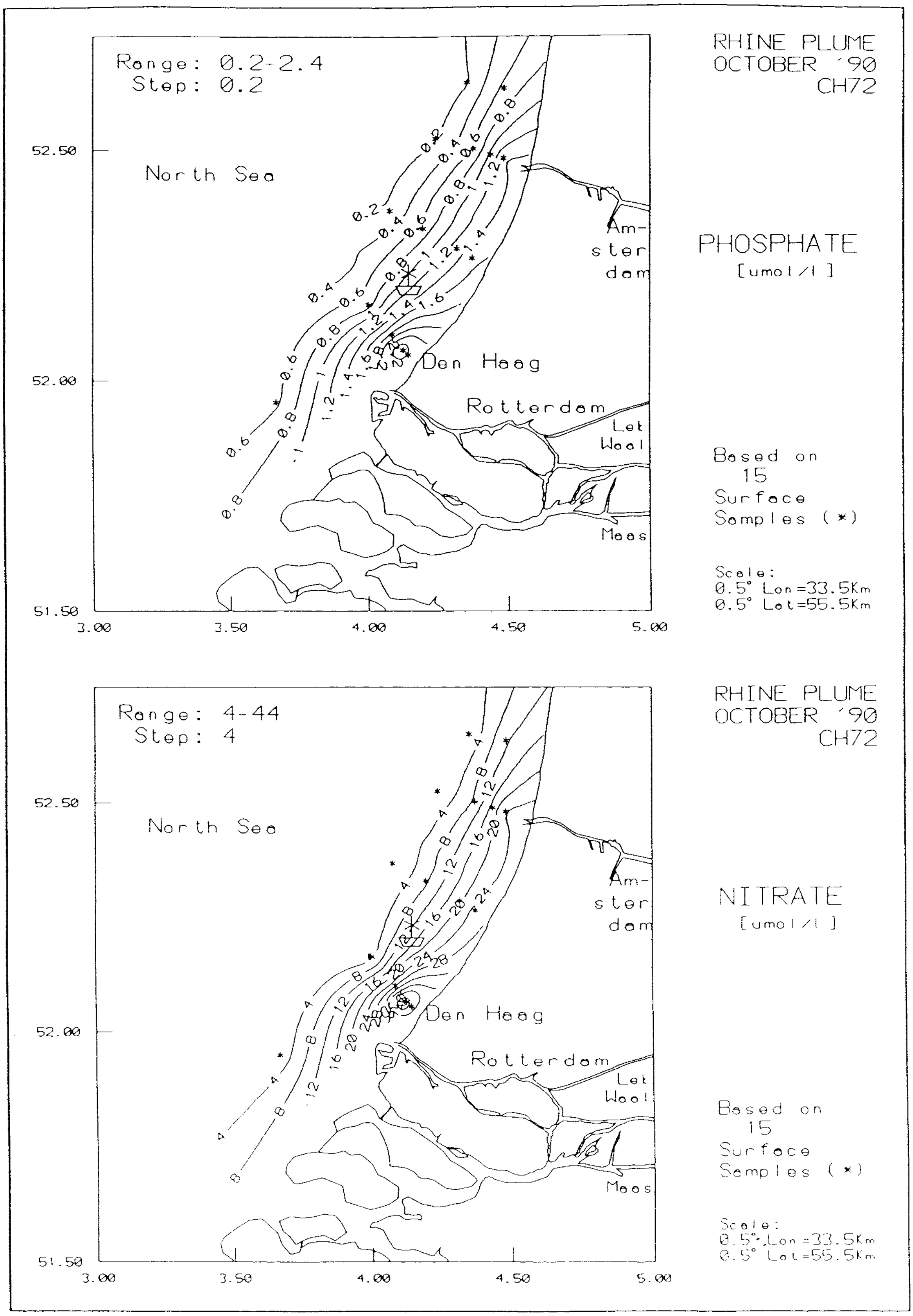

Figure 7.3: Phosphate and nitrate distributions in the Rhine plume (CH72)

7.3.2 Dissolved Trace Metal Inputs from the Nieuwe Waterweg

Time series plots of the trace metal data collected at the tidal river station in the Nieuwe Maas (51°54'N; 4°21'E) are shown in Figure 7.4 and Figure 7.5, together with those for salinity and suspended particulate matter. Trace metal data have been plotted against salinity in Figure 7.7 and Figure 7.8. No regressions against salinity have been made for data from the riverine tidal station.

Dissolved manganese concentrations (Figure 7.4) vary between 330 and 460 nmol/l, with values decreasing for the first two hours, at low salinities, followed by a slow rise back to the starting level. Bottom samples seem to be more prone to spikes, with elevated values at 13 and 15 hrs. Plotted against salinity, manganese concentrations show a sharp rise from a minimum at lowest salinities (Figure 7.7), similar to the findings from longitudinal sections by Duinker and Nolting (1978) and Duinker et al. (1979), who attributed this feature to the re-dissolution of Mn from estuarine particles. Their studies also highlight the variability of the lowest-salinity end member around the ten-year average freshwater value at Lobith of 940 nmol/l (Table 7.1): Duinker et al. (1979) give concentrations around 1800 nmol/l for both February and October 1975, compared to approx. 500 nmol/l for September 1975 (Duinker and Nolting, 1978) and only 350 nmol/l in this study. The concentration range of this study is about 25 - 30% of the levels reported by Duinker and Nolting (1978) for a fixed station at virtually the same position.

Iron concentrations, with the majority of values below 50 nmol/l, range between 16 and 245 nmol/l, about one order of magnitude less than found by Duinker and Nolting (1978) at their fixed station, but in broad agreement with the range of their longitudinal section. At high salinities, values are particularly low, and bottom samples at low salinities are most likely to show erratic high values (at 13, 15, 19, and 21 hrs, and at 11 and 21 hrs for the surface).

Nickel shows some negative correlation with salinity, with increased and more variable concentrations at low salinities. The change in cobalt concentrations is very similar to the Mn trend, showing a decrease until 12 hrs, followed by a slow, but generally persistent increase, and elevated bottom samples at 13 and 15 hrs. Maximum concentrations of both Ni and Co are well below the freshwater value at Lobith.

Copper and zinc values are consistently higher in surface than in bottom samples for a large part of the cycle (Figure 7.5), and vaguely follow the inverse of the salinity pattern, resulting in a descending line in the metal-salinity plots (Figure 7.8). Copper values range between 27 and 39 nmol/l, which is comparable to the findings of Golimowsky et al. (1990), reporting on a station at Maassluis, a few kilometres downstream, and of Duinker and Nolting (1978). Zinc concentrations, between 120 and 180 nmol/l, reach about half the level reported in Duinker and Nolting (1978), but are higher than the value reported by Golimowsky et al. (1990) for the downstream station, sampled in 1984. Lowest-salinity values are well below the freshwater estimate at Lobith, possibly reflecting reduced anthropogenic loads.

Cadmium levels are constant between 0.2 and 0.3 nmol/l in both surface and bottom water, before a sudden rise in both layers to around 0.6 nmol/l, coinciding with the SPM maxima and the sudden rise in phosphate, just before high water. As salinity decreases, concentrations fall again to below 0.4 nmol/l. The rise in cadmium concentrations with the incoming tide, and the striking correlation with phosphorus, and, less closely, turbidity, aluminium and ammonia, has its probable cause in the discharge of phosphogypsum from nearby fertilizer manufacturing plants, containing an annual load of 12 tonnes of cadmium, i.e. considerably more than the annual load passing Lobith in 1985. Alternatively, one could hypothesize a strong particle affinity of cadmium in the freshwater part of the Rhine, and subsequent release into the dissolved phase at increasing salinities, as found elsewhere (e.g. Elbaz-Poulichet et al., 1987) and as used in local Cd transport models by de Kok (pers.comm.). However, the dissolved concentration range is nearly an order of magnitude below the Lobith freshwater concentration and the levels reported by Duinker and Nolting (1977) for the Rhine estuary, and also below the value reported by Golimowsky et al. (1990). Further investigation would be necessary to decide whether the additional cadmium and phosphate inputs originate from a continuous discharge plume, or are the result of tidal mobilisation of contaminated sediments, if phosphogypsum slurry proved to be the cause of these dissolved estuarine inputs.

Lead concentrations show a clear surface - bottom separation during the first low salinity period, with elevated values in the surface layer, followed by uniformly low values around high water, rising again slowly afterwards. Bottom samples show single high values at 15, 19, and 21 hrs. Values range from 0.58 to 1.1 nmol/l, comparable to the value of Golimowsky et al. (1990) downstream, and a quarter of the mean freshwater concentration at Lobith and the levels reported for the area by Duinker and Nolting (1977).

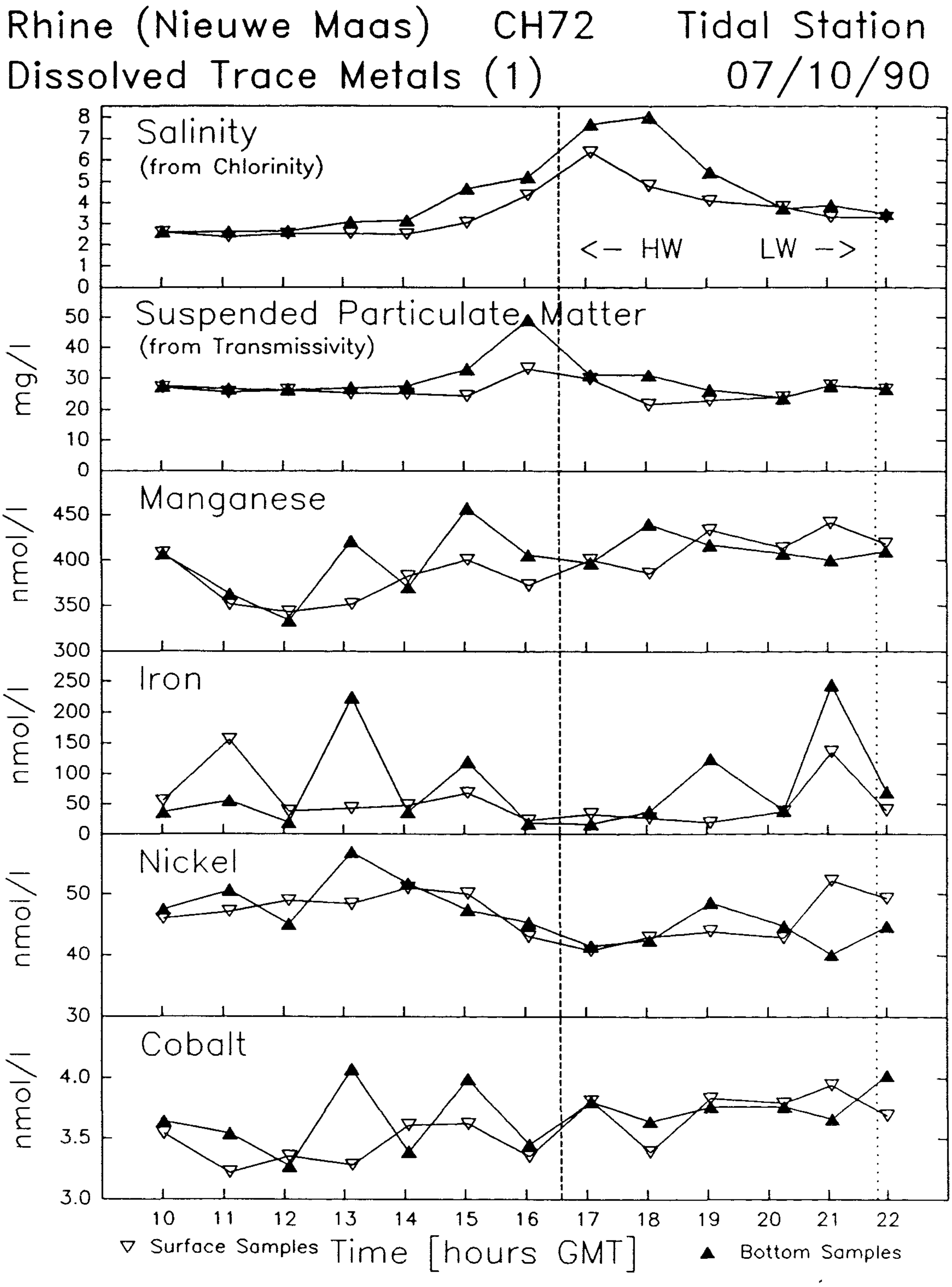

Figure 7.4: Time series of Mn, Fe, Ni and Co over a tidal cycle at the river station (CH72)

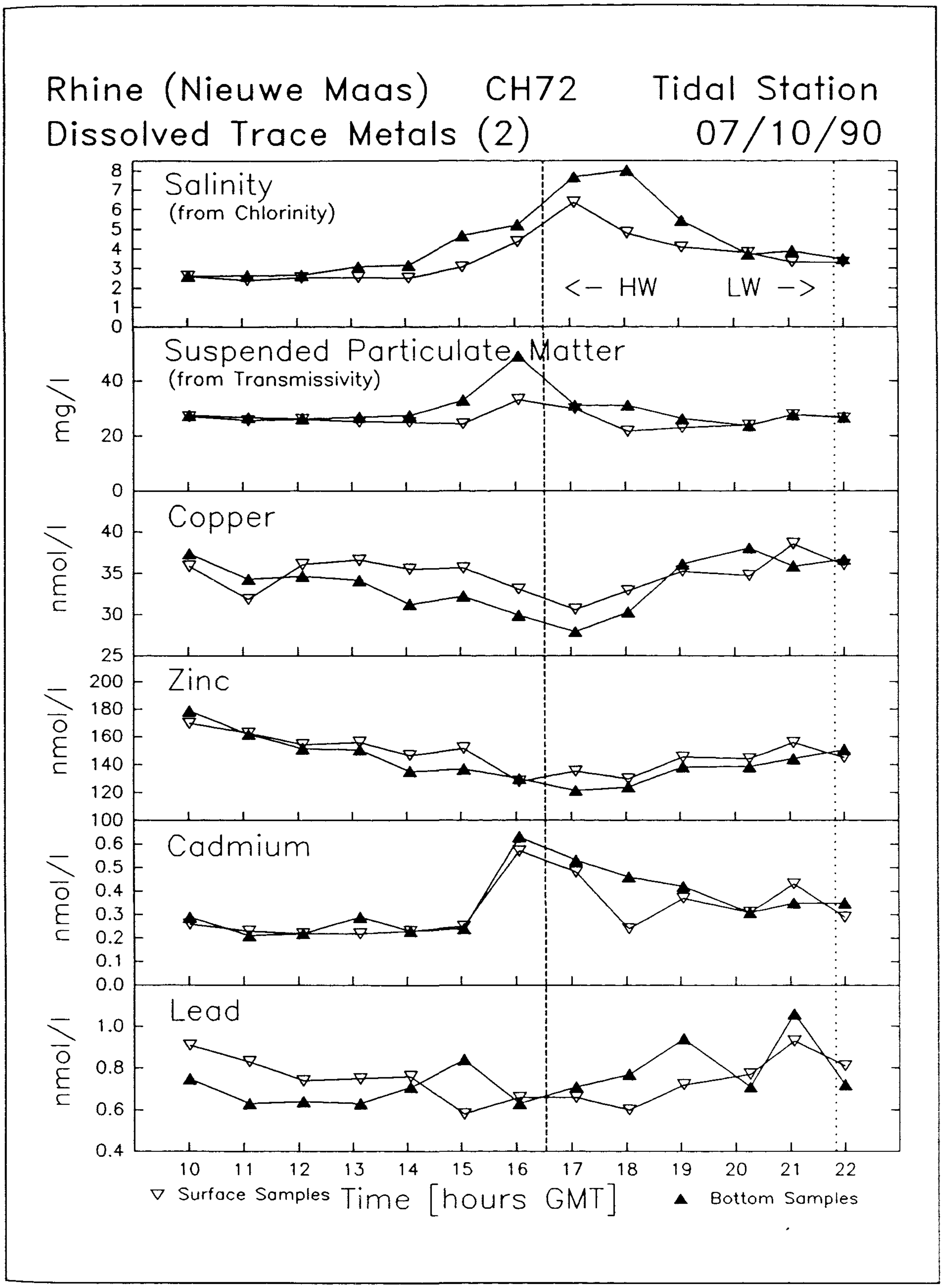

Figure 7.5: Time series of Cu, Zn, Cd and Pb over a tidal cycle at the river station (CH72)

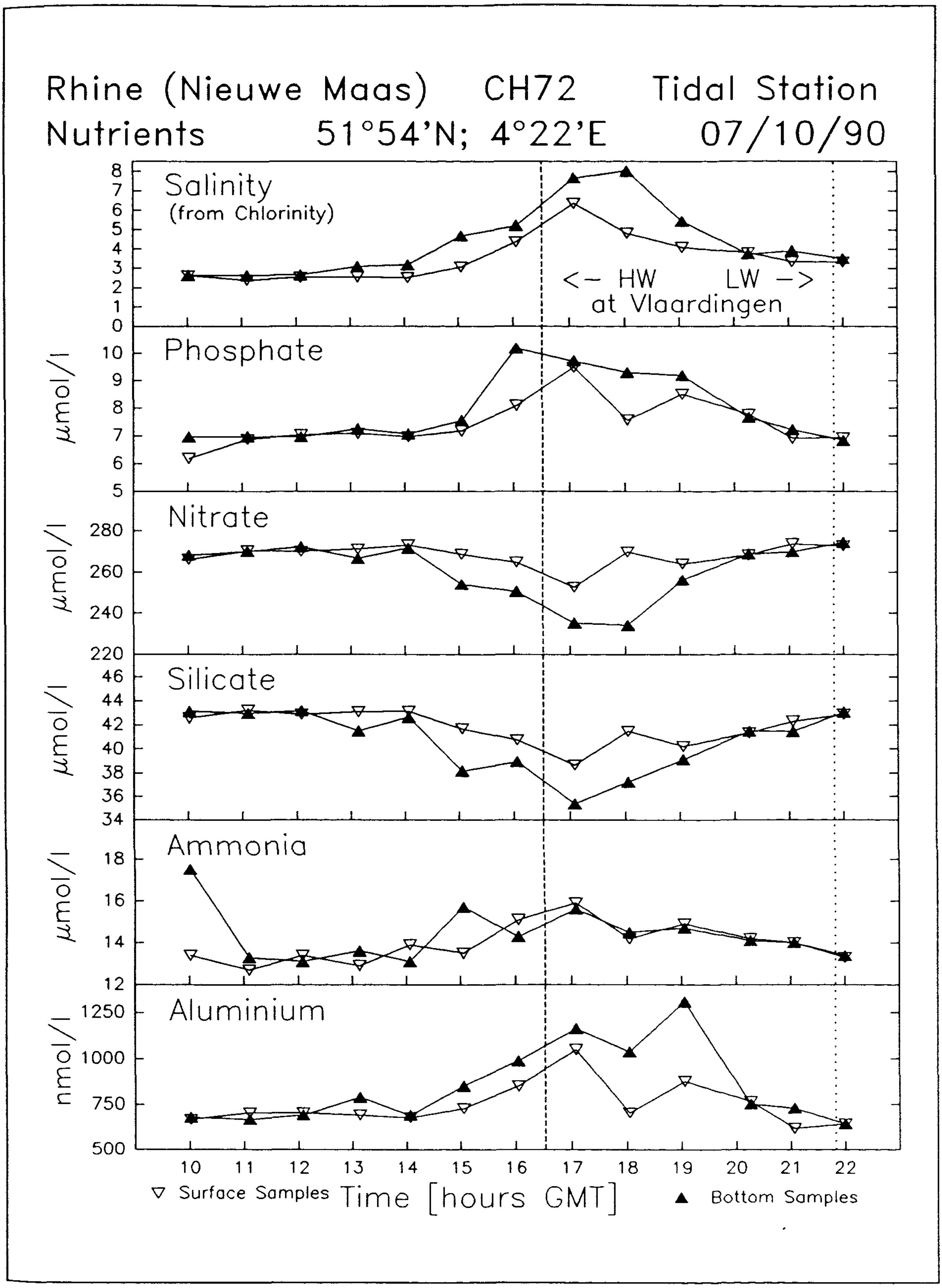

Figure 7.6: Time series of PO_4, NO_3, Si, NH_4 and Al over a tidal cycle at the river station (CH72)

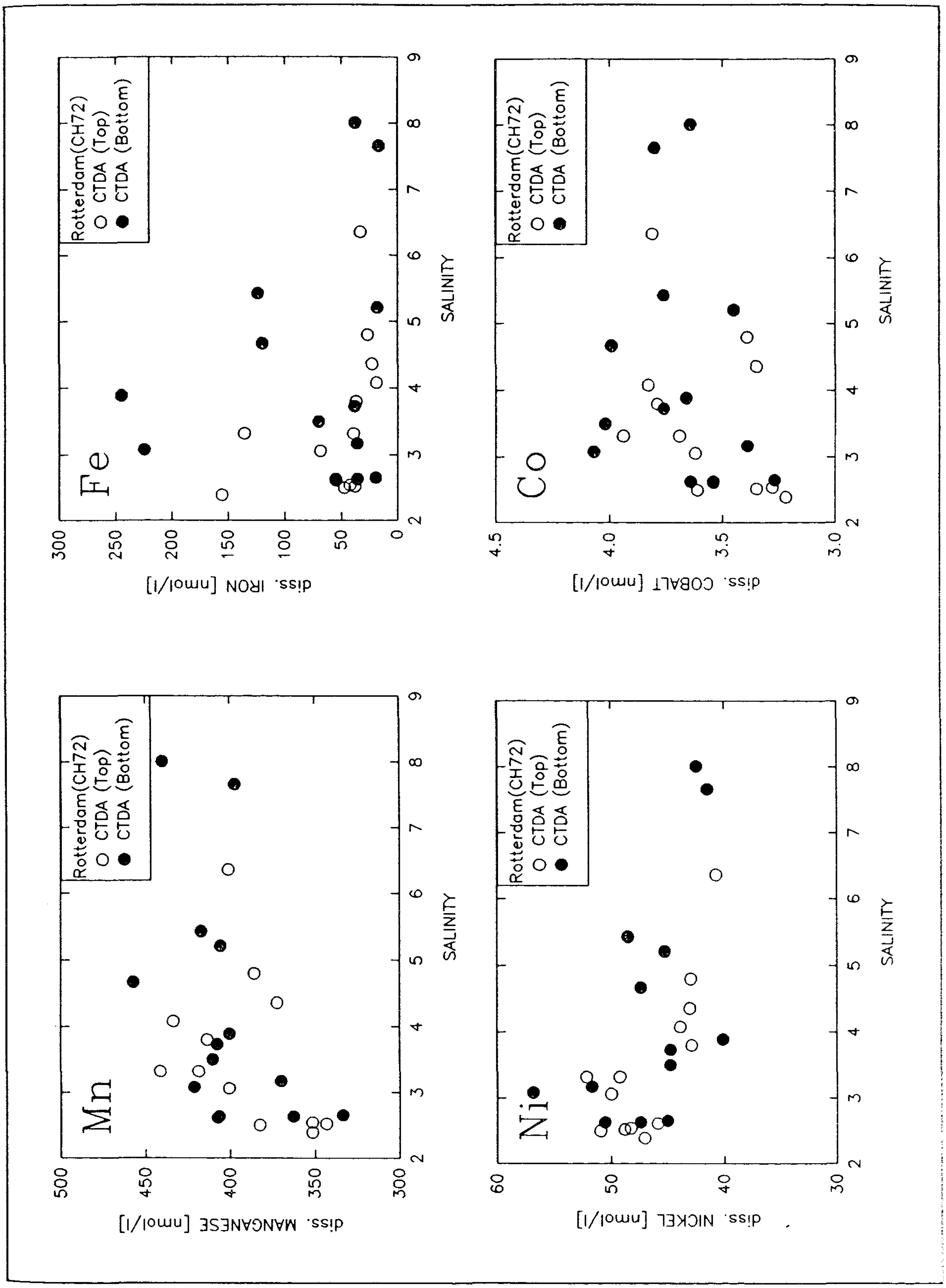

Figure 7.7: Trace metal-salinity plots for dissolved Mn, Fe, Ni and Co at the tidal river station (CH72)

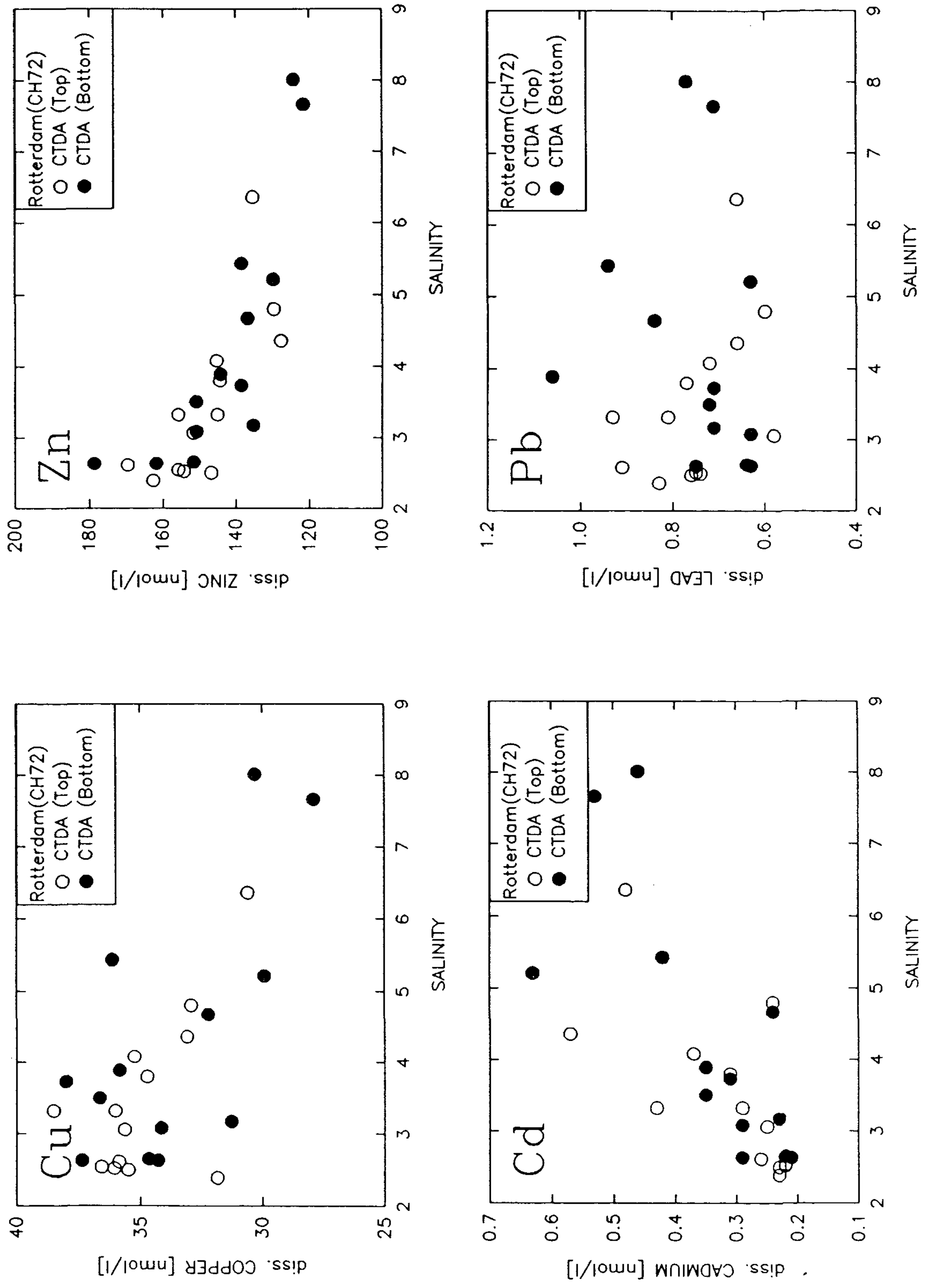

Figure 7.8: Trace metal-salinity plots for dissolved Cu, Zn, Cd and Pb at the tidal river station (CH72)

7.3.3 Trace Metals in the Rhine Plume

Contour plots of dissolved trace metal concentrations in the surface water, interpolated from the 20 stations of the regional survey, are shown in Figure 7.9 to Figure 7.12; the time series for surface and bottom concentrations at the coastal tidal station are given in Figure 7.13 and Figure 7.14, and in Figure 7.16 and Figure 7.17 trace metal concentrations from both the coastal tidal station and the 20 regional survey stations have been plotted against salinity. Three sets of trace metal data have been related to the respective salinities in a least-squares-regression: the 26 samples from the offshore tidal station; the 41 pooled samples from both the tidal station and the regional survey stations north of the outflow, the 'plume' proper; and the 10 samples of the regional survey from stations with salinity ≥34, essentially the stations less affected by the river plume, i.e. south of the outflow and at the seaward margin of the survey area. Results of the higher correlated metals (R-squared > 60%) have been compiled in Table 7.2.

7.3.3.1 Manganese

The overriding feature of the Mn-distribution are the high concentrations of 62, 88 and 44 nmol/l along the T-transect, close to the Rhine outflow. No other station even exceeds 20 nmol/l. Concentrations are particularly low south of the outflow (<7 nmol/l), at the nearshore stations N2 and N3, and stay below 10 nmol/l at the most offshore stations of transects N and T. Further north, however, values are again slightly increased, to between 10 and 20 nmol/l, with no offshore gradient. At the tidal station (Figure 7.13), there are further indications of higher offshore concentrations; values range from 5 to 19 nmol/l, and are positively correlated to salinity (Table 7.2). Extrapolating this relationship to an offshore salinity of 34.5, a marine end member concentration of 21 nmol/l is computed, comparable to levels in the high productivity area around station E5. Due to this complex pattern of both nearshore and offshore elevations, the pooled plume data do not correlate highly with salinity (Figure 7.16).

7.3.3.2 Iron

The distribution pattern for iron is at least equally complex, and values range from 3 (below LoD) to 17 nmol/l. There are indications for an offshore increase in transects T, N, and E, all north of the outflow, although T7 and N7 again show decreased values. Transects G and S show an offshore decrease. At the offshore tidal station, close to the 11 nmol/l contour on the map, concentrations fluctuate between 2 (below LoD) and 20, with no clear surface-bottom pattern and only a hint of a positive correlation with salinity. The iron-salinity plot for the entire area (Figure 7.16) appears to be virtually random-distributed.

7.3.3.3 Nickel

Nickel concentrations range from 18 nmol/l at T1, next to the outflow, to below 8 nmol/l at the offshore side of the plume. Contour lines run parallel to the coast, with nearshore values between 13 and 15 nmol/l. At the tidal station, near the 11 nmol/l contour, concentrations range between 8 and 13 nmol/l, following the change in salinity inversely, but without a clear stratification. The regression of both tidal station and plume data sets computes a zero-salinity intercept of around 90 nmol/l. This value is in remarkable agreement with the 87 nmol/l given in van der Weijden and Middelburg (1989) as the weighted average concentration in the river Rhine at the German-Dutch border at Lobith. South of the outflow, concentrations range between 9 and 11 nmol/l, leading to a cluster of elevated values ($Sal \geq 34$, $Ni \geq 9$) above the otherwise tight correlation in Figure 7.16. The regression of nickel concentrations from regional survey stations with salinities above 34, i.e. from the offshore fringe of the plume and the area south of it, yield a steeper slope and a y-axis intercept of around 190 nmol/l (Table 7.2). If it is assumed that the northern offshore values are representative for the coastal sea end member, this suggests a freshwater/estuarine source with nickel levels twice as high as the Rhine affecting this southern area, or additional, non-conservative inputs.

7.3.3.4 Cobalt

Like that for Mn, the contour plot for cobalt is dominated by three high values close to the outflow, ranging between 1.3 and 1.5 nmol/l. Concentrations then fall rapidly to around 0.8 and 0.7 nmol/l nearshore and below 0.5 nmol/l offshore and south of the plume. At the tidal station, on the 0.8 nmol/l contour, concentrations range between 0.64 and 0.94 nmol/l and inversely reflect the changing salinity within both the water column and the tidal cycling, yielding a zero-salinity intercept of 4.8 nmol/l (Table 7.2), in good agreement with the lowest-salinity value at the river station, but well below the mean dissolved concentration at Lobith. Due to the high variation at low and apparently decreased values at high salinities (Figure 7.16), the regression of the entire plume data set against salinity is less significant.

7.3.3.5 Copper

The distribution of dissolved copper is characterised by contours parallel to the coast. Nearshore values vary between 15 (near the outflow) and 12 nmol/l, about half the concentration found by Duinker and Nolting (1977) during a cruise in February 1975, and decrease offshore to below 5 nmol/l. Variation over the tidal cycle is between 6 and 10 nmol/l and inversely correlated to salinity. Correlation for the tidal station data is less significant than for the combined plume data set, yielding intercepts of 53 and 73 nmol/l, respectively, compared to 68 nmol/l quoted for the river Rhine at Lobith, and a lowest-salinity concentration below 40 nmol/l at the river station. Like in the case of Ni, stations south of the outflow show comparatively high values, leading to a steep negative slope and resultant high intercept of 215 nmol/l for the selected offshore data in Table 7.2.

7.3.3.6 Zinc

The distribution of Zn also shows a strong longshore feature, with nearshore concentrations between 30 and 26 nmol/l, again considerably lower than found by Duinker and Nolting (1977), decreasing to below 10 nmol/l offshore. At the coastal tidal station on the 20 nmol/l contour, concentrations range between 12 and 25 nmol/l, with a clear inverse correlation with salinity, reflected in both stratification and tidal cycle. Regression of both tidal station and pooled plume data sets yield a zero-salinity intercept of around 210 nmol/l, considerably less than the estimate of van der Weijden and Middelburg (1989) of 590 nmol/l, but in good agreement with the river station maximum of 180 nmol/l. South of the outflow, values are again comparatively elevated, leading to an intercept of 340 nmol/l for the high-salinity stations.

7.3.3.7 Cadmium

Whilst Cd concentrations close to the outflow are surprisingly low, not exceeding 0.20 nmol/l, there is a distinct 'hot-spot' further up the coast, reaching 0.40 nmol/l at station Y2 near IJmuiden, also suspected of having a very high SPM concentration, and stretching out to the surrounding transects and offshore. There is no corresponding feature in the phosphate distribution (Figure 7.3). Opposite the old delta, values are low, between 0.16 and 0.21, and the lowest values of the survey have been recorded offshore. At the coastal tidal station, between the 0.20 and 0.24 nmol/l contours, concentrations range between 0.15 and 0.26, with two surface values reaching 0.36 and 0.31 nmol/l, respectively. Inverse correlation with salinity is visible, but not strong. The trace metal-salinity plot for the entire coastal data set (Figure 7.17) is similarly inconclusive. All values are well below the 0.9 nmol/l given in Duinker and Nolting (1977) as the minimum contour for the area during spring 1975.

7.3.3.8 Lead

Similar to Mn and Co, dissolved lead concentrations are very high at T1, T2 and T3, close to the outflow, ranging between 0.31 and 0.40 nmol/l. They remain around 0.2 to 0.27 in most of the area north of the outflow, dropping to only 0.17 nmol/l at T7. The lowest values, however, are to be found in the comparably particle-rich, but saline environments off the old delta, At the tidal station on the 0.27 nmol/l contour, concentrations range really from 0.10 to 0.27 nmol/l, with two spikes nearly reaching 0.40 nmol/l. Indications of a freshwater source for lead are only just perceptible. Despite a lot of scatter, however, the trace metal-salinity plot shows a decrease in dissolved lead with increasing salinity (Figure 7.17), until, for the offshore samples, this trend reverses, possibly due to a combination of persistent atmospheric input and a decrease in scavenging particle populations offshore. Again, all recorded concentrations are well below the minimum 2 nmol/l contour given for this area in Duinker and Nolting (1977).

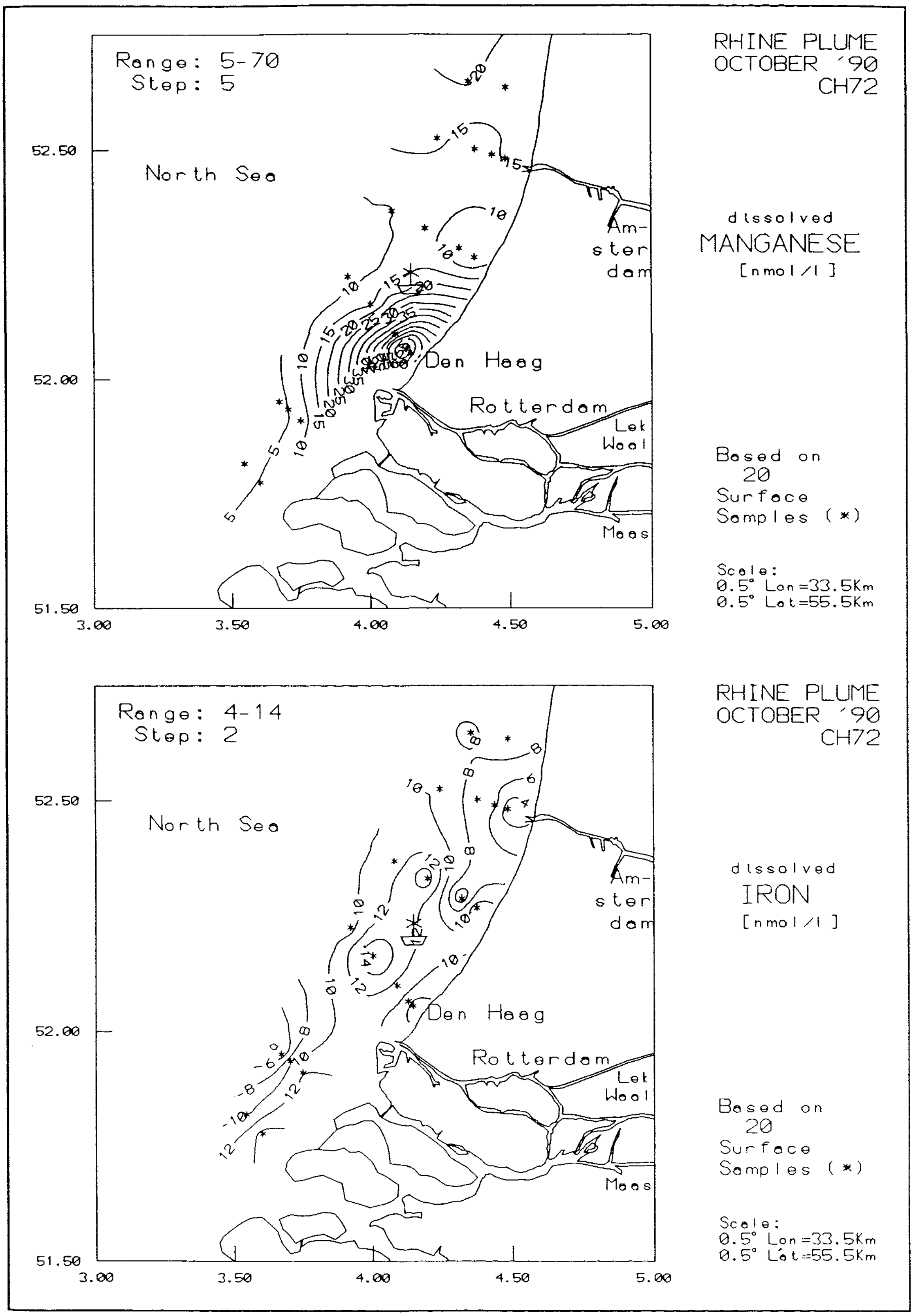

Figure 7.9: Distribution of dissolved manganese and iron in the Rhine plume (CH72)

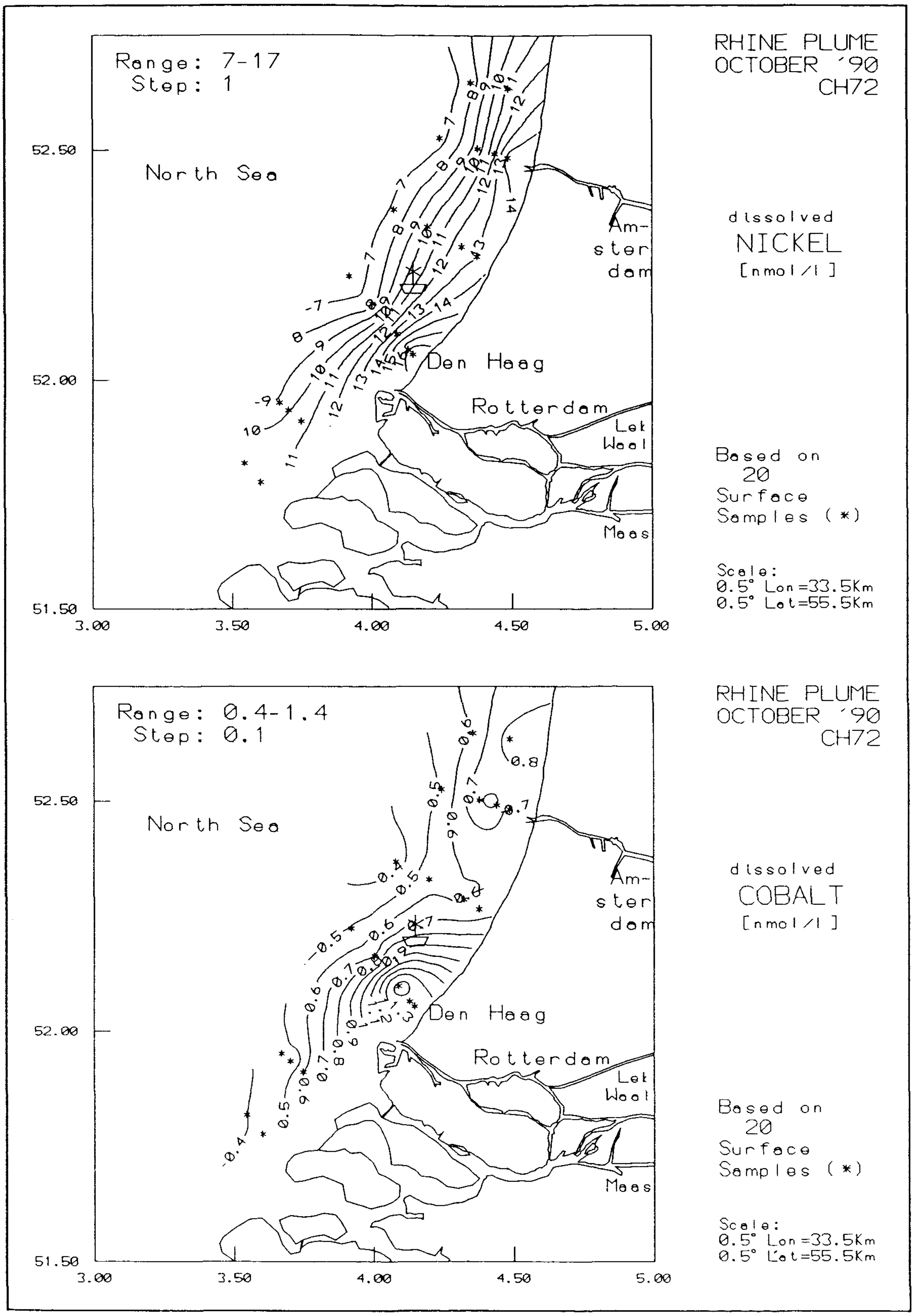

Figure 7.10: Distribution of dissolved nickel and cobalt in the Rhine plume (CH72)

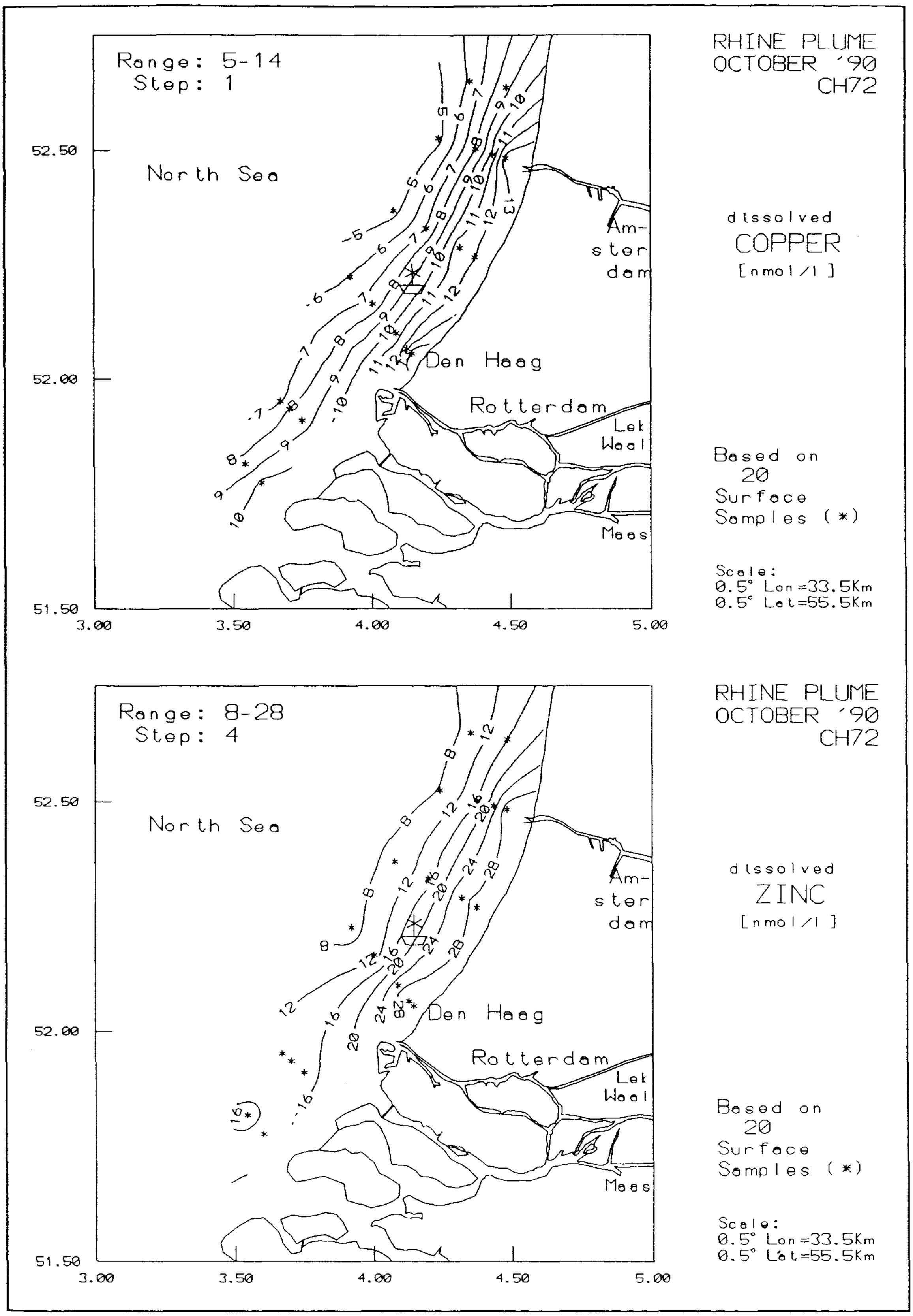

Figure 7.11: Distribution of dissolved copper and zinc in the Rhine plume (CH72)

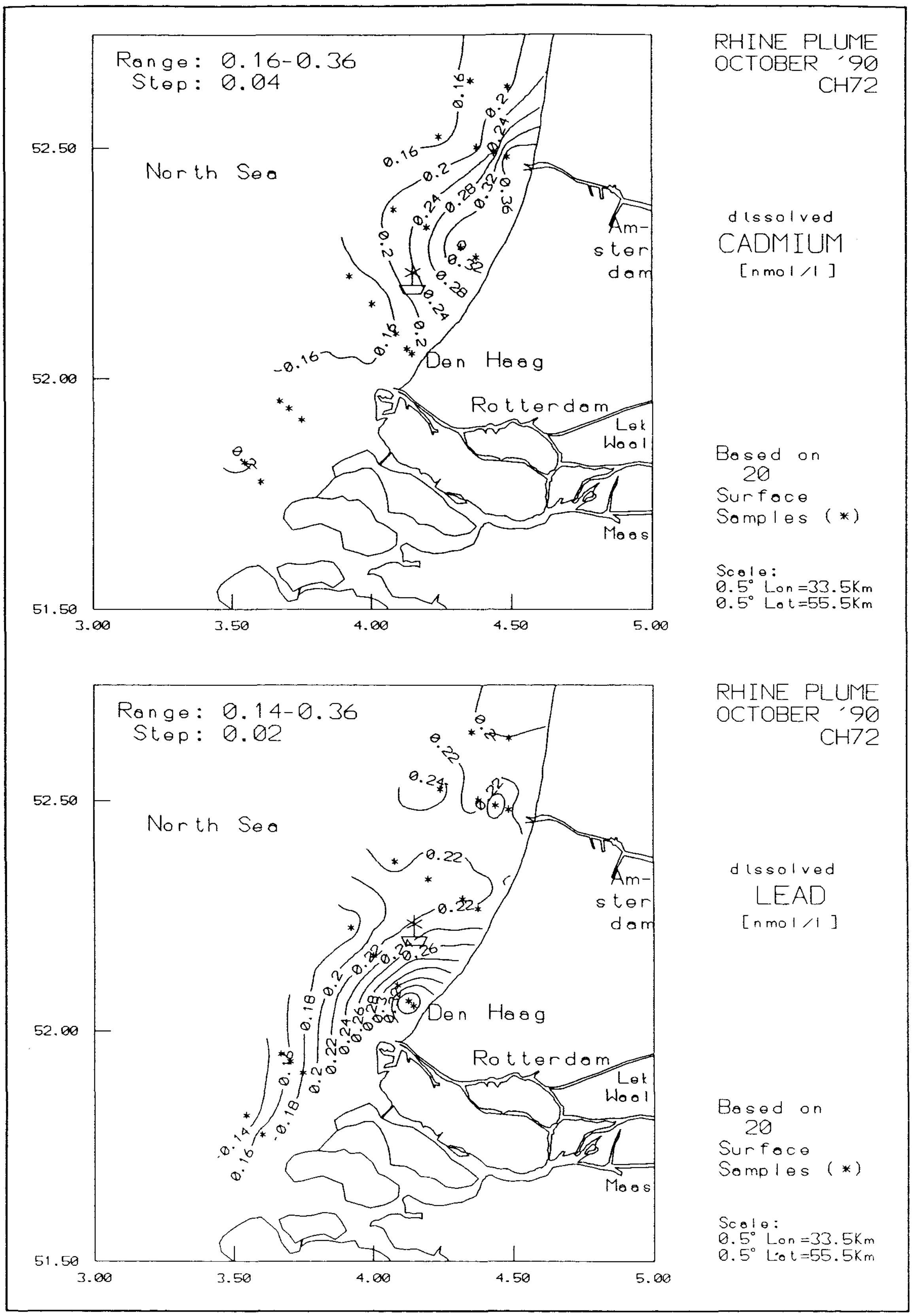

Figure 7.12: Distribution of dissolved cadmium and lead in the Rhine plume (CH72)

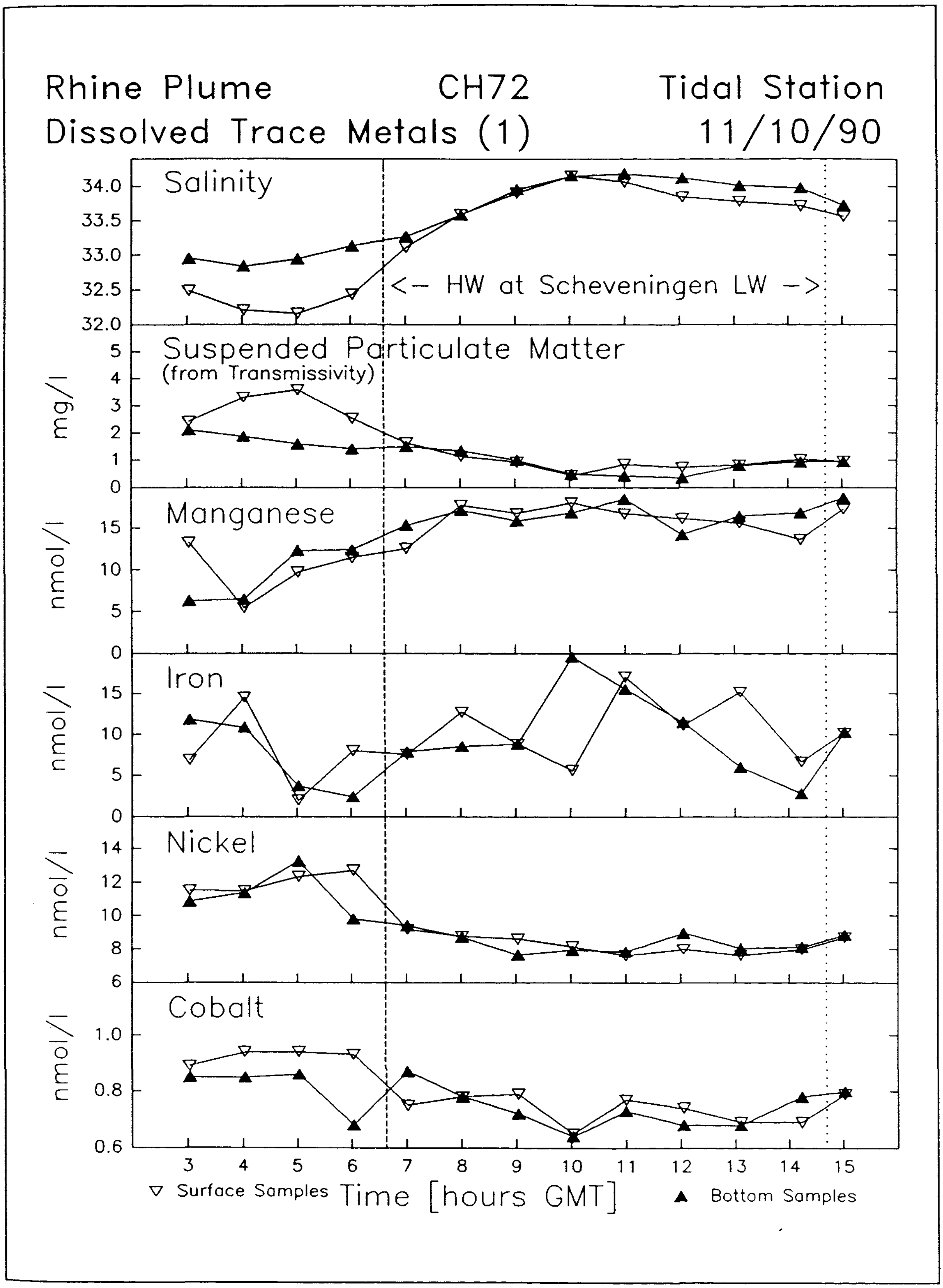

Figure 7.13: Time series of dissolved Mn, Fe, Ni and Co at the offshore tidal station (CH72)

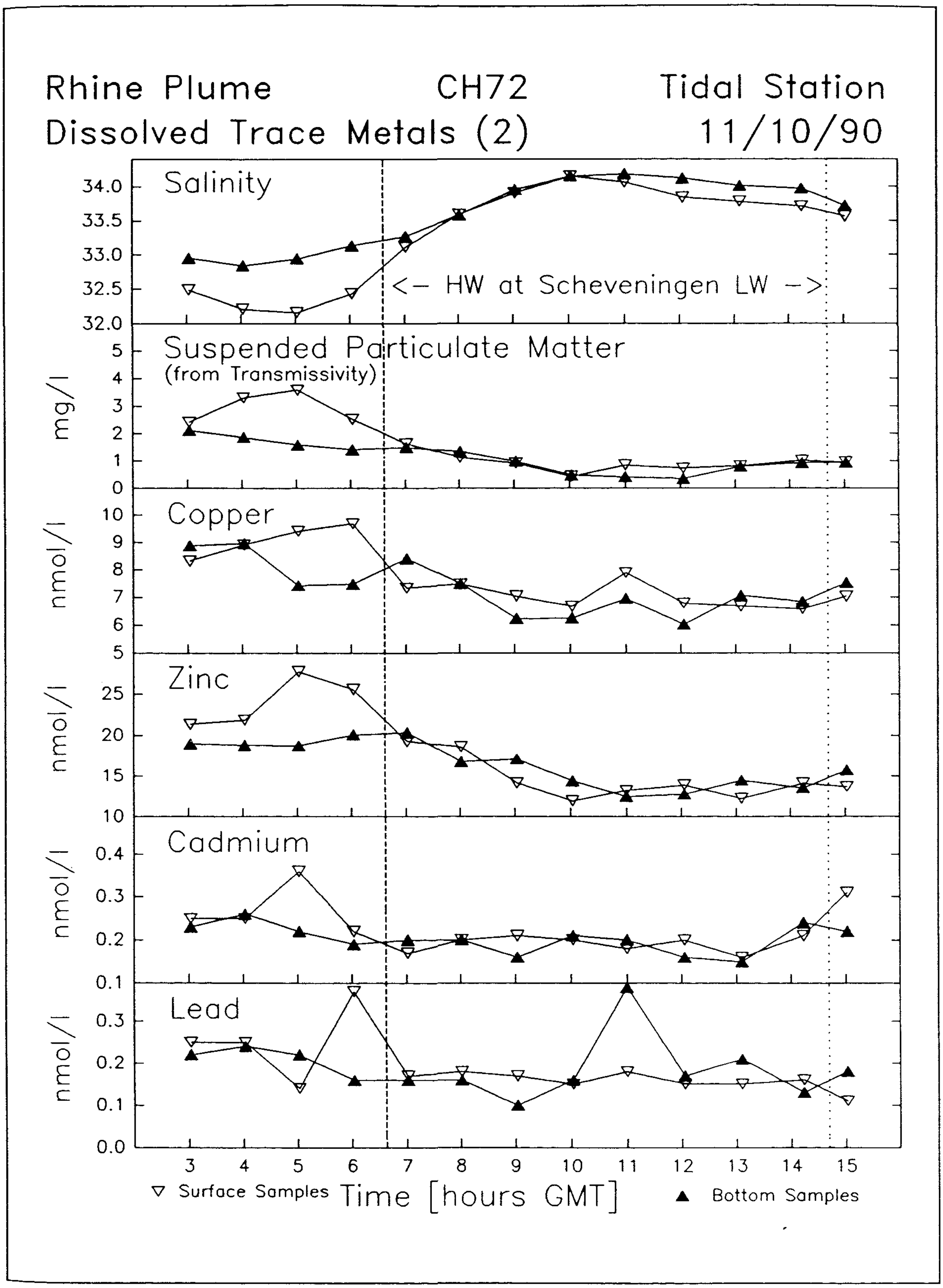

Figure 7.14: Time series of dissolved Cu, Zn, Cd and Pb at the offshore tidal station (CH72)

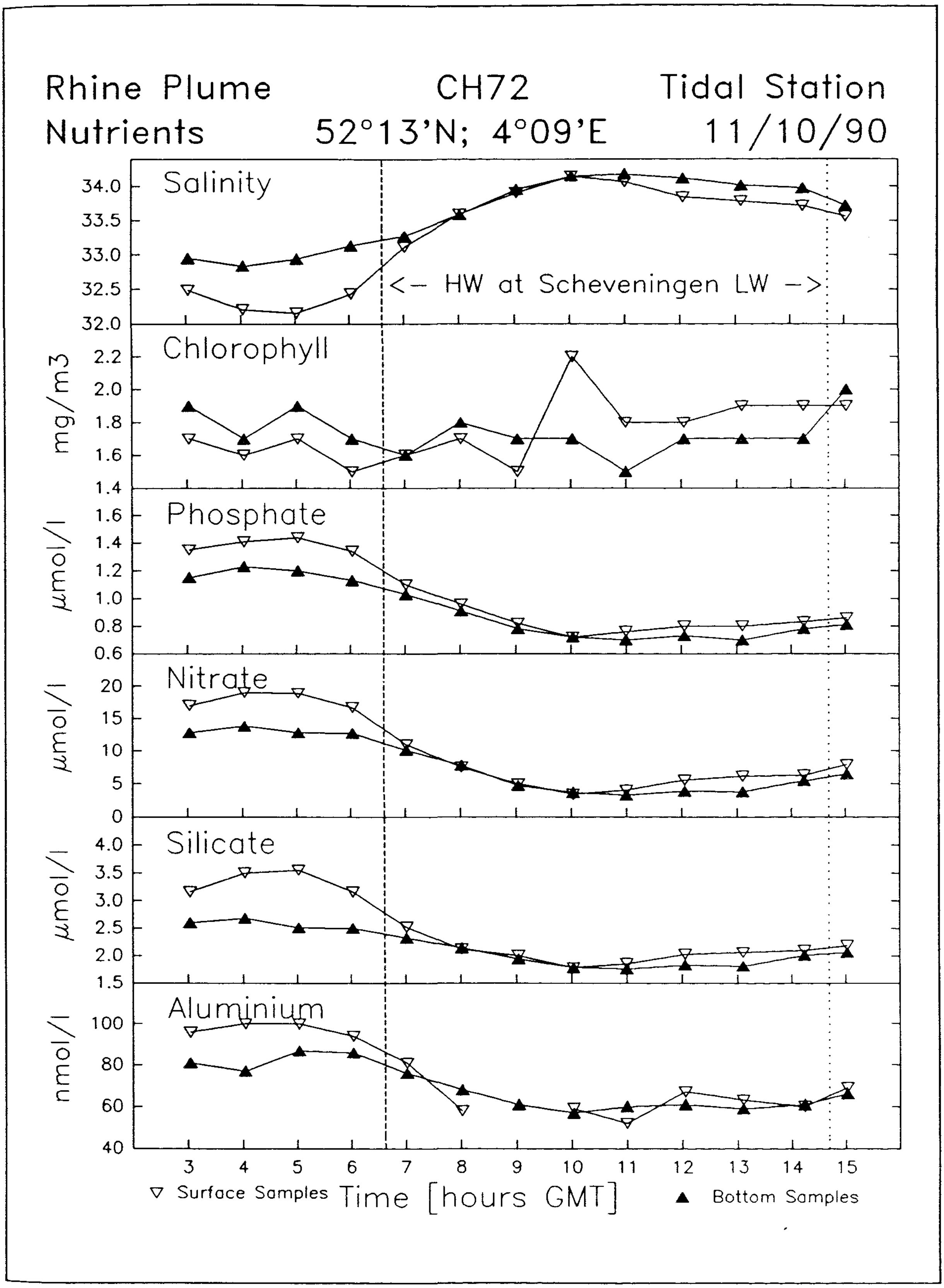

Figure 7.15: Time series of chlorophyll, PO_4, NO_3, Si and Al at the offshore tidal station (CH72)

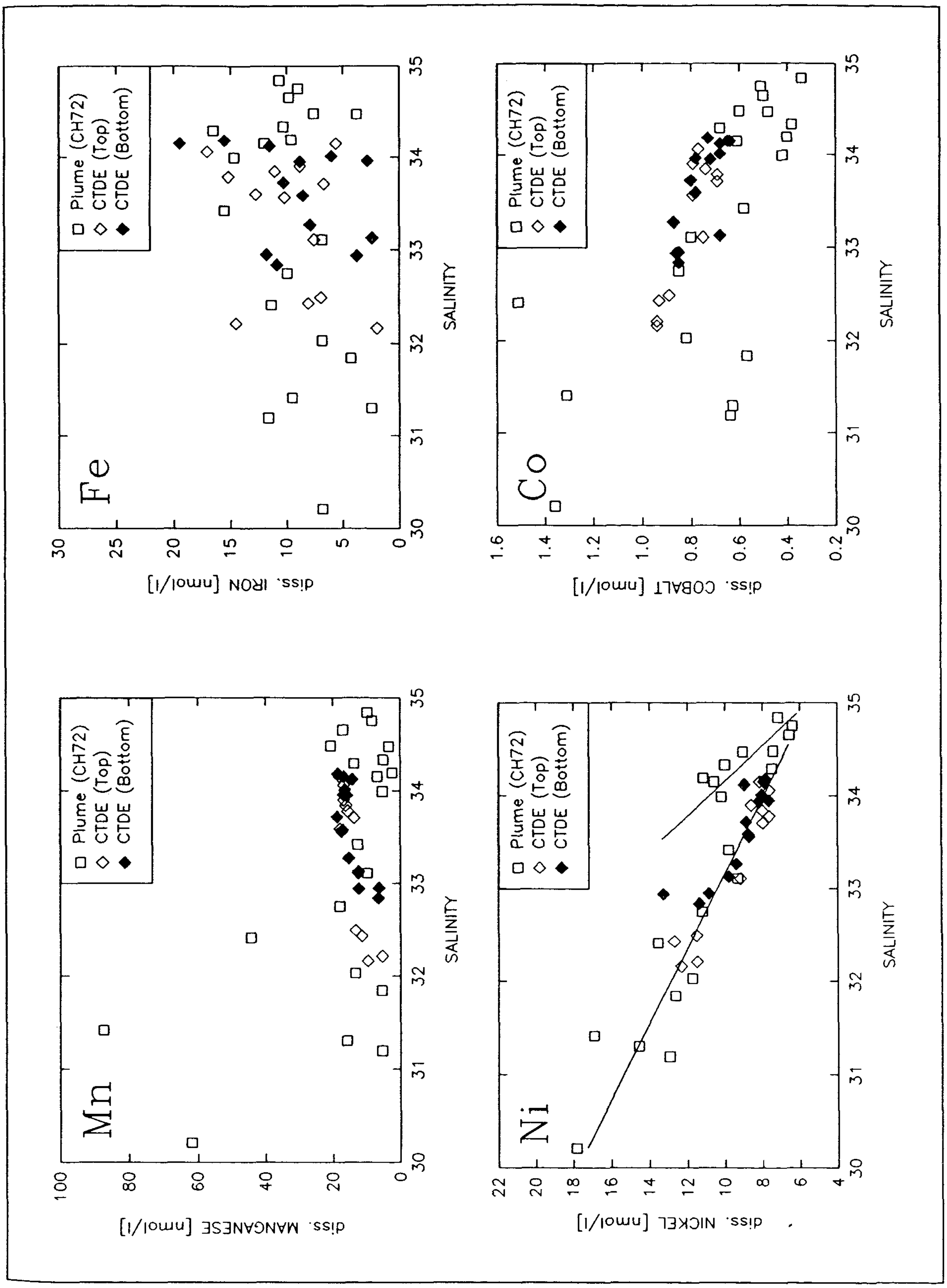

Figure 7.16: Trace metal-salinity plots for dissolved Mn, Fe, Ni and Co in the Rhine plume (CH72)

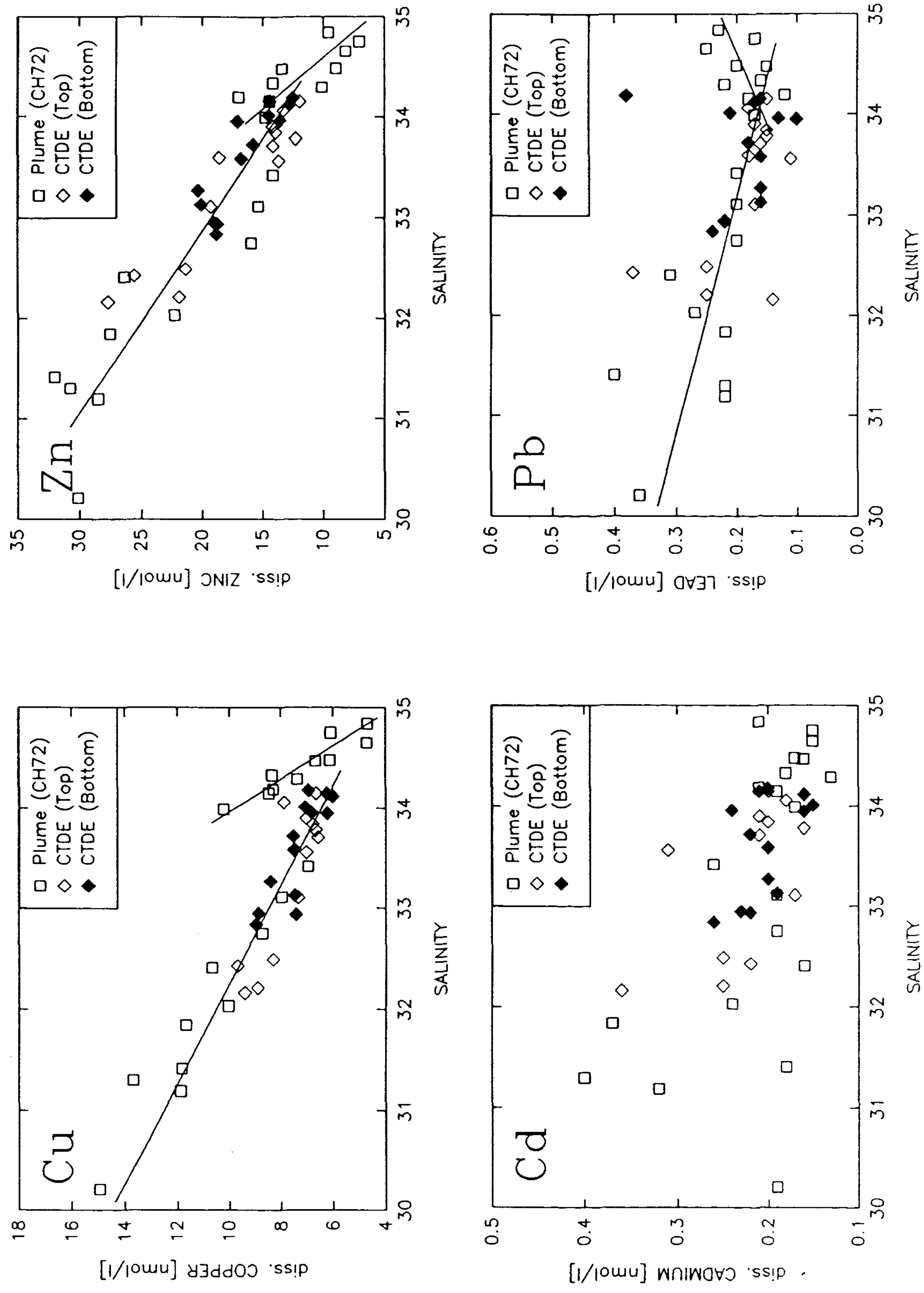

Figure 7.17: Trace metal-salinity plots for dissolved Cu, Zn, Cd and Pb in the Rhine plume (CH72)

Rhine: Regression for different data sets

Offshore Tidal Station (n=26)

Element	Intercept [nmol/l]	Slope	Probability Slope=0 (H0)	Corr.Coeff.	R-squared
Mn	-145±25	+4.8±0.7	0.00000	+0.80	63%
Ni	91±8	-2.4±0.3	0.00000	-0.90	81%
Co	4.8±0.5	-0.12±0.02	0.00000	-0.84	70%
Cu	53±6	-1.4±0.2	0.00000	-0.86	73%
Zn	216±18	-6.0±0.6	0.00000	-0.91	83%

Plume north of Hoek van Holland (n=41; pooled tidal station/regional survey data)

Element	Intercept [nmol/l]	Slope	Probability Slope=0 (H0)	Corr.Coeff.	R-squared
Ni	90±5	-2.4±0.1	0.00000	-0.94	89%
Cu	73±4	-2.0±0.1	0.00000	-0.94	89%
Zn	209±11	-5.8±0.3	0.00000	-0.94	89%

High Salinity Samples (n=10; southern and offshore stations, S ≥ 34)

Element	Intercept [nmol/l]	Slope	Probability Slope=0 (H0)	Corr.Coeff.	R-squared
Ni	194±46	-5.4±1.3	0.00356	-0.82	68%
Cu	216±28	-6.1±0.8	0.00006	-0.94	88%
Zn	344±91	-9.7±2.7	0.00654	-0.79	62%

Table 7.2: Regression of dissolved trace metal concentrations against salinity for different data sets from the Rhine plume (CH72)

7.3.4 Distribution between Dissolved and Particulate Phase

In Figure 55.21 to Figure 55.28, particle-bound percentages of the total load have been plotted, on a probability scale, against suspended matter concentrations, on a logarithmic scale. Lines corresponding to a given K_d-value have also been plotted.

In the Rhine estuary and plume, iron shows the strongest affinity to particles, with more than 90% of the total concentration bound to SPM in most samples. Lead and, in the coastal waters, manganese, is to more than 50% bound to particles. All other metals, however, exist predominantly in the dissolved phase, most extremely in the case of nickel, where more than 90% of the total load is dissolved. K_d-values are generally in agreement with the ranges given by Golimowsky et al. (1990) for the Rhine and Maas rivers and estuary.

Samples have been sub-divided into four subsets: the tidal coastal station, with its very low turbidity; the tidal river station, and the regional survey samples north and south of the outflow; the last three groups having comparable SPM concentrations around the 10 mg/l level, with the highly turbid station Y2 as an outlier.

Distribution coefficients are distinctly different between the four subsets, with characteristic patterns for both particle-reactive (Mn, Co and Pb) elements and those for which there is evidence for additional inputs at higher salinity (Ni, Cu, Zn and Cd). For manganese, the differences are most pronounced: Coastal plume samples from north of the outflow have $\log(K_d)$-values around 6, including the station Y2, but samples from south of the outflow, less influenced by the estuarine plume, have higher values, close to 7. Values from the coastal tidal station are also slightly higher, between 6 and 7, especially in particle-depleted samples. $\text{Log}(K_d)$-values below 5 are common at the tidal river station, where particles thus appear depleted in trace metals compared to the dissolved phase. The same pattern is also apparent for cobalt, with $\log(K_d)$-values in the river just above 4, and highest, above 5, at the southern stations, and lead (estuarine and coastal plume between 5 and 6, coastal tidal station and southern sites between 6 and 7).

The reverse of this behaviour can be seen for cadmium: southern stations and many coastal tidal station samples range between log(K_d)'s of 4 and 5, northern plume samples just below 5, and estuarine samples at or above the 10^5 contour. High estuarine and low southern station K_d's can also be seen for Cu, although subsets are less well separated. For zinc, K_d's south of the outflow are lower than those in the North, but on a par with the estuarine samples. The same is still essentially the case for Ni, although for this element most K_d's range in a narrow band between 1000 and 10000. Iron shows no differentiation between coastal values, but a depletion of the particulate compared to the dissolved phase for some estuarine samples.

Unfortunately, particulate trace metal concentrations cannot be corrected for different grain size distributions, which could lead to lower K_d's in areas of coarser SPM, without actual adsorption/desorption processes taking place. This is, however, not very likely to be the only reason for the observed differences, since at least three subsets have comparable SPM concentrations and thus probably not too different size spectra, and no subset shows decreased distribution coefficients for all metals. The present findings could also be interpreted as the result of offshore scavenging of Mn, Co and Pb, especially in the fairly saline and particle-rich coastal waters south of the plume, and simultaneous desorption of Cu and Cd from estuarine particles. Zinc and nickel, however, appear to be characterised by comparatively high dissolved concentrations in both the estuary and south of the outflow, possibly due to predominance of the dissolved phase in the river, followed by nearshore removal, but offshore desorption. These preliminary conclusions, however, require further investigation of distributions in the particulate phase.

7.4 SUMMARY: THE RHINE PLUME

The investigation has significantly increased our knowledge of the Rhine outflow system through the combination of intensive hydrographic profiling, the application of clean sampling methods and use of analytical techniques which have enabled information to be obtained on eight trace metals with contrasting biogeochemical behaviours. The outcome is a much more detailed understanding of the behaviour of trace metals in the estuarine and coastal mixing zone.

Regarding the data for the tidal cycle station in the low salinity region, it was found that

(i) for all metals, lowest salinity concentrations at the river station were below the ten year average dissolved concentrations at Lobith (Table 7.3), possibly due to natural variation, estuarine losses at even lower salinities or, especially for Cu, Zn, Cd and Pb, substantially reduced loads since the 1970s.

(ii) the changes in concentration of Ni, Cu and Zn could partly be explained by the mixing of sea water with trace metal-enriched river water, although the influence of other factors in this complex and industrialised environment was also evident.

(iii) the behaviour of the most particle-reactive metals, Mn, Fe, Co and Pb, is not dominated by two end-member mixing, but by processes such as re-suspension and particle-water interaction. There are strong similarities in the trends of these metals, especially in coincident short-term variability in bottom waters during the tidal cycle.

(iv) for manganese, dissolved concentrations rise sharply from the lowest salinity end, indicative of mobilisation from particulate or sedimentary sources; K_d-values here are lower than in coastal waters, underlining the enrichment of the dissolved compared to the particulate phase.

(v) concentrations of dissolved cadmium in the Nieuwe Waterweg are dominated by local sources, most possibly phosphogypsum slurries discharged from fertilizer manufacturing plants, or massive desorption from riverborne particles; K_d-values are higher than in the coastal zone.

Regarding the distribution of dissolved trace metals in the coastal water body, it was found that

(i) within the longshore river plume north of the outflow, the distributions of Ni, Co, Cu and Zn were largely correlated with the prevailing salinity distribution and thus could be partly explained by the mixing of river and sea water; for zinc and cobalt, there was good agreement between effective river end member estimates and concentrations measured at lowest salinities in the river (Table 7.3); for nickel and copper, zero-salinity intercepts from the river plume over-estimated actual riverine concentrations, indicative of additional coastal inputs.

(ii) stations south of the river plume showed dissolved concentrations of Ni, Cu and Zn higher than could be expected from salinity data, leading to steeply sloped regression lines and high zero-salinity intercepts, when related to the assumed marine background concentrations (Table 7.3); explanations include a freshwater source with higher trace metal concentrations than the river Rhine, or additional inputs within the coastal sea, possibly remobilisation from suspended particulate matter or sediments; K_d-values of these metals are generally lower here than in the plume in the North.

(iii) there was a highly productive, nutrient- and particle-depleted offshore water body with increased manganese levels in the north-west of the survey area

(iv) there was a large area off the coast near IJmuiden, where dissolved cadmium and suspended particulate matter concentrations were higher than close to the Rhine outflow, without concomitant high phosphate levels

(v) concentrations of dissolved lead were higher in offshore areas with lower concentrations of SPM, than in particle-richer areas of lower salinity, with a minimum in the comparably particle-rich and saline coastal waters south of the outflow; the two major factors that can give rise to this are the more intensive scavenging at higher particle concentrations and the inputs to offshore waters, e.g. from atmospheric and benthic sources. Together with manganese and cobalt, K_d-values for lead were generally higher in this area than in the plume north of the outflow.

(vi) for most trace metals, concentrations found during this study were significantly below levels reported earlier. It is possible that improvements in water quality may have contributed to the observed decrease but other factors, including seasonal variability and improvements in clean sampling and analysis, may also explain this finding.

[nmol/l]	Average Lobith 1975-84	River station $2.4 < Sal < 7.6$	Intercept north of outflow	Intercept south of outflow
Mn	940	330-460		
Fe	900	16-250		
Ni	87	40-57	90-91	190
Co	13	3.2-4.1	4.8	
Cu	68	28-39	53-73	220
Zn	590	120-180	210-220	340
Cd	5.0	0.21-0.63		
Pb	4.5	0.58-1.1		

Table 7.3: Freshwater concentration estimates for the river Rhine

CHAPTER 8: CONCLUDING DISCUSSIONS

Intensive surveying under contrasting seasonal conditions of dissolved trace metal concentrations in coastal water bodies and estuaries discharging into them, together with the measurement of a wide range of other relevant parameters, has substantially extended our knowledge of trace metal behaviour in the estuarine plumes of the Humber, Thames and Rhine rivers.

Coastal distributions almost always showed major influences of riverine dissolved trace metal inputs, but differ strongly between the individual metals with respect to the extent to which distributions are dominated by river-sea water mixing. Generally, a strong negative correlation with salinity was found for the dissolved concentrations of nickel, copper, zinc and cadmium, allowing the computation of effective freshwater end member concentrations. Coastal distributions of manganese, iron, cobalt and lead, however, were strongly influenced by processes other than conservative mixing. Zero-salinity extrapolations with R^2-values greater than 55% and near-freshwater concentrations from the Rhine tidal river station are compiled in Table 7.4, together with effective end member estimates based on samples from the early 1980s, representing average North Sea river water concentrations (Kremling, 1985), and estimates of world average river water concentrations (Martin and Windom, 1991). Estimates from this study are shown for estuaries, outflow areas (Humber mouth, mid-estuary Thames) and coastal water samples (Humber-Wash area, outer Thames estuary, Dutch coastal zone south and north of the Rhine outflow).

all [nmol/l]	**Mn**	**Fe**	**Ni**	**Co**	**Cu**	**Zn**	**Cd**	**Pb**
ESTUARIES: Humber Estuary, Inner Thames Estuary, Rhine River(*)								
Humber Spring			270		160		5.2	0.7
Thames Winter	100	350	260	7.2	120	650	2.3	20
Rhine Autumn		250	57	4.1	39	180	0.21	1.1
OUTFLOWS: Tidal Stations Humber, Middle Thames Estuary								
Humber Winter1			190	19	140	600	3.0	
Humber Winter2			240		100		4.0	
Humber Spring	2000		380	10	150	850	8.1	
Humber Summer	10000		520	32	200	890	9.3	
Thames Spring	90		270	8.8	200	870	4.7	6.1
COASTAL WATERS: Humber-Wash Area, Outer Thames Estuary, Rhine N, Rhine S								
Humber Winter			250		150	320	5.3	
Humber Spring			250		200	220	4.9	
Humber Summer			400		270	400	7.3	
Thames Winter			300		330	1000		8.2
Rhine N Autumn			90	4.8	73	210		
Rhine S Autumn			190		220	340		
NORTH SEA RIVERS: Zero-Salinity Estimates (Kremling, 1985)								
	140		160		92		5.8	
WORLD RIVERS: Average Dissolved Concentrations (Martin and Windom, 1991)								
	150	720	8.5	1.7	24	9.2	0.09	0.14

(*): For the Rhine estuary, lowest salinity maximum values have been used instead of zero salinity intercepts

Table 7.4: Riverine end member concentration estimates

8.1 NICKEL, COPPER, ZINC AND CADMIUM

Even the distributions of the apparently conservatively mixing elements Ni, Cu, Zn and Cd are subject to further complexities and modifications. Effective riverine concentrations reaching the coastal zone via the outflow areas increase from winter to summer, possibly in response to decreased freshwater discharges, as can be seen from the Humber tidal station estimates. This could lead to metal-salinity relationships changing with time and space, as the riverine source variation propagates through the coastal zone, which would, e.g., explain the apparent time lag of three months between plume- and outflow-derived nickel estimates. Differences in effective riverine concentrations according to the extent of the sampling zone on which the values are based, i.e. the offshore increase of the effective riverine concentrations for Ni, Cu and Zn in the Thames and for Cu in the Humber (although together with decrease for Zn), and the increased estimates for the area south of the Rhine outflow compared to those for the plume to its north, could also be due to additional inputs to the dissolved phase in the respective coastal areas. This holds also partly true for cadmium, which showed strong additional inputs in the coastal zone near IJmuiden, possibly due to a point source, and in the Nieuwe Waterweg. The latter phenomenon showed strong resemblance to the mid-salinity increases due to remobilisation from particles observed in both industrialised and less industrialised estuaries by Elbaz-Poulichet et al. (1987). In this study, however, a strong positive correlation with phosphorus pointed to local phosphogypsum discharges as the main source of dissolved cadmium. Increased dissolved concentrations of Ni and, to a lesser extent, Cu, were found near the Barrow Deep dumping ground in the Thames estuary.

Comparing the different riverine inputs, one finds a fairly good agreement between corresponding estimates for Ni, Cu and Zn in Humber and Thames rivers, with intercepts for the outer Thames estuary being elevated for Cu and Zn. Dissolved cadmium concentrations in the Humber are about twice as high as in the Thames, possibly due to higher industrial discharges or mobilisation from dredge spoils, and in agreement with earlier studies identifying this estuary as a significant source of cadmium (Balls, 1985a). Lowest salinity concentrations from the Rhine river station and effective freshwater concentrations derived from the Rhine plume in autumn lie generally well below the corresponding estimates for

Humber and Thames, pointing in the first case possibly at estuarine removal above the tidal river station, or indeed at real differences in the freshwater concentrations. Estimates using data from the area south of the outflow, however, are in good agreement with the other offshore values. Decreased dissolved concentrations of Ni, Cu, Zn and Cd in areas of high biological activity were observed in the Humber-Wash coastal zone, and in the Thames estuary levels of Zn and Cd apparently were lower in summer than in winter, all indicating potential for biological removal of these elements during the spring and summer months. No additional inputs were observed during resuspension events.

The effective freshwater concentrations for Cd found during this study agree well with the values by Kremling (1985) for average North Sea river water (5.8 nmol/l) and by Elbaz-Poulichet et al. for the Gironde (5 nmol/l), but are up to two orders of magnitude higher than the worldwide average river concentration. The estimates of Kremling (1985) for Ni and Cu seem to underestimate the contribution of the English estuaries, and extrapolations for Ni in this study also exceed recent measurements in the Scheldt and Rhône (Zhang and Wollast, 1990) by around an order of magnitude.

8.2 MANGANESE, IRON, COBALT AND LEAD

Dissolved concentrations of manganese, iron, cobalt and lead showed little or no correlation with salinity. At the tidal river and estuarine stations, manganese frequently showed maximum concentrations at the lowest salinity, and the high riverine end member estimates of 2000 and 10000 nmol/l at the Humber mouth, compared to around 100 nmol/l for the Thames and 140 for average North Sea rivers, are most likely to be the result of sedimentary inputs in the lower estuary, also observed during the estuarine transect. High manganese levels observed in the immediate vicinity of the Humber and Rhine outflows, rapidly decrease in the coastal waters, where they are probably removed by oxidative scavenging. In the coastal areas off the Humber and Thames, dissolved manganese concentrations increased from winter to summer, and in the Rhine plume, elevated offshore concentration were detected in a particle-depleted and biologically productive active area in the north west. Similar observations of seasonal changes have been made by Morley et al. (1990), who found significant increases in the concentration of Mn, Co and Pb in July compared to December in the Gulf of Lions. The reasons for these elevated levels remained unclear; photo-reductive mobilisation from particles, as described, e.g. by Sulzberger and Xyla (1990), could possibly offer an explanation. Manganese apparently is also remobilised during resuspension events, but appeared decreased in areas of high primary production in the Humber-Wash area during spring. Offshore K_d distribution coefficients were generally an order of magnitude higher than estuarine and outflow values, except for stations with elevated dissolved levels in spring off Norfolk, underlining the efficiency of nearshore removal and, in spring, offshore mobilisation.

The element cobalt seems to share some of these characteristics, including sedimentary inputs in the lower Humber estuary, rapid nearshore removal, increased summer levels off the Humber and Thames estuaries, inputs during resuspension of bed sediments and increased offshore K_d-values. No biological uptake or increased levels in the northwest of the Rhine plume were observed. In nearshore and estuarine waters, however, cobalt seems to behave fairly conservatively, in agreement with observations by Zhang and Wollast (1990) in the Rhône estuary. Effective freshwater estimates for North Sea rivers again are in some cases increased by more than an order of magnitude compared to the Rhône (1.1 nmol/kg, Zhang and Wollast) or the world-wide average.

Iron concentrations include a large number of erratic values and iron distributions remain the most difficult to explain. Acceptable river end member estimates for the Thames and Rhine remain below the world wide average. Iron is the element most strongly bound to suspended sediments, with particulate percentages exceeding 90% in Humber and Rhine, and 99% in the Thames. At some tidal stations, iron and lead concentration changes showed a remarkable degree of coincidence.

In the Humber estuary, dissolved lead concentrations increased from the particle-rich inshore areas offshore, and concentrations at the tidal station were positively correlated with salinity. In the Dutch coastal waters, elevated levels near the Rhine outflow decreased rapidly, with minimum levels in particle-rich nearshore areas rather than particle-depleted offshore stations. This behaviour is explained by removal onto particles in turbid areas, together with additional inputs offshore from the atmosphere. In the Thames and Humber estuaries, however, lead appears to behave almost conservatively, leading to freshwater end member concentrations of 0.7 nmol/l in the Humber, and 20 nmol/l in the inner Thames estuary, compared to a lowest salinity concentration of 1.1 nmol/l in the Rhine, identifying the Thames as a major source of dissolved lead, probably reflecting major urban sources, especially from leaded petrol, in the Greater London area. However, a reduced estimate for the outer Thames shows some removal between the two apparently linear transects.

Taking the results from all the elements investigated, it becomes clear that on a world wide scale, the rivers Humber, Rhine and Thames show highly elevated concentrations for most trace metals: Ni, Co and Cu are more than one order of magnitude, Zn, Cd and Pb up to two orders of magnitude higher than the world average levels, although zero-salinity extrapolation for Mn and Fe, disregarding remobilisation in the Humber, are comparably low. This differentiation indicates a strong anthropogenic contribution to the observed elevated trace metal inputs. In all areas, however, measurements conducted during this study frequently were considerably lower than previously reported, possibly a reflection of improved contamination control during analysis, or indeed the effect of improvements in river and estuary water quality over the last two decades.

8.3 ACHIEVEMENT OF OBJECTIVES

In a qualitative sense, the objectives stated in Chapter 1 have to a large extent been achieved. Horizontal dissolved trace metal distributions in the estuarine plumes of the Humber, Thames and Rhine rivers have been mapped as contour plots. Vertical distributions have been investigated at suspected resuspension sites and a few other selected locations, and at the riverine and coastal anchor station during the Rhine cruise. Seasonal changes in horizontal distributions and riverine influx have been shown in both the Humber and Thames coastal areas. Removal by and mobilisation from particles, and the effects of biological uptake, atmospheric inputs and sediment resuspension have been inferred. In a quantitative sense, the objectives have been partly achieved by the calculation of meaningful effective riverine trace metal concentrations reaching the coastal zone, which can be converted into flux estimates. So far, it has not been possible to quantify reliably the effects of biological uptake, atmospheric input or sediment resuspension in a way which would allow application in computer models.

8.4 SUGGESTIONS FOR FUTURE WORK

The full potential of the data collected during this study will only be realised through the complete integration with the results from other research groups taking part in the different cruises. Particulate trace metal determinations and the measurements of trace metal fluxes between water column and bottom sediments promise further insight into particle-water interactions and bottom sediment inputs. Radiotracer experiments conducted during some of the cruises may give information about the kinetics of trace metal adsorption and facilitate particle-water interaction modelling. Suspended sediments can be further characterised by their aluminium and organic material contents, and thus conclusion about their origin and properties may be possible. The full evaluation of the nutrient data will highlight riverine inputs and seasonal uptake and re-mineralisation, which could lead to a better understanding of similar processes expected for some trace metals. Effective riverine end member estimates should be compared with time series of real river concentrations, thus defining the impact of both average conditions and episodical events. Trace metal behaviour in the respective survey areas could described in terms of coastal residence times, and trace metal inventories and mass balances should be computed. One-dimensional linear mixing models, as used in this study, need to be complemented with hydrodynamic transport modelling. Most of these developments are being taken up in the follow up to the phase of the NSP of which the present study formed a part.

For future studies of dissolved trace metals in estuarine plumes, the following are recommended:

- a reassessment of the statistical requirements of linear (or non-linear) mixing models, and subsequent development of suitable sampling and data processing strategies, as indicated in section 3.1.

- a reassessment of the sampling strategy, tailor-made for the process under investigation. This could mean

    - more samples in the vicinity of the outflow, where the strongest changes in salinity and especially in the concentrations of some of the more particle-active metals were observed
    - more near-bottom samples, especially during resuspension events, in order to quantify sedimentary inputs (resuspension studies were undertaken during the NSP, but not specifically in the estuarine plume areas)
    - more samples in areas of high biological activity, and appropriate reference areas, in order to quantify biological removal (or mobilisation)
    - no re-sampling of stations within a short time span, unless there is reason to suspect sudden changes, and a concept to investigate them

- an improved characterisation of suspended particulate material and dynamic modelling of its transport.

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APPENDIX I

EXTRACTION LIST

(EXAMPLE)

SAMPLE LIST FOR EXTRACTION NO.7 (RHINE OUTFLOW OFFSHORE STATIONS)

Table	Vial No.	Bottle	Sal	Site	CTD-No.	pH	Commts
Row 1	5	blank		--			
Table 1	6	4382	31.0	T1	3641		
B-Extr. 1	7	4383	31.5	T2	3642		
	8	4384	32.5	T3	3643		
	9	4385	34.0	T5	3645		
	10	4386	34.5	T7	3647		
Row 2	11	STD		CASS			
	12	4387	31.0	N2	3654		
	13	4388	32.0	N3	3655		
	14	4389	34.0	N5	3657		
	15	4390	34.5	N7	3659		
	16	4391	34.5	Y6	3667		
Row 1	17	4392	33.0	Y4	3669		
Table 2	18	blank		--			
	19	4393	32.0	Y3	3670		
	20	4394	31.0	Y2	3671		
	21	4395	35.0	E5	3674		
	22	4396	33.5	E3	3676		
Row 2	23	0	*	0;	0	*	
	24	35	ul of	0.1;	5	nmol/l	
	25	70	0.2; 10	0.2;	10	in	
	26	140	umol/l	0.4;	20	LTMS	
	27	245	spike	0.7;	35	*	
	28	350	*	1;	50	*	
Row 1	29	4397	34.0	G6	3678		
Table 3	30	STD					
B-Extr. 2	31	4398	34.0	G4	3679		
	32	4399	34.0	G3	3680		
	33	4400	34.0	S1	3682		
	34	4401	34.0	S2	3683		
Row 2	35	4402		CTDE			
	36	STD		CASS			
	37	4403		CTDE			
	38	4404		CTDE			
	39	4405		CTDE			
	40	blank		--			

Table	Vial No.	Bottle	Sal	Site	CTD-No.	pH	Commts
Row 1	45	4406		CTDE			
Table 4	46	4407		CTDE			
	47	4408		CTDE			
	48	blank		--			
	49	4409		CTDE			
	50	4410		CTDE			
Row 2	51	4411		CTDE			
	52	4412		CTDE			
	53	4413		CTDE			
	54	STD		CASS			
	55	4414		CTDE			
	56	4415		CTDE			
Row 1	57	0	*	0; 0	*		
Table 5	58	35	ul of	0.1; 5	nmol/l		
B-Extr. 3	59	70	0.2; 10	0.2; 10	in		
	60	140	umol/l	0.4; 20	Standard		
	61	245	spike	0.7; 35	Seawater		
	62	350	*	1; 50	*		
Row 2	63	4416		CTDE			
	64	4417		CTDE			
	65	4418		CTDE			
	66	blank		--			
	67	STD		CASS			
	68	4419		CTDE			
Row 1	69	4420		CTDE			
Table 6	70	4421		CTDE			
	71	4422		CTDE			
	72	4423		CTDE			
	73	blank		--			
	74	4424		CTDE			
Row 2	75	4425		CTDE			
	76	4426		CTDE			
	77	4427		CTDE			
	78	STD		CASS			
	79	3532	34.9	CH46	1429		
	80	3535	34.6	CH46	1430		

SUMMARY

20 Samples Regional Survey
26 Samples Tidal Station 'E'
2 Samples CH46
6 CASS Standards (11,30,36,54,78)
6 Blanks (5,18,40,48,66,73)
12 Recovery Calibrations (23 to 28 and 57 to 62)

======

72 Samples

APPENDIX II

ANALYTICAL CALCULATION SHEET

```
26-03-91 1100B    pyro plat   FE7        10 µl inject   55.85  g/mol

                  ============================
                    RESULTS  IRON   ANALYSIS
                  ============================


AAS-SYSTEM
==========


BASELINE AND DETECTION LIMITS        PRECISION AND SENSITIVITY

Auto-Zero     avg      std                Reslope      avg      std        rsd
            0.000     low            30 µg/l         0.285    low       n.d.

rel. LOD             abs. LOD
  n.d.    µg/l         n.d.    pg        Characterist. Mass     4.63 pg

LAMP ENERGY               54             CALIBRATION FACTOR     14.2


EXTRACTION
==========


ANALYTICAL BLANKS                        PRECISION calculated from CASS
-----------------                        ---------
                  µg/l                                    nmol/l
 Samples     avg      std      rsd     Samples     avg      std       rsd
       5    10.65     4.99       47%         5    13.40     2.61        19%

Procedural Blank:     3.90 nmol/l

                                         ACCURACY compared to CASS
                                         --------
LIMIT OF DETECTION                       NRCC-est.   15.63 nmol/l  ±    1.36
------------------
in seawater            5.48 nmol/l      SUDO-est.   13.40 nmol/l  ±    2.61

in extract            14.97 µg/l        Error [%]     -14%(analytical bias)


RECOVERY            Ideal slope:          2.89
--------
   Set       Data    CorrCoeff  Slope  St.Err   Background St.Err Extr.Eff.

                                                  nmol/l   nmol/l
  REC1          4    0.9899      2.65     0.19     -2.60      1.06        92%
  REC2          5    0.9852      2.81     0.20      6.84      1.96        97%
  USED                           2.73                                     94%
```

QUALITY CONTROL SAMPLES

BLANKS

		EXTRACTS			SEA WATER	
Vial-No.	Content	nom.conc µg/l	dil.conc µg/l	Dilution Factor	undil. µg/l	EndResult nmol/l
5	blank	0.00	12.53	1	12.53	4.59
18	blank	0.00	5.36	1	5.36	1.96
40	blank	0.00	18.95	1	18.95	6.94
48	blank	0.00	10.67	1	10.67	3.91
73	blank	0.00	5.75	1	5.75	2.10
(66)	blank	0.00	57.74	1	57.74	21.14

RECOVERY

		EXTRACTS				SEA WATER	
Vial-No.	Content nmol/l	Spike nom.conc µg/l	dil.conc µg/l	Dilution Factor	undil. lessBlnk µg/l	EndResult nmol/l	Spike nmol/l
23	0	0.00	6.05	1	-4.60	-1.68	0.84
24	5	14.46	13.87	1	3.22	1.18	3.71
25	10	28.92	15.19	2	19.73	7.22	9.75
26	20	57.83	28.78	2	46.91	17.17	19.70
(27)	35	101.21	23.11	4	81.79	29.94	32.47
(28)	50	144.58	21.54	5	97.05	35.53	38.06
57	0	0.00	26.84	1	16.19	5.93	-1.11
58	5	14.46	40.20	1	29.55	10.82	3.78
59	10	28.92	32.77	2	54.89	20.09	13.06
60	20	57.83	29.32	3	77.31	28.30	21.26
61	35	101.21	31.37	4	114.83	42.04	35.00
(62)	50	144.58	28.74	5	133.05	48.71	41.67

SEAWATER REFERENCE STANDARD (CASS)

		EXTRACTS			SEA WATER		
Vial-No.	Content	nom.conc µg/l	dil.conc µg/l	Dilution Factor	undil. µg/l	EndResult nmol/l	NRCC nmol/l
11	CASS	45.20	14.47	3	43.41	11.99	15.63
30	CASS	45.20	38.76	1	38.76	10.29	15.63
54	CASS	45.20	44.71	1	44.71	12.47	15.63
67	CASS	45.20	59.72	1	59.72	17.96	15.63
78	CASS	45.20	49.69	1	49.69	14.29	15.63
(36)	CASS	45.20	43.25	3	129.75	43.60	15.63

SEAWATER SAMPLES

Vial-No.	Bottle	Station	dil.conc µg/l	Dilution Factor	undil. µg/l	EndResult nmol/l	below LoD?
6	4382	3641	8.23	3	24.69	5.14	<
7	4383	3642	10.80	3	32.40	7.96	
8	4384	3643	12.61	3	37.83	9.95	
9	4385	3645	26.31	2	52.62	15.36	
10	4386	3647	15.48	2	30.96	7.43	
12	4387	3654	38.70	1	38.70	10.27	
13	4388	3655	17.35	1	17.35	2.45	<
14	4389	3657	49.78	1	49.78	14.32	
15	4390	3659	35.77	1	35.77	9.20	
16	4391	3667	33.31	1	33.31	8.29	
17	4392	3669	24.68	1	24.68	5.14	<
19	4393	3670	24.74	1	24.74	5.16	<
20	4394	3671	12.11	1	12.11	0.53	<
21	4395	3674	26.85	1	26.85	5.93	
22	4396	3676	33.74	1	33.74	8.45	
29	4397	3678	15.83	1	15.83	1.90	<
31	4398	3679	34.71	1	34.71	8.81	
32	4399	3680	39.70	1	39.70	10.63	
33	4400	3682	47.41	1	47.41	13.46	
34	4401	3683	32.71	1	32.71	8.07	
35	4402	----	24.90	1	24.90	5.22	<
37	4403	----	39.04	1	39.04	10.39	
38	4404	----	46.95	1	46.95	13.29	
39	4405	----	36.37	1	36.37	9.41	
45	4406	----	10.72	1	10.72	0.02	<
46	4407	----	15.79	1	15.79	1.88	<
47	4408	----	28.13	1	28.13	6.40	
49	4409	----	11.91	1	11.91	0.46	<
50	4410	----	26.83	1	26.83	5.92	
51	4411	----	27.72	1	27.72	6.25	
52	4412	----	41.77	1	41.77	11.39	
53	4413	----	29.63	1	29.63	6.95	
55	4414	----	30.48	1	30.48	7.26	
56	4415	----	21.20	1	30.48	7.26	
63	4416	----	28.28	1	21.20	3.86	<
64	4417	----	61.20	1	61.20	18.50	
65	4418	----	54.26	1	54.26	15.96	
68	4419	----	49.89	1	49.89	14.36	
69	4420	----	36.95	1	36.95	9.63	
70	4421	----	38.27	1	38.27	10.11	
71	4422	----	48.85	1	48.85	13.98	
72	4423	----	22.30	1	22.30	4.26	<
74	4424	----	24.24	1	24.24	4.97	<
75	4425	----	13.09	1	13.09	0.89	<
76	4426	----	34.38	1	34.38	8.69	
77	4427	----	34.66	1	34.66	8.79	
79	3532	1429	8.72	1	8.72	-0.71	<
80	3535	1430	10.89	1	10.89	0.09	<

RECOVERY CALIBRATION

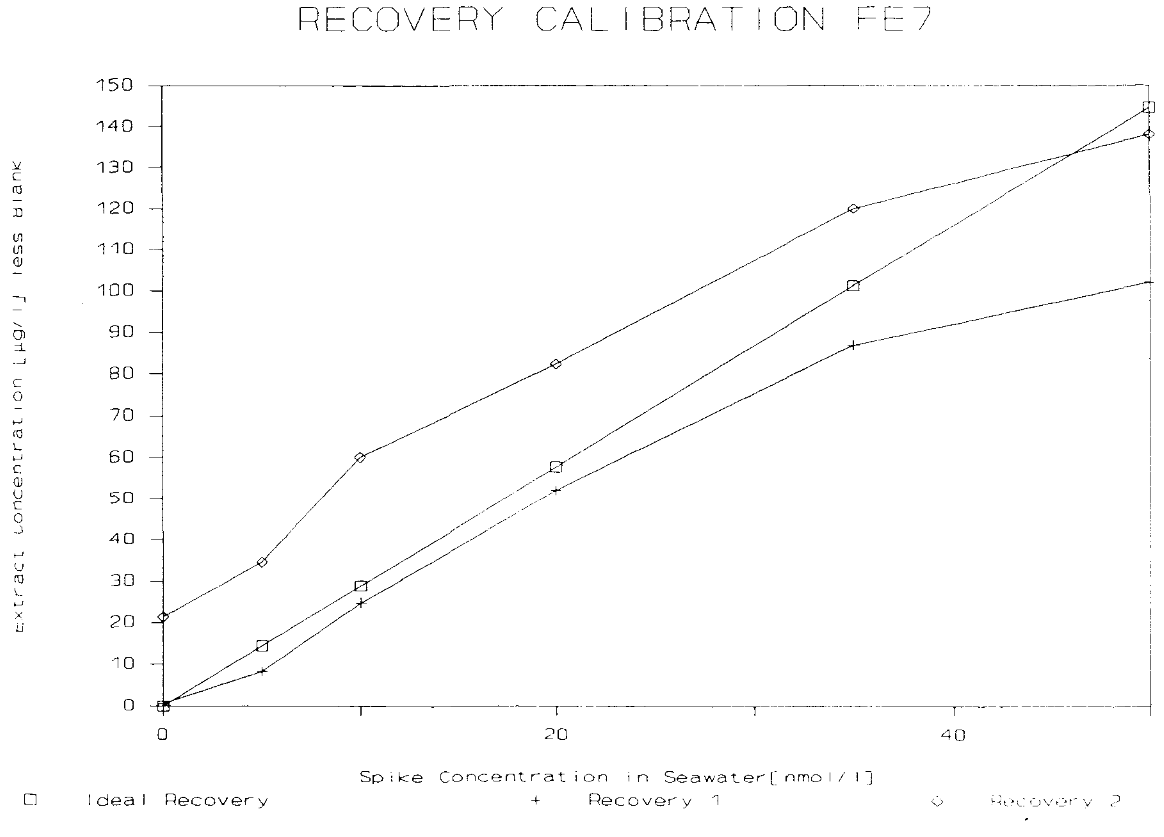
RECOVERY SET 1 (No.s 23 to 28)

```
                  Regression Output:
         Constant                            -6.91
         Std Err of Y Est                 2.806534
         R Squared                        0.989879
         No. of Observations                     4
         Degrees of Freedom                      2

         X Coefficient(s)  2.654057
         Std Err of Coef.  0.189756
```

RECOVERY SET 2 (No.s 57 to 62)

```
                  Regression Output:
         Constant                         19.22254
         Std Err of Y Est                 5.519760
         R Squared                        0.985181
         No. of Observations                     5
         Degrees of Freedom                      3
         X Coefficient(s)  2.809246
         Std Err of Coef.  0.198918
```



APPENDIX III

DATA BASE

STRUCTURE

FIELD	TYPE	LEN	DEC	CTD's in ORACLE	P-Stations in ORACLE	Description	Units
SHEET 1							
CODE	C	5	0			Code, e.g. A01, S54, A13B, T5	
TYP	C	5	0			Station Type, e.g. CTD, P, CTDA, CTDE	
STN	N	5	0	BOTTLE.CSTATN	PSTATN1.PSTATN	Station Number	
DEPTH	N	6	1	BOTTLE.DEPTH	'3.3'	Depth	m
BOTT	N	5	0	Sample Storage Bottle No.		Sample Bottle	
S	N	3	0	Extraction No.		Extraction Number	
DATE	D	8	0	STATION.TBEGNS	PSTATN1.DATIM	Sampling Date	
TIME	N	9	6	STATION.TBEGNS	PSTATN1.DATIM	Sampling Time	
LAT	N	9	4	STATION.LAT	PSTATN1.LAT	Latitude +ve North	
LON	N	9	4	STATION.LON	PSTATN1.LON	Longitude +ve East	
SAL	N	6	2	BOTCTD.SALINC	PSTATN2/1.SAL or BSAL	Salinity	
A	C	1	0	BOTCTD.FSC	G' or 'T'	Salinity Flag	
TEMP	N	6	2	BOTCTD.TEMPC	PSTATN1.TEMP	Temperature	C
B	C	1	0	BOTCTD.FTC	---	Temperature Flag	
SHEET2							
MND	N	8	2	Analysis Results		Dissolved Manganese	nmol/l
C	C	1	0	''<','?' or none		Flag for MND	
FED	N	8	2	Analysis Results		Dissolved Iron	nmol/l
D	C	1	0	''<','?' or none		Flag for FED	
NID	N	8	2	Analysis Results		Dissolved Nickel	nmol/l
E	C	1	0	''<','?' or none		Flag for NID	
COD	N	8	3	Analysis Results		Dissolved Cobalt	nmol/l
F	C	1	0	''<','?' or none		Flag for COD	
CUD	N	8	2	Analysis Results		Dissolved Copper	nmol/l
G	C	1	0	''<','?' or none		Flag for CUD	
ZND	N	8	2	Analysis Results		Dissolved Zinc	nmol/l
H	C	1	0	''<','?' or none		Flag for znd	
CDD	N	8	3	Analysis Results		Dissolved Cadmium	nmol/l
I	C	1	0	''<','?' or none		Flag for CDD	
PBD	N	8	3	Analysis Results		Dissolved Lead	nmol/l
J	C	1	0	''<','?' or none		Flag for PBD	
SHEET 3							
SWT	N	5	0	PARTMET.SWT	PSTATN2.SWT	SPM for Trace Metal Analysis	mg
SCONC	N	6	1	PARTMET.SCONC	PSTATN2.SCONC	SPM Concentration for TM Analysis	mg/l
MNP	N	8	1	PARTMET.MNP	PSTATN2.MNP	Particle-bound Manganese	nmol/l
FEP	N	8	0	PARTMET.FEP	PSTATN2.FEP	Particle-bound Iron	nmol/l
NIP	N	7	2	PARTMET.NIP	PSTATN2.NIP	Particle-bound Nickel	nmol/l
COP	N	8	2	PARTMET.COP	PSTATN2.COP	Particle-bound Cobalt	nmol/l
CUP	N	7	2	PARTMET.CUP	PSTATN2.CUP	Particle-bound Copper	nmol/l
ZNP	N	7	2	PARTMET.ZNP	PSTATN2.ZNP	Particle-bound Zinc	nmol/l
CDP	N	8	3	PARTMET.CDP	PSTATN2.CDP	Particle-bound Cadmium	nmol/l
PBP	N	8	2	PARTMET.PBP	PSTATN2.PBP	Particle-bound Lead	nmol/l

FIELD	TYPE	LEN	DEC	CTD's in ORACLE	P-Stations in ORACLE	Description	Units
SHEET 4							
THGT	N	8	5	HYCAST.THGT	PSTATN2.THGT	Total Unfiltered Mercury	nmol/l
THGD	N	8	5	DISSMET.THGD	PSTATN2.THGD	Total Dissolved Mercury	nmol/l
RHGD	N	8	5	DISSMET.RHGD	PSTATN2.RHGD	Reactive Dissolved Mercury	nmol/l
IASD	N	8	2	DISSMET.IASD	PSTATN2.IASD	Dissolved Inorganic Arsenic	nmol/l
MASD	N	8	2	DISSMET.MASD	PSTATN2.MASD	Dissolved Monomethyl Arsenic	nmol/l
DASD	N	8	2	DISSMET.DASD	PSTATN2.DASD	Dissolved Dimethyl Arsenic	nmol/l
AL	N	8	2	HYCAST.AL	PSTATN2.ALD	Aluminium and Dissolved Aluminium	nmol/l
ALP	N	8	2	PARTMET.ALP	PSTATN3.ALP	Particle-bound Aluminium	μmol/l
CRP	N	8	2	PARTMET.CRP	PSTATN3.CRP	Particle-bound Chromium	nmol/l
SHEET 5							
PO4	N	9	2	HYCAST.PO4 or underway	PSTATN1.PO4	Phosphate	μmol/l
NO2	N	9	2	HYCAST.NO2 or underway	PSTATN1.NO2	Nitrite	μmol/l
NO3	N	9	2	HYCAST.NO3 or underway	PSTATN1.NO3	Nitrate	μmol/l
SI	N	9	2	HYCAST.SI or underway	PSTATN.SI	Silicate	μmol/l
NH4	N	9	2	HYCAST.NH4 or underway	---	Ammonia	μmol/l
DOXY	N	8	1	BOTCTD.O2C	PSTATN1.DOXY	Calibrated Oxygen	μmol/l
K	C	1	0	BOTCTD.FOC	---	Flag for O2C	
CPHYLL	N	8	1	BOTCTD.CPHYLC	PSTATN1.CPHL	Calibrated Chlorophyll	mg/m3
L	C	1	0	BOTCTD.FCC	---	Flag for CPHYLC	
IBTTLE	N	8	0	BOTTLE.IBTTLE	PSTATN1.PSTATN	BODC Bottle Identifier	
SHEET 6							
TOTSED	N	9	2	BOTCTD.TSEDC	PSTATN1.DTSED	Calibrated SPM	mg/l
M	C	1	0	BOTCTD.FTSC	---	Flag for TSEDC	
ORGSED	N	9	2	BOTCTD.OSEDC	---	Calibrated Organic SPM	mg/l
N	C	1	0	BOTCTD.FOSC	---	Flag for FOSC	
INORGSED	N	9	2	BOTCTD.ISEDC	---	Calibrated Inorganic SPM	mg/l
O	C	1	0	BOTCTD.FISC	---	Flag for FISC	
POC	N	9	2	HYCAST.POC	---	Particulate Organic Carbon	μmol/l
GRAVIMET	N	9	2	HYCAST.TOTSED	PSTATN3.TSED	Measured SPM on GFC-Filter	mg/l
MAFFCU	N	8	3	from	PSTATN3.MAFCU	ASV-measured Cu (MAFF)	
MAFFCD	N	8	3	personal	PSTATN3.MAFCD	ASV-measured Cd (MAFF)	
MAFFPB	N	8	3	communication	PSTATN3.MAFPB	ASV-measured Pb (MAFF)	
SHEET 7							
LATLOW	N	9	4	Tidally Corrected Position		LAT for low water	
LONLOW	N	9	4	Tidally Corrected Position		LON for low water	
SHEET 8 (spreadsheet only)							
MNKD etc.	N	9	2	log10((MNP*10^6)/(SCONC*MND))		K_d-partitioning coefficient	

APPENDIX IV

QUALITY CONTROL CHARTS

Analytical Quality Control Chart: Trace Metals North Sea Project April 1989 to September 1991 Analyst: M.Althaus

dissolved MANGANESE	Batch 2 Apr '89 (Pre-Run)	Batch 3 Aug '89	Batch 4 Sep '89	Batch 5 Mar '90	Batch 6 May '90	Batch 7 Mar '91	Batch 8 Jun '91	Batch 9 Jul '91	Batch 10 Aug '91	Batch 11 Sep '91
Characteristic Mass [pg]	2.6	2.9	2.3	2.4	2.0	2.0	1.8	1.9	1.7	1.9
Procedural Blank [nmol/l]	0.33	0.33	0.61	0.56	0.13	1.21	0.52	0.27	0.41	0.19
(used/total samples)	8	8	6	4	6	6	6	4/6	5/6	5
Limit of Detection [nmol/l]	0.77	0.92	0.59	0.94	0.27	2.47	0.88	0.37	0.63	0.60
Precision (CASS)	5%					9%	4%	5%	4%	10%
(used/total samples)	3					6	6	6	6	5
Error (CASS)	1%					-2%	6%	4%	4%	0%
Standard Material	(CASS I)					(CASS I)	(CASS I)	(CASS II)	(CASS II)	(CASS II)
CASS [nmol/l]	42.8					40.4	43.8	37.6	37.7	36.2
Precision (2ndary Standard		3%		4%	5%		4%	7%	5%	
(used/total samples)		3		2	5/6	1	2	5/6	6	
2ndary Standard [nmol/l]		22.0		13.4	15.0	15.4	15.8	16.4	16.1	
Standard Material		(NSP I)		(NSP I)	(NSP I)	(NSP II)	(NSP II)	(NSP II)	(NSP II)	
Recovery used	97%	95%	90%	100%	100%	100%	100%	100%	100%	100%
Matrix Material	(LTMS)	(LTMS)	(LTMS)	(LTMS)	(LTMS)	(LTMS)	(NSP II)	(NSP II)	(NSP II)	(NSP II)
Recovery found	97%	95	81/90	120	100/90	75/75	95/86	106	92	65
Spike Control							90%	102%	102%	97%

Analytical Quality Control Chart: Trace Metals North Sea Project April 1989 to September 1991 Analyst: M.Althaus

dissolved IRON	Batch 2 Apr '89 (Pre-Run)	Batch 3 Aug '89	Batch 4 Sep '89	Batch 5 Mar '90	Batch 6 May '90	Batch 7 Mar '91	Batch 8 Jun '91	Batch 9 Jul '91	Batch 10 Aug '91	Batch 11 Sep '91
Characteristic Mass [pg]			5.7	6.6	5.3	4.6	5.1	5.2	5.1	5.3
Procedural Blank [nmol/l]			1.22	1.08 (set)	0.96	1.73 (set)	0.48	0.92	1.60	0.91 (set)
(used/total samples)			5/6	4	5/6	5/6	5/6	5/6	4/6	5
Limit of Detection [nmol/l]			0.62	3.13	0.88	5.18	0.46	1.35	0.68	2.31
Precision (CASS)						10%	6%	4%	8%	6%
(used/total samples)						4/6	6	6	6	5
Error (CASS)						-13%	-11%	0%	-10%	1%
Standard Material						(CASS I)	(CASS I)	(CASS II)	(CASS II)	(CASS II)
CASS [nmol/l]						13.5	13.9	21.5	19.4	21.6
Precision (2ndary Standard				22%	25%		11%	7%	7%	
(used/total samples)				2	5/6	1	2	6	6	
2ndary Standard [nmol/l]				8.8	6.8	7.6	9.5	8.9	8.9	
Standard Material				(NSP I)	(NSP I)	(NSP II)	(NSP II)	(NSP II)	(NSP II)	
Recovery used				100%	95%	100%	100%	95%	94%	95%
Matrix Material				(LTMS)	(LTMS)	(LTMS)	(NSP II)	(NSP II)	(NSP II)	(NSP II)
Recovery found				109	95/90	92/97	97/98	95	94	82
"										
Spike Control							86%	102%	101%	97%

Analytical Quality Control Chart: Trace Metals   North Sea Project   April 1989 to September 1991   Analyst: M.Althaus

dissolved NICKEL	Batch 2 Apr '89 (Pre-Run)	Batch 3 Aug '89	Batch 4 Sep '89	Batch 5 Mar '90	Batch 6 May '90	Batch 7 Mar '91	Batch 8 Jun '91	Batch 9 Jul '91	Batch 10 Aug '91	Batch 11 Sep '91
Characteristic Mass [pg]	19.3	20.6	13.5	11.0	11.5	12.6	11.0	12.0	11.5	15.5
Procedural Blank [nmol/l]	0.72	0.40	0.69	0.64	0.48	0.45	0.66 (set)	0.98	1.34	1.48
(used/total samples)	8	6/8	6	4	5/6	4/6	-/6	4/6	6	5
Limit of Detection [nmol/l]	1.09	0.41	0.70	0.50	0.90	0.26	1.00 (set)	1.24	1.87	1.90
Precision (CASS)	1%					7%	11%	9%	16%	14%
(used/total samples)	3					5/6	5/6	5/6	5/6	5
Error (CASS)	(40%)					11%	9%	6%	12%	19%
Standard Material	CASS I					CASS I	CASS I	CASS II	CASS II	CASS II
CASS [nmol/l]	(6.9)					5.5	5.4	5.4	5.7	6.1
Precision (2ndary Standard		8%		17%	17%		1%	6%	11%	
(used/total samples)		3		2	5/6	1	2	5	6	
2ndary Standard [nmol/l]		4.8		3.9	3.9	5.1	5.3	4.8	3.8	
Standard Material		(NSP I)		(NSP I)	(NSP I)	(NSP II)	(NSP II)	(NSP II)	(NSP II)	
Recovery used	77%	98%	97%	100%	101%	100%	100%	100%	100%	100%
Matrix Material	(LTMS)	(LTMS)	(LTMS)	(LTMS)	(LTMS)	(LTMS)	(NSP II)	(NSP II)	(NSP II)	(NSP II)
Recovery found	77%	98	100	119	101/106	80/78	81/92	103	94	97
Spike Control							89%	96%	108%	100%

Analytical Quality Control Chart: Trace Metals North Sea Project April 1989 to September 1991 Analyst: M.Althaus

dissolved COBALT	Batch 2 Apr '89 (Pre-Run)	Batch 3 Aug '89	Batch 4 Sep '89	Batch 5 Mar '90	Batch 6 May '90	Batch 7 Mar '91	Batch 8 Jun '91	Batch 9 Jul '91	Batch 10 Aug '91	Batch 11 Sep '91
Characteristic Mass [pg]	16.1 (3)	12.7 (4)	11.0 (4)	9.6 (4)	6.6 (4)	9.6 (4)	7.3 (1)	9.9 (3)	7.1 (2)	7.8 (3)
(multiple injections)										
Procedural Blank [nmol/l]	0.08	0.11	0.07	0.06	0.06	0.10	0.05	0.05	0.04	0.05
(used/total samples)	8	8	3/6	4	5/6	6	5/6	4/6	5/6	5
Limit of Detection [nmol/l]	0.48	0.20	0.06	0.19	0.15	0.14	0.04	0.11	0.10	0.12
Precision (CASS)	23%					11%	4%	18%	15%	8%
(used/total samples)	3					6	4/6	6	6	5
Error (CASS)	(399%)					-6%	-16%	10%	10%	-4%
Standard Material	CASS I					CASS I	CASS I	CASS II	CASS II	CASS II
CASS [nmol/l]	(1.95)					0.37	0.33	0.46	0.46	0.40
Precision (2ndary Standard		20%		16%	16%		3%	14%	14%	
(used/total samples)		3		2	4/6	1	2	5	6	
2ndary Standard [nmol/l]		0.17		0.19	0.10	0.33	0.44	0.43	0.25	
Standard Material		(NSP I)		(NSP I)	(NSP I)	(NSP II)	(NSP II)	(NSP II)	(NSP II)	
Recovery used	89%	107%	100%	94%	106%	100%	100%	100%	100%	100%
Matrix Material	(LTMS)	(LTMS)	(LTMS)	(LTMS)	(LTMS)	(LTMS)	(NSP II)	(NSP II)	(NSP II)	(NSP II)
Recovery found	89	107	100/73	94	106/89	77/80	89/87	69	103	123
Spike Control							100%	115%	101%	--

Analytical Quality Control Chart: Trace Metals North Sea Project April 1989 to September 1991 Analyst: M.Althaus

dissolved COPPER	Batch 2 Apr '89 (Pre-Run)	Batch 3 Aug '89	Batch 4 Sep '89	Batch 5 Mar '90	Batch 6 May '90	Batch 7 Mar '91	Batch 8 Jun '91	Batch 9 Jul '91	Batch 10 Aug '91	Batch 11 Sep '91
Characteristic Mass [pg]	10.6	7.0	6.4	7.3	4.7	4.6	5.5	5.5	5.7	5.3
Procedural Blank [nmol/l]	1.56	0.74	0.51	0.31	0.56	0.76 (set)	0.71	0.80	1.55	1.56
(used/total samples)	8	7/8	5/6	4	5/6	6	6	4/6	6	5
Limit of Detection [nmol/l]	2.37	0.63	0.35	0.17	0.73	1.18	0.90	1.07	1.96	1.87
Precision (CASS)	5%					12%	9%	4%	8%	11%
(used/total samples)	3					6	6	4/6	6	5
Error (CASS)	10%					-2%	11%	8%	4%	9%
Standard Material	CASS I					CASS I	CASS I	CASS II	CASS II	CASS II
CASS [nmol/l]	5.1					4.5	5.1	11.4	11.1	11.6
Precision (2ndary Standard)		7%		5%	13%		4%	8%	3%	
(used/total samples)		3		2	5/6	1	2	5	6	
2ndary Standard [nmol/l]		2.8		2.8	3.3	4.8	5.2	4.7	3.8	
Standard Material		(NSP I)		(NSP I)	(NSP I)	(NSP II)	(NSP II)	(NSP II)	(NSP II)	
Recovery used	81%	104%	100%	100%	103%	100%	100%	100%	100%	100%
Matrix Material	(LTMS)	(LTMS)	(LTMS)	(LTMS)	(LTMS)	(LTMS)	(NSP II)	(NSP II)	(NSP II)	(NSP II)
Recovery found	81	104	100/101	122	103/114	70/64	88/89	121	95	100
Spike Control							77%	98%	100%	

Analytical Quality Control Chart: Trace Metals North Sea Project April 1989 to September 1991 Analyst: M.Althaus

dissolved ZINC	Batch 2 Apr '89 (Pre-Run)	Batch 3 Aug '89	Batch 4 Sep '89	Batch 5 Mar '90	Batch 6 May '90	Batch 7 Mar '91	Batch 8 Jun '91	Batch 9 Jul '91	Batch 10 Aug '91	Batch 11 Sep '91
Characteristic Mass [pg]	6.1	6.4	8.1	8.3	5.7	9.4	9.0	7.8	7.5	9.0
Procedural Blank [nmol/l]	3.02	0.41 (set)	1.14	0.61	0.54	1.05	1.51	1.25	1.10	1.17
(used/total samples)	8	8	6	4	5/6	6	5/6	3/6	5/6	5
Limit of Detection [nmol/l]	1.75	1.56	0.97	0.97	0.55	1.21	1.98	0.73	1.57	3.94
Precision (CASS)	4%					2%	11%	4%	5%	5%
(used/total samples)	3					6	6	5/6	5/6	5
Error (CASS)	(54%)					13%	21%	25%	10%	-1%
Standard Material	CASS I					CASS I	CASS I	CASS II	CASS II	CASS II
CASS [nmol/l]	(23.1)					17.0	18.1	37.8	33.1	29.8
Precision (2ndary Standard		8%		17%	9%		15%	4%	1%	
(used/total samples)		3		2	5/6	1	2	5	6	
2ndary Standard [nmol/l]		34.4		5.6	7.4	12.9	15.2	16.4	12.5	
Standard Material		(NSP I)		(NSP I)	(NSP I)	(NSP II)	(NSP II)	(NSP II)	(NSP II)	
Recovery used	74%	112%	111%	100%	108%	100%	100%	103%	100%	100%
Matrix Material	(LTMS)	(LTMS)	(LTMS)	(LTMS)	(LTMS)	(LTMS)	(NSP II)	(NSP II)	(NSP II)	(NSP II)
Recovery found	74	112	111/116	121	108/76	99/79	75/109	103	116	90
Spike Control							91%	116%	98%	99%

Analytical Quality Control Chart: Trace Metals North Sea Project April 1989 to September 1991 Analyst: M.Althaus

dissolved CADMIUM	Batch 2 Apr '89 (Pre-Run)	Batch 3 Aug '89	Batch 4 Sep '89	Batch 5 Mar '90	Batch 6 May '90	Batch 7 Mar '91	Batch 8 Jun '91	Batch 9 Jul '91	Batch 10 Aug '91	Batch 11 Sep '91
Characteristic Mass [pg]	1.02	1.28	0.83	0.70	0.55	0.81	1.00	1.31	0.83	0.92
Procedural Blank [nmol/l]	0.08	0.03	0.03	0.04	0.02	0.15	0.03	0.03	0.02	0.01
(used/total samples)	8	8	4/6	4	5/6	6	6	6	6	5
Limit of Detection [nmol/l]	0.12	0.02	0.02	0.01	0.03	0.03	0.02	0.01	0.02	0.01
Precision (CASS)	3%					7%	13%	4%	7%	5%
(used/total samples)	2/3					5/6	6	5/6	6	5
Error (CASS)	18%					14%	5%	-3%	-6%	3%
Standard Material	CASS I					CASS I	CASS I	CASS II	CASS II	CASS II
CASS [nmol/l]	0.27					0.26	0.24	0.16	0.16	0.17
Precision (2ndary Standard		13%		0%	18%		0%	13%	4%	
(used/total samples)		3		2	5/6	1	2	5	6	
2ndary Standard [nmol/l]		0.14		0.14	0.16	0.18	0.16	0.16	0.05	
Standard Material		(NSP I)		(NSP I)	(NSP I)	(NSP II)	(NSP II)	(NSP II)	(NSP II)	
Recovery used	93%	99%	100%	90%	90%	100%	100%	100%	95%	100%
Matrix Material	(LTMS)	(LTMS)	(LTMS)	(LTMS)	(LTMS)	(LTMS)	(NSP II)	(NSP II)	(NSP II)	(NSP II)
Recovery found	93	99	100/94	90	90/85	81/85	73/74	50	95	78
Spike Control							99%	99%	99%	96%

Analytical Quality Control Chart: Trace Metals North Sea Project April 1989 to September 1991 Analyst: M.Althaus

dissolved LEAD	Batch 2 Apr '89 (Pre-Run)	Batch 3 Aug '89	Batch 4 Sep '89	Batch 5 Mar '90	Batch 6 May '90	Batch 7 Mar '91	Batch 8 Jun '91	Batch 9 Jul '91	Batch 10 Aug '91	Batch 11 Sep '91
Characteristic Mass [pg]	11.9	7.3	6.0	6.6	4.7	4.6	4.6	4.8	4.7	4.9
Procedural Blank [nmol/l]	0.01	0.05	0.02	0.01	0.01	0.00	0.02	0.02	0.02 (set)	0.02
(used/total samples)	8	8	5/6	4	5/6	6	6	5/6	6	5
Limit of Detection [nmol/l]	0.05	0.06	0.04	0.03	0.02	0.04	0.03	0.03	0.05	0.03
Precision (CASS)	5%					7%	12%	4%	19%	8%
(used/total samples)	2/3					6	3/6	5/6	6	4/5
Error (CASS)	-15%					-11%	-12%	9%	-12%	-15%
Standard Material	CASS I					CASS I	CASS I	CASS II	CASS II	CASS II
CASS [nmol/l]	1.03					1.08	1.06	0.10	0.08	0.08
Precision (2ndary Standard		4%		17%	20%		33%	13%	4%	
(used/total samples)		3		2	5/6	1	2	5	6	
2ndary Standard [nmol/l]		0.13		0.15	0.13	0.17	0.15	0.15	0.06	
Standard Material		(NSP I)		(NSP I)	(NSP I)	(NSP II)	(NSP II)	(NSP II)	(NSP II)	
Recovery used	79%	94%	101%	98%	85%;61%	90%	80%	100%	100%	80%
Matrix Material	(LTMS)	(LTMS)	(LTMS)	(LTMS)	(LTMS)	(LTMS)	(NSP II)	(NSP II)	(NSP II)	(NSP II)
Recovery found	79	94	101/86	98	85/61	78/89	64/72	88	101	78
Spike Control							93%	109%	100%	105%

APPENDIX V

CRUISE CH42

DATA BASE

CONTENT

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH42.WK1
SHEET 1: GENERAL SAMPLE PARAMETER FINAL VERSION
CH42: HUMBER PLUME CRUISE I 17/01/92 22:14:51

CODE	TYP	STN #	DEPTH m	BOTT #	S	DATE dd/mm/yy	TIME hh:mm	LAT +ve N	LONG +ve E	SAL	A	TEMP °C	B
A101	CTDA	1070	8.6	3191	5	21/12/88	13:04	53.5490	0.1053	31.22	G	6.79	O
A102	CTDA	1071	8.3	3192	6	21/12/88	13:56	53.5502	0.1040	32.71	G	7.01	G
A103	CTDA	1072	9.3	3193	6	21/12/88	14:54	53.5519	0.1042	33.18	G	7.17	O
A104	CTDA	1073	8.8	3194	6	21/12/88	15:55	53.5518	0.1043	33.48	G	7.24	I
A105	CTDA	1074	8.8	3195	6	21/12/88	17:00	53.5528	0.1052	33.57	G	7.21	O
A106	CTDA	1075	8.5	3196	5	21/12/88	17:57	53.5509	0.1068	32.97	G	7.14	I
A107	CTDA	1076	8.9	3197	5	21/12/88	18:55	53.5544	0.1056	32.45	G	6.97	G
A108	CTDA	1077	8.0	3198	5	21/12/88	19:54	53.5515	0.1062	30.95	G	6.78	G
A109	CTDA	1078	8.6	3199	5	21/12/88	20:54	53.5512	0.1069	29.73	G	6.66	I
A110	CTDA	1079	8.6	3200	5	21/12/88	22:04	53.5521	0.1059	28.87	G	6.59	I
A111	CTDA	1080	8.7	3201	5	21/12/88	23:04	53.5541	0.1061	28.25	G	6.55	O
A112	CTDA	1081	8.4	3202	5	22/12/88	00:04	53.5526	0.1057	30.17	G	6.71	O
A113	CTDA	1082	8.1	3203	5	22/12/88	01:01	53.5501	0.1025	30.85	G	6.80	G
A114	CTDA	1083	7.0	3204	5	22/12/88	02:01	53.5509	0.1037	31.99	G	6.90	O
A123	CTDA	1092	9.1	3205	5	22/12/88	11:00	53.5498	0.1070	29.75	G	6.70	I
S1	P	1	3.2	3207	6	22/12/88	14:32	53.5393	0.2537	33.83		7.68	
S2	P	2	3.2	3206	4	22/12/88	15:12	53.5363	0.4271	34.37		8.31	
S3	P	3	3.2	3208	4	22/12/88	15:48	53.5435	0.5869	34.43		8.50	
S4	CTD	1095	12.2	3209	5	22/12/88	18:19	53.4057	0.9180	34.41	G	8.29	G
S5	P	4	3.2	3210	4	22/12/88	19:19	53.2836	1.0543	34.29		7.93	
S6	P	5	3.2	3212	4	22/12/88	21:09	53.0240	1.2918	34.03		7.15	
S7	CTD	1096	17.3	3211	5	22/12/88	21:31	52.9973	1.3029	34.05	G	7.08	O
S8	CTD	1097	21.9	3213	5	22/12/88	22:41	53.0076	1.5070	34.25	G	7.40	O
S9	P	6	3.2	3214	4	23/12/88	00:42	53.2572	1.2680	34.39		7.82	
S10	CTD	1098	14.3	3215	5	23/12/88	01:38	53.4092	1.0746	34.42	G	8.06	O
S11	P	7	3.2	3218	4	23/12/88	02:17	53.4258	1.0443	34.42		8.05	
S12	P	8	3.2	3216	6	23/12/88	04:14	53.6447	0.8432	34.48		8.42	
S13	CTD	1099	33.6	3217	5	23/12/88	06:29	53.8170	0.6335	34.53	G	8.56	O
S14	CTD	1100	35.5	3219	5	23/12/88	08:28	53.8175	0.3825	34.46	G	8.70	G
S15	P	9	3.2	3220	4	23/12/88	08:32	53.8186	0.3829	34.46		8.66	
S16	CTD	1101	7.6	3221	6	23/12/88	10:19	53.8174	0.0483	34.36	G	8.12	O
S17	P	10	3.2	3222	4	23/12/88	10:55	53.7690	0.1483	34.36		8.34	
S18	P	11	3.2	3223	4	23/12/88	12:45	53.5475	0.4398	34.25		7.89	
S19	CTD	1102	8.5	3224	6	23/12/88	13:47	53.4083	0.4767	32.81	G	6.56	O
S20	P	12	3.2	3225	6	23/12/88	13:49	53.4087	0.4763	32.80		6.55	
S21	P	13	3.2	3226	4	23/12/88	15:09	53.1922	0.5100	33.62		6.65	
S22	CTD	1103	30.0	3227	6	23/12/88	16:01	53.0512	0.4616	33.69	G	6.68	G
S23	P	14	3.2	3228	4	23/12/88	17:34	53.1258	0.5587	33.42		6.41	
S24	P	15	3.2	3229	4	23/12/88	18:54	53.2252	0.7575	33.87		7.45	
S25	P	16	3.2	3230	4	23/12/88	20:05	53.0740	1.0225	33.87		7.00	
S26	CTD	1104	9.4	3231	5	23/12/88	20:41	52.9994	1.0594	33.57	G	6.63	O
S27	P	17	3.2	3233	4	23/12/88	22:05	53.0029	1.4458	34.11		7.30	
S28	P	18	3.2	3232	4	23/12/88	22:35	53.0032	1.5163	34.22		7.40	
S29	CTD	1105	21.2	3234	5	23/12/88	22:40	53.0039	1.5173	34.25	G	7.41	G
S30	P	19	3.2	3235	6	23/12/88	23:50	53.1239	1.3866	34.29		7.56	
S31	P	20	3.2	3236	6	24/12/88	01:14	53.3301	1.1698	34.35		7.95	
S32	P	21	3.2	3237	4	24/12/88	01:55	53.4231	1.0625	34.24		7.98	
S33	P	22	3.2	3238	4	24/12/88	03:43	53.6025	0.8577	34.41		8.38	
S34	P	23	3.2	3240	4	24/12/88	05:15	53.7298	0.7322	34.45		8.48	

Table V.1: General station parameters CH42

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH42.WK1
SHEET 1: GENERAL SAMPLE PARAMETER FINAL VERSION
CH42: HUMBER PLUME CRUISE I 17/01/92 22:14:51

CODE	TYP	STN	DEPTH	BOTT	S	DATE	TIME	LAT	LONG	SAL	A	TEMP	B
		#	m	#		dd/mm/yy	hh:mm	+ve N	+ve E			°C	
S35	P	24	3.2	3239	4	24/12/88	06:34	53.8093	0.5910	34.43		8.62	
S36	P	25	3.2	3241	4	24/12/88	07:38	53.8178	0.3628	34.37		8.39	
S37	CTD	1106	12.8	3242	5	24/12/88	10:01	53.8187	0.0488	34.37	G	8.04	G
S38	P	26	3.2	3243	4	24/12/88	11:07	53.7263	0.2178	34.38		8.39	
S39	P	27	3.2	3244	4	24/12/88	12:00	53.6305	0.3515	34.39		8.35	
S40	P	28	3.2	3246	4	24/12/88	13:39	53.4115	0.4757	32.49		6.61	
S41	CTD	1107	8.9	3245	5	24/12/88	13:50	53.4097	0.4722	32.51	G	6.58	G
S42	P	29	3.2	3247	6	24/12/88	15:08	53.4248	0.7590	34.09		7.86	
S43	CTD	1108	16.9	3248	5	24/12/88	15:52	53.4274	0.8835	34.38	G	8.17	G
S44	P	30	3.2	3249	4	24/12/88	17:35	53.5868	0.6788	34.46		8.48	
S45	P	31	3.2	3251	4	24/12/88	19:01	53.7445	0.4850	34.48		8.56	
S46	P	32	3.2	3253	4	25/12/88	17:20	53.6746	0.3227	34.37		8.54	
S47	P	33	3.2	3250	4	25/12/88	19:01	53.3802	0.4808	32.55		6.82	
S48	P	34	3.2	3254	4	25/12/88	19:36	53.2755	0.4930	32.90		6.38	
S49	P	35	3.2	3255	6	25/12/88	20:42	53.2137	0.6517	33.48		6.78	
S50	P	36	3.2	3256	5	25/12/88	22:01	53.1348	0.9183	33.87		7.46	
S51	P	37	3.2	3257	4	25/12/88	23:06	53.0033	1.0856	33.48		6.75	
S52	P	38	3.2	3258	4	25/12/88	23:59	53.0198	1.2866	34.02		7.22	
S53	P	39	3.2	3259	4	26/12/88	01:03	53.1865	1.1243	33.94		7.45	
S54	P	40	3.2	3260	4	26/12/88	02:58	53.5003	0.8005	34.16		7.98	
S55	P	41	3.2	3261	4	26/12/88	03:33	53.5765	0.7005	34.29		8.14	
S56	P	42	3.2	3262	4	26/12/88	04:53	53.7267	0.4935	34.43		8.54	
S57	P	43	3.2	3263	6	26/12/88	05:53	53.7980	0.4338	34.40		8.58	
S58	P	44	3.2	3264	4	26/12/88	06:51	53.7916	0.6700	34.45		8.48	
S59	P	45	3.2	3268	4	26/12/88	08:23	53.5616	0.9206	34.37		8.35	
S60	P	46	3.2	3265	4	26/12/88	09:22	53.4193	1.0780	34.36		8.14	
S61	P	47	3.2	3266	4	26/12/88	11:04	53.1670	1.3548	34.30		7.64	
S62	P	48	3.2	3269	4	26/12/88	12:19	52.9952	1.4988	34.26		7.36	
S63	P	49	3.2	3270	6	26/12/88	13:40	53.0006	1.1176	33.80		6.89	
S64	P	51	3.2	3271	4	26/12/88	15:57	53.2450	0.6763	34.02		7.55	
S65	P	52	3.2	3252	4	26/12/88	18:46	53.3157	0.7343	33.98		7.64	
S66	P	53	3.2	3267	4	26/12/88	19:30	53.4122	0.8205	34.15		7.94	
S67	P	54	3.2	3275	4	26/12/88	21:27	53.4817	0.8278	34.47		8.40	
A201	CTDA	1109	9.1	3272	3	27/12/88	11:06	53.5431	0.0989	31.92	G	7.27	G
A202	CTDA	1110	8.9	3282	3	27/12/88	12:05	53.5435	0.0992	31.20	C	7.24	C
A203	CTDA	1111	8.5	3276	3	27/12/88	13:02	53.5432	0.0999	30.51	G	7.19	I
A204	CTDA	1112	9.1	3274	3	27/12/88	14:01	53.5423	0.0988	30.26	G	7.18	O
A205	CTDA	1113	8.8	3273	4	27/12/88	15:01	53.5430	0.0983	30.34	G	7.19	I
A206	CTDA	1114	8.6	3278	3	27/12/88	16:06	53.5427	0.0978	30.54	G	7.20	G
A207	CTDA	1115	8.5	3279	3	27/12/88	17:02	53.5443	0.0968	30.91	G	7.22	O
A208	CTDA	1116	8.3	3280	3	27/12/88	18:04	53.5431	0.0972	31.70	G	7.28	O
A209	CTDA	1117	8.5	3281	3	27/12/88	19:07	53.5440	0.0968	32.43	G	7.35	I
A210	CTDA	1118	9.0	3283	3	27/12/88	20:04	53.5441	0.0976	32.67	G	7.39	I
A211	CTDA	1119	8.7	3284	3	27/12/88	21:03	53.5443	0.0982	32.78	G	7.41	O
A212	CTDA	1120	9.1	3285	3	27/12/88	22:04	53.5437	0.0984	32.44	G	7.35	I
A213	CTDA	1121	8.5	3286	5	27/12/88	23:03	53.5432	0.0983	31.74	G	7.27	O
A214	CTDA	1122	8.7	3288	6	28/12/88	00:05	53.5434	0.0988	31.17	G	7.22	O

Table V.2: General station parameter CH42 (continued)

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH42.WK1
SHEET 2: DISSOLVED TRACE METAL CONCENTRATIONS
CH42: HUMBER PLUME CRUISE I

CODE	TYP	MND nmol/l	C	FED nmol/l	D	NID nmol/l	E	COD nmol/l	F	CUD nmol/l	G	ZND nmol/l	H	CDD nmol/l	I	PBD nmol/l	J
A101	CTDA	54.19		32.66		13.17		1.132		18.80		36.18		0.583		0.085	
A102	CTDA	29.46		42.02		17.72		0.899		6.22		21.16		0.413		0.161	
A103	CTDA	14.77		7.85		12.98		0.585		11.55		16.36		0.335		0.203	
A104	CTDA																
A105	CTDA	30.43		1437.11		14.52		1.023		10.31		14.04		0.322		0.645	
A106	CTDA	20.86		19.86		15.14		0.523		11.33		28.98		0.333		0.012	<
A107	CTDA	110.62		3537.60		17.77		2.023		16.10		52.20		0.293		2.249	
A108	CTDA	99.10		4017.20		23.49		3.471		20.66		76.56		0.376		2.522	
A109	CTDA	102.75		402.58		30.30		2.107		21.28		63.28		0.581		0.322	
A110	CTDA	206.76		2902.97		32.68		3.764		27.29		84.84		0.585		1.979	
A111	CTDA	701.16		2940.82		43.84		4.255		32.32		117.91		0.776		1.888	
A112	CTDA	131.00		626.60		35.90		1.289		20.31		61.13		0.712		0.837	
A113	CTDA	418.65		5183.80		29.61		2.344		22.11		108.46		0.562		2.975	
A114	CTDA	129.32		854.84		23.36		1.292		15.29		30.47		0.476		1.674	
A123	CTDA	260.52		4146.82		35.33		1.842		24.09		86.89		0.633		2.389	
S1	P	19.11		381.69	?	8.47		0.638		8.56		9.87		0.224		0.330	
S2	P	1.82		2.02		4.83		0.119		5.50		13.15		0.166		0.157	
S3	P	2.42		2.99		3.24		0.063		3.71		4.32		0.146		0.165	
S4	CTD	3.13		10.45		4.31		0.171	<	4.55		4.16		0.137		0.254	
S5	P	2.28		3.90		5.16		0.011	<	5.96		8.70		0.197		0.102	
S6	P	2.81		2.01		7.80		0.027	<	7.04		13.28		0.243		0.086	
S7	CTD	2.57		8.95		10.67		0.171	<	7.02		13.13		0.222		0.166	
S8	CTD	1.71		28.73		6.48		0.098	<	5.69		8.19		0.195		0.220	
S9	P	3.72		1.35		4.02		0.001	<	4.44		5.24		0.158		0.133	
S10	CTD	1.66		20.03		4.24		0.098	<	4.19		5.36		0.149		0.220	
S11	P	3.69		0.31	<	4.47		0.162		4.36		9.45		0.158		0.116	
S12	P	1.82		3.90		4.43		0.219		4.00		5.27		0.201		0.175	
S13	CTD	2.48		16.61		4.13		0.011	<	3.89		4.65		0.147		0.291	
S14	CTD	1.36		1.94		3.58		0.001	<	3.69		7.93		0.170		0.311	
S15	P	2.70		2.52		4.29		0.119		4.86		5.84		0.189		0.198	
S16	CTD	2.39		2.39		6.84		0.278		5.54		12.44		0.203		0.281	
S17	P	1.97		1.88		5.03		0.113		5.55		9.60		0.168		0.216	
S18	P	2.87		2.70		6.24		0.122		6.78		10.81		0.199		0.111	
S19	CTD	1.85		1.64		16.77		0.154		9.36		19.99		0.438		0.067	
S20	P	1.99		1.72		14.54		0.083	<	10.02		18.29		0.392		0.129	
S21	P	2.14		3.01		10.35		0.158		9.88		14.70		0.273		0.098	
S22	CTD	2.20		1.13		11.53		0.179		8.28		15.21		0.323		0.105	
S23	P	2.74		1.13		13.95		0.280		11.52		17.61		0.336		0.073	
S24	P	2.12		8.97		9.98		0.217		8.10		12.73		0.273		0.054	
S25	P	5.43		19.02		11.04		0.188		9.02		14.49		0.343		0.122	
S26	CTD	3.38		33.69		9.21		0.081	<	8.59		13.65		0.276		0.128	
S27	P	3.08		3.10		6.15		0.152		6.14		10.28		0.228		0.058	
S28	P	3.93		4.61		5.16		0.136		5.15		8.88		0.195		1.245	?
S29	CTD	1.15		12.63		4.99		0.008	<	4.61		5.43		0.191		0.110	
S30	P	2.09		4.12		4.47		0.033	<	4.27		8.69		0.185		0.093	
S31	P	2.56		2.56		3.86		0.064	<	4.30		6.49		0.155		0.111	
S32	P	2.12		1.84		6.18		0.116		6.22		8.08		0.197		0.152	
S33	P	1.89		1.48		4.59		0.057	<	4.57		5.48		0.173		0.114	
S34	P	2.06		8.50		3.75		0.034	<	5.20		7.17		0.189		0.110	

Table V.3: Dissolved trace metal concentrations CH42

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH42.WK1
SHEET 2: DISSOLVED TRACE METAL CONCENTRATIONS
CH42: HUMBER PLUME CRUISE I

CODE	TYP	MND nmol/l	C	FED nmol/l	D	NID nmol/l	E	COD nmol/l	F	CUD nmol/l	G	ZND nmol/l	H	CDD nmol/l	I	PBD nmol/l	J
S35	P	1.51		1.62		3.36		0.076		3.59		3.65		0.146		0.116	
S36	P	1.44		1.90		4.70		0.076		5.11		5.61		0.161		0.189	
S37	CTD	2.31		8.01		7.69		0.084	<	6.37		7.54		0.166		0.276	
S38	P	1.82		16.99		3.72		0.070		5.40		5.92		0.165		0.217	
S39	P	1.75		1.51		4.36		0.070		5.49		7.01		0.161		0.185	
S40	P	2.46		1.10		16.94		0.076	<	12.12		22.06		0.427		0.108	
S41	CTD	2.47		29.90		16.52		0.091	<	11.86		23.91		0.449		0.121	
S42	P	2.71		2.82		5.28		0.064	<	5.33		5.76		0.182		0.169	
S43	CTD	2.42		4.51		5.12		0.036	<	6.12		6.56		0.174		0.266	
S44	P	2.64		3.45		4.21		0.054	<	3.15		3.98		0.149		0.174	
S45	P	3.32		21.38		3.65		0.031	<	3.01		2.85		0.144		0.191	
S46	P	1.67		2.81		4.38		0.037	<	4.05		5.72		0.151		0.236	
S47	P	6.81		3.03		16.86		0.224		11.92		24.29		0.380		0.095	
S48	P	2.85		1.63		16.01		0.109		12.41		21.13		0.423		0.132	
S49	P	2.32		1.72		10.14		0.067	<	9.45		13.39		0.496	?	0.072	
S50	P	2.05		1.87		4.83		0.050	<	7.86		10.24		0.252		0.144	
S51	P	2.46		2.13		11.97		0.778		9.02		12.76		0.308		0.166	
S52	P	1.77		4.09		6.95		0.014	<	6.71		11.09		0.211		0.138	
S53	P	4.50		8.32		9.26		0.037	<	7.43		12.17		0.240		0.152	
S54	P	1.37		2.16		6.43		0.113		6.76		11.30		0.209		0.148	
S55	P	1.62		3.05		8.09		0.188		7.33		12.53		0.228		0.171	
S56	P	2.28		2.43		3.27		0.014	<	3.66		3.15		0.142		0.205	
S57	P	1.94		2.40		2.95		0.050	<	2.83		2.95		0.143		0.094	
S58	P	2.57		3.03		3.31		0.060	<	3.12		2.63		0.161		0.145	
S59	P	1.72		1.31		3.29		0.021	<	3.30		3.75		0.141		0.162	
S60	P	4.53		1.58		4.06		0.057	<	4.46		6.42		0.165		0.182	
S61	P	1.69		1.31		5.20		0.080		4.92		7.59		0.192		0.177	
S62	P	2.00		8.35		6.70		0.093		5.85		21.99	?	0.214		0.241	
S63	P	16.82		502.42	?	8.94		0.362		7.51		10.80		0.320		0.559	?
S64	P	5.39		19.89		8.05		0.099		7.60		13.19		0.240		0.275	
S65	P	1.85		0.62		9.40		0.054	<	8.05		11.56		0.237		0.147	
S66	P	2.34		1.49		6.50		0.080		6.54		10.43		0.195		0.138	
S67	P	2.61		6.60		3.84		0.132		3.78		4.68		0.144		0.176	
A201	CTDA	32.44				22.80		0.793		14.11		38.39		0.596			
A202	CTDA	38.68				32.97		0.818		16.13		49.44		0.589		0.096	
A203	CTDA	106.46				35.23		1.262		17.98		59.13		0.603		0.083	
A204	CTDA	208.27				42.64		1.868		22.12		77.82		0.767		0.118	
A205	CTDA	95.16		9.35		33.64		0.896		21.21		58.32		0.679		0.076	
A206	CTDA	65.59				34.98		2.116		21.65		56.64		1.103	?	0.321	
A207	CTDA	34.67				28.81		1.026		19.98		65.59		0.605		0.109	
A208	CTDA	31.33				24.98		0.790		17.04		56.64		0.513		0.114	
A209	CTDA	19.44				21.46		0.634		15.55		51.45		0.459		0.098	
A210	CTDA	19.81				21.72		0.658		14.40		45.12		0.405		0.119	
A211	CTDA	49.98				22.86		1.121		15.25		49.99		0.464		0.776	
A212	CTDA	15.35				20.89		0.594		14.49		48.72		0.429		0.069	
A213	CTDA	24.18		9.89		23.95		0.662		16.27		40.12		0.539		0.065	
A214	CTDA	25.58		19.64		25.02		0.589		12.79		36.30		0.640		0.123	

Table V.4: Dissolved trace metal concentrations CH42 (continued)

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH42.WK1
SHEET 3: PARTICULATE TRACE METAL CONCENTRATIONS
CH42: HUMBER PLUME CRUISE I

CODE	TYP	SWT mg	SCONC mg/l	MNP nmol/l	FEP nmol/l	NIP nmol/l	COP nmol/l	CUP nmol/l	ZNP nmol/l	CDP nmol/l	PBP nmol/l
A101	CTDA										
A102	CTDA										
A103	CTDA										
A104	CTDA	197	26.9	357.4	12437	18.79	9.13	9.78	42.39		14.41
A105	CTDA	268	33.1	439.8	14545	23.12	8.99	11.04	50.13		12.30
A106	CTDA	283	31.9	487.7	18570	22.83	8.66	13.10	65.88		14.16
A107	CTDA	282	43.1	651.2	22126	35.25	12.43	16.41	94.28		16.85
A108	CTDA	367	61.7	1134.3	40679	48.36	19.89	30.10	171.78		25.91
A109	CTDA	641	120.0	2380.9	85412	87.92	34.62	65.34	357.96	0.320	64.29
A110	CTDA										
A111	CTDA										
A112	CTDA	446	52.8	1047.6	39548	44.08	17.92	29.67	160.73	0.235	28.54
A113	CTDA	717	79.2	1557.0	54330	60.73	25.53	43.50	222.93	0.141	40.90
A114	CTDA	490	54.1	896.1	32278	40.56	14.69	22.90	130.76		22.20
A123	CTDA										
S1	P		9.9	138.8	4382			3.44	15.60		
S2	P		2.6	45.0	626				6.08		
S3	P										
S4	CTD										
S5	P		2.8	41.8	758				4.11		
S6	P										
S7	CTD	66	8.7	110.9	3542			2.59	12.38	0.054	
S8	CTD	53	6.0	84.1	2153	4.29		1.61	9.27		2.72
S9	P		3.7	39.7	988	2.21			4.19		
S10	CTD	28	3.1	33.9	1081			0.85	3.08	0.017	
S11	P										
S12	P		2.7	35.9	825				3.68		
S13	CTD	8	0.9	13.3	222				1.36		
S14	CTD										
S15	P		1.2	17.0	286				1.60		
S16	CTD	30	3.7	66.0	1312	2.46		0.89	5.60		
S17	P										
S18	P		5.8	90.8	1390				7.81		
S19	CTD	268	40.0	655.3	18121	26.58	12.22	14.42	74.04	0.142	21.24
S20	P										
S21	P		38.5	679.8	20909	30.18		11.94	98.36	0.343	
S22	CTD	260	32.8	561.2	17866	24.59	10.02	12.75	70.25		17.10
S23	P		48.2	833.5	22172	34.49	14.72	18.21	101.75	0.257	26.99
S24	P		9.1	152.4	4074	5.89	2.16	2.96	16.84	0.032	5.18
S25	P										
S26	CTD	142	16.0	262.1	6695	10.90	3.80	5.24	32.55	0.085	9.04
S27	P		7.4	111.8	2360	4.16		1.56	10.98	0.086	
S28	P										
S29	CTD	57	6.3	91.7	2176	3.54		1.78	9.45		
S30	P										
S31	P										
S32	P		3.7	58.6	1172	1.89		0.84	5.43		
S33	P										
S34	P										

Table V.5: Particulate trace metal concentrations CH42

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH42.WK1
SHEET 3: PARTICULATE TRACE METAL CONCENTRATIONS
CH42: HUMBER PLUME CRUISE I

CODE	TYP	SWT mg	SCONC mg/l	MNP nmol/l	FEP nmol/l	NIP nmol/l	COP nmol/l	CUP nmol/l	ZNP nmol/l	CDP nmol/l	PBP nmol/l
S35	P		2.1	22.2	316				2.15		
S36	P		3.5	50.3	737	1.37			3.80	0.050	
S37	CTD	36	4.1	75.4	1473	1.96		1.16	6.46		
S38	P										
S39	P		2.7	38.8	470						
S40	P										
S41	CTD										
S42	P										
S43	CTD	32	3.6	55.7	1245	1.72		1.20	5.51		
S44	P										
S45	P										
S46	P		2.8	43.3	670	1.34			3.34		
S47	P		15.2	265.6	7888				67.20		
S48	P		34.4	644.9	23585			16.51	87.88		17.60
S49	P										
S50	P		8.7	137.8	3483	5.34		2.74	15.04	0.031	5.75
S51	P		22.6	370.2	10028	14.63		7.33	43.91	0.121	11.02
S52	P										
S53	P		6.1	82.2	1933	3.74			8.40		
S54	P										
S55	P		4.4	72.1	1500	2.92			7.47		
S56	P		1.1	21.2	348	0.79			1.87		
S57	P										
S58	P										
S59	P										
S60	P										
S61	P										
S62	P										
S63	P										
S64	P										
S65	P		7.9	122.2	3532			0.84	12.93		
S66	P		4.7	67.6	1378			1.03	6.97		2.88
S67	P										
A201	CTDA	561	60.7	1171.2	39226	46.54	19.57	32.48	169.93		30.47
A202	CTDA	507	119.0	2469.3	81887	89.22	38.37	67.23	360.44	0.106	56.86
A203	CTDA	880	127.0	2566.0	89962	97.38	43.10	74.35	390.50	0.226	64.36
A204	CTDA	831	96.1	1976.7	68814	73.68	30.98	57.02	321.95	0.086	53.34
A205	CTDA	464	51.6	1080.1	37679	41.32	19.26	24.93	168.92	0.046	25.90
A206	CTDA	593	76.6	1659.2	60227	61.34	26.00	42.44	247.25	0.136	46.58
A207	CTDA	1147	177.0	3672.9	114795	129.68	60.07	99.45	484.67	0.472	93.12
A208	CTDA	875	101.0	1967.1	67638	74.00	32.56	51.98	296.65	0.359	53.13
A209	CTDA	345	66.4	1244.9	42612	50.91	25.91	31.56	174.71		32.69
A210	CTDA	430	49.1	902.7	31747	38.48	17.50	25.35	92.39		24.41
A211	CTDA	323	35.7	643.3	18666	27.98	11.51	16.97	105.95		17.57
A212	CTDA	381	41.6	779.9	27658	32.60	12.71	22.26	118.37		19.07
A213	CTDA	494	54.3	1067.5	37239	44.41	20.27	29.82	183.57		26.47
A214	CTDA										

Table V.6: Particulate trace metal concentrations CH42 (continued)

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH42.WK1
SHEET 4: NUTRIENTS, BIOLOGICAL PARAMETER AND UNFILTERED ALUMINIUM
CH42: HUMBER PLUME CRUISE I

CODE	TYP	PO4 umol/l	NO2 umol/l	NO3 umol/l	SI umol/l	O2 umol/l	K	CPHYLL mg/m3		Lunflt.AL nmol/l
A101	CTDA	0.80	0.05	49.52	11.44	299.7	G	0.7	G	23.55
A102	CTDA	0.79	0.07	43.95	10.93	299.1	G	0.6	G	25.59
A103	CTDA					298.0	G	0.5	G	26.26
A104	CTDA		0.46	21.11	7.28	298.6	G	0.6	G	23.10
A105	CTDA	0.77	0.52	21.05	7.42	298.0	G	0.5	G	31.36
A106	CTDA	0.78	0.54	39.46	10.53	299.1	G	0.6	G	34.45
A107	CTDA	0.83	0.57	50.65	12.69	299.8	G	0.6	G	43.49
A108	CTDA	0.80	0.57	54.27	13.63	300.4	G	0.7	G	41.29
A109	CTDA	0.77	0.55	63.11	15.01	300.1	G	0.8	G	27.16
A110	CTDA	0.65	0.53	72.10	17.53	299.5	G	0.8	G	26.26
A111	CTDA	0.41	0.54	77.57	19.18	297.6	G	0.9	G	29.65
A112	CTDA	0.74	0.52	73.30	17.77	299.5	G	0.8	G	30.09
A113	CTDA	0.83	0.53	57.80	13.50	299.8	G	0.7	G	32.07
A114	CTDA	0.83	0.54	46.36	11.02	299.8	G	0.7	G	32.22
A123	CTDA	0.76	0.43	71.10	17.98	298.6	G	0.8	G	28.61
S1	P	0.92	0.24	11.05	5.77			0.1		33.80
S2	P	0.91	0.20	1.89	4.16			0.1		30.24
S3	P	0.86	0.22		3.92			0.1		18.77
S4	CTD	0.88	0.22	6.00	3.98	295.9	G	0.5	G	23.99
S5	P		0.21	7.98	4.20	368.0		0.1		24.67
S6	P	0.86	0.28	11.73	4.63			0.1		22.41
S7	CTD	0.88	0.30	11.92	4.77	297.7	G	0.5	G	23.70
S8	CTD	0.82	0.29	8.52	4.02	298.4	G	0.5	G	23.70
S9	P	0.82	0.41	5.65	3.54			0.1		18.55
S10	CTD	0.84	0.36	5.39	3.80	296.2	G	0.5	G	
S11	P	0.86	0.40	5.72	4.00			0.1		
S12	P	0.74	0.40	4.11	3.92			0.1		18.11
S13	CTD	0.79	0.34	3.44	4.06	295.0	G	0.7	G	12.65
S14	CTD	0.67	0.40	4.25	4.33	295.4	G	0.6	G	18.75
S15	P	0.68	0.39	4.24	4.28			0.1		
S16	CTD	0.90	0.44	7.31	5.02	296.0	G	0.4	G	35.34
S17	P	0.91	0.41	6.45	4.75			0.1		31.27
S18	P	0.89	0.57	9.58	5.46			0.1		31.50
S19	CTD	1.08	0.51	26.93	8.67	300.2	G	0.6	G	34.78
S20	P	1.08	0.51	27.15	8.72	370.2		0.1		
S21	P	1.32	0.58	17.99	7.23			0.1		27.01
S22	CTD	1.26	0.51	17.55	7.64	299.6	I	0.7	G	36.57
S23	P	1.36	0.53	20.63		371.3		0.1		19.81
S24	P	1.17	0.53	12.99	6.90			0.1		29.27
S25	P	1.22	0.54	13.10	7.66	368.7		0.1		17.88
S26	CTD	1.48	0.66	19.03	8.19	301.0	G	0.6	G	16.26
S27	P	1.18	0.51	8.42	6.81	370.6		0.1		30.09
S28	P	1.19	0.52	7.51	6.69	369.0		0.1		
S29	CTD	1.18	0.53	7.48	6.68	301.7	G	0.6	G	23.32
S30	P					369.6		0.1		
S31	P	0.68	0.29	6.18	4.52			0.1		25.52
S32	P	0.70	0.31	8.11	5.08			0.1		25.97
S33	P	0.62	0.34	3.79	4.40			0.1		21.82
S34	P	0.83	0.31	3.03	4.67			0.1		13.84

Table V.7: Nutrients, biological parameter and aluminium CH42

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH42.WK1
SHEET 4: NUTRIENTS, BIOLOGICAL PARAMETER AND UNFILTERED ALUMINIUM
CH42: HUMBER PLUME CRUISE I

CODE	TYP	PO4 umol/l	NO2 umol/l	NO3 umol/l	SI umol/l	O2 umol/l	K	CPHYLL mg/m3		Lunflt.AL nmol/l
S35	P	0.85	0.28	3.24	5.14	364.5		0.1		14.32
S36	P	0.92	0.27	5.52	6.22	366.6		0.1		35.24
S37	CTD	0.96	0.34	6.79	5.01	298.8	G	0.5	G	32.88
S38	P	1.05	0.33	5.47	4.97	365.5		0.1		22.22
S39	P	0.93	0.29	5.47	4.99			0.1		24.00
S40	P	0.87	0.33	29.09	9.89			0.1		
S41	CTD	0.88	0.32	28.99	10.00	299.1	G	0.7	G	27.68
S42	P	0.76	0.35	9.57	6.32	368.5		0.1		29.42
S43	CTD	0.76	0.31	6.77	5.98	296.2	G	0.5	G	29.69
S44	P	0.70	0.36	3.50	5.61	366.7		0.1		14.43
S45	P	0.69	0.28	3.15	6.14			0.1		12.76
S46	P	0.98	0.22	6.03	4.39	370.6		0.1		15.92
S47	P	1.09	0.28	31.27	9.05			0.1		16.88
S48	P	1.26	0.16	28.41	9.06	376.1		0.1		14.39
S49	P	1.27	0.24	20.63	6.83			0.1		19.00
S50	P	1.10	0.25	14.58	7.00			0.1		22.67
S51	P	1.30	0.38	22.04	8.09	374.3		0.1		15.99
S52	P	1.00	0.25	12.22	5.91			0.1		20.70
S53	P	1.01	0.30	12.88	6.32			0.1		23.56
S54	P	0.96	0.31	10.62	5.84			0.1		21.74
S55	P	0.95	0.29	8.48	5.51			0.1		25.30
S56	P	0.89	0.25	5.04	4.71	373.6		0.1		11.72
S57	P	0.81	0.16	4.96	4.57	370.7		0.1		9.79
S58	P	0.75	0.19	4.71		370.6		0.1		7.98
S59	P	0.79	0.21	5.63	4.59	368.0		0.1		17.10
S60	P	0.88	0.23	8.16	4.87	368.3		0.1		21.52
S61	P		0.17					0.1		20.33
S62	P	0.85		4.67	5.24			0.1		20.92
S63	P		0.20	14.46	7.11			0.1		22.67
S64	P	1.01	0.09	12.04	6.59			0.1		
S65	P	1.04	0.12	12.59	6.85			0.1		23.26
S66	P	1.00	0.19	10.25	6.40			0.1		32.65
S67	P	0.97	0.23	5.31	4.46			0.1		21.59
A201	CTDA	0.94		51.32	14.12	297.2	G	0.6	G	18.04
A202	CTDA	0.97		45.11	12.26	299.2	C	0.7	C	21.28
A203	CTDA	0.89		55.89	15.18	300.4	G	0.8	G	20.24
A204	CTDA	0.78		63.08	18.13	297.3	G	0.7	G	25.93
A205	CTDA	0.83		62.36	17.78	298.9	G	0.6	G	25.18
A206	CTDA	0.93		56.84	15.48	299.1	G	0.7	G	26.37
A207	CTDA	0.97		47.15	12.62	297.6	G	0.7	G	17.45
A208	CTDA	0.97		38.38	10.64	295.5	G	0.7	G	19.86
A209	CTDA	0.98		30.53	9.02	296.3	G	0.6	G	21.76
A210	CTDA	1.01		31.45	9.05	297.3	G	0.6	G	24.74
A211	CTDA	1.00		38.49	10.70		N	0.5	G	27.16
A212	CTDA	0.99		44.95	12.08		N	0.5	G	27.38
A213	CTDA	0.99		48.33	13.53		N	0.6	G	23.84
A214	CTDA	1.02		46.92	12.68		N	0.7	G	24.63

Table V.8: Nutrients, biological parameter and aluminium CH42 (continued)

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH42.WK1
SHEET 5: SUSPENDED PARTICULATE MATTER, TIDALLY CORRECTED POSITIONS AND
CH42: HUMBER PLUME CRUISE I ADDITIONAL TRACE METAL DATA

CODE	TYP	TOTSED mg/l		MGRAVIMET mg/l	LAT corrected	LON to low water	MAFFCU nmol/l	MAFFCD nmol/l	MAFFPB nmol/l
A101	CTDA		N	121.70	53.5353	0.0984	6.29	0.46	0.80
A102	CTDA		N	54.60	53.5372	0.1030		0.33	0.19
A103	CTDA	40.71	G	39.40	53.5429	0.1060		0.50	0.24
A104	CTDA	37.60	G	35.90			5.35	0.41	0.77
A105	CTDA	41.86	G	38.70	53.5584	0.1022	5.11	0.28	0.99
A106	CTDA	34.02	G	32.90	53.5655	0.0978	8.18	0.37	0.08
A107	CTDA	45.79	C	44.60	53.5710	0.0914		0.42	3.19
A108	CTDA		N	69.50	53.5618	0.0811		0.53	3.96
A109	CTDA		N	103.50	53.5378	0.0729	13.69	0.62	0.87
A110	CTDA		N	90.00	53.5247	0.0669	23.60	0.73	3.81
A111	CTDA	43.57	G	49.50	53.5492	0.0872		1.16	2.94
A112	CTDA	45.55	C	54.70	53.5465	0.0920		0.58	0.47
A113	CTDA		N	90.40	53.5371	0.0913	18.88	0.69	8.21
A114	CTDA		N	73.00	53.5374	0.1012	10.07	0.49	2.80
A123	CTDA	45.47	C	55.20	53.5490	0.0827			
S1	P	13.90		19.40	53.5260	0.2396	2.67	0.24	0.11
S2	P	3.90		6.40	53.5084	0.4327	2.67	0.13	0.08
S3	P	1.70			53.5264	0.5942	2.83	0.13	0.31
S4	CTD	3.28	G	2.20	53.4225	0.8879	2.83	0.10	0.20
S5	P	5.00		3.10	53.3098	1.0010	2.52	0.13	0.09
S6	P	12.40		8.50	53.0322	1.1683	5.35	0.33	0.16
S7	CTD	9.04	G	10.70	52.9881	1.1682	4.88	0.09	0.10
S8	CTD	6.00	G	6.50	53.0252	1.3689	10.54	0.20	0.18
S9	P	3.80		3.30	53.2367	1.2169	2.20	0.13	0.16
S10	CTD	3.28	G	3.80	53.3588	1.0710			
S11	P	4.50			53.3770	1.0487	3.31	0.10	0.19
S12	P	3.30		3.10	53.6262	0.8447		0.46	0.16
S13	CTD	1.96	G	1.20	53.8239	0.6462	2.20	0.12	0.24
S14	CTD	2.13	G	1.40	53.7838	0.3693	2.52	0.04	0.22
S15	P	0.70		1.40	53.7828	0.3717	2.36	0.14	0.25
S16	CTD	4.88	G	5.10	53.8039	0.0634	3.15	0.12	0.25
S17	P	5.00		4.50	53.7178	0.1660	8.50	0.16	0.32
S18	P	5.90		6.60	53.4671	0.4229	5.19	0.09	0.07
S19	CTD	35.55	G	46.90	53.3416	0.4761			
S20	P				53.3425	0.4755	7.71	0.16	0.10
S21	P			47.60	53.1629	0.5045	6.14	0.14	0.33
S22	CTD	32.95	G	35.20	53.0520	0.4635	4.25	0.21	0.16
S23	P				53.1236	0.5586	6.53	0.27	0.11
S24	P	11.90			53.2368	0.7450			
S25	P	15.90		14.70	53.0840	0.9722	5.04	0.13	0.09
S26	CTD	16.63	G	23.10	52.9951	0.9923	6.92	0.19	0.14
S27	P	9.00			53.0233	1.3090	3.62	0.17	0.11
S28	P	8.30			53.0250	1.3741			
S29	CTD	6.97	G	6.97	53.0243	1.3773	4.09	0.20	0.23
S30	P	5.30			53.1352	1.2667	4.56	0.51	0.21
S31	P	4.00			53.2987	1.1321	2.99	0.12	0.12
S32	P	4.50			53.3706	1.0501	1.89	0.11	0.10
S33	P	2.30			53.5587	0.8591		0.18	0.16
S34	P	0.40			53.7128	0.7311	1.89	0.13	0.09

Table V.9: Suspended particulate matter, tidally corrected positions and additional trace metal data CH42

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH42.WK1
SHEET 5: SUSPENDED PARTICULATE MATTER, TIDALLY CORRECTED POSITIONS AND
CH42: HUMBER PLUME CRUISE I ADDITIONAL TRACE METAL DATA

CODE	TYP	TOTSED mg/l		MGRAVIMET mg/l	LAT corrected	LON to low water	MAFFCU nmol/l	MAFFCD nmol/l	MAFFPB nmol/l
S35	P	0.10			53.8119	0.5865			
S36	P	2.90			53.8099	0.3510	2.83	0.13	0.24
S37	CTD	5.19	G	5.19	53.8054	0.0621	3.46	0.13	0.22
S38	P	3.20			53.6497	0.2638	4.09	0.13	0.31
S39	P	3.50			53.5328	0.3189	7.55	0.13	0.27
S40	P				53.3392	0.4736			
S41	CTD	25.18	G	25.18	53.3383	0.4737	5.82	0.44	0.13
S42	P	6.50			53.3471	0.7683	4.41	0.13	0.18
S43	CTD	4.58	G	4.58	53.3783	0.9076	3.30	0.15	0.29
S44	P	1.00			53.5765	0.6767	5.19	0.16	0.29
S45	P				53.7452	0.4799	1.89	0.13	0.21
S46	P	1.90			53.6465	0.3145	1.39	0.11	0.19
S47	P	30.70			53.3816	0.4829	5.67	0.47	0.09
S48	P				53.2718	0.4929	9.29	0.45	0.13
S49	P	28.10			53.2203	0.6451	6.92	0.28	0.09
S50	P	11.20			53.1395	0.8438	5.04	0.20	0.15
S51	P	25.00			52.9932	0.9869	5.67	0.23	0.14
S52	P	9.30			53.0230	1.1478			
S53	P	6.90			53.1757	1.0311	4.09	0.14	0.13
S54	P	4.90			53.4171	0.7933	5.19	0.27	0.28
S55	P	4.20			53.5034	0.6783	3.46	0.14	0.11
S56	P	0.20			53.6654	0.5053	2.20	0.14	0.22
S57	P				53.7733	0.4541	2.05	0.13	0.20
S58	P				53.7828	0.6676	8.18	0.07	0.14
S59	P	2.20			53.5703	0.9057	2.67	0.12	0.15
S60	P	3.50			53.4403	1.0410	2.99	0.12	0.19
S61	P	3.70			53.1984	1.2652	10.86	0.13	0.15
S62	P	9.90			53.0141	1.3672		0.20	0.24
S63	P	17.80			52.9903	0.9932	4.72	0.20	0.07
S64	P	10.20			53.1219	0.6284	4.56	0.77	0.10
S65	P	10.50			53.2999	0.7377	5.98	0.20	0.16
S66	P	5.10			53.4084	0.8238	2.83	0.20	0.08
S67	P	2.10			53.4887	0.8055			
A201	CTDA	45.52	C	39.10	53.5363	0.0706	10.39	0.44	0.48
A202	CTDA		N	117.60	53.5300	0.0630	11.33	0.54	0.15
A203	CTDA		N	106.50	53.5251	0.0602	18.88	0.98	0.25
A204	CTDA		N	81.20	53.5419	0.0549	15.74	0.89	0.04
A205	CTDA		N	61.30	53.5362	0.0646	15.58	0.65	4.01
A206	CTDA		N	75.90	53.5327	0.0763	14.48	0.52	0.03
A207	CTDA		N	131.20	53.5333	0.0860	10.70	0.58	0.14
A208	CTDA		N	114.00	53.5339	0.0952	11.33	0.48	0.19
A209	CTDA		N	70.50	53.5391	0.0983	9.60	0.51	0.07
A210	CTDA	39.69	G	54.00	53.5431	0.0985	10.23	0.42	0.10
A211	CTDA	32.31	G	45.60	53.5480	0.0917	8.97	0.45	0.53
A212	CTDA	41.10	G	46.80	53.5454	0.0818			
A213	CTDA	45.09	C	59.30	53.5370	0.0704	12.12	0.61	0.05
A214	CTDA		N	139.30	53.5304	0.0625			

Table V.10: Suspended particulate matter, tidally corrected positions and additional trace metal data CH42 (continued)

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH42.WK1
SHEET 8: log10 Kd-VALUES
CH42: HUMBER PLUME CRUISE I

log 10 values of ratio of nmol/kg sediment to nmol/l water

CODE	TYP	MNkd	FEkd	NIkd	COkd	CUkd	ZNkd	CDkd	PBkd
A101	CTDA								
A102	CTDA								
A103	CTDA								
A104	CTDA								
A105	CTDA	5.64	5.49	4.68	5.42	4.51	5.03		5.76
A106	CTDA	5.87	7.47	4.67	5.72	4.56	4.85		7.57
A107	CTDA	5.14	5.16	4.66	5.15	4.37	4.62		5.24
A108	CTDA	5.27	5.22	4.52	4.97	4.37	4.56		5.22
A109	CTDA	5.29	6.25	4.38	5.14	4.41	4.67	3.66	6.22
A110	CTDA								
A111	CTDA								
A112	CTDA	5.18	6.08	4.37	5.42	4.44	4.70	3.80	5.81
A113	CTDA	4.67	5.12	4.41	5.14	4.40	4.41	3.50	5.24
A114	CTDA	5.11	5.84	4.51	5.32	4.44	4.90		5.39
A123	CTDA								
S1	P	5.87	6.06			4.61	5.20		
S2	P	6.98	8.08				5.25		
S3	P								
S4	CTD								
S5	P	6.82	7.84				5.23		
S6	P								
S7	CTD	6.70	7.66			4.63	5.03	4.45	
S8	CTD	6.91	7.10	5.04		4.67	5.28		6.31
S9	P	6.46	8.30	5.17			5.33		
S10	CTD	6.82	7.24			4.82	5.27	4.57	
S11	P								
S12	P	6.86	7.89				5.41		
S13	CTD	6.78	7.17				5.51		
S14	CTD								
S15	P	6.72	7.98				5.36		
S16	CTD	6.87	8.17	4.99		4.64	5.09		
S17	P								
S18	P	6.74	7.95				5.10		
S19	CTD	6.95	8.44	4.60	6.30	4.59	4.97	3.91	6.90
S20	P								
S21	P	6.92	8.26	4.88		4.50	5.24	4.51	
S22	CTD	6.89	8.68	4.81	6.23	4.67	5.15		6.70
S23	P	6.80	8.61	4.71	6.04	4.52	5.08	4.20	6.88
S24	P	6.90	7.70	4.81	6.04	4.60	5.16	4.11	7.02
S25	P								
S26	CTD	6.69	7.09	4.87	6.47	4.58	5.17	4.28	6.64
S27	P	6.69	8.01	4.96		4.54	5.16	4.71	
S28	P								
S29	CTD	7.10	7.44	5.05		4.79	5.44		
S30	P								
S31	P								
S32	P	6.87	8.24	4.92		4.56	5.26		
S33	P								
S34	P								

Table V.11: K_d-distribution coefficients CH42

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH42.WK1
SHEET 8: log10 Kd-VALUES
CH42: HUMBER PLUME CRUISE I

log 10 values of ratio of nmol/kg sediment to nmol/l water

CODE	TYP	MNkd	FEkd	NIkd	COkd	CUkd	ZNkd	CDkd	PBkd
S35	P	6.85	7.97				5.45		
S36	P	7.00	8.04	4.92			5.29	4.95	
S37	CTD	6.90	7.65	4.79		4.65	5.32		
S38	P								
S39	P	6.91	8.06						
S40	P								
S41	CTD								
S42	P								
S43	CTD	6.81	7.88	4.97		4.74	5.37		
S44	P								
S45	P								
S46	P	6.97	7.93	5.04			5.32		
S47	P	6.41	8.23				5.26		
S48	P	6.82	8.62			4.59	5.08		6.59
S49	P								
S50	P	6.89	8.33	5.10		4.60	5.23	4.15	6.66
S51	P	6.82	8.32	4.73		4.56	5.18	4.24	6.47
S52	P								
S53	P	6.48	7.58	4.82			5.05		
S54	P								
S55	P	7.00	8.05	4.91			5.13		
S56	P	6.93	8.11	5.34			5.73		
S57	P								
S58	P								
S59	P								
S60	P								
S61	P								
S62	P								
S63	P								
S64	P								
S65	P	6.92	8.86			4.12	5.15		
S66	P	6.79	8.29			4.53	5.15		6.65
S67	P								
A201	CTDA	5.77		4.53	5.61	4.58	4.86		
A202	CTDA	5.73		4.36	5.60	4.54	4.79	3.18	6.70
A203	CTDA	5.28		4.34	5.43	4.51	4.72	3.47	6.79
A204	CTDA	4.99		4.25	5.24	4.43	4.63	3.07	6.67
A205	CTDA	5.34	7.89	4.38	5.62	4.36	4.75	3.12	6.82
A206	CTDA	5.52		4.36	5.21	4.41	4.76	3.21	6.28
A207	CTDA	5.78		4.41	5.52	4.45	4.62	3.64	6.68
A208	CTDA	5.79		4.47	5.61	4.48	4.71	3.84	6.66
A209	CTDA	5.98		4.55	5.79	4.49	4.71		6.70
A210	CTDA	5.97		4.56	5.73	4.55	4.62		6.62
A211	CTDA	5.56		4.54	5.46	4.49	4.77		5.80
A212	CTDA	6.09		4.57	5.71	4.57	4.77		6.82
A213	CTDA	5.91	7.84	4.53	5.75	4.53	4.93		6.88
A214	CTDA								

Table V.12: K_d-distribution coefficients CH42 (continued)

APPENDIX VI

CRUISE CH46

DATA BASE

CONTENT

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH46.WK1
SHEET 1: GENERAL SAMPLE PARAMETER Updated: 01/01/92 14:09
CH46: THAMES PLUME I

CODE	STN #	TYP	DEPTH m	BOTT #	S	DATE dd/mm/yy	TIME hh:mm	LAT +ve N	LONG +ve E	SAL	A	TEMP °C	B
S1	100	P	3.3	3412	9	13/02/89	01:07	51.6791	1.3017	34.70		6.95	
S2	101	P	3.3	3454	9	13/02/89	02:10	51.5445	1.0510	34.70		6.95	
S3	102	P	3.3	3455	9	13/02/89	03:06	51.4937	0.7865	33.50		6.67	
T1	103	P	3.3	3456	8	13/02/89	04:05	51.5030	0.5091	28.40		6.99	
T2	104	P	3.3	3480	8	13/02/89	05:12	51.4488	0.4233	26.20		7.19	
A1	1405	CTDA	7.8	3481	6	13/02/89	12:11	51.4494	0.4248	19.81	G	8.20	I
A2	1406	CTDA	8.1	3482	6	13/02/89	13:17	51.4494	0.4249	19.84	G	8.20	G
A3	1407	CTDA	8.0	3483	6	13/02/89	14:12	51.4497	0.4243	20.52	G	8.15	G
A4	1408	CTDA	8.0	3488	5	13/02/89	15:07	51.4487	0.4240	21.83	G	7.95	O
A5	1409	CTDA	8.9	3489	5	13/02/89	16:07	51.4485	0.4241	22.40	G	7.86	I
A6	1410	CTDA	8.7	3490	5	13/02/89	17:04	51.4485	0.4244	23.46	G	7.71	I
A7	1411	CTDA	9.1	3491	6	13/02/89	18:04	51.4487	0.4239	25.04	G	7.45	O
A8	1412	CTDA	9.0	3492	6	13/02/89	19:06	51.4487	0.4249	25.77	G	7.33	I
A9	1413	CTDA	8.7	3493	6	13/02/89	20:12	51.4490	0.4248	23.01	G	7.83	I
A10	1414	CTDA	6.0	3494	6	13/02/89	21:14	51.4492	0.4247	21.42	G	8.03	G
A11	1415	CTDA	6.5	3495	8	13/02/89	22:11	51.4490	0.4254	20.07	G	8.23	O
A12	1416	CTDA	7.1	3496	8	13/02/89	23:08	51.4487	0.4256	19.68	G	8.31	G
A13	1417	CTDA	7.3	3497	8	14/02/89	00:07	51.4487	0.4257	19.23	G	8.38	O
A14	1418	CTDA	7.8	3506	8	14/02/89	01:07	51.4486	0.4254	19.45	G	8.29	I
T3	105	P	3.3	3507	9	14/02/89	12:10	51.5002	0.6408	28.20		6.87	
S4	106	P	3.3	3508	9	14/02/89	13:15	51.4811	0.9518	34.30		6.81	
S5	107	P	3.3	3509	9	14/02/89	14:10	51.4917	1.0309	34.40		6.84	
S6	108	P	3.3	3510	9	14/02/89	15:44	51.5715	1.2272	34.50		6.81	
S7	109	P	3.3	3511	9	14/02/89	16:54	51.6726	1.4458	34.50		6.69	
S8	110	P	3.3	3512	9	14/02/89	18:09	51.7312	1.4852	34.50		6.70	
S9	111	P	3.3	3513	9	14/02/89	20:10	51.8647	1.7257	34.30		6.52	
S10	112	P	3.3	3514	9	14/02/89	20:58	51.8573	1.6453	34.40		6.67	
S11	113	P	3.3	3515	9	15/02/89	00:01	51.6351	1.2422	34.30		6.40	
S12	114	P	3.3	3516	9	15/02/89	00:57	51.5398	1.0943	34.40		6.79	
T4	115	P	3.3	3517	9	15/02/89	02:01	51.4808	0.9114	31.30		6.60	
S13	116	P	3.3	3518	9	15/02/89	03:02	51.4942	1.0284	33.50		6.65	
S14	117	P	3.3	3519	9	15/02/89	04:17	51.5548	1.3132	34.50		6.89	
S15	118	P	3.3	3520	9	15/02/89	05:03	51.4822	1.4362	34.60		7.17	
S16	119	P	3.3	3521	9	15/02/89	07:06	51.3325	1.6125	34.40		7.04	
S17	120	P	3.3	3522	9	15/02/89	08:17	51.4138	1.8630	34.90		8.59	
S18	121	P	3.3	3526	9	15/02/89	08:51	51.5035	1.9584	34.90		8.46	
S19	1429	CTD	9.3	3523	7	15/02/89	11:00	51.6886	1.9873	34.94	G	7.78	G
S20	122	P	3.3	3524	9	15/02/89	15:29	51.3297	1.6030	34.50		7.22	
S21	123	P	3.3	3528	9	15/02/89	18:07	51.5886	1.7384	34.40		6.94	
S22	1430	CTD	8.3	3525	7	15/02/89	18:32	51.5877	1.7353	34.63	G	6.92	I
S23	124	P	3.3	3529	9	15/02/89	20:44	51.7973	1.9517	34.60		7.36	
S24	125	P	3.3	3527	9	15/02/89	22:50	51.7240	1.7732	34.40		6.80	
S25	126	P	3.3	3530	9	15/02/89	23:34	51.6312	1.6875	34.40		6.88	
S26	1431	CTD	8.2	3531	9	16/02/89	01:17	51.4687	1.4999	34.64	G	7.07	I
S27	127	P	3.3	3532	9	16/02/89	02:27	51.5303	1.4100	34.60		7.07	
S28	1432	CTD	8.2	3533	9	16/02/89	03:58	51.6888	1.6023	34.63	G	6.81	O
S29	128	P	3.3	3534	9	16/02/89	05:11	51.7882	1.7305	34.40		6.65	
S30	1433	CTD	7.9	3535	9	16/02/89	06:07	51.8629	1.8264	34.52	G	6.74	I
S31	129	P	3.3	3536	9	16/02/89	07:34	51.8653	1.6242	34.30		6.45	
S32	1434	CTD	8.5	3537	9	16/02/89	08:51	51.7552	1.4125	34.55	G	6.53	O

Table VI.1: General station parameters CH46

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH46.WK1
SHEET 1: GENERAL SAMPLE PARAMETER Updated: 01/01/92 14:09
CH46: THAMES PLUME I

CODE	STN #	TYP	DEPTH m	BOTT #	S	DATE dd/mm/yy	TIME hh:mm	LAT +ve N	LONG +ve E	SAL	A	TEMP °C	B
S33	130	P	3.3	3543	9	16/02/89	19:20	51.6585	1.8184	34.60		7.21	
S34	131	P	3.3	3542	9	16/02/89	20:32	51.4755	1.6198	34.40		6.80	
S35	133	P	3.3	3539	9	16/02/89	22:45	51.4648	1.7578	34.50		7.02	
S36	134	P	3.3	3538	9	16/02/89	23:49	51.6209	1.9302	34.80		7.75	
S37	135	P	3.3	3540	9	17/02/89	01:16	51.6983	2.1678	34.70		8.05	
S38	136	P	3.3	3541	9	17/02/89	04:07	51.3207	1.7625	35.00		8.42	
S39	137	P	3.3	3565	9	17/02/89	04:56	51.2270	1.6271	34.70		7.50	
S40	139	P	3.3	3558	9	17/02/89	09:13	51.4853	1.2939	34.50		6.79	
S41	140	P	3.3	3559	9	17/02/89	10:52	51.4938	0.8365	33.70		6.53	
S42	141	P	3.3	3560	9	17/02/89	11:21	51.5015	0.7137	32.40		6.48	
T5	142	P	3.3	3566	9	17/02/89	11:47	51.5052	0.6071	30.80		6.38	
T6	143	P	3.3	3567	9	17/02/89	12:02	51.5043	0.5479	29.60		6.61	
T7	144	P	3.3	3568	8	17/02/89	12:26	51.4901	0.4653	27.90		6.80	
T8	145	P	3.3	3569	8	17/02/89	12:42	51.4592	0.4426	26.20		7.16	
T9	146	P	3.3	3570	8	17/02/89	13:10	51.4470	0.4034	23.20		7.75	
T10	147	P	3.3	3571	8	17/02/89	14:16	51.4470	0.4036	21.60		7.95	
T11	148	P	3.3	3564	8	17/02/89	16:56	51.4473	0.4036	20.10		8.26	
P43A	1435	CTD	5.2	3552	9	17/02/89	21:00	51.5703	1.1301	34.53	G	6.43	I
S43	1435	CTD	7.9	3551	9	17/02/89	21:00	51.5703	1.1301	34.52	G	6.43	O
P43C	1435	CTD	11.8	3562	9	17/02/89	21:00	51.5703	1.1301	34.53	G	6.43	O
P43D	1435	CTD	14.7	3561	9	17/02/89	21:00	51.5703	1.1301	34.53	G	6.43	G
P43E	1435	CTD	17.0	3563	9	17/02/89	21:00	51.5703	1.1301	34.53	G	6.43	G
P44	155	P	3.3	3544	9	19/02/89	00:54	51.4970	0.7190	32.60		6.82	
T12	156	P	3.3	3545	8	19/02/89	01:27	51.5032	0.5973	30.20	S	7.07	
T13	157	P	3.3	3546	8	19/02/89	02:01	51.5024	0.5104	27.60		7.45	
T14	158	P	3.3	3547	8	19/02/89	02:34	51.4583	0.4403	26.41	S	7.64	
T15	159	P	3.3	3548	8	19/02/89	03:03	51.4504	0.3778	22.60		8.15	
T16	160	P	3.3	3549	8	19/02/89	03:40	51.4695	0.3159	19.50		8.58	
T17	161	P	3.3	3550	8	19/02/89	04:11	51.4637	0.2626	16.80		8.75	
T18	162	P	3.3	3553	8	19/02/89	04:52	51.4866	0.1847	12.60		8.82	
T19	163	P	3.3	3554	8	19/02/89	05:38	51.5129	0.1101	7.40		8.81	
T20	164	P	3.3	3555	8	19/02/89	06:22	51.4968	0.0547	5.00		8.42	
T21	165	P	3.3	3556	8	19/02/89	06:57	51.5133	0.1386	7.80		8.59	
T22	166	P	3.3	3557	8	19/02/89	08:26	51.4598	0.2835	15.54	S	8.78	

Table VI.2: General station parameter CH46 (continued)

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH46.WK1
SHEET 2: DISSOLVED TRACE METAL CONCENTRATIONS
CH46: THAMES PLUME I

CODE	STN #	MND nmol/l	C	FED nmol/l	D	NID nmol/l	E	COD nmol/l	F	CUD nmol/l	G	ZND nmol/l	H	CDD nmol/l	I	PBD nmol/l	J
S1	100	3.81		36.96	?	31.01	?	0.98	?	12.76		23.09		0.27		0.97	?
S2	101	5.63		2.73		11.38		0.62		9.27		18.97		0.23		0.23	
S3	102	10.57		7.25		23.52		0.88		16.54		55.44		0.32		0.43	
T1	103	33.15		9.34		62.73		1.63		34.14		138.52		0.78		2.30	
T2	104	38.42		19.08		74.08		2.05		50.05		178.70		0.83		2.34	
A1	1405	38.88		36.66		98.83		2.09		38.98		302.88		1.21		9.15	
A2	1406	45.01		267.04		118.92		2.02		42.01		270.07		1.33		9.68	
A3	1407	43.00		46.27		112.81		2.66		38.98		252.04		1.21		8.09	
A4	1408	39.71		34.32		47.02		2.23		54.04		253.38		1.04		4.04	
A5	1409	39.36		69.57		46.79		1.91		52.10		251.91		1.18		4.23	
A6	1410	37.75		38.33		42.55		2.69		47.36		239.92		1.12		4.27	
A7	1411	40.50		24.50		74.64		2.34		30.52		196.23		1.47		5.56	
A8	1412	31.19		23.55		69.17		1.74		26.15		158.32		1.10		3.35	
A9	1413	33.41		20.66		48.41		2.55		30.41		231.45		1.25		6.66	
A10	1414	38.66		22.47		44.99		2.78		31.29		240.38		1.25		7.35	
A11	1415	58.36		93.59		146.86		3.32		81.47		372.77		1.08		3.77	
A12	1416	57.66		30.85		113.65		3.04		72.36		324.68		0.96		6.40	
A13	1417	67.47		28.50		115.42		3.11		72.33		281.76		0.94		6.36	
A14	1418	69.77		21.64		99.75		3.64		61.41		470.61		1.11		3.90	
T3	105	26.49		29.00		66.79		2.08		34.70		182.76		0.60		1.91	
S4	106	5.49		17.18		15.30		0.70		14.84		36.49		0.24		0.34	
S5	107	9.68		5.60		12.91		0.73		11.70		21.82		0.35		0.21	
S6	108	7.23		6.01		11.75		0.76		10.06		17.91		0.28		0.13	
S7	109	2.59		6.38		13.63		0.53		10.46		14.92		0.29		0.10	
S8	110	2.71		5.29		13.11		0.55		11.10		16.04		0.35		0.15	
S9	111	6.74		136.14	?	11.17		0.51		10.47		16.59		0.24		0.14	
S10	112	7.58		7.47		13.90		0.68		12.59		27.34		0.28		0.14	
S11	113	4.45		3.51		12.67		0.56		11.89		27.06		0.27		0.15	
S12	114	5.13		4.31		10.61		0.55		9.66		25.23		0.24		0.18	
T4	115	19.68		9.29		11.70		1.33		7.25		110.90		0.49		1.02	
S13	116	13.03		10.45		12.18		1.08		8.59		76.94		0.38		0.56	
S14	117	3.36		2.10		11.52		0.44		10.78		19.30		0.28		0.19	
S15	118	2.76		1.10	<	9.47		0.42		11.37		16.14		0.23		0.12	
S16	119	2.32		0.61	<	11.87		0.39		11.66		20.23		0.28		0.18	
S17	120	2.50		4.02		4.68		0.19		5.04		11.05		0.16		0.12	
S18	121	2.29		4.38		5.35		0.19		5.78		11.24		0.17		0.11	
S19	1429	1.73	<	1.29	<	9.16		0.37		8.79		12.72		0.32		0.11	
S20	122	3.68		1.81		11.12		0.43		10.13		20.16		0.23		0.14	
S21	123	0.76		5.50		11.03		0.30		9.76		16.72		0.19		0.11	
S22	1430	0.37	<	2.04	<	10.44		0.38		10.63		12.97		0.32		0.14	
S23	124	2.96		14.95		8.71		0.29		8.31		15.41		0.20		0.12	
S24	125	1.13		2.21		11.59		0.29		10.45		15.76		0.20		0.08	
S25	126	1.41		1.79		10.64		0.39		10.58		16.63		0.22		0.05	
S26	1431	2.78		1.93		10.49		0.37		9.36		23.59		0.23		0.17	
S27	127	2.66		8.00		8.79		0.29		8.71		17.34		0.20		0.10	
S28	1432	2.82		1.47		11.07		0.35		9.98		20.13		0.24		0.12	
S29	128	2.73		1.54		11.27		0.24		11.48		16.89		0.23		0.10	
S30	1433	1.89		1.92		10.93		0.26		8.42		16.78		0.22		0.10	
S31	129	1.32		1.10	<	10.88		0.22		11.04		16.15		0.24		0.08	
S32	1434	1.79		8.78		12.40		0.34		12.05		48.81	?	0.24		0.12	

<u>Table VI.3</u>: Dissolved trace metal concentrations CH46

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH46.WK1
SHEET 2: DISSOLVED TRACE METAL CONCENTRATIONS
CH46: THAMES PLUME I

CODE	STN #	MND nmol/l	C	FED nmol/l	D	NID nmol/l	E	COD nmol/l	F	CUD nmol/l	G	ZND nmol/l	H	CDD nmol/l	I	PBD nmol/l	J
S33	130	2.51		16.07		9.75		0.25		8.38		17.02		0.21		0.11	
S34	131	2.12		17.36		12.64		0.40		11.41		17.25		0.25		0.11	
S35	133	1.99		11.77		11.08		0.23		10.10		16.63		0.25		0.15	
S36	134	1.82		5.90		7.11		0.22		6.84		13.37		0.18		0.12	
S37	135	1.62		8.61		5.61		0.14		4.91		10.90		0.16		0.12	
S38	136	2.01		3.05		5.63		0.14		4.38		12.71		0.12		0.20	
S39	137	1.96		1.88		8.17		0.27		7.67		13.79		0.20		0.12	
S40	139	2.53		1.23	<	11.23		0.49		9.14		17.74		0.25		0.16	
S41	140	5.28		0.80	<	17.56		0.49		12.27		37.90		0.32		0.31	
S42	141	11.85		3.66		28.77		0.91		8.58		82.42		0.41		0.61	
T5	142	22.49		5.14		45.06		1.32		8.18		130.49		0.56		1.03	
T6	143	24.03		6.82		49.23		1.20		8.74		156.28		0.59		1.49	
T7	144	36.41		7.60		56.61		1.93		39.33		197.86		0.88		2.94	
T8	145	41.76		11.15		65.50		2.14		44.70		262.21		0.97		2.97	
T9	146	42.59		12.47		76.93		2.55		51.81		344.79		1.10		2.62	
T10	147	49.26		17.17		87.55		3.43		59.88		418.49		1.25		3.58	
T11	148	51.62		28.61		79.60		2.83		57.03		351.49		1.08		6.89	
S43A	1435	5.14		0.52	<	12.28		0.50		13.43		34.35		0.29		0.32	
S43	1435	4.49		2.82		12.95		0.52		10.48		24.86		0.23		0.21	
S43C	1435	3.95		8.04		16.45		0.56		13.03		198.18		0.35		1.27	
S43D	1435	6.42		8.76		12.90		0.55		11.42		28.22		0.29		0.19	
S43E	1435	4.53		3.10		12.81		0.44		12.44		22.52		0.26		0.24	
S44	155	9.49		19.82		26.22		0.92		8.91		70.54		0.41		0.68	
T12	156	17.94		28.14		39.02		1.46		27.02		117.18		0.58		1.36	
T13	157	28.10		256.16		58.53		2.19		36.06		189.95		0.82		2.41	
T14	158	39.80		53.17		72.45		2.46		41.48		243.14		0.90		3.25	
T15	159	40.10		120.28		90.45		2.88		54.36		313.69		1.14		3.96	
T16	160	57.64		131.08		113.42		3.51		65.09		323.49		1.21		7.37	
T17	161	88.89		174.54		141.90		4.32		75.25		408.32		1.29		7.64	
T18	162	65.16		254.83		176.54		4.66		82.32		436.86		1.18		11.43	
T19	163	85.80		273.15		116.19		5.34		94.56		488.76		1.13		13.70	
T20	164	43.78		282.56		122.65		6.74		87.37		486.73		1.38		17.07	
T21	165	83.78		288.45		124.15		5.75		85.74		534.79		1.31		17.47	
T22	166	95.90		178.27		162.22		4.01		81.08		442.82		1.36		13.10	

Table VI.4: Dissolved trace metal concentrations CH46 (continued)

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH46.WK1
SHEET 3: PARTICULATE TRACE METAL CONCENTRATIONS
CH46: THAMES PLUME I

CODE	STN #	SWT mg	SCONC mg/l	MNP nmol/l	FEP nmol/l	NIP nmol/l	COP nmol/l	CUP nmol/l	ZNP nmol/l	CDP nmol/l	PBP nmol/l
S1	100	248	34.6	289.7	12310	24.16	9.39	11.49	48.69	0.123	12.02
S2	101										
S3	102	215	30.9	286.8	11652			11.86	54.35		12.38
T1	103	287	38.7	436.7	15106	24.39	9.85	25.58	85.24		19.05
T2	104	195	34.2	398.4	14892	20.39	7.54	28.90	88.93		25.75
A1	1405	225	47.9	566.7	16724	27.74	14.63	36.86	106.97		33.52
A2	1406	214	57.9	706.1	21522	35.50	16.70	45.37	158.52	0.206	38.29
A3	1407	238	44.1	489.6	14079	24.04	9.73	31.16	93.76		35.33
A4	1408	648	151.0	2088.8	70268	97.73	53.81	128.31	408.79	0.134	105.68
A5	1409	912	217.0	2922.8	93017	133.06	66.28	182.00	541.01	0.386	143.49
A6	1410	667	167.0	1975.8	69611	102.40	45.34	134.28	416.35	0.297	110.43
A7	1411	716	159.0	2112.7	72084	100.20	45.87	127.10	384.25	0.283	99.76
A8	1412	249	75.5	865.8	27429	45.01	17.94	55.24	133.96	0.067	49.19
A9	1413	338	241.0	3114.5	93466	155.99	61.34	194.17	593.47		158.19
A10	1414	665	289.0	3734.8	129054	187.06	78.47	239.20	800.08	1.286	191.10
A11	1415	548	274.0	3590.8	119363	172.68	79.04	232.39	737.60	0.731	193.08
A12	1416	539	189.0	2683.3	87072	128.77	54.52	165.65	505.89	0.504	146.87
A13	1417	303	97.7	1262.6	38380	64.90	26.53	77.18	271.97	0.348	67.90
A14	1418	328	88.7	1114.0	36814	58.92	27.09	73.42	236.06	0.395	59.51
T3	105	95	28.7	303.0	10709	17.11	8.28	16.26	59.26	0.434	18.28
S4	106	140	19.1	159.9	6703	11.39		6.37	27.17	0.034	8.57
S5	107										
S6	108	57	16.4	119.4	4240	8.94		4.65	21.07		14.25
S7	109										
S8	110	122	25.5	213.5	10232	15.64	6.92	7.46	31.59		10.71
S9	111	135	16.6	160.1	6450	10.46	4.23	5.28	22.60		6.49
S10	112										
S11	113	185	25.7	219.9	10147	14.88	6.54	8.45	34.20		10.17
S12	114	148	22.0	180.2	7922	13.12	6.35	6.40	28.94		8.60
T4	115	161	17.7	154.6	6202	9.65	4.20	7.88	33.57	0.079	8.12
S13	116	61	11.8	100.9	3543	8.44		4.88	17.69	0.052	
S14	117	197	39.4	337.1	14215	22.82	10.70	11.47	53.03	0.210	12.74
S15	118	186	24.8	189.6	8752	14.78	5.89	6.20	28.83		5.75
S16	119	279	38.7	317.0	15043	21.75	12.48	10.90	47.35		16.06
S17	120										
S18	121	23	2.0	20.0	566	1.29		0.31	2.78		
S19	1429										
S20	122	179	18.1	148.3	7149	11.41	4.91	5.44	27.41	0.129	7.16
S21	123										
S22	1430	86	10.2	76.1	3216	5.21	2.94	2.55	12.32		4.38
S23	124	61	8.0	61.2	1925	4.09		1.64	8.93	0.050	2.82
S24	125	109	12.5	109.2	4926	7.66	3.82	3.70	16.06		4.65
S25	126	182	19.3	168.6	7506	11.51	5.24	5.31	28.34	0.052	5.59
S26	1431										
S27	127	185	20.6	157.5	7591	11.23	4.89	5.96	24.89	0.055	6.46
S28	1432										
S29	128	92	16.2	153.3	6057	10.76		5.35	22.30	0.029	7.43
S30	1433										
S31	129										
S32	1434										

Table VI.5: Particulate trace metal concentrations CH46

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH46.WK1
SHEET 3: PARTICULATE TRACE METAL CONCENTRATIONS
CH46: THAMES PLUME I

CODE	STN	SWT	SCONC	MNP	FEP	NIP	COP	CUP	ZNP	CDP	PBP
	#	mg	mg/l	nmol/l	nmol/l	nmol/l	nmol/l	nmol/l	nmol/l	nmol/l	nmol/l
S33	130										
S34	131										
S35	133										
S36	134										
S37	135										
S38	136										
S39	137	55	4.9	37.5	1254	3.25		0.80	5.55	0.052	1.75
S40	139	156	32.4	218.2	10059	17.66	7.15	6.93	37.17		12.04
S41	140	133	30.3	248.2	10970	16.52	7.71	8.53	39.86		11.85
S42	141	79	26.3	225.0	8990	14.33		7.16	39.82	0.047	
T5	142	62	20.5	194.0	6104	11.17		7.16	34.49	0.055	
T6	143	83	27.7	252.1	9126	15.10		11.90	47.45	0.173	18.32
T7	144	96	23.3	250.2	8928	12.30		13.86	48.11		17.09
T8	145	120	36.4	371.0	11901	19.22		20.62	78.50	0.130	24.42
T9	146	191	47.3	533.8	18302	29.00	10.43	34.61	107.07	0.210	28.54
T10	147	932	210.0	2637.4	87083	132.35	60.58	170.84	507.49		135.82
T11	148	721	219.0	2870.0	100187	141.75	63.18	182.30	582.84	0.195	151.15
S43A	1435										
S43	1435	168	18.2	145.8	6263	10.54	4.63	5.79	23.10	0.081	8.52
S43C	1435										
S43D	1435										
S43E	1435										
S44	155										
T12	156										
T13	157										
T14	158										
T15	159										
T16	160										
T17	161										
T18	162										
T19	163										
T20	164										
T21	165										
T22	166										

Table VI.6: Particulate trace metal concentrations CH46 (continued)

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH46.WK1
SHEET 4: SUSPENDED PARTICULATE MATTER AND MAFF DATA
CH46: THAMES PLUME I

CODE	STN #	TOTSED mg/l	M	CPHYLL mg/m3		LGRAVIMET mg/l	MAFFCU nmol/l	MAFFCD nmol/l	MAFFPB nmol/l
S1	100			0.7		39.70	6.92	0.334	0.198
S2	101	31.30		0.7		43.90	7.24	0.249	0.101
S3	102	26.02		0.8		39.60	10.54	0.400	0.381
T1	103	34.18				39.80	31.47	1.335	2.172
T2	104					31.20	36.19	0.979	3.765
A1	1405		N	1.1	G	75.80	36.19	1.512	9.170
A2	1406	56.73	G	1.0	G	42.20	48.78	0.961	8.688
A3	1407	57.78	C	0.9	G	43.70	40.91	0.890	6.757
A4	1408		N	1.0	G	179.00	44.06	1.868	7.240
A5	1409		N	1.0	G	326.00	36.19	1.601	6.757
A6	1410		N	1.1	G	147.00	28.32	1.157	4.826
A7	1411		N	1.1	G	140.00	20.46	1.423	3.982
A8	1412		N	0.9	G	156.00	18.88	1.512	4.103
A9	1413		N	1.0	G	158.00	17.31	1.157	4.006
A10	1414		N	0.9	G	247.00	44.06	1.512	7.240
A11	1415		N	0.9	G	357.00	42.49	1.423	6.757
A12	1416		N	1.0	G	221.00	34.62	1.423	7.722
A13	1417		N	1.1	G	123.00		1.246	7.240
A14	1418		N	1.0	G	95.60	36.19	1.512	8.205
T3	105	28.88				33.30	17.31	0.747	2.075
S4	106	25.90		0.7		26.00	6.14	0.267	0.188
S5	107	25.59		0.9			8.03	0.347	0.212
S6	108	23.60		0.8		18.90	6.29	0.418	0.159
S7	109	30.44		0.7		26.20	4.88	0.383	0.140
S8	110	31.62		0.4		37.10	3.15	0.107	0.077
S9	111	20.65		0.4		16.40	6.29	0.302	0.121
S10	112			0.5		69.90	7.40	0.347	0.285
S11	113	28.98		0.5		28.50	5.82	0.356	0.125
S12	114	26.84		0.6		28.70	5.66	0.400	0.227
T4	115	18.54		0.7		16.90	18.88	0.863	0.917
S13	116	19.90		0.6		17.40	10.54	0.454	0.531
S14	117			0.7		37.50	5.51	0.276	0.159
S15	118	27.82		0.5		25.50	5.04	0.276	0.092
S16	119			0.7		37.20	2.83	0.214	0.077
S17	120	3.83		0.4		3.60	3.30	0.142	0.058
S18	121	4.17		0.4		4.20	2.05	0.107	0.053
S19	1429	7.06	G	0.2	G	8.00	1.89	0.294	0.193
S20	122	25.90		0.5		23.10	4.56	0.311	0.246
S21	123	11.61		0.4					
S22	1430	12.74	G	0.4	G	12.20	5.51	0.338	0.072
S23	124	10.66		0.4		10.70	8.03	0.267	0.212
S24	125	15.57		0.4		15.10	7.24	0.498	0.179
S25	126	23.62		0.4		21.90	4.25	0.285	0.072
S26	1431	26.76	G	0.5	G	25.10	8.03	0.160	0.232
S27	127	22.95		0.5		23.50	4.72	0.267	0.082
S28	1432	31.01	G	0.5	G	32.50	5.35	0.285	0.082
S29	128	20.34		0.4		22.00	4.72	0.329	0.087
S30	1433	17.70	G	0.3	G	17.30	3.46	0.329	0.068
S31	129			0.6		40.50	4.41	0.249	0.111
S32	1434	33.99	G	0.5	G	43.10	5.35	0.454	0.241

Table VI.7: Suspended particulate matter, chlorophyll and additional trace metal data CH46

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH46.WK1
SHEET 4: SUSPENDED PARTICULATE MATTER AND MAFF DATA
CH46: THAMES PLUME I

CODE	STN #	TOTSED mg/l	M CPHYLL mg/m3	LGRAVIMET mg/l	MAFFCU nmol/l	MAFFCD nmol/l	MAFFPB nmol/l
S33	130	10.04	0.4	12.20	6.92	0.276	0.072
S34	131	21.33	0.4	24.30			
S35	133	11.39	0.4	12.00	4.41	0.391	0.111
S36	134	3.73	0.4	4.80	3.62	0.222	0.058
S37	135	3.11	0.4	4.00	2.99	0.214	0.082
S38	136	2.74	0.4	4.10	2.52	0.240	0.135
S39	137	5.75	0.4	5.90	2.68	0.231	0.106
S40	139		1.0	35.60		0.276	0.212
S41	140			34.70	7.71	0.667	0.676
S42	141	26.85		39.80	12.75	0.810	1.400
T5	142	20.12		20.60	8.03	0.792	1.207
T6	143	23.98		25.60	23.60	1.246	1.351
T7	144	28.86		26.10	18.88	0.890	2.220
T8	145	34.79		39.30	25.18	1.335	2.751
T9	146	34.87		44.70	48.78	1.690	4.489
T10	147		0.4	167.00	42.49	1.335	4.730
T11	148			133.00	23.60	1.335	3.909
S43A	1435	26.13 G	0.5 G				
S43	1435	43.60 G	0.7 G	40.90			
S43C	1435	40.45 G	0.7 G				
S43D	1435	47.19 G	0.8 G				
S43E	1435	45.99 G	0.9 G				
S44	155	29.68	1.0	34.00	7.40	0.525	0.627
T12	156	30.36		42.10	13.85	0.738	1.448
T13	157	34.43		35.40	20.46	1.112	2.124
T14	158			12.10	20.46	0.685	2.510
T15	159			71.70			
T16	160			19.30			
T17	161						
T18	162			24.20			
T19	163			84.80			
T20	164			24.20			
T21	165			25.90			
T22	166			13.40			

Table VI.8: Suspended particulate matter, chlorophyll and additional trace metal data CH46 (continued)

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH46.WK1
SHEET 5: log10 Kd-VALUES
CH46: THAMES PLUME I

CODE	STN #	MNkd	FEkd	NIkd	COkd	CUkd	ZNkd	CDkd	PBkd
		log 10 values of ratio of nmol/kg sediment to nmol/l water							
S1	100	6.34	6.98	4.35	5.44	4.42	4.78	4.12	5.55
S2	101								
S3	102	5.94	7.72			4.37	4.50		5.97
T1	103	5.53	7.62	4.00	5.19	4.29	4.20		5.33
T2	104	5.48	7.36	3.91	5.03	4.23	4.16		5.51
A1	1405	5.48	6.98	3.77	5.16	4.30	3.87		4.88
A2	1406	5.43	6.14	3.71	5.15	4.27	4.01	3.43	4.83
A3	1407	5.41	6.84	3.68	4.92	4.26	3.93		5.00
A4	1408	5.54	7.13	4.14	5.20	4.20	4.03	2.93	5.24
A5	1409	5.53	6.79	4.12	5.20	4.21	4.00	3.18	5.19
A6	1410	5.50	7.04	4.16	5.00	4.23	4.02	3.20	5.19
A7	1411	5.52	7.27	3.93	5.09	4.42	4.09	3.08	5.05
A8	1412	5.57	7.19	3.94	5.14	4.45	4.05	2.91	5.29
A9	1413	5.59	7.27	4.13	5.00	4.42	4.03		4.99
A10	1414	5.52	7.30	4.16	4.99	4.42	4.06	3.55	4.95
A11	1415	5.35	6.67	3.63	4.94	4.02	3.86	3.39	5.27
A12	1416	5.39	7.17	3.78	4.98	4.08	3.92	3.44	5.08
A13	1417	5.28	7.14	3.76	4.94	4.04	3.99	3.58	5.04
A14	1418	5.26	7.28	3.82	4.92	4.13	3.75	3.60	5.24
T3	105	5.60	7.11	3.95	5.14	4.21	4.05	4.40	5.52
S4	106	6.18	7.31	4.59		4.35	4.59	3.87	6.12
S5	107								
S6	108	6.00	7.63	4.67		4.45	4.86		6.83
S7	109								
S8	110	6.49	7.88	4.67	5.69	4.42	4.89		6.45
S9	111	6.16	6.46	4.75	5.70	4.48	4.91		6.45
S10	112								
S11	113	6.28	8.05	4.66	5.66	4.44	4.69		6.42
S12	114	6.20	7.92	4.75	5.72	4.48	4.72		6.34
T4	115	5.65	7.58	4.67	5.25	4.79	4.23	3.96	5.65
S13	116	5.82	7.46	4.77		4.68	4.29	4.06	
S14	117	6.41	8.24	4.70	5.79	4.43	4.84	4.28	6.23
S15	118	6.44	8.51	4.80	5.75	4.34	4.86		6.29
S16	119	6.55	8.80	4.68	5.92	4.38	4.78		6.36
S17	120								
S18	121	6.64	7.81	5.08		4.43	5.09		
S19	1429	6.35	8.34	4.75	5.80	4.47	4.88	4.49	6.45
S20	122	6.35	8.34	4.75	5.80	4.47	4.88	4.49	6.45
S21	123	6.41	7.21	4.77		4.39	4.86	4.49	6.47
S22	1430	7.30	8.19	4.69	5.88	4.37	4.97		6.49
S23	124	6.41	7.21	4.77	5.84	4.39	4.86	4.49	6.47
S24	125	6.89	8.25	4.72	6.02	4.45	4.91		6.67
S25	126	6.79	8.34	4.75	5.84	4.42	4.95	4.09	6.76
S26	1431	6.46	7.66	4.79	5.91	4.52	4.84	4.13	6.50
S27	127	6.46	7.66	4.79	5.91	4.52	4.84	4.13	6.50
S28	1432								
S29	128	6.54	8.39	4.77		4.46	4.91	3.89	6.66
S30	1433								
S31	129								
S32	1434								

Table VI.9: K_d distribution coefficients CH46

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH46.WK1
SHEET 5: log10 Kd-VALUES
CH46: THAMES PLUME I

CODE	STN	MNkd	FEkd	NIkd	COkd	CUkd	ZNkd	CDkd	PBkd
	#	log 10 values of ratio of nmol/kg sediment to nmol/l water							
S33	130								
S34	131								
S35	133								
S36	134								
S37	135								
S38	136								
S39	137	6.59	8.13	4.91		4.33	4.91	4.72	6.47
S40	139	6.43	8.40	4.69	5.65	4.37	4.81		6.37
S41	140	6.19	8.66	4.49	5.72	4.36	4.54		6.10
S42	141	5.86	7.97	4.28		4.50	4.26	3.64	
T5	142	5.62	7.76	4.08		4.63	4.11	3.68	
T6	143	5.58	7.68	4.04		4.69	4.04	4.02	5.65
T7	144	5.47	7.70	3.97		4.18	4.02		5.40
T8	145	5.39	7.47	3.91		4.10	3.92	3.57	5.35
T9	146	5.42	7.49	3.90	4.94	4.15	3.82	3.61	5.36
T10	147	5.41	7.38	3.86	4.92	4.13	3.76		5.26
T11	148	5.40	7.20	3.91	5.01	4.16	3.88	2.92	5.00
S43A	1435								
S43	1435	6.25	8.09	4.65	5.69	4.48	4.71	4.29	6.35
S43C	1435								
S43D	1435								
S43E	1435								
S44	155								
T12	156								
T13	157								
T14	158								
T15	159								
T16	160								
T17	161								
T18	162								
T19	163								
T20	164								
T21	165								
T22	166								

Table VI.10: K_d distribution coefficients CH46 (continued)

APPENDIX VII

CRUISE CH65

DATA BASE

CONTENT

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH65.WK1
SHEET 1: GENERAL SAMPLE PARAMETER Update: 16/01/92 08:30
CH65: HUMBER PLUME CRUISE II

CODE	TYP	STN #	DEPTH m	BOTT #	S	DATE dd/mm/yy	TIME hh:mm	LAT +ve N	LONG +ve E	SAL	A	TEMP °C	B
S1	P	201	3.3	4084	10	06/05/90	18:31	53.1462	0.5680	33.75	X	10.96	
S2	P	202	3.3	4085	10	06/05/90	21:28	53.5438	0.2097	32.12	X	11.96	
A1	CTDA	2975	0.8	4086	10	06/05/90	23:24	53.5409	0.1440	30.75	C	12.37	C
A2	CTDA	2976	0.8	4087	10	07/05/90	00:29	53.5421	0.1419	31.50	C	12.19	C
A3	CTDA	2977	0.5	4088	10	07/05/90	01:25	53.5409	0.1430	32.00	C	11.96	C
A4	CTDA	2978	0.9	4089	10	07/05/90	02:23	53.5443	0.1409	33.02	G	11.31	G
A5	CTDA	2979	0.7	4090	10	07/05/90	03:29	53.5412	0.1411	33.42	C	10.93	C
A6	CTDA	2980	0.6	4091	10	07/05/90	04:25	53.5402	0.1431	33.46	C	10.85	C
A7	CTDA	2981	0.6	4092	10	07/05/90	05:25	53.5410	0.1433	33.29	C	11.00	C
A8	CTDA	2982	0.5	4093	10	07/05/90	06:25	53.5407	0.1437	33.00	C	11.25	C
A9	CTDA	2983	0.5	4094	10	07/05/90	07:29	53.5413	0.1439	32.69	C	11.55	C
A10	CTDA	2984	0.6	4095	10	07/05/90	08:28	53.5415	0.1440	32.26	C	11.86	C
A11	CTDA	2985	0.8	4096	10	07/05/90	09:30	53.5413	0.1442	31.58	C	12.20	C
A12	CTDA	2986	0.6	4097	10	07/05/90	10:27	53.5418	0.1437	30.82	C	12.45	C
A13	CTDA	2987	0.6	4098	10	07/05/90	11:31	53.5420	0.1422	30.90	C	12.65	C
A18	CTDA	2992	0.6	4099	10	07/05/90	16:32	53.5417	0.1422	33.48	C	11.17	C
A24	CTDA	2999	0.7	4100	10	07/05/90	22:30	53.5481	0.1468	30.68	C	12.50	C
S3	P	203	3.3	4101	11	07/05/90	23:40	53.5670	0.3603	33.94	X	10.66	
O1	P	204	3.3	4102		08/05/90	00:45	53.6019	0.5737	34.30	X	9.72	
S4	P	205	3.3	4103	11	08/05/90	02:28	53.7689	0.5116	34.49	X	8.83	
S5	CTD	3000	0.5	4104	11	08/05/90	03:41	53.7501	0.3606	34.38	C	8.60	C
O2	P	206	3.3	4105		08/05/90	04:40	53.7367	0.1846	34.36	X	8.91	
O3	P	207	3.3	4106		08/05/90	05:50	53.8587	0.0028	34.33	X	9.62	
O4	P	208	3.3	4107		08/05/90	07:35	53.9761	0.3048	34.37	X	9.70	
O5	P	209	3.3	4108		08/05/90	08:30	54.0438	0.5153	34.41	X	9.99	
O6	P	210	3.3	4109		08/05/90	13:13	53.6572	0.9725	34.50	X	9.79	
S6	P	211	3.3	4110	11	08/05/90	13:53	53.5972	0.8951	34.40	X	9.87	
O7	P	212	3.3	4111		08/05/90	17:56	53.4771	0.5844	34.36	X	10.16	
O8	P	213	3.3	4112		08/05/90	19:40	53.4441	0.3370	33.90	X	10.93	
O9	P	214	3.3	4113		08/05/90	20:58	53.3351	0.4460	33.33	X	11.62	
S7	P	215	3.3	4114	11	08/05/90	22:27	53.4194	0.7645	34.15	X	9.99	
O10	P	216	3.3	4115		08/05/90	23:47	53.2605	0.6550	33.85	X	11.11	
S8	CTD	3001	0.7	4116	11	09/05/90	03:39	53.0798	0.5002	33.84	C	10.81	C
O11	P	217	3.3	4117		09/05/90	05:16	53.2016	0.6422	33.90	X	10.57	
O12	P	218	3.3	4118		10/05/90	17:33	54.4843	4.8345	34.63	X	12.70	?
O13	CTD	3002	2.3	4119		10/05/90	17:45	54.5851	4.8375	34.48	G	12.74	O
O14	CTD	3003	1.2	4120		11/05/90	11:03	54.0443	0.5025	34.27	C	9.07	C
O15	CTD	3004	1.1	4121		11/05/90	12:50	53.8792	0.3137	34.31	G	8.53	C
S9	CTD	3005	1.5	4122	11	11/05/90	14:15	53.7204	0.1326	34.17	G	9.51	O
O16	CTD	3006	0.6	4123		11/05/90	15:40	53.5389	0.2442	33.42	C	11.07	C
O17	CTD	3007	1.0	4124		11/05/90	17:48	53.6021	0.6279	34.36	G	9.17	C
O18	CTD	3008	1.4	4125		11/05/90	19:41	53.7652	0.8336	34.54	G	8.94	C
S10	CTD	3018	1.1	4126	11	12/05/90	09:58	53.1360	0.9163	34.01	O	10.49	C
S11	CTD	3019	1.4	4127	11	12/05/90	11:14	53.0012	1.0696	33.67	C	12.66	C
O19	CTD	3020	1.5	4128		12/05/90	13:23	53.2563	1.2744	34.43	U	10.39	U
S12	CTD	3021	1.8	4129	11	12/05/90	15:24	53.0865	1.3883	34.43	G	10.58	G
S13	CTD	3022	1.8	4130	11	12/05/90	17:09	52.9029	1.5120	34.10	G	10.99	C
S14	CTD	3023	2.3	4131	11	12/05/90	18:59	52.7158	1.8171	34.10	G	10.70	O
S15	CTD	3024	3.0	4132	11	12/05/90	20:07	52.7072	2.0623	34.00	G	10.57	G
S16	CTD	3025	2.6	4133	11	12/05/90	21:21	52.6973	2.2989	34.05	G	10.26	O
B16	CTD	3025	42.7	4134	10	12/05/90	21:21	52.6973	2.2989	34.15	G	10.11	G

Table VII.1: General station parameters CH65

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH65.WK1
SHEET 1: GENERAL SAMPLE PARAMETER Update: 16/01/92 08:30
CH65: HUMBER PLUME CRUISE II

CODE	TYP	STN #	DEPTH m	BOTT #	S	DATE dd/mm/yy	TIME hh:mm	LAT +ve N	LONG +ve E	SAL	A	TEMP °C	B
S17	CTD	3026	1.5	4135	11	12/05/90	23:41	52.9438	2.2015	34.67	U	10.29	U
S18	CTD	3027	1.3	4136	11	13/05/90	01:55	53.0799	1.7538	34.63	C	10.49	C
S19	CTD	3028	1.6	4137	11	13/05/90	03:04	53.1707	1.5145	34.66	G	10.61	C
S20	CTD	3029	1.2	4138	11	13/05/90	04:13	53.2491	1.2790	34.49	C	10.34	C
S21	CTD	3030	1.4	4139	11	13/05/90	06:25	53.4802	1.0013	34.43	G	10.12	O
O20	CTD	3031	1.1	4140		13/05/90	08:08	53.6466	0.9659	34.51	C	9.41	C
S22	CTD	3032	1.8	4141	11	13/05/90	16:27	53.5492	0.6482	34.32	G	9.73	C
S23	CTD	3033	2.4	4142	11	13/05/90	17:34	53.4974	0.5002	34.30	G	10.05	G
S24	CTD	3034	1.8	4143	11	13/05/90	18:46	53.4460	0.3318	33.93	G	10.76	C
O21	CTD	3035	2.8	4144		13/05/90	19:44	53.3861	0.3757	33.76	G	11.06	G
S25	CTD	3036	2.9	4145	11	13/05/90	20:34	53.3247	0.4155	33.37	G	11.65	G
B25	CTD	3036	16.6	4146	10	13/05/90	20:34	53.3247	0.4155	33.38	G	11.65	G
S26	CTD	3037	2.8	4147	11	13/05/90	21:39	53.2418	0.5022	33.35	G	11.98	O
B26	CTD	3037	18.2	4148	10	13/05/90	21:39	53.2418	0.5022	33.37	G	11.95	I
O22	CTD	3038	2.1	4149		13/05/90	22:49	53.1817	0.6250	33.67	G	11.80	O
S27	CTD	3039	1.0	4150	11	14/05/90	00:58	53.0025	0.4022	33.40	C	12.80	C
O23	CTD	3040	1.3	4151		14/05/90	03:11	53.2551	0.6990	33.90	G	11.02	C
S28	CTD	3041	1.6	4152	11	14/05/90	04:19	53.3295	0.7266	33.99	O	10.75	C
O24	CTD	3042	1.0	4153		14/05/90	05:20	53.4143	0.7634	34.21	U	10.23	U
S29	CTD	3043	1.8	4154	11	14/05/90	06:51	53.3232	1.0083	34.29	U	10.31	U
O25	CTD	3044	2.2	4155		14/05/90	07:57	53.1631	1.0391	34.22	G	10.58	G
S30	CTD	3045	2.5	4156	11	14/05/90	10:15	53.1247	1.1831	34.18	G	10.87	G
O26	CTD	3046	1.5	4157		14/05/90	14:28	52.8125	1.6643	34.05	U	12.09	U
O27	P	219	3.3	4158		14/05/90	14:48	52.8052	1.6812	34.05	X	12.17	U
S31	P	220	3.3	4159	12	15/05/90	09:29	53.4372	0.3409	34.22	X	10.75	
S32	P	221	3.3	4160	12	15/05/90	13:24	53.0015	0.4029	33.55	X	13.74	
O28	CTD	3047	1.0	4162		15/05/90	14:16	53.0024	0.4037	33.51	U	13.95	U
S33	P	222	3.3	4161	12	15/05/90	14:31	53.0037	0.4047	33.54	X	13.95	U
S34	CTD	3048	0.8	4163	12	15/05/90	15:24	53.1214	0.5413	33.83	U	12.09	U
S35	CTD	3049	1.0	4164	12	15/05/90	16:33	53.2486	0.6761	33.90	C	11.39	C
O29	CTD	3050	0.9	4165		15/05/90	17:51	53.4141	0.7669	34.18	C	10.66	C
X1	CTD	3051	1.3	4166	12	16/05/90	01:56	52.7140	1.8165	34.12	C	11.18	C
O30B	CTD	3051	29.1	4167		16/05/90	01:56	52.7140	1.8165	34.22	G	11.09	G
O31	CTD	3052	0.7	4168		16/05/90	03:12	52.7040	2.0635	34.30	C	10.63	C
O31B	CTD	3052	28.3	4169		16/05/90	03:12	52.7040	2.0635	34.31	G	10.63	O
H1	P	223	3.3	4170	10	17/05/90	05:21	53.5545	0.1184	31.58	X	12.83	
H2	P	224	3.3	4171	10	17/05/90	05:36	53.5753	0.0582	30.66	X	13.11	
H3	P	225	3.3	4172	10	17/05/90	05:47	53.5880	0.0064	29.60	X	13.22	
H4	P	226	3.3	4173	10	17/05/90	06:03	53.6074	-0.0707	27.75	X	13.42	
H5	P	227	3.3	4174	10	17/05/90	06:17	53.6255	-0.1378	26.67	X	13.64	
H6	P	228	3.3	4175	10	17/05/90	06:32	53.6581	-0.1811	23.62	X	13.89	
H7	P	229	3.3	4176	10	17/05/90	06:47	53.6915	-0.2219	22.62	X	14.03	
H8	P	230	3.3	4177	10	17/05/90	06:59	53.7184	-0.2545	20.60	X	14.26	

Table VII.2: General station parameters CH65 (continued)

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH65.WK1
SHEET 2: DISSOLVED TRACE METAL CONCENTRATIONS
CH65: HUMBER PLUME CRUISE II

CODE	TYP	MND nmol/l	C	FED nmol/l	D	NID nmol/l	E	COD nmol/l	F	CUD nmol/l	G	ZND nmol/l	H	CDD nmol/l	I	PBD nmol/l	J
S1	P	4.83		0.04	<	12.65		0.270		10.00		14.36		0.250		0.050	<
S2	P	85.61		116.49		41.86		0.730		19.13		72.94		0.810		0.180	
A1	CTDA	165.68		3.65		63.41	?	1.300		26.76		105.13		0.960		0.120	
A2	CTDA	84.96		136.57		43.83		0.970		23.49		79.76		0.780		0.210	
A3	CTDA	55.26		1.55		34.60		0.900		20.47		68.04		0.660		0.070	
A4	CTDA	33.77		68.84		25.43		0.380		16.49		44.32		0.430		0.180	
A5	CTDA	26.38		0.91		18.51		0.370		14.67		35.26		0.370		0.060	<
A6	CTDA	44.47		542.87		16.16		0.660		15.59		53.48		0.440		0.750	
A7	CTDA	25.60		19.74		18.08		0.420		14.19		44.09		0.450		0.050	<
A8	CTDA	58.20		606.40		19.36		0.560		15.17		52.58		0.510		0.910	
A9	CTDA	40.67		13.37		30.16		0.490		17.10		54.97		0.550		0.070	
A10	CTDA	62.42		100.03		29.42		0.800		19.11		71.45		0.630		0.120	
A11	CTDA	146.14		3.66		37.54		0.960		20.80		83.71		0.830		0.020	<
A12	CTDA	186.67		8.49		47.16		1.160		25.66		115.74		1.040		0.050	<
A13	CTDA	128.78		1.47		41.83		0.860		22.44		97.66		1.020		0.040	<
A18	CTDA	23.07		2.11		14.87		0.340		13.32		42.63		0.400		0.050	<
A24	CTDA	237.62		9.63		46.12		1.300		24.67		110.14		1.060		0.050	<
S3	P	13.38		5.54		10.47		0.334		10.19		21.06		0.268		0.061	
01	P																
S4	P	6.70		2.77		5.14		0.170		5.26		7.15		0.123		0.190	
S5	CTD	5.57		4.19		4.61		0.167		5.74		14.19		0.125		0.205	
02	P																
03	P																
04	P																
05	P																
06	P																
S6	P	7.60		3.99		5.09		0.148		6.92		7.94		0.147		0.144	
07	P																
08	P																
09	P																
S7	P	6.69		1.95	<	11.77		0.298		9.37		15.75		0.206		0.154	
010	P																
S8	CTD	13.17		5.89		9.93		0.249		10.33		24.50		0.233		0.133	
011	P																
012	P																
013	CTD																
014	CTD																
015	CTD																
S9	CTD	9.61		5.11		5.44		0.272		7.41		12.19		0.156		0.125	
016	CTD																
017	CTD																
018	CTD																
S10	CTD	10.20		3.82		7.57		0.154		9.15		17.07		0.221		0.103	
S11	CTD	22.76		5.15		8.79		0.344		10.41		8.65		0.218		0.107	
019	CTD																
S12	CTD	19.06		9.63		5.34		0.266		5.02		10.76		0.141		0.110	
S13	CTD	10.91		4.14		6.77		0.193		8.14		9.62		0.184		0.057	
S14	CTD	7.74		8.18		6.86		0.246		8.32		11.87		0.192		0.080	
S15	CTD	7.82		9.20		6.70		0.397		7.84		9.66		0.173		0.105	
S16	CTD	16.48		5.61		5.36		0.423		7.59		8.85		0.168		0.096	
B16	CTD	33.00		3.42		7.08		0.580		4.92		7.98		0.160		0.230	

Table VII.3: Dissolved trace metal concentrations CH65

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH65.WK1
SHEET 2: DISSOLVED TRACE METAL CONCENTRATIONS
CH65: HUMBER PLUME CRUISE II

CODE	TYP	MND nmol/l	C	FED nmol/l	D	NID nmol/l	E	COD nmol/l	F	CUD nmol/l	G	ZND nmol/l	H	CDD nmol/l	I	PBD nmol/l	J
S17	CTD	29.48		5.85		3.86		0.226		4.54		6.04		0.115		0.143	
S18	CTD	26.83		7.53		6.25		0.256		4.94		8.44		0.127		0.107	
S19	CTD	27.67		9.34		4.11		0.262		4.81		9.04		0.132		0.103	
S20	CTD	20.62		7.06		3.71		0.177		5.25		7.42		0.141		0.185	
S21	CTD	22.33		8.11		4.01		0.203		4.38		6.35		0.132		0.136	
O20	CTD																
S22	CTD	9.17		3.43		4.07		0.180		6.24		10.36		0.141		0.157	
S23	CTD	8.28		3.67		5.67		0.230		6.95		11.82		0.163		0.123	
S24	CTD	11.98		1.80	<	9.83		0.292		9.82		21.04		0.280		0.077	
O21	CTD																
S25	CTD	7.97		1.38	<	15.10		0.269		13.01		26.80		0.409		0.073	
B25	CTD	4.15		1.82		20.04		0.330		12.60		27.68		0.380		0.070	
S26	CTD	4.44		1.71	<	16.40		0.305		12.87		20.75		0.386		0.076	
B26	CTD	6.64		3.44		19.40		0.260		11.73		25.52		0.380		0.070	
O22	CTD																
S27	CTD	13.81		2.57		8.80		0.410		12.69		8.50		0.208		0.084	
O23	CTD																
S28	CTD	7.55		3.50		11.21		0.230		11.18		16.08		0.240		0.101	
O24	CTD																
S29	CTD	18.54		3.95		6.08		0.190		6.46		11.81		0.190		0.143	
O25	CTD																
S30	CTD	28.43		5.87		7.41		0.302		8.79		11.90		0.223		0.175	
O26	CTD																
O27	P																
S31	P	36.70		7.40		8.87		0.400		6.48		14.12		0.190		0.040	
S32	P	14.65		1.15		9.71		0.510		8.03		5.96		0.160		0.110	
O28	CTD																
S33	P	12.36		0.35		8.90		0.360		7.59		5.52		0.190		0.110	
S34	CTD	18.55		2.73		11.71		0.200		6.53		10.50		0.220		0.070	
S35	CTD	7.57		4.52		10.41		0.230		6.48		12.42		0.240		0.190	
O29	CTD																
X1	CTD	9.85		2.62		8.66		0.150		5.92		12.17		0.210		0.090	
O30B	CTD																
O31	CTD																
O31B	CTD																
H1	P	71.50		1.16		32.39		0.850		18.38		48.60		0.770		0.070	
H2	P	753.73		180.61		51.72		2.490		28.53		104.15		1.290		0.050	<
H3	P	824.59		100.67		63.39		2.690		30.93		139.84		1.480		0.060	<
H4	P	688.50		9.08		73.46		2.120		34.12		139.14		1.520		0.070	
H5	P	799.41		46.80		99.48		2.980		49.62		211.58		2.330		0.140	
H6	P	130.57		6.81		99.26		0.840		55.26		157.38		2.220		0.190	
H7	P	152.23		10.64		104.00		1.030		55.96		164.14		2.170		0.220	
H8	P	180.75		14.03		116.69		1.360		69.13		175.49		2.360		0.260	

Table VII.4: Dissolved trace metal concentrations CH65 (continued)

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH65.WK1
SHEET 3: PARTICULATE TRACE METAL CONCENTRATIONS
CH65: HUMBER PLUME CRUISE II

CODE	TYP	SWT mg	SCONC mg/l	MNP nmol/l	FEP nmol/l	NIP nmol/l	COP nmol/l	CUF nmol/l	ZNP nmol/l	CDP nmol/l	PBP nmol/l
S1	P	56	3.5	49.5	800	0.55	0.34	2.47	7.68	0.090	1.66
S2	P	383	23.5	642.1	16259	12.77	5.30	15.90	106.08		6.65
A1	CTDA										
A2	CTDA	265	35.3	1093.2	23394	18.18	8.57	24.35	161.11	0.160	7.52
A3	CTDA	298	41.4	1265.7	28104	16.64	8.01	30.36	181.12	0.110	16.72
A4	CTDA	88	12.6	325.0	7544	5.01	2.03	6.33	46.08	0.090	6.99
A5	CTDA										
A6	CTDA	111	7.2	169.8	3635	2.22	1.11	3.11	29.16		4.88
A7	CTDA	155	9.8	230.3	5036	3.16	1.35	4.12	35.85	0.010	6.18
A8	CTDA	121	9.1	219.0	4781	3.12	2.05	3.78	36.33	0.010	5.49
A9	CTDA	137	16.9	450.0	9205	7.12	2.53	8.20	70.10	0.030	
A10	CTDA	317	30.8	812.4	19103	14.74	3.55	17.39	132.33	0.030	13.30
A11	CTDA										
A12	CTDA	239	28.1	749.4	17568	12.74	5.68	14.16	130.82	0.080	14.07
A13	CTDA	220	25.3	804.7	16239	11.33	5.11	15.92	121.15	0.070	13.39
A18	CTDA	62	7.3	171.2	3685	1.60	0.92	15.84	26.19	0.010	3.75
A24	CTDA	241	27.7	753.3	18932	13.03	6.06	100.18	139.07	0.070	11.74
S3	P										
O1	P	39	2.2	33.2	503		0.12	0.82	3.99	0.002	1.13
S4	P	20	1.3	7.1	36			0.14		0.009	0.17
S5	CTD	19	1.1	11.8	80		0.03	0.81	2.23		
O2	P	45	3.4	47.3	271			0.80	3.80	0.012	1.28
O3	P	50	2.4	32.2	384		0.14	0.56	3.25	0.004	0.62
O4	P	21	1.6	15.7	117				2.95		
O5	P	20	1.4	5.0	28			0.18	2.24	0.017	0.14
O6	P	15	1.8							0.008	
S6	P	17	1.5		34			0.17		0.007	0.14
O7	P	53	3.2	35.6	593	0.45	0.20		4.60	0.003	0.65
O8	P	105	5.3	82.7	1584		0.56		11.27	0.009	2.51
O9	P	144	14.0	233.9	5124		2.09	3.23	31.34	0.050	6.21
S7	P	75	4.0	54.8	833		0.29	1.33	7.02	0.004	1.91
O10	P	42	2.5	30.7	536		0.13	0.35	5.02	0.004	0.59
S8	CTD	61	5.4	49.2			0.39	2.10	7.97		1.56
O11	P	78	4.1	52.4	1031		0.39	1.02	7.42	0.007	2.19
O12	P	19	1.0						2.02	0.014	
O13	CTD	8	0.5		26			0.06	1.44	0.010	0.07
O14	CTD	30	2.0	10.3	137		0.11		4.47	0.010	0.54
O15	CTD	34	2.2	25.7	310		0.14	0.36	3.50		0.71
S9	CTD	42	2.5	32.1	518		0.23	0.28	3.55		1.30
O16	CTD	74	8.2	118.2	3531	3.21	1.31		29.03	0.010	7.89
O17	CTD	23	1.4	5.7	70			0.13	3.12	0.010	0.20
O18	CTD	24	1.2					0.07		0.010	0.06
S10	CTD	41	4.8	53.5	1159	1.16	0.37	2.08	10.59		1.26
S11	CTD										
O19	CTD	28	1.8	4.5	44						
S12	CTD										
S13	CTD	24	3.5	13.4	164	0.35		0.57	4.50		
S14	CTD	17	3.6	23.7	359					0.030	0.30
S15	CTD	15	3.6	15.9	219					0.020	0.36
S16	CTD	19	2.2	7.6	162			0.39	3.42	0.020	0.24
B16	CTD	279	35.8	192.1	9172	0.73	3.40		39.54	0.060	11.00

Table VII.5: Particulate trace metal concentrations CH65

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH65.WK1
SHEET 3: PARTICULATE TRACE METAL CONCENTRATIONS
CH65: HUMBER PLUME CRUISE II

CODE	TYP	SWT mg	SCONC mg/l	MNP nmol/l	FEP nmol/l	NIP nmol/l	COP nmol/l	CUP nmol/l	ZNP nmol/l	CDP nmol/l	PBP nmol/l
S17	CTD	10	1.1		78						0.06
S18	CTD	15	0.6		29			0.06	1.32	0.010	0.06
S19	CTD	7	0.8		35						
S20	CTD	5	0.6		45					0.010	0.10
S21	CTD	4	0.5		37			0.34		0.020	0.07
O20	CTD	18	1.2					0.25			0.51
S22	CTD	19	2.4	22.8	376		0.12	0.79	3.84	0.040	0.63
S23	CTD	45	2.6	36.6	578		0.23		4.19		
S24	CTD	89	5.1	98.4	1812		0.56		12.84	0.010	1.25
O21	CTD	94	7.6	133.3	2548		0.81	2.01	18.11	0.010	4.62
S25	CTD										
B25	CTD	116	13.8	271.7	5349		1.69		36.68	0.020	11.72
S26	CTD	63	6.4	101.3	1509			0.91	11.83	0.020	2.55
B26	CTD	88	8.9	161.7	3818		0.97	1.14	25.67	0.030	3.56
O22	CTD	45	16.1	73.3	1096	0.25		2.81	13.60		1.76
S27	CTD										
O23	CTD	35	5.9	34.0	489		0.21		6.41	0.050	0.95
S28	CTD	37	4.6	43.8	717		0.26	0.95	6.26	0.020	1.04
O24	CTD	31	1.9	19.6	268		0.07	0.40	1.83	0.010	0.30
S29	CTD	26	2.2	15.8	214			0.32	2.66	0.010	0.23
O25	CTD	14	2.2	21.6	252			0.38		0.010	0.13
S30	CTD	20	1.5	10.5	55			0.26		0.010	0.23
O26	CTD	4	1.7		125			0.45		0.040	0.13
O27	P	5	2.7		165					0.017	
S31	P										
S32	P										
O28	CTD	4	3.0		343					0.030	
S33	P	9	15.0		1305					0.187	1.85
S34	CTD										
S35	CTD										
O29	CTD	4	0.4	10.1	146			0.16			0.13
X1	CTD	13	0.8	9.1	52			0.16			0.09
O30B	CTD	4	0.4		49						0.06
O31	CTD	10	0.5	6.3	25			0.10	1.06		0.05
O31B	CTD										
H1	P										
H2	P										
H3	P										
H4	P										
H5	P										
H6	P										
H7	P										
H8	P										

Table VII.6: Particulate trace metal concentrations CH65 (continued)

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH65.WK1
SHEET 4: NUTRIENTS,BIOLOGICAL PARAMETER AND UNFILTERED ALUMINIUM
CH65: HUMBER PLUME CRUISE II

CODE	TYP	PO4 umol/l	NO2 umol/l	NO3 umol/l	SI umol/l	K	CPHYLL mg/m3	Lunflt.AL nmol/l
S1	P	0.60	0.38	7.20	4.08		4.1	
S2	P	0.72	0.42	21.35	6.34		4.9	
A1	CTDA	0.85	0.38	65.49	10.95		1.9	C 115.08
A2	CTDA	0.91	0.38	55.07	8.85		2.4	C 102.35
A3	CTDA	0.93	0.37	48.28	8.13		2.8	C 96.70
A4	CTDA	0.94	0.36	31.68	6.62		2.3	G 99.59
A5	CTDA	0.99	0.37	25.24	6.38		2.2	C 91.25
A6	CTDA	0.97	0.35	23.70	6.21		2.1	C 98.14
A7	CTDA	1.01	0.35	26.93	6.34		2.3	C 95.01
A8	CTDA	1.03	0.34	31.55	6.55		2.9	C 99.21
A9	CTDA						2.0	C 98.96
A10	CTDA	0.93	0.35	44.08	7.11		3.5	C 115.08
A11	CTDA	0.80	0.33	55.56	8.24		3.3	C 124.48
A12	CTDA	0.72	0.33	66.15	9.60		3.3	C 116.96
A13	CTDA	0.81	0.32	64.67	9.42		3.0	C 123.54
A18	CTDA	0.92	0.30	25.11	5.63		2.2	C 101.47
A24	CTDA	0.88	0.29	69.04	8.17		2.7	C
S3	P	0.88	0.29	21.00	2.86		3.5	
O1	P	0.96	0.24	8.50	2.86		3.0	
S4	P	0.78	0.18	2.00	1.43		3.8	
S5	CTD	1.02	0.35	6.22	3.15		2.5	C 43.15
O2	P	1.13	0.36	7.65	3.92		2.5	
O3	P	1.29	0.39	8.85	4.17		3.0	
O4	P						5.6	
O5	P	0.42	0.17		4.10		3.6	
O6	P	0.25	0.10				2.1	
S6	P	0.22	0.12		2.75		4.6	
O7	P	0.58	0.28	7.15	4.22		3.6	
O8	P						3.8	
O9	P	0.96	0.41	31.80	5.46		2.4	
S7	P	0.76	0.33	11.40	4.17		2.7	
O10	P	0.66	0.31	14.85	3.15		6.6	
S8	CTD	0.58	0.31	12.04	3.94		5.2	C 82.15
O11	P	0.74	0.33	16.05			2.9	
O12	P						1.9	
O13	CTD						-99.0	N
O14	CTD	0.42	0.25	1.94	5.18		4.4	C 19.32
O15	CTD						2.9	G 47.16
S9	CTD	0.69	0.37	6.92	5.42		2.9	G 51.11
O16	CTD						2.5	C
O17	CTD	0.36	0.13	0.77	3.28		3.0	G 31.98
O18	CTD	0.32	0.09	0.49	3.13		2.9	G 15.05
S10	CTD	0.71	0.33	14.39	3.27		3.1	O 67.60
S11	CTD	0.22	0.10		2.57		18.9	C 15.36
O19	CTD	0.32	0.14				1.8	G
S12	CTD						2.1	G 17.43
S13	CTD	0.28	0.12		2.26		11.2	G 29.98
S14	CTD	0.20	0.20		2.28		13.3	G 46.53
S15	CTD	0.14	0.12		2.27		12.5	G 49.67
S16	CTD	0.18	0.19		2.55		8.9	G 46.53
B16	CTD						9.8	G

Table VII.7: Nutrients, biological parameter and aluminium CH65

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH65.WK1
SHEET 4: NUTRIENTS,BIOLOGICAL PARAMETER AND UNFILTERED ALUMINIUM
CH65: HUMBER PLUME CRUISE II

CODE	TYP	PO4 umol/l	NO2 umol/l	NO3 umol/l	SI umol/l	K CPHYLL mg/m3		Lunflt.AL nmol/l
S17	CTD	0.38	0.11		2.16	1.3	O	24.33
S18	CTD					1.4	C	
S19	CTD					1.6	G	17.43
S20	CTD					2.1	C	15.99
S21	CTD	0.26	0.13	0.27	2.50	3.6	G	19.75
O20	CTD	0.29	0.16	0.19	2.68	2.1	C	21.95
S22	CTD	0.67	0.28	4.74	4.33	3.0	G	44.53
S23	CTD	0.79	0.28	6.34	5.70	2.8	G	56.13
S24	CTD					2.8	G	85.16
O21	CTD					2.6	G	83.09
S25	CTD	0.56	0.41	8.06	2.63	2.6	G	94.38
B25	CTD					3.1	G	
S26	CTD	0.54	0.41	8.96	2.70	3.1	G	89.99
B26	CTD					3.4	G	
O22	CTD	0.15	0.25	2.48	2.96	19.5	G	
S27	CTD			0.54	3.43	23.6	C	
O23	CTD		0.32			10.3	G	
S28	CTD	0.89	0.35	12.38	3.33	5.3	O	
O24	CTD	0.89	0.35	8.72	3.65	3.0	C	
S29	CTD	0.78	0.31	5.64	2.73	4.2	G	41.70
O25	CTD	0.88	0.31	6.43	2.56	2.5	G	49.23
S30	CTD	0.53	0.26	0.18	2.30	2.8	G	36.50
O26	CTD	0.11	0.14	0.37	2.61	7.9	C	37.94
O27	P	0.18	0.14	0.38	2.50	6.3		
S31	P					1.9		
S32	P	0.28	0.12	0.04	2.64	13.2		
O28	CTD	0.17	0.11	0.38	2.65	11.9	G	
S33	P	0.18	0.13	0.36	2.75	19.0		
S34	CTD	0.24	0.16	0.56	2.60	14.4	G	
S35	CTD	0.35	0.28	5.37	2.79	13.3	C	
O29	CTD	0.56	0.32	8.87	3.00	4.3	C	
X1	CTD	0.26	0.18	0.04	2.41	2.4	C	
O30B	CTD					2.5	G	
O31	CTD	0.38	0.20	0.72	2.01	2.0	C	
O31B	CTD					2.2	G	
H1	P					2.4		
H2	P					2.2		
H3	P					2.5		
H4	P					2.7		
H5	P					2.7		
H6	P					2.8		
H7	P					2.8		
H8	P					2.9		

Table VII.8: Nutrients, biological parameter and aluminium CH65 (continued)

NORTH SEA PROJECT DATA BASEFILE: CH65.WK1
SHEET 5: SUSPENDED PARTICULATE MATTER AND TIDALLY CORRECTED POSITIONS
CH65: HUMBER PLUME CRUISE II

CODE	TYP	TOTSED		MGRAVIMET	CODE	LAT	LONG
		mg/l		mg/l		at low	water
S1	P	4.80		4.00		53.2620	0.5822
S2	P	18.00		15.50		53.5436	0.2082
A1	CTDA	30.65	C	21.09			
A2	CTDA	36.76	C	40.63			
A3	CTDA	40.85	C	40.58			
A4	CTDA	20.98	G	21.09			
A5	CTDA	10.90	C	12.49			
A6	CTDA	8.74	C	10.06			
A7	CTDA	9.38	C	9.33			
A8	CTDA	12.37	C	10.24			
A9	CTDA	19.42	C	28.29			
A10	CTDA	30.69	C	31.05			
A11	CTDA	42.21	C	42.67			
A12	CTDA	38.57	C	37.80			
A13	CTDA	31.05	C	30.53			
A18	CTDA	8.09	C	11.60			
A24	CTDA	38.31	C	36.44			
S3	P	6.10		6.20		53.5682	0.3653
O1	P	4.00		3.50		53.6076	0.5804
S4	P	2.10		1.40		53.8123	0.5138
S5	CTD	1.31	C			53.8254	0.3568
O2	P	3.30		2.30		53.8035	0.1727
O3	P	3.60		3.30		53.8769	0.0095
O4	P	3.90		3.90			
O5	P	3.50		3.50			
O6	P	2.10		3.10		53.6561	1.0071
S6	P	2.80		4.10		53.6085	0.9336
O7	P	4.90		5.90		53.5571	0.5982
O8	P	5.70		7.70		53.4961	0.3362
O9	P	6.00		6.20		53.3575	0.4235
S7	P	4.80		5.90		53.4333	0.7591
O10	P	5.80		5.50		53.2573	0.6559
S8	CTD	5.12	C	2.28		53.1390	0.5192
O11	P	6.20		8.30		53.3046	0.6763
O12	P	2.20					
O13	CTD	1.20	G				
O14	CTD	2.51	C	4.00			
O15	CTD	2.27	G	5.10		53.8781	0.3194
S9	CTD	2.62	G	5.52		53.7268	0.1297
O16	CTD	8.15	C	8.54		53.5730	0.2718
O17	CTD	1.39	G	1.37		53.6840	0.6191
O18	CTD	1.23	G	0.75		53.8385	0.8345
S10	CTD	4.34	O	7.77		53.1740	0.9511
S11	CTD	12.86	C	9.95		53.0093	1.0843
O19	CTD	1.92	G	3.68		53.2505	1.2802
S12	CTD	1.73	G	0.90		53.0677	1.4598
S13	CTD	4.35	G			52.8802	1.5977
S14	CTD	5.90	G	2.79			
S15	CTD	6.33	G	3.00			
S16	CTD	3.97	G	2.27			
B16	CTD	33.80	G				

Table VII.9: Suspended particulate matter and tidally corrected positions CH65

NORTH SEA PROJECT DATA BASEFILE: CH65.WK1
SHEET 5: SUSPENDED PARTICULATE MATTER AND TIDALLY CORRECTED POSITIONS
CH65: HUMBER PLUME CRUISE II

CODE	TYP	TOTSED mg/l	MGRAVIMET mg/l	CODE	LAT at low water	LONG
S17	CTD	1.25 O	3.99			
S18	CTD	0.99 C	3.20		53.0798	1.7538
S19	CTD	0.97 G	2.72		53.1498	1.5596
S20	CTD	1.92 C	2.93		53.2258	1.3375
S21	CTD	2.16 G	2.80		53.5165	1.0483
O20	CTD	1.28 C	3.49		53.7044	0.9980
S22	CTD	1.89 G	1.75		53.5617	0.6675
S23	CTD	2.58 G	2.97		53.5386	0.5280
S24	CTD	5.12 G	5.95		53.4983	0.3564
O21	CTD	5.18 G	6.53		53.4425	0.3759
S25	CTD	4.51 G	6.78		53.3440	0.3863
B25	CTD	7.04 G				
S26	CTD	7.99 G	9.52		53.2824	0.4718
B26	CTD	15.91 G				
O22	CTD	12.44 G	8.14		53.2815	0.6421
S27	CTD	14.87 C	8.83		53.0079	0.4182
O23	CTD	6.02 G	5.58		53.2412	0.7047
S28	CTD	4.19 O	7.10		53.3331	0.7436
O24	CTD	2.21 C	5.55		53.4274	0.7960
S29	CTD	2.35 G	1.80		53.3370	1.0726
O25	CTD	1.94 G	1.40		53.1691	1.1330
S30	CTD	2.05 G	0.90		53.1447	1.2369
O26	CTD	7.57 C	3.65		52.8129	1.6685
O27	P	5.20				
S31	P	3.90			53.4979	0.3433
S32	P	8.50			53.0135	0.4385
O28	CTD	12.00 G	6.80		53.0048	0.4107
S33	P	9.00			53.0040	0.4057
S34	CTD	9.33 G	5.86		53.1166	0.5430
S35	CTD	6.47 C	6.04		53.2433	0.6836
O29	CTD	2.55 C	4.68		53.4174	0.7980
X1	CTD	1.46 C	5.56			
O30B	CTD	1.50 G				
O31	CTD	0.99 C	4.32			
O31B	CTD	1.10 G				
H1	P	15.40	12.60			
H2	P	11.30	14.10			
H3	P	13.10	10.90			
H4	P	30.20	29.80			
H5	P	23.40	27.10			
H6	P	30.50	30.80			
H7	P	28.00	28.80			
H8	P	29.10	39.80			

Table VII.10: Suspended particulate matter and tidally corrected positions CH65 (continued)

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH65.WK1
SHEET 6: log10 Kd-VALUES
CH65: HUMBER PLUME CRUISE II

log 10 values of ratio of nmol/kg sediment to nmol/l water

CODE	STN #	MNkd	FEkd	NIkd	COkd	CUkd	ZNkd	CDkd	PBkd
S1	201	6.47	9.76	4.09	5.56	4.85	5.18	5.01	6.98
S2	202	5.50	6.77	4.11	5.49	4.55	4.79		6.20
A1	2975								
A2	2976	5.56	6.69	4.07	5.40	4.47	4.76	3.76	6.01
A3	2977	5.74	8.64	4.07	5.33	4.55	4.81	3.60	6.76
A4	2978	5.88	6.94	4.19	5.63	4.48	4.92	4.22	6.49
A5	2979								
A6	2980	5.72	5.97	4.28	5.37	4.44	4.88		5.96
A7	2981	5.96	7.42	4.25	5.52	4.47	4.92	3.36	7.10
A8	2982	5.62	5.94	4.25	5.60	4.44	4.88	3.33	5.82
A9	2983	5.82	7.61	4.15	5.49	4.45	4.88	3.51	
A10	2984	5.63	6.79	4.21	5.16	4.47	4.78	3.19	6.56
A11	2985								
A12	2986	5.15	7.87	3.98	5.24	4.29	4.60	3.44	7.00
A13	2987	5.39	8.64	4.03	5.37	4.45	4.69	3.43	7.12
A18	2992	6.01	8.38	4.17	5.57	5.21	4.93	3.53	7.01
A24	2999	5.06	7.85	4.01	5.23	5.17	4.66	3.38	6.93
S3	203								
O1	204								
S4	205	5.91	7.00			4.31		4.75	5.84
S5	3000	6.28	7.24		5.21	5.11	5.15		
O2	206								
O3	207								
O4	208								
O5	209								
O6	210								
S6	211		6.75			4.21		4.50	5.81
O7	212								
O8	213								
O9	214								
S7	215	6.31	8.03		5.39	4.55	5.05	3.69	6.49
O10	216								
S8	3001	5.84			5.46	4.58	4.78		6.34
O11	217								
O12	218								
O13	3002								
O14	3003								
O15	3004								
S9	3005	6.13	7.61		5.53	4.18	5.07		6.62
O16	3006								
O17	3007								
O18	3008								
S10	3018	6.04	7.80	4.50	5.70	4.68	5.11		6.41
S11	3019								
O19	3020								
S12	3021								
S13	3022	5.55	7.05	4.17		4.30	5.13		
S14	3023	5.93	7.09					4.64	6.02
S15	3024	5.75	6.82					4.51	5.98
S16	3025	5.32	7.12			4.37	5.24	4.73	6.06
B16	3025	5.21	7.87	3.46	5.21		5.14	4.02	6.13

Table VII.11: K_d-distribution coefficients CH65

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH65.WK1
SHEET 6: log10 Kd-VALUES
CH65: HUMBER PLUME CRUISE II

CODE	STN	MNkd	FEkd	NIkd	COkd	CUkd	ZNkd	CDkd	PBkd
	#	log 10 values of ratio of nmol/kg sediment to nmol/l water							
S17	3026		7.08						5.58
S18	3027		6.81			4.31	5.42	5.12	5.97
S19	3028		6.67						
S20	3029		7.03					5.07	5.95
S21	3030		6.96			5.19		5.48	6.01
O20	3031								
S22	3032	6.02	7.66		5.44	4.72	5.19	5.07	6.22
S23	3033	6.23	7.78		5.59		5.13		
S24	3034	6.21	8.30		5.58		5.08	3.85	6.50
O21	3035								
S25	3036								
B25	3036	6.68	8.33		5.57		4.98	3.58	7.08
S26	3037	6.55	8.14			4.04	4.95	3.91	6.72
B26	3037	6.44	8.10		5.62	4.04	5.05	3.95	6.76
O22	3038								
S27	3039								
O23	3040								
S28	3041	6.10	7.65		5.39	4.27	4.93	4.26	6.35
O24	3042								
S29	3043	5.59	7.39			4.35	5.01	4.38	5.86
O25	3044								
S30	3045	5.39	6.80			4.29		4.48	5.94
O26	3046								
O27	219								
S31	220								
S32	221								
O28	3047		8.40					4.82	6.05
S33	222		8.40					4.82	6.05
S34	3048								
S35	3049								
O29	3050								
X1	3051	6.06	7.39			4.53			6.10
O30B	3051								
O31	3052								
O31B	3052								
H1	223								
H2	224								
H3	225								
H4	226								
H5	227								
H6	228								
H7	229								
H8	230								

Table VII.12: K_d-distribution coefficients CH65 (continued)

APPENDIX VIII

CRUISE CH69

DATA BASE

CONTENT

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=============================================================================
NORTH SEA PROJECT DATA BASE (SUDO)                        FILE:    CH69.WK1
SHEET 1: GENERAL SAMPLE PARAMETER
CH69: THAMES II AND HUMBER III CRUISE          16/01/92 09:28:49
-----------------------------------------------------------------------------
CODE TYP    STN DEPTH BOTT S  DATE     TIME  LAT      LONG     SAL   A TEMP B
             #    m     #     dd/mm/yy hh:mm +ve N    +ve E             °C
=============================================================================
T1   P      301   3.3 4284 10 28/07/90 07:45  51.4251   1.5076 33.27 X17.43
T2   P      302   3.3 4285 10 28/07/90 08:43  51.5242   1.3459 33.82 X17.35
T3   P      303   3.3 4286 10 28/07/90 09:45  51.5227   1.1437 34.23 X18.20
T4   P      304   3.3 4287 10 28/07/90 10:35  51.4829   0.9437 34.18 X19.33
T5   P      305   3.3 4288 10 28/07/90 11:41  51.5020   0.6442 34.26 X19.84
T6   P      306   3.3 4289 10 28/07/90 12:20  51.5004   0.5039 34.28 X20.44
T7   P      307   3.3 4290 10 28/07/90 13:25  51.4922   0.7401 34.34 X19.64
T8   P      308   3.3 4291 10 28/07/90 14:24  51.5138   0.9524 34.20 X18.63
T9   P      309   3.3 4292 10 28/07/90 15:25  51.5848   1.1593 33.84 X18.20
T10  P      310   3.3 4293 10 28/07/90 16:40  51.6709   1.3050 33.63 X18.01
T11  P      311   3.3 4294 10 28/07/90 18:16  51.7775   1.4781 34.11 X17.87
O1   CTD   3481  41.5 4295    30/07/90 12:35  54.5914   4.8251 34.57 G14.37 O
O1A  CTD   3481  22.0 4296    30/07/90 12:35  54.5914   4.8251 34.55 G14.55 I
O1B  CTD   3481   1.5 4297    30/07/90 12:35  54.5914   4.8251 34.56 C16.68 C
O2   CTD   3482   3.2 4298    31/07/90 07:13  54.0361   0.5146 34.15 G14.53 I
O3   CTD   3483   3.2 4299    31/07/90 10:10  53.8562  -0.0268 34.22 C15.59 O
O4   CTD   3484   4.0 4300    31/07/90 14:21  53.8914   0.6714 34.33 G14.48 O
O5   P      320   3.3 4301    31/07/90 18:16  53.5664   0.2873 34.18 X15.90
S1   P      322   3.3 4302 11 31/07/90 19:18  53.4869   0.3661 33.70  16.94
S2   P      324   3.3 4303 11 31/07/90 20:56  53.5100   0.6695 33.90  17.04
S3   CTD   3486   1.9 4304 11 01/08/90 00:16  53.6474   0.9738 34.27 C14.85 C
S4   CTD   3487   1.6 4305 11 01/08/90 01:38  53.4773   0.9955 34.26 G15.14 C
S5   P      328   3.3 4306 11 01/08/90 03:16  53.4113   0.7747 34.10  16.10
S6   P      330   3.3 4307 11 01/08/90 06:41  53.1848   0.6231 34.10  17.03
O6   P      332   3.3 4308    01/08/90 11:54  53.2529   0.7117 34.10  17.16
S7   P      334   3.3 4309 11 01/08/90 13:45  53.0720   1.0216 34.20  16.63
S8   P      336   3.3 4310 11 01/08/90 15:46  52.9789   1.3847 34.20  16.54
S9   P      338   3.3 4311 11 01/08/90 17:22  52.8042   1.6721 34.20  17.19
S10  P      339   3.3 4312 11 01/08/90 19:12  52.7075   2.0945 34.30 X16.73
S11  CTD   3489   1.5 4313 11 01/08/90 22:16  52.9519   2.1983 34.39 G16.76 C
S12  P      342   3.3 4314 11 01/08/90 23:42  53.0416   1.8912 34.40 X16.03
S13  CTD   3490   1.5 4315 11 02/08/90 00:36  53.0840   1.7499 34.26 G15.97 C
S14  P      344   3.3 4316 11 02/08/90 02:05  53.1851   1.4627 34.53 X15.91
S15  CTD   3491   1.0 4317 11 02/08/90 03:15  53.2487   1.2972 34.32 C15.76 C
S16  P      346   3.3 4318 11 02/08/90 04:51  53.3410   0.9723 34.45 X16.10
S17  P      348   3.3 4319 11 02/08/90 06:41  53.4767   0.4991 33.83 X17.66
S18  P      349   3.3 4320 11 02/08/90 07:40  53.5458   0.2313 33.42 X16.95
A1   CTDA  3492   0.9 4321 10 02/08/90 09:30  53.5427   0.1078 30.86 C18.75 C
A2   CTDA  3493   0.8 4322 10 02/08/90 10:31  53.5425   0.1077 31.71 C18.33 C
A3   CTDA  3494   1.2 4323 10 02/08/90 11:33  53.5423   0.1077 32.13 C18.25 C
A4   CTDA  3495   1.1 4324 10 02/08/90 12:32  53.5427   0.1077 32.21 C18.46 C
A5   CTDA  3496   1.0 4325 10 02/08/90 13:31  53.5423   0.1080 32.72 C18.16 C
A6   CTDA  3497   1.2 4326 10 02/08/90 14:30  53.5421   0.1079 32.88 C17.71 C
A7   CTDA  3498   0.9 4327 10 02/08/90 15:32  53.5419   0.1078 32.89 C17.70 C
A8   CTDA  3499   1.0 4328 10 02/08/90 16:30  53.5420   0.1078 32.79 C18.26 C
A9   CTDA  3500   1.0 4329 10 02/08/90 17:33  53.5425   0.1092 32.28 C18.24 C
A10  CTDA  3501   0.9 4330 10 02/08/90 18:32  53.5415   0.1093 31.86 C18.46 C
A11  CTDA  3502   1.3 4331 10 02/08/90 19:31  53.5420   0.1085 31.91 G18.36 C
A12  CTDA  3503   1.1 4332 10 02/08/90 20:35  53.5449   0.1078 31.64 C18.46 C
A13  CTDA  3504   1.0 4333 10 02/08/90 21:31  53.5432   0.1088 30.92 C18.61 C
```

Table VIII.1: General station parameters CH69

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH69.WK1
SHEET 1: GENERAL SAMPLE PARAMETER
CH69: THAMES II AND HUMBER III CRUISE 16/01/92 09:28:49

CODE	TYP	STN #	DEPTH m	BOTT #	S	DATE dd/mm/yy	TIME hh:mm	LAT +ve N	LONG +ve E	SAL	A	TEMP °C	B
A14	CTDA	3505	1.3	4334	10	02/08/90	22:33	53.5445	0.1070	31.30	G	18.72	C
A15	CTDA	3506	4.4	4335	10	02/08/90	23:31	53.5476	0.1075	31.88	G	18.39	I
O7	P	350	3.3	4336		03/08/90	09:26	53.5462	0.2477	33.10		17.39	
O8	P	351	3.3	4337		03/08/90	10:12	53.5484	0.4549	33.80		17.60	
O9	P	352	3.3	4338		03/08/90	11:25	53.5512	0.7240	34.10		16.40	
S19	P	353	3.3	4339	11	03/08/90	13:18	53.6290	0.4468	34.20		15.56	
S20	P	354	3.3	4340	11	03/08/90	14:44	53.7323	0.1650	34.20		14.67	
S21	P	355	3.3	4341	11	03/08/90	16:00	53.7815	0.5066	34.20		14.74	
O10	P	357	3.3	4342		03/08/90	19:35	53.5285	0.5977	34.10		16.14	
O11	P	358	3.3	4343		03/08/90	20:08	53.4912	0.4719	33.90		17.96	
S22	P	359	3.3	4344	11	03/08/90	20:53	53.4292	0.3438	33.50		18.47	
S23	P	360	3.3	4345	11	03/08/90	21:38	53.3321	0.4114	34.10		18.81	
S24	P	361	3.3	4346	11	03/08/90	22:27	53.3744	0.6019	34.10		17.09	
O12	P	362	3.3	4347		03/08/90	23:12	53.4157	0.7649	34.20		15.94	
S25	P	364	3.3	4348	11	04/08/90	05:24	53.2279	0.5142	34.10		18.30	
S26	P	365	3.3	4349	11	04/08/90	07:26	53.0073	0.4036	34.20		18.23	
S27	P	367	3.3	4350	11	04/08/90	09:44	53.2016	0.8008	34.10		17.23	
S28	P	368	3.3	4351	11	04/08/90	11:36	53.0067	1.0723	34.20		17.85	
S29	P	369	3.3	4352	11	04/08/90	12:36	53.1520	1.1811	34.20		16.50	
O13	CTD	3529	1.1	4353		06/08/90	00:44	53.1758	1.0237	34.15	C	17.12	C
S30	CTD	3530	2.1	4354	11	07/08/90	04:00	52.9031	1.5208	34.22	G	16.99	G
S31	CTD	3531	1.1	4355	11	07/08/90	05:46	52.7148	1.8190	34.19	G	17.11	C

Table VIII.2: General station parameter CH69 (continued)

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH69.WK1
SHEET 2: DISSOLVED TRACE METAL CONCENTRATIONS
CH69: THAMES II AND HUMBER III CRUISE

CODE	TYP	MND nmol/l	C	FED nmol/l	D	NID nmol/l	E	COD nmol/l	F	CUD nmol/l	G	ZND nmol/l	H	CDD nmol/l	I	PBD nmol/l	J
T1	P	5.62		10.05		8.95		0.870		8.37		7.24		0.160		0.110	
T2	P	13.67		841.69		9.01		1.690		9.01		12.87		0.160		1.070	
T3	P	4.26		7.43		12.02		0.640		10.84		13.53		0.190		0.180	
T4	P	6.80		2.49		30.36		1.240		22.92		37.63		0.370		0.400	
T5	P	23.94		68.93		52.37		2.420		44.67		129.28		0.880		1.240	
T6	P	30.58		8.12		82.54		2.780		61.47		260.31		1.440		1.770	
T7	P	8.74		3.35		31.55		1.600		29.12		62.63		0.490		0.440	
T8	P	6.75		8.97		11.97		0.740		13.51		13.10		0.200		0.200	
T9	P	8.60		28.32		9.75		0.830		9.93		8.79		0.140		0.200	
T10	P	14.59		4.57		8.68		0.780		9.12		7.21		0.130		0.140	
T11	P	4.39		2.24		14.45	?	0.580		12.52		7.64		0.190		0.140	
O1	CTD																
O1A	CTD																
O1B	CTD																
O2	CTD																
O3	CTD																
O4	CTD																
O5	P																
S1	P	32.31		9.17		12.14		0.384		11.81		16.15		0.293		0.103	
S2	P	23.23		2.66		10.12		0.446		8.78		8.76		0.211		0.111	
S3	CTD	10.57		1.96	<	4.13		0.269		4.35		9.59		0.118		0.185	
S4	CTD	17.51		5.70		4.36		0.305		5.09		8.68		0.122		0.128	
S5	P	24.67		4.55		8.16		0.344		8.00		8.63		0.184		0.112	
S6	P	37.72		7.15		9.97		0.397		9.13		9.55		0.187		0.120	
O6	P																
S7	P	43.55		7.77		6.67		0.534		7.92		7.07		0.163		0.107	
S8	P	18.88		5.22		5.94		0.357		7.63		6.87		0.171		0.057	
S9	P	30.35		9.88		6.67		0.407		7.79		6.94		0.175		0.098	
S10	P	6.14		2.84		7.91		0.289		7.84		7.16		0.184		0.084	
S11	CTD	8.05		2.77		4.84		0.239		5.62		6.02		0.130		0.122	
S12	P	13.93		4.02		4.74		0.134		5.32		4.50		0.134		0.135	
S13	CTD	11.78		4.81		5.55		0.259		5.69		17.79	?	0.158		0.142	
S14	P	11.72		2.04	<	4.01		0.236		4.34		3.71		0.120		0.139	
S15	CTD	8.19		3.44		4.09		0.269		4.42		5.69		0.127		0.155	
S16	P	17.06		3.81		11.50	?	0.305		6.54		6.17		0.141		0.163	
S17	P	35.32		5.76		10.62		0.410		10.31		9.73		0.226		0.106	
S18	P	29.80		1.00	<	16.23		0.410		12.45		20.02		0.347		0.077	
A1	CTDA	661.03		2.01		48.74		2.170		29.93		101.29		1.140		0.020	<
A2	CTDA	211.60		1.40		35.83		0.970		24.07		56.54		0.810		0.050	<
A3	CTDA	141.28		1.86		30.97		0.740		21.24		48.79		0.730		0.060	
A4	CTDA	138.64		4.24		35.03	?	0.840		21.85		49.86		0.750		0.070	
A5	CTDA	58.25		1.98		24.03		0.560		16.72		35.87		0.560		0.070	
A6	CTDA	42.55		1.68		21.61		0.400		15.93		32.81		0.490		0.080	
A7	CTDA	47.79		0.52	<	22.54		0.510		17.10		37.07		0.530		0.090	
A8	CTDA	54.06		3.08		25.30		0.550		18.89		35.98		0.530		0.070	
A9	CTDA	130.93		2.84		35.64		0.920		23.13		51.91		0.670		0.070	
A10	CTDA	222.55		9.67		41.03		0.950		24.08		65.43		0.820		0.050	<
A11	CTDA	216.84		2.18		34.99		1.120		24.06		63.19		0.880		0.040	<
A12	CTDA	259.90		2.29		45.10		1.450		26.19		79.32		0.860		0.060	<
A13	CTDA	770.86		4.28		52.06		2.760		25.46		76.27		0.940		0.050	<

Table VIII.3: Dissolved trace metal concentrations CH69

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH69.WK1
SHEET 2: DISSOLVED TRACE METAL CONCENTRATIONS
CH69: THAMES II AND HUMBER III CRUISE

CODE	TYP	MND nmol/l	C	FED nmol/l	D	NID nmol/l	E	COD nmol/l	F	CUD nmol/l	G	ZND nmol/l	H	CDD nmol/l	I	PBD nmol/l	J
A14	CTDA	418.88		3.05		54.41	?	1.950		25.67		62.02		0.930		0.060	<
A15	CTDA	214.36		2.89		42.67		1.170		21.42		45.42		0.740		0.060	
O7	P																
O8	P																
O9	P																
S19	P	23.15		2.61		5.47		0.295		5.47		7.09		0.127		0.118	
S20	P	18.16		4.25		3.73		0.279		4.00		4.63		0.110		0.122	
S21	P	10.28		1.46	<	3.89		0.210		4.33		4.19		0.110		0.179	
O10	P																
O11	P																
S22	P	66.46		4.78		13.88		0.531		11.21		12.79		0.300		0.078	
S23	P	63.59		8.45		9.28		0.380		10.10		11.93		0.204		0.061	
S24	P	45.40		7.16		7.22		0.361		7.01		9.16		0.158		0.164	
O12	P																
S25	P	63.73		6.75		9.14		0.387		8.89		11.80		0.192		0.082	
S26	P	67.23		13.53		7.96		0.413		8.09		9.17		0.161		0.168	
S27	P	27.78		6.32		7.43		0.436		7.13		7.95		0.163		0.150	
S28	P	50.91		12.56		7.16		0.528		7.18		8.40		0.170		0.132	
S29	P	18.67		3.32		5.48		0.348		5.49		7.07		0.141		0.117	
O13	CTD																
S30	CTD	25.57		8.62		5.23		0.285		5.74		12.15		0.153		0.117	
S31	CTD	16.13		6.17		5.66		0.298		6.42		9.25		0.170		0.110	

Table VIII.4: Dissolved trace metal concentrations CH69 (continued)

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH69.WK1
SHEET 4: NUTRIENTS, BIOLOGICAL PARAMETER AND UNFILTERED ALUMINIUM
CH69: THAMES II AND HUMBER III CRUISE

CODE	TYP	PO4 umol/l	NO2 umol/l	NO3 umol/l	SI umol/l	K CPHYLL mg/m3		Lunflt.AL nmol/l
T1	P	0.78	0.27	1.08	3.96	1.2		
T2	P	0.54	0.29	0.36	3.58	2.3		
T3	P	1.05	0.40	1.22	3.28	2.1		
T4	P	4.70	1.19	22.33	4.28	2.3		
T5	P	14.77	1.44	83.57	12.12	2.9		
T6	P	21.28	0.80	83.74	23.44	4.4		
T7	P	9.14	1.27	49.86	5.69	2.4		
T8	P			0.88		2.3		
T9	P	0.74	0.21	0.69	3.26	2.2		
T10	P	0.87	0.23	0.75	2.95	2.2		
T11	P	1.10	0.33	1.87	3.12	1.9		
O1	CTD					0.7	G	
O1A	CTD					0.9	G	
O1B	CTD					0.4	C	
O2	CTD	0.39	0.12	0.07	2.11	0.5	G	117.21
O3	CTD	0.48	0.09	0.13	2.29	0.6	G	
O4	CTD	0.42	0.08	0.14	1.08	0.3	G	
O5	P	0.75	0.29	7.90	2.19	1.0		
S1	P	0.80	0.39	7.50	2.89	1.1		
S2	P	0.29	0.17	0.11	3.11	2.1		
S3	CTD		0.14		1.28	1.3	O	
S4	CTD	0.28	0.21	0.26	1.95	0.6	G	
S5	P	0.26	0.18	0.51	1.32	1.0		
S6	P	0.41	0.17	0.35	1.65	0.9		
O6	P	0.33	0.12	0.16	3.25	1.1		
S7	P	0.31	0.20		5.46	1.1		
S8	P	0.40	0.20	0.33	4.34	0.6		
S9	P	0.36	0.19	0.51	4.19	1.0		
S10	P	0.25	0.05	0.01	3.92	0.7		
S11	CTD					0.7	G	
S12	P					0.8		
S13	CTD	0.32	0.10	0.22	2.78	0.8	G	
S14	P	0.32	0.08	0.31	2.25	0.8		
S15	CTD	0.38	0.10	0.34	2.38	0.8	C	
S16	P	0.36	0.09	0.33	1.99	1.8		
S17	P	0.36	0.14	0.43	1.74	1.9		
S18	P	0.97	0.42	15.05	2.76	1.2		
A1	CTDA	1.23	0.67	49.99	6.43	2.1	C	205.74
A2	CTDA	1.29	0.59	38.84	5.45	1.5	C	227.05
A3	CTDA	1.24	0.53	31.66	4.63	1.9	C	209.34
A4	CTDA					1.7	C	216.39
A5	CTDA	0.89	0.35	22.50	3.96	1.8	C	240.49
A6	CTDA	0.89	0.33	19.87	3.23	1.8	C	215.25
A7	CTDA	0.91	0.34	19.53	3.07	1.5	C	203.28
A8	CTDA	0.83	0.37	19.40	2.96	5.1	C	204.92
A9	CTDA	0.98	0.42	28.23	3.61	3.5	C	198.85
A10	CTDA	1.10	0.48	34.89	4.37	2.7	C	198.36
A11	CTDA	1.13	0.48	33.96	4.48	1.6	G	224.59
A12	CTDA	1.21	0.53	37.64	5.17	2.1	C	247.54
A13	CTDA	1.25	0.61	46.76	6.50	1.2	C	209.34

Table VIII.5: Nutrients, biological parameter and aluminium CH69

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH69.WK1
SHEET 4: NUTRIENTS, BIOLOGICAL PARAMETER AND UNFILTERED ALUMINIUM
CH69: THAMES II AND HUMBER III CRUISE

CODE	TYP	PO4 umol/l	NO2 umol/l	NO3 umol/l	SI umol/l	K	CPHYLL mg/m3	Lunflt.AL nmol/l
A14	CTDA	1.35	0.58	43.06	5.71		2.8	G 215.25
A15	CTDA	1.32	0.52	36.16	4.96		1.7	G 307.70
O7	P	0.87	0.37	11.60	3.56		1.4	
O8	P	0.43	0.11	0.28	2.54		1.0	
O9	P	0.28	0.07	1.59	2.67		1.0	
S19	P	0.27	0.05	2.02	2.56		0.9	
S20	P	0.24	0.03	1.75	2.26		0.9	
S21	P	0.29	0.07	1.51	2.96		0.6	
O10	P	0.28	0.09	1.59	3.01		1.2	
O11	P	0.22	0.10	1.53	2.57		2.3	
S22	P	0.25	0.12	1.64	2.70		2.0	
S23	P	0.45	0.16	1.86	3.15		0.7	
S24	P	0.43	0.08	1.55	3.29		1.2	
O12	P	0.40	0.08	1.51	3.14		1.1	
S25	P	0.51	0.05	1.73			0.9	
S26	P	0.56		1.77			1.0	
S27	P						0.6	
S28	P						0.7	
S29	P						1.0	
O13	CTD	0.40	0.10		2.52		0.8	C
S30	CTD						1.8	G
S31	CTD						0.6	G

Table VIII.6: Nutrients, biological parameter and aluminium CH69 (continued)

NORTH SEA PROJECT DATA BASEFILE: CH69.WK1
SHEET 5: SUSPENDED PARTICULATE MATTER AND TIDALLY CORRECTED POSITIONS
CH69: THAMES II AND HUMBER III CRUISE

CODE	TYP	TOTSED		MGRAVIMET	LAT	LONG
		mg/l		mg/l	at low	water
T1	P					
T2	P					
T3	P					
T4	P					
T5	P					
T6	P					
T7	P					
T8	P					
T9	P					
T10	P					
T11	P					
O1	CTD	2.22	G			
O1A	CTD	1.60	G			
O1B	CTD	1.90	C	0.89		
O2	CTD	0.91	G	1.16		
O3	CTD	0.42	G	0.69	53.8620	-0.0240
O4	CTD	1.78	G	1.12	53.9515	0.6901
O5	P	1.50			53.5666	0.2873
S1	P	1.50			53.4863	0.3706
S2	P	1.60			53.5115	0.6868
S3	CTD	0.67	O	0.86	53.7009	1.0079
S4	CTD	0.37	G	0.94	53.5231	1.0257
S5	P	1.10			53.4815	0.7749
S6	P	1.20			53.1941	0.6248
O6	P	1.40			53.3152	0.7374
S7	P	1.20			53.0857	1.1250
S8	P	1.00			52.9751	1.4530
S9	P	1.40				
S10	P	1.00				
S11	CTD	0.64	G	1.01		
S12	P	0.90				
S13	CTD	0.60	G	0.75	53.0907	1.7499
S14	P	1.00			53.1555	1.5782
S15	CTD	0.66	C	0.94	53.2494	1.3715
S16	P	1.40			53.3951	0.9701
S17	P	1.50			53.5025	0.4935
S18	P	2.00			53.5454	0.2302
A1	CTDA	6.72	C	3.60		
A2	CTDA	4.53	C	4.24		
A3	CTDA	3.41	C	2.97		
A4	CTDA	2.96	C	3.41		
A5	CTDA	2.15	C	2.41		
A6	CTDA	2.14	C	3.22		
A7	CTDA	2.08	C	2.03		
A8	CTDA	2.79	C	2.26		
A9	CTDA	2.59	C	2.49		
A10	CTDA	3.41	C	2.80		
A11	CTDA	4.06	G	4.03		
A12	CTDA	5.39	C	4.95		
A13	CTDA	12.59	C	6.81		

Table VIII.7: Suspended particulate matter and tidally corrected positions CH69

NORTH SEA PROJECT DATA BASEFILE: CH69.WK1
SHEET 5: SUSPENDED PARTICULATE MATTER AND TIDALLY CORRECTED POSITIONS
CH69: THAMES II AND HUMBER III CRUISE

CODE	TYP	TOTSED mg/l	MGRAVIMET mg/l	LAT at low water	LONG
A14	CTDA	6.65 G	4.02		
A15	CTDA	4.22 G	4.20		
O7	P	3.00		53.5461	0.2476
O8	P	2.30		53.5457	0.4612
O9	P	1.90		53.5456	0.7342
S19	P	1.90		53.6867	0.4448
S20	P	2.20		53.7733	0.1520
S21	P	2.10		53.8529	0.5144
O10	P	2.00		53.5698	0.5887
O11	P	2.50		53.5171	0.4656
S22	P	2.50		53.4345	0.3506
S23	P	2.60		53.3320	0.4116
S24	P	1.90		53.3678	0.6027
O12	P	1.80		53.3995	0.7831
S25	P	2.40		53.3061	0.4934
S26	P	2.20		53.0326	0.4779
S27	P	2.10		53.2134	0.7972
S28	P	2.80		53.0040	1.0913
S29	P	3.20		53.1341	1.2245
O13	CTD	1.31 C	2.61	53.1603	1.0483
S30	CTD	2.20 G	2.29	52.8736	1.6085
S31	CTD	1.25 G			

Table VIII.8: Suspended particulate matter and tidally corrected positions CH69 (continued)

APPENDIX IX

CRUISE CH72

DATA BASE

CONTENT

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH72.WK1
SHEET 1: GENERAL SAMPLE PARAMETER Update: 11/02/92 21:26
CH72: RHINE PLUME CRUISE

CODE	TYP	STN #	DEPTH m	BOTT #	S #	DATE dd/mm/yy	TIME hh:mm	LAT +ve N	LONG +ve E	SAL	A TEMP B °C
A01T	CTDA	3626	0.5	4356	8	07/10/90	10:01	51.9007	4.3668	2.63	15.58
A01B	CTDA	3626	4.6	4357	8	07/10/90	10:01	51.9007	4.3668	2.80	15.55
A02T	CTDA	3627	0.5	4358	8	07/10/90	11:06	51.9008	4.3670	2.73	15.58
A02B	CTDA	3627	4.6	4359	8	07/10/90	11:06	51.9008	4.3670	2.80	15.56
A03T	CTDA	3628	0.5	4360	8	07/10/90	12:05	51.9002	4.3662	2.64	15.57
A03B	CTDA	3628	4.3	4361	8	07/10/90	12:05	51.9002	4.3662	2.70	15.57
A04T	CTDA	3629	0.5	4362	8	07/10/90	13:08	51.9007	4.3670	2.54	15.60
A04B	CTDA	3629	4.2	4363	8	07/10/90	13:08	51.9007	4.3670	3.14	15.58
A05T	CTDA	3630	0.5	4364	8	07/10/90	14:04	51.9008	4.3670	2.44	15.57
A05B	CTDA	3630	4.2	4365	8	07/10/90	14:04	51.9008	4.3670	3.38	15.54
A06T	CTDA	3631	0.5	4366	8	07/10/90	15:03	51.9007	4.3668	2.61	15.56
A06B	CTDA	3631	4.2	4367	8	07/10/90	15:03	51.9007	4.3668	4.59	15.49
A07T	CTDA	3632	0.5	4368	8	07/10/90	16:03	51.9008	4.3665	3.80	15.50
A07B	CTDA	3632	4.5	4369	8	07/10/90	16:03	51.9008	4.3665	4.97	15.47
A08T	CTDA	3633	0.5	4370	8	07/10/90	17:05	51.9007	4.3672	6.46	15.41
A08B	CTDA	3633	3.5	4371	8	07/10/90	17:05	51.9007	4.3672	7.54	15.39
A09T	CTDA	3634	0.5	4372	8	07/10/90	18:03	51.9008	4.3673	3.35	15.49
A09B	CTDA	3634	4.7	4373	8	07/10/90	18:03	51.9008	4.3673	6.86	15.43
A10T	CTDA	3635	0.5	4374	8	07/10/90	19:03	51.9012	4.3695	4.06	15.38
A10B	CTDA	3635	4.8	4375	8	07/10/90	19:03	51.9012	4.3695	5.32	15.40
A11T	CTDA	3636	0.5	4376	8	07/10/90	20:16	51.9010	4.3679	3.88	15.33
A11B	CTDA	3636	4.5	4377	8	07/10/90	20:16	51.9010	4.3679	3.92	15.37
A12T	CTDA	3637	0.5	4378	8	07/10/90	21:04	51.9007	4.3669	3.91	15.34
A12B	CTDA	3637	4.6	4379	8	07/10/90	21:04	51.9007	4.3669	4.00	15.35
A13T	CTDA	3638	0.5	4380	8	07/10/90	22:00	51.9007	4.3670	3.58	15.40
A13B	CTDA	3638	3.6	4381	8	07/10/90	22:00	51.9007	4.3670	3.59	15.39
T1	CTD	3641	1.2	4382	7	08/10/90	17:22	52.0544	4.1443	30.21	14.37
T2	CTD	3642	0.5	4383	7	08/10/90	18:00	52.0650	4.1261	31.41	14.59
T3	CTD	3643	0.5	4384	7	08/10/90	19:12	52.0988	4.0872	32.41	14.77
T5	CTD	3645	0.5	4385	7	08/10/90	20:34	52.1630	4.0018	34.29	15.02
T7	CTD	3647	0.5	4386	7	08/10/90	21:46	52.2233	3.9203	34.75	15.08
N2	CTD	3654	0.5	4387	7	09/10/90	03:24	52.2652	4.3750	31.19	14.37
N3	CTD	3655	8.0	4388	7	09/10/90	04:09	52.2859	4.3202	31.84	14.48
N5	CTD	3657	0.5	4389	7	09/10/90	05:27	52.3293	4.1972	33.42	14.67
N7	CTD	3659	0.6	4390	7	09/10/90	06:39	52.3680	4.0778	34.84	14.84
Y6	CTD	3667	0.5	4391	7	09/10/90	13:11	52.5250	4.2423	34.65	14.60
Y4	CTD	3669	0.8	4392	7	09/10/90	16:47	52.5019	4.3781	33.11	14.36
Y3	CTD	3670	1.7	4393	7	09/10/90	17:38	52.4897	4.4393	32.03	14.31
Y2	CTD	3671	0.5	4394	7	09/10/90	18:16	52.4812	4.4857	31.30	14.28
E5	CTD	3674	0.7	4395	7	09/10/90	22:08	52.6476	4.3551	34.48	14.44
E3	CTD	3676	0.5	4396	7	09/10/90	23:35	52.6344	4.4875	32.75	14.26
G6	CTD	3678	0.5	4397	7	10/10/90	07:30	51.9513	3.6702	34.47	15.06
G4	CTD	3679	0.5	4398	7	10/10/90	07:56	51.9347	3.7027	34.33	14.97
G3	CTD	3680	0.8	4399	7	10/10/90	08:30	51.9100	3.7483	34.15	14.72
S1	CTD	3682	0.6	4400	7	10/10/90	10:42	51.7757	3.6014	33.99	14.36
S2	CTD	3683	0.8	4401	7	10/10/90	11:21	51.8175	3.5428	34.19	14.85
B01T	CTDE	3694	0.5	4402	7	11/10/90	03:02	52.2177	4.1550	32.49	14.52
B01B	CTDE	3694	17.0	4403	7	11/10/90	03:02	52.2177	4.1550	32.95	14.59
B02T	CTDE	3696	0.5	4404	7	11/10/90	04:02	52.2183	4.1573	32.21	14.46
B02B	CTDE	3696	17.1	4405	7	11/10/90	04:02	52.2183	4.1573	32.84	14.57

Table IX.1: General station parameters CH72

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NORTH SEA PROJECT DATA BASE (SUDO)                      FILE:    CH72.WK1
SHEET 1: GENERAL SAMPLE PARAMETER              Update: 11/02/92 21:26
CH72: RHINE PLUME CRUISE
----------------------------------------------------------------------------
CODE TYP  STN  DEPTH BOTT S  DATE     TIME  LAT      LONG     SAL    A TEMP B
          #      m     #  #  dd/mm/yy hh:mm +ve N    +ve E              °C
============================================================================
B03T CTDE 3698   0.5 4406  7 11/10/90 05:02  52.2188   4.1564 32.16  14.46
B03B CTDE 3698  16.1 4407  7 11/10/90 05:02  52.2188   4.1564 32.94  14.56
B04T CTDE 3700   0.5 4408  7 11/10/90 06:02  52.2190   4.1563 32.43  14.50
B04B CTDE 3700  16.3 4409  7 11/10/90 06:02  52.2190   4.1563 33.13  14.58
B05T CTDE 3701   0.5 4410  7 11/10/90 07:01  52.2187   4.1595 33.11  14.61
B05B CTDE 3701  17.7 4411  7 11/10/90 07:01  52.2187   4.1595 33.27  14.63
B06T CTDE 3703   0.5 4412  7 11/10/90 08:01  52.2204   4.1568 33.59  14.68
B06B CTDE 3703  17.9 4413  7 11/10/90 08:01  52.2204   4.1568 33.58  14.68
B07T CTDE 3705   0.5 4414  7 11/10/90 09:02  52.2171   4.1593 33.90  14.70
B07B CTDE 3705  17.3 4415  7 11/10/90 09:02  52.2171   4.1593 33.95  14.71
B08T CTDE 3707   0.5 4416  7 11/10/90 10:02  52.2191   4.1545 34.15  14.73
B08B CTDE 3707  17.6 4417  7 11/10/90 10:02  52.2191   4.1545 34.15  14.74
B09T CTDE 3709   0.5 4418  7 11/10/90 11:00  52.2159   4.1547 34.06  14.75
B09B CTDE 3709  17.4 4419  7 11/10/90 11:00  52.2159   4.1547 34.18  14.75
B10T CTDE 3711   0.5 4420  7 11/10/90 12:03  52.2171   4.1597 33.84  14.72
B10B CTDE 3711  16.5 4421  7 11/10/90 12:03  52.2171   4.1597 34.12  14.75
B11T CTDE 3713   0.5 4422  7 11/10/90 13:06  52.2162   4.1473 33.78  14.74
B11B CTDE 3713  16.4 4423  7 11/10/90 13:06  52.2162   4.1473 34.01  14.75
B12T CTDE 3715   0.5 4424  7 11/10/90 14:14  52.2067   4.1344 33.71  14.73
B12B CTDE 3715  17.7 4425  7 11/10/90 14:14  52.2067   4.1344 33.96  14.74
B13T CTDE 3717   0.5 4426  7 11/10/90 15:02  52.1979   4.1288 33.56  14.73
B13B CTDE 3717  15.8 4427  7 11/10/90 15:02  52.1979   4.1288 33.72  14.74
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Table IX.2: General station parameters CH72 (continued)

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH72.WK1
SHEET 2: DISSOLVED TRACE METAL CONCENTRATIONS
CH72: RHINE PLUME CRUISE

CODE	TYP	MND nmol/l	C	FED nmol/l	D	NID nmol/l	E	COD nmol/l	F	CUD nmol/l	G	ZND nmol/l	H	CDD nmol/l	I	PBD nmol/l	J
A01T	CTDA	407.39		54.76		45.91		3.540		35.87		169.59		0.260		0.910	
A01B	CTDA	406.51		35.77		47.42		3.640		37.37		178.71		0.290		0.750	
A02T	CTDA	351.56		155.44		47.08		3.220		31.85		162.68		0.230		0.830	
A02B	CTDA	362.73		54.97		50.58		3.540		34.28		161.79		0.210		0.630	
A03T	CTDA	343.40		37.96		48.86		3.350		36.06		154.28		0.220		0.740	
A03B	CTDA	333.69		19.36		45.02		3.270		34.66		151.54		0.220		0.640	
A04T	CTDA	351.73		42.39		48.31		3.280		36.58		155.80		0.220		0.750	
A04B	CTDA	421.32		224.43		56.88		4.070		34.15		150.74		0.290		0.630	
A05T	CTDA	382.49		47.34		50.98		3.610		35.50		146.79		0.230		0.760	
A05B	CTDA	370.12		36.08		51.74		3.390		31.27		135.23		0.230		0.710	
A06T	CTDA	400.62		68.53		50.03		3.620		35.64		151.67		0.250		0.580	
A06B	CTDA	457.24		119.76		47.38		3.990		32.21		136.81		0.240		0.840	
A07T	CTDA	372.27		22.75		43.03		3.350		33.09		127.76		0.570		0.660	
A07B	CTDA	405.60		17.94		45.25		3.450		29.92		129.73		0.630		0.630	
A08T	CTDA	400.79		32.89		40.71		3.810		30.60		135.40		0.480		0.660	
A08B	CTDA	397.01		16.37		41.46		3.800		27.91		121.47		0.530		0.710	
A09T	CTDA	385.67		26.60		42.94		3.390		32.91		129.69		0.240		0.600	
A09B	CTDA	439.97		37.41		42.43		3.640		30.31		124.20		0.460		0.770	
A10T	CTDA	433.52		18.97		43.87		3.830		35.25		145.34		0.370		0.720	
A10B	CTDA	416.94		123.71		48.52		3.760		36.13		138.39		0.420		0.940	
A11T	CTDA	413.42		37.22		42.85		3.790		34.73		144.37		0.310		0.770	
A11B	CTDA	407.40		38.48		44.72		3.760		38.02		138.52		0.310		0.710	
A12T	CTDA	441.34		135.78		52.21		3.940		38.52		155.75		0.430		0.930	
A12B	CTDA	400.19		244.92		40.10		3.660		35.85		144.24		0.350		1.060	
A13T	CTDA	418.57		39.43		49.28		3.690		36.02		145.03		0.290		0.810	
A13B	CTDA	410.07		70.09		44.74		4.020		36.65		150.83		0.350		0.720	
T1	CTD	61.83		6.81		17.84		1.360		14.95		30.14		0.190		0.360	
T2	CTD	87.58		9.48		16.93		1.310		11.82		32.03		0.180		0.400	
T3	CTD	44.37		11.36		13.56		1.510		10.67		26.34		0.160		0.310	
T5	CTD	13.74		16.48		7.50		0.680		7.37		10.10		0.130		0.220	
T7	CTD	8.36		8.98		6.37		0.510		6.08		7.05		0.150		0.170	
N2	CTD	5.47		11.66		12.94		0.640		11.88		28.50		0.320		0.220	
N3	CTD	5.51		4.27	<	12.64		0.570		11.67		27.55		0.370		0.220	
N5	CTD	12.65		15.49		9.82		0.580		6.95		14.17		0.260		0.200	
N7	CTD	9.73		10.65		7.16		0.340		4.68		9.59		0.210		0.230	
Y6	CTD	16.86		9.80		6.55		0.500		4.70		8.17		0.150		0.250	
Y4	CTD	9.76		6.81		9.34		0.800		7.97		15.35		0.190		0.200	
Y3	CTD	13.46		6.83		11.75		0.820		10.03		22.30		0.240		0.270	
Y2	CTD	15.95		2.46	<	14.55		0.630		13.68		30.75		0.400		0.220	
E5	CTD	20.46		7.56		7.41		0.600		6.11		8.96		0.170		0.200	
E3	CTD	17.91		9.94		11.21		0.850		8.73		15.94		0.190		0.200	
G6	CTD	3.31		3.75	<	9.04		0.480		6.67		13.37		0.160		0.150	
G4	CTD	5.16		10.28		10.02		0.380		8.34		14.14		0.180		0.160	
G3	CTD	6.86		12.01		10.59		0.610		8.48		14.40		0.190		0.180	
S1	CTD	5.35		14.67		10.19		0.420		10.21		14.72		0.170		0.170	
S2	CTD	2.50		9.59		11.17		0.400		8.30		16.97		0.210		0.120	
B01T	CTDE	13.26		6.89		11.53		0.890		8.31		21.35		0.250		0.250	
B01B	CTDE	6.29		11.78		10.86		0.850		8.87		18.98		0.230		0.220	
B02T	CTDE	5.43		14.52		11.49		0.940		8.91		21.88		0.250		0.250	
B02B	CTDE	6.48		10.85		11.36		0.850		8.96		18.79		0.260		0.240	

Table IX.3: Dissolved trace metal concentrations CH72

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH72.WK1
SHEET 2: DISSOLVED TRACE METAL CONCENTRATIONS
CH72: RHINE PLUME CRUISE

CODE	TYP	MND nmol/l	C	FED nmol/l	D	NID nmol/l	E	COD nmol/l	F	CUD nmol/l	G	ZND nmol/l	H	CDD nmol/l	I	PBD nmol/l	J
B03T	CTDE	9.73		1.98	<	12.33		0.940		9.41		27.68		0.360		0.140	
B03B	CTDE	12.29		3.73	<	13.26		0.860		7.42		18.75		0.220		0.220	
B04T	CTDE	11.47		8.00		12.72		0.930		9.68		25.55		0.220		0.370	
B04B	CTDE	12.40		2.39	<	9.81		0.680		7.47		20.08		0.190		0.160	
B05T	CTDE	12.52		7.55		9.19		0.750		7.33		19.28		0.170		0.170	
B05B	CTDE	15.33		7.86		9.41		0.870		8.40		20.33		0.200		0.160	
B06T	CTDE	17.75		12.72		8.77		0.780		7.47		18.59		0.200		0.180	
B06B	CTDE	17.08		8.52		8.72		0.780		7.49		16.78		0.200		0.160	
B07T	CTDE	16.72		8.82		8.61		0.790		7.03		14.16		0.210		0.170	
B07B	CTDE	15.85		8.82		7.65		0.720		6.23		17.07		0.160		0.100	
B08T	CTDE	18.05		5.61		8.16		0.650		6.66		11.93		0.200		0.150	
B08B	CTDE	16.82		19.45		7.93		0.640		6.25		14.39		0.210		0.160	
B09T	CTDE	16.70		17.04		7.62		0.770		7.89		13.23		0.180		0.180	
B09B	CTDE	18.50		15.53		7.85		0.730		6.94		12.47		0.200		0.380	
B10T	CTDE	16.10		11.06		8.00		0.740		6.78		13.89		0.200		0.150	
B10B	CTDE	14.21		11.51		8.97		0.680		6.03		12.74		0.160		0.170	
B11T	CTDE	15.63		15.17		7.62		0.690		6.67		12.23		0.160		0.150	
B11B	CTDE	16.42		5.99		8.05		0.680		7.07		14.47		0.150		0.210	
B12T	CTDE	13.62		6.66		7.98		0.690		6.57		14.13		0.210		0.160	
B12B	CTDE	16.82		2.80	<	8.13		0.780		6.83		13.53		0.240		0.130	
B13T	CTDE	17.26		10.17		8.71		0.790		7.02		13.69		0.310		0.110	
B13B	CTDE	18.63		10.26		8.86		0.800		7.52		15.75		0.220		0.180	

Table IX.4: Dissolved trace metal concentrations CH72 (continued)

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH72.WK1
SHEET 3: PARTICULATE TRACE METAL CONCENTRATIONS
CH72: RHINE PLUME CRUISE

CODE	TYP	SWT mg	SCONC mg/l	MNP nmol/l	FEP nmol/l	NIP nmol/l	COP nmol/l	CUP nmol/l	ZNP nmol/l	CDP nmol/l	PBP nmol/l
A01T	CTDA	49	10.3	269.2	2671	1.52	0.87	6.56	78.99	0.305	2.46
A01B	CTDA	41	10.6	200.7	2126	1.24	0.63	6.66	60.00	0.300	2.63
A02T	CTDA	60	13.2	254.8	2440	1.35	0.78	6.26	71.53	0.316	2.05
A02B	CTDA	41	12.9	151.3	1511	0.95	0.51	4.42	46.36	0.256	2.60
A03T	CTDA	45	14.2	255.4	2461	1.47	0.78	6.92	72.40	0.366	2.71
A03B	CTDA	40	12.0	253.7	2443	1.50	0.80	6.66	75.79	0.353	2.77
A04T	CTDA	41	9.4	216.8	2054	1.28	0.71	5.89	60.76	0.324	2.23
A04B	CTDA	52	11.9	245.6	2453	1.37	0.79	6.65	69.80	0.390	2.42
A05T	CTDA	52	12.3	250.1	2364	1.42	0.81	6.34	70.97	0.338	2.47
A05B	CTDA	48	10.7	258.1	2527	1.45	0.84	8.10	74.52	0.401	2.39
A06T	CTDA	69	13.6	237.3	2289	1.50	0.74	5.93	64.60	0.341	2.09
A06B	CTDA	77	14.4	289.5	3069	1.67	0.90	6.96	82.42	0.472	2.80
A07T	CTDA	92	17.2	300.1	3109	1.75	0.98	7.47	84.65	0.495	2.11
A07B	CTDA	142	25.6	416.8	4097	2.63	1.34	11.47	116.82	0.639	3.36
A08T	CTDA	63	13.1	273.6	2775	1.59	0.92	7.99	74.84	0.466	2.94
A08B	CTDA	73	16.7	340.2	3347	1.73	1.05	6.67	82.75	0.591	3.01
A09T	CTDA	44	10.3	151.0	2275	1.22	0.66	5.65	58.73	0.336	3.24
A09B	CTDA	84	18.8	250.3	3827	2.10	1.14	9.54	92.96	0.717	4.79
A10T	CTDA	49	11.3	563.0	2525	1.50	0.85	11.92	72.47	0.456	4.26
A10B	CTDA	43	14.8	659.1	2843	1.63	0.95	8.37	77.85	0.471	4.83
A11T	CTDA	36	9.8	620.9	2568	1.41	0.89	8.77	75.74	0.461	4.32
A11B	CTDA	46	10.8	511.0	2155	1.22	0.74	5.60	67.95	0.382	4.20
A12T	CTDA	52	11.9	563.6	2451	1.37	0.82	6.36	74.52	0.430	3.92
A12B	CTDA	78	15.5	338.6	3040	1.84	1.02	8.71	97.46	0.566	3.97
A13T	CTDA	56	14.4	352.1	3251	1.76	1.05	6.71	100.77	0.547	5.32
A13B	CTDA	62	16.2	376.6	3551	1.88	1.15	7.88	106.67	0.597	4.58
T1	CTD	78	9.1	214.9	1335	0.45	0.32	1.64	24.28	0.142	1.57
T2	CTD	102	12.5	236.5	1813	0.49	0.41	2.45	15.23	0.166	1.64
T3	CTD	48	5.4	145.0	795	0.50	0.21	0.89	14.70	0.070	0.91
T5	CTD	21	1.7	87.6	235	0.14	0.10	0.20	3.26	0.024	0.34
T7	CTD	24	2.4	69.9	198	0.16	0.09	0.30	4.09	0.036	0.42
N2	CTD	134	12.6	291.5	1743	0.88	0.48	1.59	26.24	0.133	0.96
N3	CTD	66	5.9	134.9	624	0.26	0.21	0.55	12.74	0.039	0.52
N5	CTD	60	9.1	206.3	615	0.53	0.31	0.84	18.04	0.090	0.70
N7	CTD	59	6.0	90.9	333	0.25	0.12	0.67	12.60	0.063	0.61
Y6	CTD	51	8.2	104.9	384	0.50	0.14	0.62	6.91	0.069	0.58
Y4	CTD	43	7.1	171.4	691	0.31	0.41	1.27	13.34	0.086	0.80
Y3	CTD	92	12.5	288.9	1601	0.61	0.73	2.87	26.45	0.138	1.23
Y2	CTD	166	63.9	1083.7	12221	4.70	5.10	7.72	176.31	1.014	4.95
E5	CTD	25	2.9	62.5	149	0.12	0.13	0.03	2.31	0.026	0.78
E3	CTD	38	4.3	120.0	445	0.19	0.24	0.41	7.16	0.042	1.78
G6	CTD	110	12.7	266.7	1372	0.49	0.75	0.79	5.46	0.067	0.48
G4	CTD	57	6.8	183.8	675	0.27	0.51	0.44	3.97	0.035	3.21
G3	CTD	30	3.3	79.3	313	0.09	0.18	0.11	3.28	0.017	0.95
S1	CTD	44	5.2	143.5	778	0.20	0.36	0.69	4.90	0.029	1.55
S2	CTD	85	9.6	215.3	1290	0.32	0.66	0.54	4.24	0.035	0.36
B01T	CTDE	6	0.7	50.6	169	0.06	0.11	0.09	3.09	0.014	0.55
B01B	CTDE	19	2.1	58.8	202	0.12	0.13	0.15	2.80	0.016	0.75
B02T	CTDE	11	1.0	49.8	205	0.07	0.13	0.12	3.06	0.016	0.56
B02B	CTDE	21	2.0	50.1	132	0.03	0.09	0.08	3.30	0.012	0.49

Table IX.5: Particulate trace metal concentrations CH72

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH72.WK1
SHEET 3: PARTICULATE TRACE METAL CONCENTRATIONS
CH72: RHINE PLUME CRUISE

CODE	TYP	SWT mg	SCONC mg/l	MNP nmol/l	FEP nmol/l	NIP nmol/l	COP nmol/l	CUP nmol/l	ZNP nmol/l	CDP nmol/l	PBP nmol/l
B03T	CTDE	25	2.1	48.0	196	0.07	0.13	0.17	3.97	0.015	0.76
B03B	CTDE	28	2.6	46.8	136	0.05	0.10	0.13	3.32	0.000	0.58
B04T	CTDE	16	1.7	28.6	123	0.05	0.08	0.03	2.10	0.008	0.47
B04B	CTDE	16	1.8	47.6	132	0.07	0.10	0.08	2.97	0.009	0.46
B05T	CTDE	20	1.9	43.5	110	0.04	0.08	0.17	2.24	0.010	0.43
B05B	CTDE	24	2.1	54.4	142	0.04	0.11	0.05	2.41	0.012	0.93
B06T	CTDE	20	1.8	49.0	130	0.08	0.10	0.11	2.69	0.011	0.65
B06B	CTDE	20	1.7	42.7	114	0.06	0.08	0.10	2.12	0.010	0.43
B07T	CTDE	22	2.3	57.5	136	0.08	0.09	0.11	2.55	0.013	0.69
B07B	CTDE	16	1.5	54.6	151	0.04	0.10	0.11	2.69	0.011	0.75
B08T	CTDE	15	1.7	47.8	98	0.04	0.07	0.07	1.88	0.010	0.60
B08B	CTDE	11	1.2	47.0	96	0.08	0.07	0.07	2.87	0.009	0.38
B09T	CTDE	16	1.6	43.0	86	0.03	0.06	0.04	1.77	0.008	0.38
B09B	CTDE	12	1.2	46.2	87	0.04	0.06	0.05	1.98	0.008	0.41
B10T	CTDE	13	1.3	41.6	84	0.05	0.07	0.05	1.91	0.007	0.50
B10B	CTDE	13	1.3	44.1	86	0.01	0.06	0.05	1.96	0.007	0.37
B11T	CTDE	12	1.3	44.7	90	0.07	0.07	0.06	2.40	0.009	0.38
B11B	CTDE	10	1.2	46.1	129	0.05	0.08	0.07	1.83	0.007	0.47
B12T	CTDE	17	1.9	54.3	145	0.04	0.09	0.10	2.58	0.012	0.56
B12B	CTDE	14	1.8	56.3	165	0.06	0.10	0.09	4.47	0.009	1.12
B13T	CTDE	16	1.7	45.6	115	0.07	0.08	0.07	2.86	0.008	0.25
B13B	CTDE	15	1.6	52.1	140	0.05	0.08	0.07	2.46	0.008	0.55

Table IX.6: Particulate trace metal concentrations CH72 (continued)

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH72.WK1
SHEET 4: NUTRIENTS, BIOLOGICAL PARAMETER AND UNFILTERED ALUMINIUM
CH72: RHINE PLUME CRUISE

CODE	TYP	PO4 µmol/l	NO2 µmol/l	NO3 µmol/l	SI µmol/l	NH4 µmol/l	O2 µmol/l	K	CPHYLL mg/m3	Lunflt.AL nmol/l
A01T	CTDA	6.18		266.10	42.57	13.40			5.0	666.00
A01B	CTDA	6.95		268.20	43.12	17.50			4.7	678.00
A02T	CTDA	6.87		270.40	43.22	12.70			5.1	703.00
A02B	CTDA	6.97		270.10	42.96	13.30			4.8	666.00
A03T	CTDA	7.03		270.10	42.88	13.40			5.3	703.00
A03B	CTDA	6.96		272.30	43.17	13.10			4.8	691.00
A04T	CTDA	7.08		271.20	43.08	12.90			4.9	691.00
A04B	CTDA	7.24		266.70	41.49	13.60			4.7	789.00
A05T	CTDA	6.96		273.20	43.11	13.90			5.1	678.00
A05B	CTDA	7.06		271.60	42.66	13.10			4.7	691.00
A06T	CTDA	7.17		268.60	41.69	13.50			5.0	728.00
A06B	CTDA	7.54		254.00	38.15	15.70			4.8	850.00
A07T	CTDA	8.08		264.70	40.76	15.10			5.0	850.00
A07B	CTDA	10.18		250.50	38.93	14.30			4.7	987.00
A08T	CTDA	9.48		252.60	38.64	15.90			4.6	1048.00
A08B	CTDA	9.72		235.20	35.37	15.60			4.3	1160.00
A09T	CTDA	7.56		269.80	41.46	14.20			4.4	703.00
A09B	CTDA	9.29		234.10	37.21	14.50			4.2	1036.00
A10T	CTDA	8.50		264.00	40.21	14.90			4.5	876.00
A10B	CTDA	9.18		256.20	39.11	14.70			4.1	1307.00
A11T	CTDA	7.76		268.30	41.33	14.20			4.2	765.00
A11B	CTDA	7.65		268.70	41.47	14.10			4.2	752.00
A12T	CTDA	6.90		273.70	42.31	14.00			4.6	616.00
A12B	CTDA	7.21		269.80	41.45	14.00			4.3	728.00
A13T	CTDA	6.92		272.80	42.88	13.30			4.5	641.00
A13B	CTDA	6.83		274.40	43.06	13.40			4.4	641.00
T1	CTD	2.25		38.50	7.24				2.5	201.00
T2	CTD	2.80		53.80	10.33				2.7	258.00
T3	CTD	1.80		26.20	5.27				1.5	156.00
T5	CTD	0.71		1.90	1.84				1.8	57.00
T7	CTD								3.2	
N2	CTD	1.52		25.00	5.71				1.9	107.00
N3	CTD	1.28		19.20	3.45				1.8	104.00
N5	CTD	0.69		7.10	1.96				2.6	66.00
N7	CTD	0.24		0.10	0.83				7.3	42.00
Y6	CTD	0.18		0.50	0.36				8.3	49.00
Y4	CTD	0.60		8.50	2.63				2.5	71.00
Y3	CTD	1.02		17.00	3.83				2.3	89.00
Y2	CTD	1.38		24.20	5.44				3.4	99.00
E5	CTD	0.18		0.30	0.22				9.9	54.00
E3	CTD	0.65		11.40	2.75				2.1	75.00
G6	CTD	0.55		1.30	1.84				2.4	53.00
G4	CTD								2.7	
G3	CTD								2.5	56.00
S1	CTD								3.1	53.00
S2	CTD								3.0	58.00
B01T	CTDE	1.35		17.00	3.16				1.7	96.00
B01B	CTDE	1.15		12.80	2.60				1.9	81.00
B02T	CTDE	1.41		19.00	3.50				1.6	100.00
B02B	CTDE	1.23		13.80	2.68				1.7	77.00

Table IX.7: Nutrients, biological parameter and aluminium CH72

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH72.WK1
SHEET 4: NUTRIENTS, BIOLOGICAL PARAMETER AND UNFILTERED ALUMINIUM
CH72: RHINE PLUME CRUISE

CODE	TYP	PO4 µmol/l	NO2 µmol/l	NO3 µmol/l	SI µmol/l	NH4 µmol/l	O2 µmol/l	K CPHYLL mg/m3	Lunflt.AL nmol/l
B03T	CTDE	1.44		18.90	3.55			1.7	100.00
B03B	CTDE	1.20		12.80	2.51			1.9	87.00
B04T	CTDE	1.34		16.70	3.16			1.5	94.00
B04B	CTDE	1.13		12.70	2.50			1.7	86.00
B05T	CTDE	1.10		11.00	2.52			1.6	81.00
B05B	CTDE	1.03		10.10	2.32			1.6	76.00
B06T	CTDE	0.96		7.50	2.12			1.7	58.00
B06B	CTDE	0.91		7.80	2.14			1.8	68.00
B07T	CTDE	0.82		5.00	2.00			1.5	
B07B	CTDE	0.78		4.70	1.94			1.7	61.00
B08T	CTDE	0.72		3.40	1.78			2.2	59.00
B08B	CTDE	0.72		3.70	1.78			1.7	57.00
B09T	CTDE	0.76		4.00	1.86			1.8	52.00
B09B	CTDE	0.70		3.30	1.76			1.5	60.00
B10T	CTDE	0.80		5.60	2.03			1.8	67.00
B10B	CTDE	0.73		3.90	1.83			1.7	61.00
B11T	CTDE	0.80		6.20	2.06			1.9	63.00
B11B	CTDE	0.70		3.80	1.81			1.7	59.00
B12T	CTDE	0.83		6.30	2.10			1.9	60.00
B12B	CTDE	0.78		5.50	2.01			1.7	61.00
B13T	CTDE	0.86		7.90	2.19			1.9	69.00
B13B	CTDE	0.81		6.50	2.06			2.0	66.00

Table IX.8: Nutrients, biological parameter and aluminium CH72 (continued)

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH72.WK1
SHEET 5: SUSPENDED PARTICULATE MATTER AND CHLORINITY-SALINITY
CH72: RHINE PLUME CRUISE

CODE	TYP	TOTSED mg/l	M ORGSED mg/l	N INORGSEDO mg/l	GRAVIMET mg/l	CL_SAL
A01T	CTDA	26.99	4.93	21.89		2.61
A01B	CTDA	27.46	5.01	22.29		2.63
A02T	CTDA	25.47	4.70	20.61		2.39
A02B	CTDA	26.54	4.86	21.51		2.63
A03T	CTDA	26.08	4.79	21.12		2.52
A03B	CTDA	26.30	4.83	21.31		2.65
A04T	CTDA	25.08	4.64	20.29		2.54
A04B	CTDA	26.85	4.91	21.77		3.08
A05T	CTDA	24.97	4.62	20.19		2.50
A05B	CTDA	27.44	5.00	22.27		3.17
A06T	CTDA	24.22	4.51	19.56		3.06
A06B	CTDA	32.89	5.84	26.85		4.67
A07T	CTDA	33.12	5.87	27.05		4.36
A07B	CTDA	49.08	8.32	40.47		5.21
A08T	CTDA	29.85	5.37	24.29		6.36
A08B	CTDA	31.05	5.56	25.31		7.66
A09T	CTDA	21.50	4.09	17.27		4.80
A09B	CTDA	31.03	5.55	25.29		8.01
A10T	CTDA	22.83	4.30	18.39		4.08
A10B	CTDA	26.21	4.81	21.23		5.43
A11T	CTDA	23.83	4.45	19.23		3.80
A11B	CTDA	23.72	4.43	19.14		3.73
A12T	CTDA	27.69	5.04	22.48		3.32
A12B	CTDA	27.61	5.03	22.41		3.89
A13T	CTDA	26.38	4.84	21.37		3.32
A13B	CTDA	26.69	4.89	21.64		3.50
T1	CTD	22.97	4.32	18.51	15.87	
T2	CTD	32.26	5.74	26.32		
T3	CTD	9.93	2.32	7.54		
T5	CTD	3.46	1.33	2.09	5.69	
T7	CTD	3.21	1.29	1.88	4.01	
N2	CTD	34.83	6.13	28.49	14.81	
N3	CTD	12.28	2.68	9.51		
N5	CTD	8.64	2.12	6.45		
N7	CTD	3.53	1.34	2.15		
Y6	CTD	2.97	1.25	1.69		
Y4	CTD	9.10	2.19	6.84		
Y3	CTD	17.91	3.54	14.25	11.10	
Y2	CTD					
E5	CTD	3.72	1.37	2.32	4.05	
E3	CTD	6.93	1.86	5.01	5.26	
G6	CTD	15.53	3.18	12.25		
G4	CTD	16.66	3.35	13.20	20.69	
G3	CTD	11.98	2.63	9.27		
S1	CTD	7.83	2.00	5.77	7.31	
S2	CTD	13.66	2.89	10.68	13.43	
B01T	CTDE	2.42	1.17	1.22	3.33	
B01B	CTDE	2.11	1.12	0.96	5.89	
B02T	CTDE	3.31	1.30	1.97	2.23	
B02B	CTDE	1.86	1.08	0.75	2.42	

Table IX.9: Suspended particulate matter and chlorinity-salinity CH72

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH72.WK1
SHEET 5: SUSPENDED PARTICULATE MATTER AND CHLORINITY-SALINITY
CH72: RHINE PLUME CRUISE

CODE	TYP	TOTSED mg/l	M ORGSED mg/l	N INORGSEDO mg/l	GRAVIMET mg/l	CL_SAL
B03T	CTDE	3.59	1.35	2.20	2.80	
B03B	CTDE	1.58	1.04	0.51	2.42	
B04T	CTDE	2.53	1.18	1.32	2.38	
B04B	CTDE	1.40	1.01	0.36	2.97	
B05T	CTDE	1.63	1.05	0.55	2.04	
B05B	CTDE	1.49	1.03	0.44	2.53	
B06T	CTDE	1.13	0.97	0.14		
B06B	CTDE	1.33	1.00	0.30	1.91	
B07T	CTDE	0.91	0.94	-0.05		
B07B	CTDE	0.99	0.95	0.02	2.52	
B08T	CTDE	0.43	0.86	-0.45	2.02	
B08B	CTDE	0.47	0.87	-0.42	2.18	
B09T	CTDE	0.84	0.93	-0.11	2.28	
B09B	CTDE	0.41	0.86	-0.47	2.21	
B10T	CTDE	0.73	0.91	-0.20	3.03	
B10B	CTDE	0.35	0.85	-0.52	1.77	
B11T	CTDE	0.81	0.92	-0.14		
B11B	CTDE	0.79	0.92	-0.15	2.32	
B12T	CTDE	1.01	0.95	0.04	1.61	
B12B	CTDE	0.92	0.94	-0.04	1.44	
B13T	CTDE	0.95	0.94	-0.02		
B13B	CTDE	0.93	0.94	-0.03		

Table IX.10: Suspended particulate matter and chlorinity-salinity CH72 (continued)

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH72.WK1
SHEET 6: log10 Kd-VALUES
CH42: HUMBER PLUME CRUISE I

log 10 values of ratio of nmol/kg sediment to nmol/l water

CODE	TYP	MNkd	FEkd	NIkd	COkd	CUkd	ZNkd	CDkd	PBkd
A01T	CTDA	4.81	6.68	3.51	4.38	4.25	4.66	5.06	5.42
A01B	CTDA	4.67	6.75	3.39	4.21	4.23	4.50	4.99	5.52
A02T	CTDA	4.74	6.08	3.34	4.26	4.17	4.52	5.02	5.27
A02B	CTDA	4.51	6.33	3.16	4.05	4.00	4.35	4.98	5.51
A03T	CTDA	4.72	6.66	3.33	4.21	4.13	4.52	5.07	5.41
A03B	CTDA	4.80	7.02	3.44	4.31	4.20	4.62	5.13	5.56
A04T	CTDA	4.82	6.71	3.45	4.36	4.23	4.62	5.19	5.50
A04B	CTDA	4.69	5.96	3.31	4.21	4.21	4.59	5.05	5.51
A05T	CTDA	4.73	6.61	3.35	4.26	4.16	4.59	5.08	5.42
A05B	CTDA	4.81	6.82	3.42	4.36	4.38	4.71	5.21	5.50
A06T	CTDA	4.64	6.39	3.34	4.18	4.09	4.50	5.00	5.42
A06B	CTDA	4.64	6.25	3.39	4.19	4.18	4.62	5.14	5.36
A07T	CTDA	4.67	6.90	3.37	4.23	4.12	4.59	4.70	5.27
A07B	CTDA	4.60	6.95	3.36	4.18	4.18	4.55	4.60	5.32
A08T	CTDA	4.72	6.81	3.47	4.27	4.30	4.63	4.87	5.53
A08B	CTDA	4.71	7.09	3.40	4.22	4.16	4.61	4.82	5.40
A09T	CTDA	4.58	6.92	3.44	4.28	4.22	4.64	5.13	5.72
A09B	CTDA	4.48	6.74	3.42	4.22	4.22	4.60	4.92	5.52
A10T	CTDA	5.06	7.07	3.48	4.29	4.48	4.64	5.04	5.72
A10B	CTDA	5.03	6.19	3.36	4.23	4.19	4.58	4.88	5.54
A11T	CTDA	5.19	6.85	3.53	4.38	4.41	4.73	5.18	5.76
A11B	CTDA	5.06	6.71	3.40	4.26	4.13	4.66	5.06	5.74
A12T	CTDA	5.03	6.18	3.34	4.24	4.14	4.60	4.92	5.55
A12B	CTDA	4.74	5.90	3.47	4.25	4.20	4.64	5.02	5.38
A13T	CTDA	4.77	6.76	3.39	4.30	4.11	4.68	5.12	5.66
A13B	CTDA	4.75	6.50	3.41	4.25	4.12	4.64	5.02	5.59
T1	CTD	5.58	7.33	3.44	4.41	4.08	4.95	4.91	5.68
T2	CTD	5.33	7.18	3.36	4.40	4.22	4.58	4.87	5.52
T3	CTD	5.78	7.11	3.83	4.41	4.19	5.01	4.91	5.74
T5	CTD	6.57	6.92	4.04	4.94	4.20	5.28	5.04	5.96
T7	CTD	6.54	6.96	4.02	4.87	4.31	5.38	5.00	6.01
N2	CTD	6.63	7.07	3.73	4.77	4.03	4.86	4.52	5.54
N3	CTD	6.62	7.39	3.54	4.80	3.90	4.89	4.25	5.60
N5	CTD	6.25	6.64	3.77	4.77	4.12	5.15	4.58	5.59
N7	CTD	6.19	6.72	3.76	4.77	4.38	5.34	4.70	5.65
Y6	CTD	5.88	6.68	3.97	4.53	4.21	5.01	4.75	5.45
Y4	CTD	6.39	7.16	3.67	4.86	4.35	5.09	4.80	5.75
Y3	CTD	6.23	7.27	3.62	4.85	4.36	4.98	4.66	5.56
Y2	CTD	6.03	7.89	3.70	5.10	3.95	4.95	4.60	5.55
E5	CTD	6.02	6.83	3.75	4.87	3.23	4.95	4.72	6.13
E3	CTD	6.19	7.02	3.60	4.82	4.04	5.02	4.71	6.32
G6	CTD	6.80	7.46	3.63	5.09	3.97	4.51	4.52	5.40
G4	CTD	6.72	6.98	3.60	5.30	3.89	4.62	4.46	6.47
G3	CTD	6.54	6.90	3.41	4.95	3.59	4.84	4.43	6.20
S1	CTD	6.71	7.01	3.58	5.22	4.11	4.81	4.52	6.24
S2	CTD	6.95	7.15	3.47	5.24	3.83	4.42	4.24	5.49
B01T	CTDE	6.74	7.54	3.87	5.25	4.19	5.32	4.90	6.50
B01B	CTDE	6.65	6.91	3.72	4.86	3.91	4.85	4.52	6.21
B02T	CTDE	6.96	7.15	3.78	5.14	4.13	5.15	4.81	6.35
B02B	CTDE	6.59	6.78	3.12	4.72	3.65	4.94	4.36	6.01

Table IX.11: K_d-distribution coefficients CH72

NORTH SEA PROJECT DATA BASE (SUDO) FILE: CH72.WK1
SHEET 6: log10 Kd-VALUES
CH42: HUMBER PLUME CRUISE I

log 10 values of ratio of nmol/kg sediment to nmol/l water

CODE	TYP	MNkd	FEkd	NIkd	COkd	CUkd	ZNkd	CDkd	PBkd
B03T	CTDE	6.37	7.67	3.43	4.82	3.93	4.83	4.30	6.41
B03B	CTDE	6.17	7.15	3.16	4.65	3.83	4.83	2.35	6.01
B04T	CTDE	6.17	6.96	3.36	4.70	3.26	4.68	4.33	5.87
B04B	CTDE	6.33	7.49	3.60	4.91	3.77	4.91	4.42	6.20
B05T	CTDE	6.26	6.88	3.36	4.75	4.09	4.79	4.49	6.12
B05B	CTDE	6.23	6.93	3.31	4.78	3.45	4.75	4.46	6.44
B06T	CTDE	6.19	6.75	3.70	4.85	3.91	4.91	4.49	6.30
B06B	CTDE	6.17	6.90	3.61	4.78	3.90	4.87	4.47	6.20
B07T	CTDE	6.17	6.83	3.61	4.69	3.83	4.89	4.43	6.25
B07B	CTDE	6.36	7.06	3.54	4.97	4.07	5.02	4.66	6.70
B08T	CTDE	6.19	7.01	3.46	4.80	3.79	4.97	4.47	6.37
B08B	CTDE	6.37	6.61	3.92	4.96	3.97	5.22	4.55	6.30
B09T	CTDE	6.21	6.50	3.39	4.69	3.50	4.92	4.44	6.12
B09B	CTDE	6.32	6.67	3.63	4.84	3.78	5.12	4.52	5.95
B10T	CTDE	6.30	6.77	3.68	4.86	3.75	5.02	4.43	6.41
B10B	CTDE	6.38	6.76	2.93	4.83	3.80	5.07	4.53	6.22
B11T	CTDE	6.34	6.66	3.85	4.89	3.84	5.18	4.64	6.29
B11B	CTDE	6.37	7.25	3.71	4.99	3.92	5.02	4.59	6.27
B12T	CTDE	6.32	7.06	3.42	4.84	3.90	4.98	4.48	6.27
B12B	CTDE	6.27	7.52	3.61	4.85	3.86	5.26	4.32	6.68
B13T	CTDE	6.19	6.82	3.67	4.78	3.77	5.09	4.18	6.13
B13B	CTDE	6.24	6.93	3.55	4.80	3.76	4.99	4.36	6.28

Table IX.12: K_d-distribution coefficients CH72 (continued)