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Processes Influencing the Fate of Trace Metals in the North Sea [and Discussion]

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Processes influencing the fate of trace metals in the North Sea

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Measurements were made in the southern North Sea of trace metals (dissolved and particulate Mn, Fe, Ni, Co, Cu, Zn, Cd, Pb) with contrasting biogeochemical behaviours. The extent to which distributions of dissolved metals over the survey area were determined by the mixing of river waters with seawater varied among the metals, and also seasonally; even for nickel and copper, which behaved most conservatively, other processes were significant. Specific instances of the effects of scavenging by particles and of inputs from benthic recycling are evident from the data and these processes lead generally to modifications of fluxes of dissolved metals in estuarine plumes. While the effect of atmospheric inputs on dissolved concentrations of metals is, on the basis of other evidence, a factor contributing to spatial and temporal variability, specific features arising from them were not identified; they probably account, however, for increased concentrations of dissolved lead observed at high salinities in the Humber plume. Seasonal variations in concentrations of dissolved metals, paralleling those of micronutrients, were not identified but manganese showed a pronounced seasonal variability related to its reduction–oxidation chemistry. Wide differences occurred in the partition between dissolved and particulate fractions, although for copper and zinc the partition could be described by a narrow range of distribution coefficients under certain conditions.

1. Introduction

Of the categories of constituents entering the North Sea, trace metals have been among the most investigated (Kersten *et al.* 1988). This reflects the geochemical importance of some of these elements and the significance of others as potential pollutants. Application to this environment of clean sampling and analytical methods, necessary to obtain accurate measurements at low concentrations of metals, is, however, comparatively recent (see, for example, Mart *et al.* 1980). Most investigations have focused on the estuarine environments and coastal region of the Southern and German Bights (Kersten *et al.* 1988). Much less attention has been given to western coastal waters (see, for example, Balls 1985*a*; Harper 1988) and information remains sparse on shelf waters remote from coastal influence despite several studies (Balls 1985*b*; Kremling *et al.* 1987). As a consequence there has been a limited basis on which to evaluate the relative importance of processes determining

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the distributions and transfers of metals; such an evaluation is essential if these constituents are to be incorporated into water quality models for the North Sea.

The NERC North Sea Project (NSP) afforded an opportunity to investigate systematically a group of trace metals in the water column of a large sector of the North Sea, including the major areas directly influenced by river discharge. The metals investigated were chosen to represent a variety of biogeochemical characteristics. Manganese, iron and lead, and to some extent cobalt, are particle-reactive metals. The aquatic chemistry of manganese is strongly influenced by reduction–oxidation reactions, with highly dynamic cycling associated with the mobilization into solution of the metal as Mn(+II), where reduction occurs, and its conversion to Mn(+III) and Mn(+IV), which are of much more limited solubility, in environments which are oxidizing for manganese. While iron has a somewhat similar reduction–oxidation chemistry, Fe(+II) is more rapidly oxidized than Mn(+II) and is thus less mobile in oxygenated waters or sediments. Nickel, copper, zinc and cadmium are less particle reactive although in the stratified open ocean their concentrations are influenced by down-column transport in association with biogenous particulate material, a behaviour which is particularly marked for zinc and cadmium. Of the metals studied, cadmium is on the U.K. Priority Red List of substances of concern in relation to discharge to the North Sea; copper is also particularly important from the standpoint of potential ecotoxicological effects (Langston 1990).

The importance of having simultaneous information on both dissolved and particulate fractions of metals, to constrain interpretations of results for coastal waters, has become well recognized (Balls 1988) but of the investigations in the North Sea, very few have provided such data and indeed information of this kind is scarce for any coastal or shelf environment. In this work the particulate fractions of metals were measured on a substantial proportion of the samples analysed for dissolved metals.

Continuous methods for the measurement of trace metals are still under development and the procedures available considerably restrict the number of analyses which can be made. Although the spatial and temporal resolution is thus inferior to that attainable for some other constituents, the NSP database for trace metals is believed to be the most comprehensive for any shelf region. This paper illustrates some of the principal features observed and discusses the processes which can give rise to them.

2. Field sampling and analytical methods

Seawater samples were collected during four cruises of RRS *Challenger* (CH33/88, August 1988; CH43/88, December 1988 to January 1989; CH51/89, April to May 1989; CH61/89, September to October 1989) from stations along the NSP survey track. These are referred to as the mid-summer, winter, spring, and late-summer cruises, respectively. Further samples were collected during cruises that focused on the Thames (CH46/89, February 1989) and Humber (CH42/88, December 1988) plumes; additional studies on the Thames, Humber and Rhine plumes were undertaken in 1990 (Althaus 1992).

All samples were collected and analysed using clean techniques. Dissolved and particulate fractions of metals were separated by pressure filtration through 0.4 μm Nuclepore filters. Concentrations in suspended particulate material (SPM) refer to the metals leached by 1 M hydrochloric acid. Dissolved metals were determined by solvent extraction of dithiocarbamate complexes, followed by graphite furnace atomic absorption spectrophotometry. Methods for clean sampling and shipboard handling, including filtration, have been described by Morley *et al.* (1988); details of the analytical procedures for particulate and dissolved metals, respectively, are given in Turner *et al.* (1991) and Tappin (1988). Within batch analytical precisions of the methods for particulate and dissolved metals are less than 10% (relative standard deviation); accuracy for dissolved metals was verified by regular analyses of a standard reference coastal sea water sample (CASS-1 supplied by the National Research Council of Canada).

3. Results and discussion

(*a*) *Role of water mixing in determining the concentrations of dissolved metals*

Major fluxes of dissolved metals into the southern North Sea are associated with the inputs of fresh water by rivers and of sea water from the English Channel and the northern North Sea. The large difference in concentrations of the metals investigated between shelf waters of high salinity and river waters entering the southern North Sea is exemplified by the data in table 1. A convenient starting point for interpretation of the distributions of the dissolved metals is to consider the extent to which they behave conservatively during the mixing of these different water bodies. The concentrations of metals in coastal waters will often be influenced by the mixing of several river waters and saline end-members, which can also vary temporally in composition. This will lead to scatter in the property–salinity relationships used to evaluate the extent to which behaviour is conservative. To reduce the scatter, relationships have been examined, using the data from the four surveys, for different hydrographic regimes of the North Sea which may be identified on the basis of salinity and other parameters, following the approach of the International Commission for the Exploration of the Sea (1983). The four zones are described as English coastal, English Channel/Thames, Continental coastal, and central North Sea waters; there were small variations among the surveys in the location of the boundaries of these zones.

Linear regression analysis showed that there were statistically significant ($P < 0.05$) inverse relationships with salinity for every metal in at least one of the 16 groups of data, but it was only for copper, and to a lesser extent, nickel, that salinity accounted for a major or dominant part of the variance in the majority of cases. For the English Channel/Thames zone, the only significant relationship was for copper in spring; the general lack of significant relationships in this region probably reflects the small number of samples from the zone and their narrow range of salinity. For the central North Sea waters, such relationships were more frequent, but only for copper in winter did salinity account dominantly for the variance ($r^2 = 0.52$). The influence of fresh water was clearer in the two coastal zones. Thus in the English coastal water in winter, the values of r^2 for cadmium, zinc and nickel were, respectively, 0.70, 0.63 and 0.58. In the continental coastal water, values of r^2 for copper for the four cruises ranged from 0.47 to 0.76, those for nickel from 0.31 to 0.75. The particle reactive metals (Mn, Fe, Co, Pb) showed few significant relationships overall and where these occurred salinity generally accounted for only a minor part of the variance.

These results show that the concentrations of all the metals examined, but

Table 1. *Concentrations of dissolved trace metals in the central zone of the southern North Sea and in the Rhine Estuary*

(Concentrations are in nmol dm^{-3}. The concentration given for the central zone of the southern North Sea (see text) is the mean, with standard deviation, for the winter cruise; data for the Rhine Estuary are from Althaus (1992).)

element	Mn	Fe	Co	Ni
Central southern North Sea ($S > 34.5$)	6.2 ± 7.0	3.4 ± 2.5	0.16 ± 0.10	4.3 ± 2.5
Rhine Estuary ($S = 2.4$–7.6)	330–460	16–250	3.2–4.1	40–57
element	Cu	Zn	Cd	Pb
Central southern North Sea ($S > 34.5$)	2.8 ± 2.0	3.7 ± 2.0	0.17 ± 0.07	0.11 ± 0.06
Rhine Estuary ($S = 2.4$–7.6)	28–39	120–180	0.21–0.63	0.6–1.1

particularly the more particle-reactive metals, were substantially influenced by factors other than conservative mixing of river and sea waters, namely particle–solution interactions and non-riverine (benthic and atmospheric) inputs. Since the zones considered here are still relatively large and subject to the influence of several river inputs, the total effect of these factors is compounded with variability due to the hydrographic factors already discussed.

The intensive studies on specific estuarine plume regions provide a more constrained basis for interpretation. Measurements on the Thames Estuary and adjacent waters in February 1989 showed that in the topographically restricted inner estuary, over a salinity range from 5.0 to 31.3, the concentrations of dissolved nickel, cobalt, copper, zinc, cadmium and lead were dominantly controlled by conservative mixing over most of the transect. Greater divergence from this behaviour was apparent in the results from sampling over a tidal cycle at a fixed station, during which large variations in the concentration of SPM occurred, indicative of sediment resuspension and consequent benthic exchanges. Addition of manganese occurred over the lower part of the salinity range, an estuarine feature generally caused by inputs from reducing sediments (Burton 1988). Above a salinity of 20, iron was generally depleted relative to the values predicted for conservative mixing. This probably reflects scavenging by SPM which showed a maximum concentration in the salinity range 21–22.

Results from regression analysis of the relationships between metal concentrations and salinity for the inner Thames Estuary and for the outer estuary and plume, with salinities in the range from 32.4 to 35.0, are given in table 2. For nickel, the intercepts at zero salinity, which represent the effective concentration of the metal in the freshwater end-member of the mixing series, were similar for both data-sets; the values of r^2 were also similar. The flux of nickel through the estuarine plume region was thus little modified relative to that through the inner estuary. The plume region appears, however, to be a zone of net removal for lead and iron, and of net addition for the other metals. Net removal is attributable to particle scavenging; while net addition may be attributable in part to release from particles, it can also occur by inputs at the benthic and atmospheric boundaries. The values of r^2 for the plume

Table 2. *Results from regressions of dissolved trace metals on salinity for the Thames Estuary, February 1989*

metal	estuarine zone	number of samples	intercept $S = 0$ nmol dm^{-3}	regression coefficient	r^2
Mn	inner[a]	22	100 ± 9	-2.3 ± 0.4	0.63
	outer[b]	44	150 ± 51	-4.3 ± 0.6	0.54
Fe	inner	22	350 ± 40	-11 ± 2	0.68
	outer	42	100 ± 51	-2.7 ± 1.5	0.08
Ni	inner	19	260 ± 14	-7.3 ± 0.6	0.91
	outer	43	300 ± 20	-8.3 ± 0.6	0.83
Co	inner	22	7.2 ± 0.2	-0.19 ± 0.01	0.97
	outer	43	11 ± 2	-0.32 ± 0.05	0.53
Cu	inner	22	120 ± 6	-3.0 ± 0.3	0.88
	outer	39	330 ± 46	-9.2 ± 1.3	0.56
Zn	inner	22	650 ± 30	-16 ± 1	0.89
	outer	43	1000 ± 70	-30 ± 2	0.85
Cd	inner	18	2.3 ± 0.1	-0.055 ± 0.004	0.90
	outer	44	3.4 ± 0.5	-0.09 ± 0.01	0.53
Pb	inner	22	20 ± 1	-0.64 ± 0.04	0.93
	outer	44	8.2 ± 0.7	-0.23 ± 0.02	0.77

[a] Salinity range: 5.0–31.3. [b] Salinity range: 32.4–35.0.

region are lower than for the inner estuary but generally a more coherent influence of fresh water is seen than for the larger zones discussed earlier.

Results for the Humber Estuary and the Humber–Wash plume are broadly consistent with the findings for the Thames although detailed differences occurred between the two systems and among three periods during which the Humber system was investigated. There was evidence for removal of dissolved zinc in the Humber plume region relative to the flux from the estuary. The particle reactive metals, manganese, iron, cobalt and lead, were dominantly influenced by processes other than conservative mixing. Within the estuary, inputs of dissolved manganese, iron and cobalt were clearly identifiable in the salinity range 26–31. A notable feature in the plume region is an increase in the average concentration of dissolved lead above a salinity of about 33.5, the concentrations increasing for example in December 1988 from an average of 0.10 ± 0.03 nmol dm^{-3} in the salinity range 32.5–33.5 to 0.20 ± 0.17 nmol dm^{-3} at salinities close to 34.5. This feature, which was also observed by Balls (1985*a*), is believed to reflect the combined effects of the less efficient scavenging in water of high salinity with lower concentrations of SPM, and additional atmospheric inputs of lead to these waters.

(*b*) *Relationships between particulate and dissolved metals*

The variations in the concentrations of particulate metals in estuaries, coastal and shelf waters arise through differences in the total concentration of SPM and in the composition of the particles. Large fluctuations are therefore attributable not only to the sources and transport of riverine and marine particles but also the resuspension and settling of sediment. The distribution of a metal between solution and particles is determined by its concentration in solution and in SPM, and the total concentration of SPM. Partition between solution and SPM is expressed by the distribution coefficient K_d, the ratio of the concentration of the metal per unit mass of particulate matter to the concentration of the metal per unit mass of sea water; frequently the

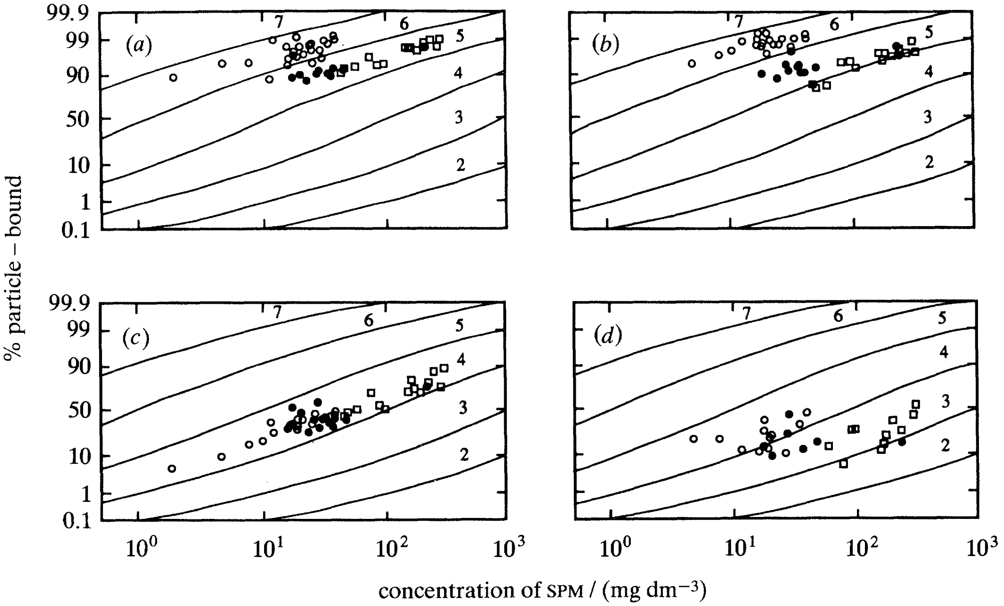

Figure 1. The partition of trace metals between the dissolved and suspended particulate fractions in relation to the concentration of SPM: results for the Thames Estuary, February 1989 for (*a*) Mn, (*b*) Pb, (*c*) Cu, and (*d*) Cd. Samples from the inner and outer estuaries (see table 2) are indicated, respectively, by filled and open circles; squares indicate samples taken over a tidal cycle in the estuary, salinities ranging from 19.2 to 25.8.

dissolved concentration per unit volume is used and this will not significantly alter the numerical values. If equilibrium existed between the particulate metal and that in solution the fraction in solution under a wide range of conditions could be predicted from a knowledge of the appropriate value of K_d. In practice the partition between the phases often varies widely because of differences in the characteristics of SPM, such as bulk composition and particle size. Differences in chemical speciation in either phase may also affect the partition. Kinetic factors are important in many reactions at particle surfaces, e.g. in the oxidative scavenging of manganese (Yeats & Strain 1990). Moreover, analytical determinations of particulate metals provide only a first-order measure of the fraction of the particle-associated metal available for exchange. The value of K_d therefore often describes the distribution empirically without the implication that the metal is equilibrated between phases.

Figure 1 shows, for the Thames Estuary, the relationship between the concentration of SPM and the fraction of the total metal (dissolved plus acid-leachable particulate) which is associated with SPM; the use of a probability scale for the latter has been adopted to provide a better resolution of points which fall within a narrow linear range. Lines of constant log K_d are shown in figure 1 and it is clear that for manganese and lead the observed distribution coefficients exhibit large differences between the inner estuary and the plume region. Within these regions differences occur but they are generally smaller. These features apply also to the other metals (Fe, Ni, Co, Zn) which are not illustrated here. Thus, for all the metals except copper and cadmium the distribution coefficient is about ten times lower in the inner than in the outer estuary. Investigations of a number of North Sea estuaries (Turner *et al.* 1991) have shown that the concentrations of trace metals in SPM generally decrease seawards due to mixing of riverine and marine particles. In the Thames Estuary systematic changes in the concentrations of metals in SPM along the salinity gradient are relatively small (Turner *et al.* 1991). The average concentrations of metals in the SPM from the inner estuary and the plume region are also generally similar but clear differences are apparent for copper (means for inner estuary and plume, 46 ± 10 and 18 ± 4 µg g^{-1} respectively) and zinc (154 ± 23 and 87 ± 10 µg g^{-1}).

The observed differences in distribution coefficients within the estuary-plume system may be partly attributable to different properties of SPM and the additional factor of markedly higher concentrations of dissolved metals in the inner estuary. The data for cadmium for the inner estuary and plume samples show no systematic change in the fraction of the metal associated with particles over the ranges of concentration of SPM. The results for dissolved cadmium are consistent with some degree of desorption with increasing salinity, a process which has been observed with this metal in some other estuaries (Elbaz-Poulichet *et al.* 1987). This probably explains at least part of the difference between the behaviour of cadmium and other metals. A significant exception to the wide variability of distribution coefficients is seen with copper for which the observed values fall within a comparatively narrow range; this is apparent also in the Humber and, to a lesser extent, the Rhine plumes (Althaus 1992).

Examination of the corresponding plots for the survey cruises shows that under winter conditions, iron and lead are dominantly associated with solid phases over the whole range of concentrations of SPM; this generally applies also to manganese but the range of distribution coefficients increases markedly at lower concentrations of SPM with the dissolved fraction dominating in some samples. For all three metals, wide variations in log K_d are apparent. Copper and zinc, for which the dissolved fraction dominates at all but the highest concentrations of SPM, show values close to 4.5 and 5.0 respectively over much of the range of concentrations of SPM, but with a tendency towards higher values at low concentrations of SPM. It is only for these metals and in winter that the use of a single K_d value would enable a reasonable prediction to be made of the partitioning between particles and solution. In spring, greater variability is evident and for zinc, at least, log K_d values are lower, mostly between 4.5 and 5.0. A tendency to lower and more variable distribution coefficients is apparent also for the particle-reactive metals in the spring survey. Manganese, in particular, shows a wide scatter in the relation of partition between solution and particles to the concentration of SPM.

The change in distribution coefficients from winter to spring is attributable both to increases in dissolved concentrations as discussed below, and to variations in the nature of SPM. For all the metals examined, except copper and possibly cadmium, a marked decrease in the concentration of the element in SPM was evident between the surveys. This may reflect the dilution of the lithogenous component of SPM with biogenous particles. The range in chlorophyll *a* concentrations had increased from the winter values of 0.3–1.5 µg dm^{-3} to 0.5–32 µg dm^{-3} at the time of the spring cruise. During the late-summer cruise chlorophyll *a* concentrations were towards the lower end of the range 0.3–24 µg dm^{-3} and there was a slight increase in distribution coefficients.

(*c*) *Seasonal variability in concentrations of dissolved metals*

Temporal variations were apparent in the effective freshwater end-member concentrations derived from measurements at different periods in the estuaries and plumes of the Thames and Humber. For nickel, which behaved largely con-

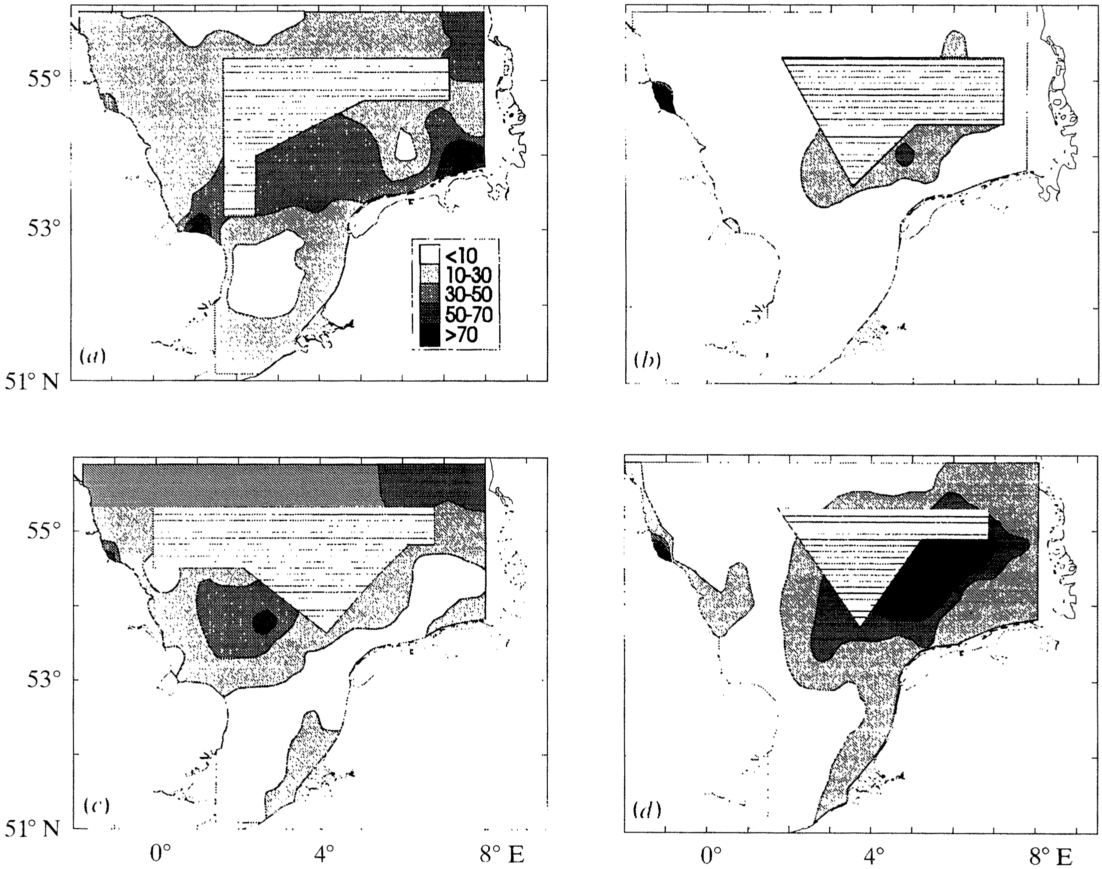

Figure 2. Temporal variations in the concentrations (nmol dm^{-3}) of dissolved manganese: results of survey cruises (*a*) August 1988, (*b*) December 1988 to January 1989, (*c*) April to May 1989, and (*d*) September to October 1989. Within the areas enclosed by straight lines contouring is not considered meaningful because of the lack of sampling points.

servatively, values extrapolated from plume measurements varied by a factor of less than two. For the particle-reactive metals larger changes were found reflecting variability in processes leading to addition or removal, as well as any changes in the actual concentration in river water. Although these differences are locally important they cannot account for the temporal changes seen for some metals in waters remote from the immediate influence of estuarine inputs. Other inputs, from benthic and atmospheric sources, and *in situ* processes leading to changes in concentration, must be considered.

For the particle-reactive metals, large overall ranges in concentration were found with localized features often apparent. For example, the concentrations of dissolved manganese varied overall by a factor of 400. This metal nevertheless showed well defined seasonal changes in dissolved concentrations, although with some differences in their pattern within the survey area (figure 2). Concentrations in winter were low (generally less than 10 nmol dm^{-3}) except at two stations, one close to the mouth of the Tees, the other in the area of the Oyster Grounds, at *ca.* 54° N, 5° E. For each of the four zones there was an increase in mean concentration in the spring which was particularly marked in the central North Sea, and in the northeastern part of the Continental coastal zone. High concentrations were found along the whole of the northern transect at this time and concentrations were an order of magnitude higher than in winter at a group of stations in the area of the Outer Silver Pit (*ca.* 54° N, 2° E). These changes were associated with increases in concentrations of iron, zinc and cadmium, and to a lesser extent, in that of lead. The spring increase was evident in the area adjoining the Rhine, Meuse and Scheldt estuaries but in the extensive area of *Phaeocystis pouchetti* blooms in the Southern Bight concentrations of dissolved manganese remained relatively low.

In the central North Sea, the increase in the concentration of dissolved manganese in spring was accompanied by a marked increase in concentration of dissolved iron. Generally the concentrations of both these metals were higher in deeper waters. The increases are considered to be due to enhanced benthic fluxes associated with changes in the reduction–oxidation conditions in sediments caused by deposition of planktonic material (Jago *et al.*, this symposium). The sedimentation of material from the diatom bloom before the time of the spring observations is evidenced by the occurrence of low concentrations of dissolved silicon and of chlorophyll *a* in surface waters but elevated concentrations of chlorophyll *a* in some deeper water samples; increased concentrations of dissolved ammonium at some stations support the hypothesis. Dehairs *et al.* (1989) attributed enrichment of iron and manganese in SPM after the spring bloom in the North Sea to benthic fluxes of the dissolved metals followed by uptake by particles. The results of the present work for these metals in SPM (see above) are generally consistent with those of Dehairs *et al.* with some differences in the timing of seasonal changes. Increased dissolved concentrations of particle-reactive metals in spring or summer have been reported also for the English Channel (Tappin *et al.* 1993) and the shelf waters of the Gulf of Lions (Morley *et al.* 1990).

At the time of the late-summer (1989) survey, particularly high concentrations of dissolved manganese were associated with an area (*ca.* 54–55° N, 4–7° E) which includes the Oyster Grounds and Elbe Rinne. This feature coincides with elevated concentrations of dissolved silicon and ammonium and occurs in waters overlying extensive mud and sandy mud deposits (Eisma & Kalf 1987). The results of the mid-summer (1988) cruise show relatively high concentrations only in the western part of this area; the occurrence of a high concentration in winter at a station in the Oyster Grounds has already been noted.

Pronounced systematic seasonal variations in the concentrations of the other metals were not found over the survey area although some significant changes in mean concentrations occurred between seasons within particular zones. Concentrations of dissolved cadmium and zinc increased in the spring, not only along the northern transect as already noted, but also in the Southern Bight and adjacent waters where blooms of *Phaeocystis pouchetti* were abundant. Although these metals and, to a lesser extent, nickel and copper, develop nutrient-like profiles in the water column of the stratified ocean, the coupling of their cycles to the utilization and regeneration of nutrients in the North Sea is not detectable. This confirms the findings from less extensive measurements made by Kremling *et al.* (1987) and accords with observations on the English Channel (Tappin *et al.* 1993). Because of the relatively high concentrations of cadmium and zinc in shelf waters, the uptake of these metals by plankton, which is demonstrated by studies using radioactive tracers (Turner *et al.* 1992), does not produce sufficient depletion for the effects to be seen against the variations due to external inputs and those due to recycling.

4. Conclusions

Processes other than conservative mixing of river and sea waters must be taken into account to explain the distributions within the North Sea of the trace metals considered here. The data provide clear evidence for the roles of particle scavenging and inputs from benthic recycling. Atmospheric inputs of metals are a potential additional source but they occur with considerable short-term variability (Chester *et al.*, this symposium); identification from the present observations of specific enhancements due to these inputs is thus problematic although an influence on the distribution of lead in the Humber plume is probable. Processes in estuarine plumes can substantially modify the fluxes of most dissolved metals to shelf waters.

Manganese is a valuable indicator of benthic recycling processes. For this metal benthic inputs led to a clear seasonal variability in dissolved concentrations which was paralleled to a lesser degree by other particle-reactive metals. Seasonal changes in dissolved concentrations of metals directly coupled to those of the micronutrients were not observable; this reflects the relatively high concentrations and the difficulty of identifying small changes against the background of other processes.

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References

Althaus, M. 1992 Dissolved trace metals in the estuarine plumes of the Humber, Thames and Rhine rivers. (331 pp.) Ph.D thesis, University of Southampton.

Balls, P. W. 1985*a* Copper, lead and cadmium in coastal waters of the western North Sea. *Mar. Chem.* **15**, 363–378.

Balls, P. W. 1985*b* Trace metals in the northern North Sea. *Mar. Poll. Bull.* **16**, 203–207.

Balls, P. W. 1988 The control of trace metal concentrations in coastal seawater through partition onto suspended particulate matter. *Neth. J. Sea Res.* **22**, 213–218.

Burton, J. D. 1988 Riverborne materials and the continent-ocean interface. In *Physical and chemical weathering in geochemical cycles* (ed. A. Lerman & M. Meybeck), pp. 299–321. Dordrecht: Kluwer.

Dehairs, F., Baeyens, W. & Van Gansbeke, D. 1989 Tight coupling between enrichment of iron and manganese in North Sea suspended matter and sedimentary redox processes: evidence for seasonal variability. *Est. coast. Shelf Sci.* **29**, 457–471.

Eisma, D. & Kalf, J. 1987 Dispersal, concentration and deposition of suspended matter in the North Sea. *J. geol. Soc. Lond.*. **144**, 161–178.

Elbaz-Poulichet, F., Martin, J. M., Huang, W. W. & Zhu, J. X. 1987 Dissolved Cd behaviour in some selected French and Chinese estuaries. Consequences on Cd supply to the ocean. *Mar. Chem.* **22**, 125–136.

Harper, D. J. 1988 Dissolved cadmium and lead in the Thames Estuary. *Mar. Poll. Bull.* **19**, 535–538.

International Commission for the Exploration of the Sea 1983 *Flushing times of the North Sea.* ICES Cooperative Research Rep. no. 123, 159 pp.

Kersten, M. *et al.* 1988 Distribution and fate of heavy metals in the North Sea. In *Pollution of the North Sea. An assessment* (ed. W. Salomons, B. L. Bayne, E. K. Duursma & U. Förstner), pp. 300–347. Berlin: Springer-Verlag.

Kremling, K., Wenck, A. & Pohl, C. 1987 Summer distribution of dissolved Cd, Co, Cu, Mn, and Ni in central North Sea waters. *Deutsche Hydrographische Z.* **40**, 103–114.

Langston, W. J. 1990 Toxic effects of metals and the incidence of pollution in marine systems. In *Heavy metals in the marine environment* (ed. R. W. Furness & P. S. Rainbow), pp. 101–122. Boca Raton, Florida: CRC Press.

Mart, L., Nürnberg, H. W. & Valenta, P. 1980 Comparative baseline studies on Pb levels in European coastal waters. In *Lead in the marine environment* (ed. M. Branica & Z. Konrad), pp. 155–179. Oxford: Pergamon Press.

Morley, N. H., Fay, C. W. & Statham, P. J. 1988 Design and use of a clean shipboard handling system for seawater samples. *Adv. underwater Technol. Ocean Sci. Offshore Engng* **16**, 283–289.

Morley, N. H., Burton, J. D. & Statham, P. J. 1990 Observations on dissolved trace metals in the Gulf of Lions. *Water Poll. Res. Rep.* no. 20, 309–328.

Tappin, A. D. 1988 Trace metals in shelf seas of the British Isles. (279 pp.) Ph.D thesis, University of Southampton.

Tappin, A. D., Hydes, D. J., Statham, P. J. & Burton, J. D. 1993 Concentrations, distributions and seasonal variability of dissolved Cd, Co, Cu, Mn, Ni, Pb and Zn in the English Channel. *Cont. Shelf Res.* (In the press.)

Turner, A., Millward, G. E. & Morris, A. W. 1992 Particulate metals in five major North Sea estuaries. *Est. coast. Shelf Sci.* **32**, 325–346.

Turner, A., Millward, G. E., Bale, A. J. & Morris, A. W. 1992 The solid–solution partitioning of trace metals in the southern North Sea – *in situ* radiochemical experiments. *Cont. Shelf Res.* **12**, 1311–1329.

Yeats, P. A. & Strain, P. M. 1990 The oxidation of manganese in seawater: rate constants based on field data. *Est. coast. Shelf Sci.* **31**, 11–24.

Discussion

P. Balls (*SOAFD Marine Laboratory, Aberdeen, U.K.*). Given that biologically related seasonal variations are apparent for dissolved metals such as Cd in the Baltic, is the absence of such variation in the data related to the relatively short water residence times in the study area?

J. D. Burton. Given the fact that marked seasonal depletion of nutrients occurs in both environments, water residence time will be a potentially significant factor when the metals released in the decomposition of biological material with which they have become associated are not restored to the biologically productive surface waters on the timescale of the seasonal cycle of primary productivity. How important this may be in relation to possible differences between the North and Baltic Seas is uncertain from present evidence, and indeed the extent of any differences between the systems in seasonal variability of concentrations of trace metals, is not unequivocally established. The results of Kremling & Petersen (1978) for a station in the Bornholm Sea suggest a similar situation to that in the North Sea; no significant depletions of copper, zinc or cadmium were observed in the upper layers of a strongly stratified water column in which a diatom bloom had occurred. From a simplified model of uptake of metals by phytoplankton, it was concluded that any effects on the concentrations of these metals were too small to be detected. A comparison of surface transects in the Baltic Sea at two different seasons (but not in the same year or in consecutive years) did, however, show significant differences in concentrations of nickel, copper and cadmium, correlated with changes in concentrations of phosphate and nitrate (Kremling 1988).

Additional references

Kremling, K. 1988 Metal cycles in coastal environments. In *Metals in coastal environments of Latin America* (ed. U. Seeliger, L. D. de Lacerda & S. R. Patchineelam), pp. 202–214. Berlin: Springer-Verlag.

Kremling, K. & Petersen, H. 1978 The distribution of Mn, Fe, Zn, Cd and Cu in Baltic seawater: a study on the basis of one anchor station. *Mar. Chem.* **6**, 155–170.

A. R. D. Stebbing (*Plymouth Marine Laboratory, U.K.*). To what extent does the conclusion that the transport of particulate material determines the fate of metals also apply to persistent organic microcontaminants like some pesticides?

J. D. Burton. As with the metals, the fractions of persistent organic micropollutants associated with SPM depend on the distribution coefficient for the compound and the concentration of SPM. The spatial distributions of organic compounds of low solubility in water are strongly influenced by sediment transport. These compounds include high molecular mass polycyclic aromatic hydrocarbons, polychlorinated biphenyls with higher degrees of chlorine substitution, hexachlorobenzene, dieldrin and compounds of the DDT group. The situation is different for more polar compounds; for example, transport in solution is reported to be a major factor influencing the distributions of α-hexachlorocyclohexane and lindane (Lohse 1988).

Additional reference

Lohse, J. 1988 Distribution of organochlorine pollutants in North Sea sediments. *Mitt. Geol.-Paläont. Inst. Univ. Hamburg* **65**, 345–365.

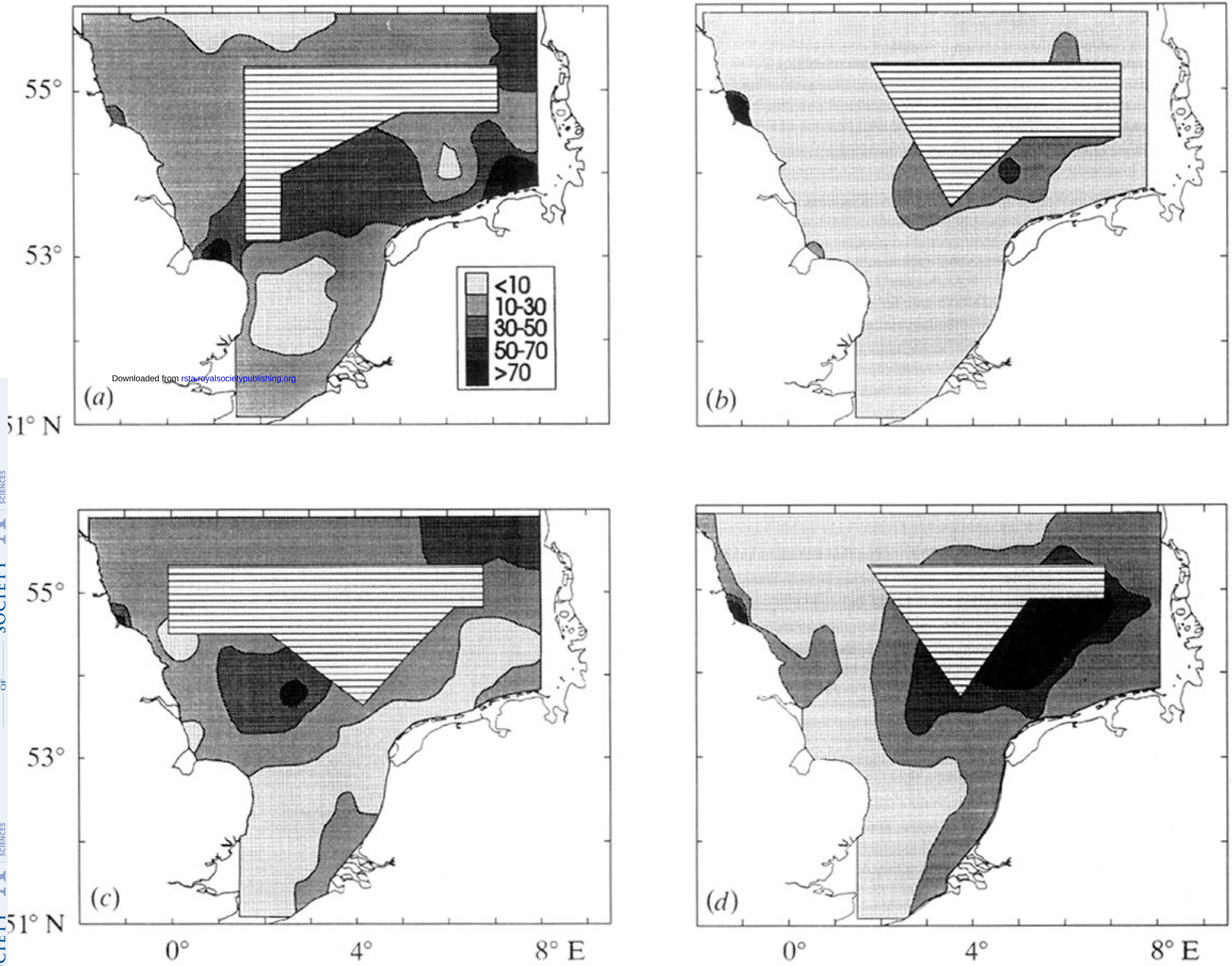

Figure 2. Temporal variations in the concentrations (nmol dm^{-3}) of dissolved manganese: results of survey cruises (*a*) August 1988, (*b*) December 1988 to January 1989, (*c*) April to May 1989, and (*d*) September to October 1989. Within the areas enclosed by straight lines contouring is not considered meaningful because of the lack of sampling points.