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PROCESSES AFFECTING THE BEHAVIOUR OF CONTAMINANTS (METALS AND ORGANOCHLORINES) DURING ESTUARINE MIXING AND IN COASTAL AREAS, WITH PARTICULAR REFERENCE TO THE SOUTHERN NORTH SEA

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INTRODUCTION

We have been studying the distribution and fate of selected chemicals (metals and organochlorines) in the marine environment for several years. Attention has been focused on riverborne components introduced into the North Sea. Measurements have also been made in the Northern North Sea and in the open ocean (North Equatorial Current system and other water systems), allowing comparison of data.

It has been found (especially for some metals) that the distribution of chemical components over the different dissolved and particulate forms can be modified significantly in estuaries and adjacent coastal areas. In the studies of the fate of components derived from the rivers Rhine, Meuse, Scheldt, Ems, Weser, Elb and Varde Å (Fig. 1) several problems were found that may have applicability to other estuaries as well. This paper responds to the agreement at the 67th Statutory Meeting in Warsaw to pay attention to "Environmental quality in coastal and estuarine systems", as well as to a request by the chairman of MEQ Committee. It is the aim to identify some of the problems and to describe our approach to overcome them. Trace metals will be discussed in the first part along with general considerations that will also apply to organochlorines, discussed in the second part.

DEFINITION AND ANALYSIS OF COMPONENTS IN SOLUTION AND SUSPENSION

It is often assumed that the concentrations of particles in open ocean waters are so low that the concentrations of any chemical component in suspension may be neglected with respect to its concentration in solution. This assumption is not justified in shallow and productive seas with larger concentrations of seston, such as the Southern Bight (North Sea). However, concentrations vary considerably, both in time and place.

Water and particulates are subjected to different physical transport mechanisms, both in rivers, estuaries and the marine environment. Also, biogeochemical processes are different for dissolved and particulate components. It is essential therefore -though by no means trivial- to distinguish dissolved and particulate fractions. From a practical point of view, this ditribution is not defined unambiguously for seawater and other natural waters. The main reason is that the size of particles in seawater suspension covers a continuous range from colloidal up to sand grain size fractions.

The problems involved can be "solved" by filtration of samples, using filters with some arbitrarily selected nominal pore size (usually 0.45 µm). Serious problems are associated with this operational definition because of the change of effective pore size during filtration, due to clogging. So, the average size of the particles collected on the filter may depend on the total concentration and on the size distribution of particles in suspension. Like many others, we have adopted filtration over 0.45 µm filters as the commonly used method to obtain solutes and particulates for separate analysis. An all-teflon pressure filtration unit has been developed for metal analysis. Samples for organochlorine analysis are filtered over glass fibre GF/C filters; if necessary when large samples are required, preceded by a continuous centrifugation step.

Sampling and processing techniques for the determination of trace metals in solution and suspension in coastal waters.

We have found that accurate particulate metal concentration data (in terms of amount per unit sediment dry weight) are obtained by measuring, in each individual sample, the amount of both metal and particulate matter. This results in more accurate data than can be obtained by measuring each of the properties in separate samples. Another source of error is eliminated by analyzing the entire content of a sampler instead of only part of it because of sample inhomogeneity introduced by settling of particles in the sampler.
The removal of sea salt from the filter content is neceassay for obtaining accurate seston weight data. Treatment of the filter content with the distilled water might result in the loss of metals from the filter. However, we found no loss of Cu,Cd,Zn,Cr,Si,Fe,Mn and Al, with a possible exception of Cd.

We have compared some methods for separating solutes and particulates, i.e. filtration, centrifugation and settling techniques. (Duinker, Van Eck & Nolting, 1974; Duinker, Nolting & Van der Sloot 1979).
a. Comparison of filtration and settling.
Studies in the Dutch Wadden Sea demonstrated that filtered suspended matter has appreciably higher contents of copper and zinc (lower contents of iron) than the particulates obtained by allowing particulates to settle in the laboratory from samples of the same positions at which the filter contents had been obtained. No difference was found for manganese.

The copper and zinc contents in filtered material were also higher (lower for iron) than in the < 16µm size fraction in bottom sediments in the same area (no difference for Mn). On this basis the existence of a "fine" fraction of suspended matter was postulated. This fraction, consisting of particles with an equivaltent diameter < 50µm and having an important content of elements like Cu and Zn, would be in suspension continuously, at least in the coastal area. It may consist of colloidal iron and manganese oxides including trace elements. The levels of some metals in total suspended matter are diluted with heavier particles with lower metal content eroded from the bottom. The levels in suspended matter cannot be reproduced by the mere process of bottom erosion even after correction for the particle size effect (fraction < 16µm).

b. Comparison of filtration and centrifugation.

The effects of filtration and centrifugation on the contents of several metals in coastal suspended matter were studied recently. The different results were interpreted in terms of varying contributions of larger and denser bottom-derived particles with higher contents of K,Fe,Al and Mn and of smaller, less dense, continuously suspended particles with higher contents of Cu,Cd,Pb and Zn. No dependence on size or density were found for Cr,Si,Mg and Ca. Filtration resulted in higher contents of Cu,Cd,Pb and Zn. For the orther elements, centrifugation resulted in contents that are at least similar to those in particulates obtained by filtration, or even larger for elements with relatively large differences between the contents in the different fractions, such as K.

Elemental contents in particulate suspended matter.

Thus, several elements are not distributed homogeneously over particles belonging to different size/density fractions. It occurs because a) the composition of particulate matter in terms of its main components such as iron and manganese (hydrous) oxides, quartz, clay minerals and organic matter, may vary with particle size fraction, b) these components have different elemental contents and c) surface sorption processes are relatively more important in smaller size fractions.

Ideally, for a proper analysis, it would be desirable to separate particulate matter into the different mineral and organic constituents in order to allow analysis of each individual component. This is difficult to achieve, in particular because various minerals and organic matter in seawater usually occur in associations. Application of chemical procedures, extracting elements from specific binding sites in bottom sediments (Patchineelam & Förstner, 1977 ; Tessier, Campbell & Bisson 1979) may have limited value in suspended matter because of modifications in the natural state of aggregation of suspended matter expected to occur during sampling and separating techniques (settling, filtration and centrifugation). Alternatively, elemental X/Al and X/organic C ratios in bulk suspended matter (Spencer & Sachs, 1970 ; Price & Calvert 1973), may assist in studying elemental partition.

We have applied this approach to study the degree of association of some metals (Fe,Mn,Al,K,Mg,Cu,Zn) with inorganic and organic constituents in the Southern North Sea (October 1975). Additionally, a study has been made of its dependence on total suspended matter concentration (Duinker, 1980a). The distributions of salinity and seston concentration in transects off the Dutch coast are represented in Fig. 2. Seston concentrations are lowest (0.5-1.0 $mg.L^{-1}$) in an area east of the axis of maximum salinity. The distribution of metal concentrations per water volume ($\mu g.L^{-1}$) is, at least qualitatively, similar to the distribution of total suspended matter, values descreasing in transects from the coast toward the central part of the Bight. However, the rate of change is distinctly different for the various elements. This can be observed from plots of the distribution of elemental contents in terms of seston dry weight ($\mu g\ g^{-1}$ or %) : those of Fe, Al and K pass through a minimum and those of Mg,Cu,Zn and organic C through a maximum (Fig. 3.). Minima and maxima do not coincide with the axis of maximum salinity but rather with the minima in seston concentrations and maxima in organic C content.

Elemental contents of Fe,Al and K are higher at higher than at lower seston concentrations while those of Mg,Cu,Zn and organic C are higher at lower seston concentrations. A critical change occurs at about 5 $mg\ L^{-1}$ (Fig. 4). The behaviour of Mn is different: its more complicated distribution pattern and the less regular relations of its content in seston with both salinity (Fig. 3) and seston concentrations (Fig. 4) result form processes that cause transitions between dissolved and particulate Mn species in the estuarine and coastal environment. We shall return to this aspect later. Aluminium is closely related to total suspended matter (Fig. 5); it may be considered as almost entirely associated with Al-silicates, mainly clay minerals. The elemental content of an element X in particulate matter is altered when varying amounts of components with low content of X (e.g. quartz) are mixed with fine-grained Al-minerals with higher contents of X. However, X/Al ratios are not altered. X/Al ratios in the present data are practically constant at seston concentrations above 10-20 $mg.L^{-1}$ (Fig. 6). This applies to the plots of all elements considered here. In addition, the X/Al ratios increase strongly with decreasing seston concentration below 5 $mg\ L^{-1}$. This is obvious (from the data of Fig. 4) for Mg.Cu,Zn and organic C: these relations are not given here. It also applies to Fe,Mn and K: these relations are represented in Fig. 6.

Different seston fractions at different seston concentrations.

The data are consistent with the model postulated earlier. A seston fraction consisting of low density - small sized particles that resist settling, dominates at los seston concentrations. Another fraction, derived from the bottom, dominates at high seston concentrations. These fractions have different settling properties and different contents of metals and organic matter. Thus, relatively high contents of Fe,Al and K occur in material present at high seston concentrations and high contents of Mg,Cu,Zn and organic C in material present at low seston concentrations. The X/Al ratios above 10-20 $mg.L^{-1}$ for the major elements (Fe/Al 0.5 ; Mn/Al 0.02 ; K/Al 0.3 ; Mg/Al 0.2) are very similar to the values reported for fine grained sediments (0.5 ; 0.01 ; 0.29 and 0.17 respectively, Goldschmidt 1954 ; Krauskopf 1965). This supports the idea that suspended matter at high seston concentration contains a relatively high fraction of bottom-derived material. Additional evidence for higher contents of e.g. Cu and Zn in particulate suspended matter at low seston concentrations ($\leq 1\ mg.L^{-1}$) was obtained from samples obtained in the region off the Danish and German coasts in April 1974 (Figs. 7 and 8). The significance of the mechanism described above is also demonstrated by measurements of mineral and chemical composition of suspended matter in vertical profiles during a tidal cycle in the Varde Å estuary (Duinker et al., 1980 in press).

Variations of elemental contents with total seston concentrations as result of varying contributions of larger, denser particles may remain undetected when concentrations are expressed on a volume ($\mu g.L^{-1}$) rather than on a sediment dry weight basis ($\mu g.g^{-1}$). The mechanism suggested above assists in distinguishing, e.g. in an estuarine environment, original fluviatile from marine derived material (Fig. 9) and it may also prove to be a useful fool in explaining data reported by others e.g. for estuaries (Sholkovitz, 1979), coastal regions (Sundby & Loring, 1978) and open ocean regions (Wallace, Hoffman & Duce, 1979).

Elemental partition.

The metals studied here are partitioned over organic matter and minerals. The strong increase in the X/Al ratios at low seston concentrations suggests that the elemental contents in the continuously suspended fraction are determined primarily by mineral components such as Fe and Mn hydrous oxides rather than by Al-silicates.

Contents of particulate Mg, Cu and Zn covary with organic carbon content ; a negative correlation is observed for Al (Fig. 9), Fe and K. No such conclusion can be drawn for Mn. Therefore, Mg, Cu and Zn may be associated with organic matter or, alternatively with mineral fragments such as oxide coatings, occuring in associations with organic matter (Pillai et al., 1971; Neihof & Loeb, 1972; Senesi et al. 1977). We have tried to determine the role of living phytoplankton as a possible site for trace elements. Practically pure samples of dinoflagellates and diatoms were obtained at some stations at low seston concentrations off the Dutch coast in April 1979. The contents of Cu,Zn,Fe and Mn were found to be far below the levels found in total suspended matter at low concentrations (Table 1). The relatively unimportant role of living phytoplankton in the Southern Bight was also reported in earlier work (Duinker & Nolting, 1976). Wollast (1979) reported a strong correlation between trace metals and organic matter in bottom sediments of the North Sea. These results, in combination with the strong correlation between the contents of several elements and organic C in seston (Fig. 9), suggest that detrital organic matter rather than living phytoplankton should be considered as a -potentially- significant site for the metals in our data.

However, mineral components such as Fe and Mn hydrous oxides, covarying with organic matter, possibly as aggregates, may also be important sites for trace metals, in particular at low seston concentrations. We have not been able to distinguish between these

these possibilities and we feel that this aspect deserves more attention than it has been given in most reports in the literature, stating the association of trace metals with organic matter in cases where only a positive correlation with organic C had been found. Application of advanced optical methods (scanning electron microscopy) and significant improvements in chemical leaching techniques are important steps required in future work.

Leachable portion of suspended metals.

It is useful to have a suitable method to distinguish, in suspended matter and bottom sediments, the fraction of trace metals incorporated into the sediments from river and seawater from the fraction that occurs in pre-existing minerals. We investigated a number of chemical agents, such as hydrochloric acid (0.01-2.0 N), acetic acid (5-25 %), hydroxylamine HCl (1 M) and a mixture of hydroxylamine HCl (1 M) and acetic acid (25 %). Considering effectiveness and selectivity in terms of clay mineral lattice breakdown, treatment with 0.1 N HCl during 18 hours was selected as the most preferable leaching agent in order to distinguish the fraction of any particular element that is included as structural element from the fraction adsorbed by clay minerals, or included in hydrous iron-manganese oxides, colloidal "free iron aquate", carbonates and organic matter (Duinker, Van Eck & Nolting, 1974). This distriction may be important for ecological aspects as it differentiates between that fraction of an element that is readily available or may become available after diagenetic transformations from the fraction that is essentially non-available.

It is interesting to observe that the percentage leachable fraction of a particular metal varies with total content in particulate matter for several elements. For instance, it decreased with increasing content of Cd,Zn,Cu,Pb,Fe and Mg. This is another argument for the difference between seston present at high and low concentrations (Duinker et al., 1980 in press).

Metals in seawater solution.

From an operational definition, dissolved components are defined as those components that have passed through a 0.45 µm nominal pore size membrane filter. Serious problems are encountered in the analysis of several trace metals at their natural levels in seawater. Errors are likely to be introduced during sampling, filtration, storing and analyzing the samples due to undesired introduction or removal of constituents to be analyzed.

Only three analytical methods, i.e. neutron activation analysis, flameless atomic absorption spectrometry and anodic stripping voltammetry (ASV) have sufficient sensitivity to allow direct measurement of some trace metals in seawater. Only ASV allows a distinction of different chemical forms ; however, for a limited number of elements only (Zn,Cd, Pb,Cu and possibly some more). Metal species in solution can be classified as free (hydrated) ions and as complexed metal species, both labile and non-labile (Matson, 1968). These complexed forms can be distinguished by ASV on the basis of the difference between the dissociation rate constant of the complex (K_{diss}) and the reaction rate constant for the reduction of the free metal ion into metal amalgam at the electrode (K_r). Labile species are characterized by $K_{diss}>K_r$, non-labile species by $K_{diss}<K_r$. It is assumed that species that are classified as non-labile under the particular experimental conditions are non-electro active and thus do not contribute to the analytical result. These considerations were applied in order to study the uptake of ionic metal spikes into non-labile complexes in filtered North Sea water. This resulted in the first observation on the existence of complexity of seawater for trace metals (copper). Fig. 10 demonstrates the removal of an ionic copper spike to seawater into what appeared to be non-labile organic complexes. The observed removal does not occur in Uv-irradiated or acidified seawater. Consecutive additons of ionic copper result in a break in the analytical response curve at about 20 $\mu g.L^{-1}$ Cu (Fig. 11). Thus, it was concluded that the seawater sample contained organic ligands in a concentration equivalent to 3.0 10^{-7} M Cu. In addition, it was found in a series of North Sea water samples that the fraction of dissolved copper, present in organically complexed forms was about 80 % of total dissolved copper content. The corresponding number for Pb,Zn and Cd were 87, 60 and 0 % respectively. It was also found that zinc, although present in seawater solution in an organically complexed form to an appreciably extent, did not reach equilibrium whithin the time of the measurement (hours, Fig 12). The removal of copper from the ionic form after addition to seawater has to be taken into account in ASV analyses in order to avoid inaccurate concentration data (Duinker & Kramer, 1977).

Recent work has shown that sediment extracted humic and fulvic acids, when added to seawater, are able to complex significant amount of copper.

Complex formation with fulvic acids proceeded much more rapid than with humic acids (Kramer and Duinker, 1980).

TRACE METALS AND ESTUARINE MIXING

In estuaries, where riverwater and coastal or oceanic waters of widely different compositions are mixed, strong gradients in chemical and physico-chemical properties occur (Dyer, 1972; Phillips 1972, Burton, 1976). As a result, the relative contributions of the various chemical species of any element to these forms can be modified considerably. Components in solution are able to leave the estuary out into the coastal area and eventually the open ocean.

Estuaries act as sinks for particulate matter derived from the river as well as from the marine environment. In addition, recent data suggest that large scale removal of dissolved species occurs in several estuaries (Duinker, 1980 b). It is important therefore to understand the effects of estuarine processes on trace metal behaviour for prediction of the geochemical behaviour of each individual element and its possible effects on organisms, as well as the role of estuaries in the mass balance between rivers and oceans (Mackenzie and Garrels, 1966 ; Burton 1976 ; Bewers and Yeats, 1977).

The interpretation of the trace metal composition of estuarine water and particles in terms of relevant processes is fraught with problems. Important factors are

a) the complexity of estuarine processes.

An estuary is a dynamical system in which the distribution patterns of dissolved and particulate components result form the physical mixing characteristics of natural waters of widely different composition and a variety of chemical and biogenic reactions taking place independently and simultaneously. Additional variations in meteorological conditions, flow characteristics and biological activity are responsible for variations in the concentrations of trace metals in estuaries, with different time scales (Turekian, 1971). In order to understand the role of estuaries in the biogeochemical cycling of trace metals it is essential to distinguish the effects of biological and chemical from hydrodynamic processes.

b) non-linearity.

Several properties do not vary linearly with the parameter that characterizes the mixing series between river water and seawater, such as chlorinity or salinity. This has been observed for several basic properties as suspended load, pH and dissolved oxygen concentration.

Chemical processes taking place during estuarine mixing have been investigated by field and laboratory studies in various laboratories. Our group has focused on an integrated study of components in solution, particulate suspended and bottom sediment particles in field studies. A number of rivers, their estuaries and adjacent coastal regions has been studied. In these studies, physical and chemical data have been obtained at fixed station in different salinity regimes of the various estuaries during complete tidal cycles, and in addition chemical data were obtained in longitudinal surveys.

Dissolved components (trace metals) during estuarine mixing.

Mixing curves of dissolved trace metal concentrations, measured over the whole estuarine salinity range against a suitable index of mixing such as chlorinity (or less accurately salinity), have been used to distinguish conservative from non-conservative behaviour. The main problems in the interpretation of these curves are related to variations in end-member concentrations, the possibility of input of material into the estuary from other sources and the correct choice of end-members (Boyle et al., 1974).

As an example, the results of measurements in the Rhine estuary in December 1974 and September 1975 will be summarized (Fig. 13-18). Complete tidal cycles were measured at the fixed stations 6,8 and 17 (Fig. 13) at 1-hour intervals in the period 11 to 19 December 1974. The stations were selected on the basis of their tidal salinity distribution. Station 6 is a fresh water station. At station 8 the only deviations from the fresh water salinity occur at high tide. Station 17 is characterized by permanent stratification. A severe gale of 10 to 11 Beaufort from westerly directions was blowing during sampling at this last station and during the 3 preceding days.

Surface samples were also obtained at the station 6 to 18 (Fig. 13) during a survey throughout the estuary in the period 22 to 29 September 1975.

The concentrations of dissolved Fe,Zn,Cu and Cd at low salinities in the longitudinal profile and those for Mn at higher salinity are below the ideal dilution line (Fig. 14 a). The residence time of fresh water in the Rhine estuary is in the order of 3 to 6 days. Relatively small variations (10 to 20 %) were observed in the concentrations of Fe,Mn, Zn,Cu and Cd in the fresh water region during the days prior to the observations in the mixing area. The negative deviation from the ideal dilution line that is observed for these elements can therefore be attributed to removal processes.

The removal from solution does not result in a positive deviation in the plot of particulate trace metal concentrations against salinity. In fact, a net removal of particulate matter and the associated trace metals is observed (Fig. 14 b).

The plots of dissolved iron and manganese against salinity for the fixed stations (Fig. 15) are very similar to the presently and also earlier reported surveys in the estuary (Duinker & Nolting, 1976, 1977). However, zinc and copper appear to behave in a conservative way. It is worthwhile in this respect to analyze the dissolved concentrations of the fixed stations more closely. Considerable variations occur in the dissolved iron concentrations at the fixed stations in the fresh water area (Fig. 16). Variations are smaller for Mn,Zn and Cu. However, the variations in the concentrations of dissolved Fe,Mn, Zn and Cu in the surface samples reflect those in the corresponding near-bottom samples very closely. As the samples are synoptic and independent, the variations most probably reflect real fluctuations rather than procedural or analytical errors.

The concentrations of dissolved Zn and Cu - and less pronounced also those of Fe - in the samples of station 6 are higher than in the fresh water samples of station 8. This may be due to removal of dissolved components in the fresh water region, resulting from the interaction with sediment particles transported upstream from the lower estuary beyond the limit of marine salt intrusion (Van Veen, 1937 ; Postma 1980). Increased suspended sediment concentrations favour the removal of dissolved trace metals (Aston & Chester, 1973). This effect is enhanced by the presence of freshly precipitated iron (and manganese) oxide and hydroxide species, that are known to act as effective scavengers for trace metals (Goldberg, 1954 ; Krauskopf, 1965). Particles derived from the lower estuary are enriched in iron and manganese oxides (Duinker & Nolting, 1976, 1977). The importance of their presence for the removal of dissolved Zn and Cu may follow from the observation of increased dissolved Mn concentrations in the samples of the fixed station 8 at high tide (Fig. 16). This increase can only be caused by interactions involving sediment particles derived from the lower estuary (Duinker, Wollast & Billen, 1979).

Therefore, the data of station 6 represent the fresh water end member concentrations of Fe,Zn and Cu. Including the data of station 8 would tend to obscure any removal process - if present - during estuarine mixing.

A second mechanism that is important in this respect concerns the contribution of trace metals from interstitital water to the overlying water. This may be important under dynamic conditions such as during dredging operations (Wakeman, 1976), bioturbation (Petr, 1977) or storms (Windom, Beck & Smith, 1971; Duinker, Van Eck & Nolting, 1974 ; Sanders 1978). The importance in the present results is demonstrated by the occurrence of - slightly - increased dissolved concentrations in near-bottom samples at the fixed station 17 compared to surface samples (Fig. 15). The magnitude of the interstitially dissolved concentrations in the mixing area is large enough to account for these observations (Table 2).

Concluding these considerations , we may state that the dissolved metal-salinity plots for Zn and Cu do not exclude removal processes from contributing to the concentrations in the water. Even so, the data at least indicate conservative behaviour and give no evidence for mobilization processes.

Particulate trace metals during estuarine mixing

The relations between salinity and particulate leacheable contents of Fe,Mn,Zn,Cr and Cu for the data of the fixed station 17 are almost linear (Fig. 17) and it appears that the surface and near-bottom contents fit the same linear relation with a fair degree of reliability. The slope of the regression line is positive for Mn and negative for Fe,Zn, Cr and Cu. It may be concluded that suspended matter derived from near the bottom was mixed into the surface layer in nearly the same ratio as the saline water in which it was suspended. The extreme meteorological conditions during and prior to sampling may have contributed to the situation observed. A few near-bottom data for Zn,Cr and Cu at high salinities (Fig. 17) are clearly above the mixing line. They are associated with the low suspended load samples at slack water, suggesting that the highest concentrations occur in finer grained material that does not settle (Duinker, Van Eck & Nolting, 1974). The contribution of near-bottom sediment particles to the concentrations in the surface layer is dominated by the coarser fraction. The value obtained by extrapolating the correlation line in Fig. 17 to 0.4 $^{o}/oo$ S (Table 3) is lower than the average content in the fresh water suspended matter for Mn,Zn,Cr and Cu. This agrees with the model just developed. The extrapolated value for leacheable Fe is higher, however. This can be attributed to the relatively large contribution of dissolved iron that is transformed into particulate forms in the early stages of mixing, increasing the leacheable - and total - iron concentrations in particulate matter to values even above the characteristic fresh water concentrations (Fig. 18). The positive slope for particulate manganese (Fig. 17) is due to the transition of Mn (II) into oxidized and particulate forms in the lower estuary in response to increased pH and dissolved O_2 concentrations.

Suspended trace metal contents in the surface layer can thus be accounted for in terms of mixing of fluviatile and marine derived particles, with additional contributions of originally dissolved riverborne components that are removed from solution during estuarine mixing. The same mechanism has to be taken into account to explain bottom sediment data in the Rhine estuary (Müller & Förstner 1975; Duinker & Nolting, 1976 ; Salomons & Mook 1977). The removal of suspended matter and trace metals from the surface layer is indicated by the present Fig. 14b. However, the net vertical exchange of particles is highly variable in time (Fig. 19).

Cycling of manganese within the estuary

Observations on a series of trace metals in solution and suspension during various surveys in the Scheldt and Rhine estuaries demonstrated some unique features of manganese: a) a positive deviation from the ideal dilution line for the dissolved species at low salinities, b) a negative deviation at higher salinities, c) the high particulate contents in the lower estuary and d) the higher particulate contents in the near-bottom layer than in the surface layer during the tidal cycle measurements. An equilibrium model of the behaviour of Mn during estuarine mixing of river and seawater was established on the basis of published thermodynamic data about manganese species in natural waters. The chemical control parameters taken into consideration are ionic strength, pH, oxygen concentration and total dissolved carbonate content. This model was shown to account for at least the general trends of dissolved manganese variations observed in the Rhine and Scheldt estuaries (Fig. 20). Some data about the kinetics of the processes involved in manganese transformations in these two environments suggest that the close approach of the thermodynamic equilibrium is a consequence of the high turbidity and the intense microbiological activity present in these heavily polluted estuaries.

It is suggested that the overall behaviour of Mn is determined by cyclic processes: removal from solution at salinities above 1-15 ^{o}/oo S accounts for the high suspended Mn concentrations in the lower estuaries and along the Dutch and Belgian coasts. Parts of the newly formed particulate Mn is transported back into the upper estuary. Once in contact with low pH or low Eh estuarine water (Fig. 20) or after deposition in sediment and subsequent reduction, Mu may return into the dissolved compartment within the water column (Wollast, Billen & Duinker 1979 ; Duinker, Wollast, Billen, 1979). An attempt was made to establish a mass balance for manganese in the Scheldt estuary (Fig. 21).

Laboratory studies on sorption of trace metals during estuarine mixing

The complex interplay between physical, chemical and biological processes in estuaries is the main reason for the problems encountered in designing laboratory experiments that might represent estuarine situations. Thus, several attempts have been made to study sorption processes by exposing sediment particles to various solutions and measuring the resultant changes in sediment and solution compositions. In an approach of this kind, involving fluvial sediment and seawater, the effect of important parameters that are known to occur during actual estuarine mixing may not be included, e.g. the initial decrease in pH in the early stages of mixing riverwater and seawater (Mook and Koene, 1975), and the absence of dissolved organic matter in artificial seawater. Alternatively, in studies involving sediment-free riverwater and seawater, the effects of pre-existing particles that are known to act as nucleation centres (Aston & Chester, 1973) are not included. Additionally, it is difficult to estimate the contact time of sediment particles with - and their concentrations in - solutions of varying composition (salinity) in the estuary. It is difficult therefore to estimate how well laboratory conditions may represent actual situations.

Field studies

In studies on the fate of riverborne trace metals in estuaries, efforts should be made to include both dissolved and particualte forms. In some cases, the evidence given for either release or removal processes would have been supported by additional information, particularly

of dissolved species. The value of such integrated studies has been demonstrated in several cases (Carpenter et al., 1975 ; Troup & Bricker, 1975 ; Duinker & Nolting, 1976,1977,1978 ; Wollast, Billen & Duinker 1979 ; Duinker, Wollast & Billen, 1979).
Bottom sediment in estuaries is a significant source for trace metals in the overlying water. This has been established in several cases for diagenetically modified anoxic sediments. On the other hand, it has not been taken into account in several cases where it might have contributed to an explanation of the data on dissolved and particulate suspended trace metal concentrations. It is important that a clear distinction is made between the desorption of trace metals from riverborne suspended particles upon contact with seawater and the desorption from bottom sediments or the contributions from interstitial water once the sediments have been diagenetically modified.

The decrease in the concentrations of a range of trace and major elements in bottom sediments in a seaward direction in the Rhine and Ems estuaries have been interpreted in terms of mobilization from suspended matter into solution as metal-organic complexes (De Groot, 1966, 1973). Manganese, that was considered to remain fixed to particles, was used as a reference for estimating the degree of mobilization of several elements. In that case, more that 50 % of the riverborne suspended Fe,Cd, Zn,Pb,Cr would have gone into solution near the head of the estuary. A relatively large and measurable increase in dissolved concentrations would be expected. However, we have not found any mobilization of Fe,Cu,Pb, Cd and Zn from the dissolved salinity plots. Instead, Fe,Cu,Cd and in some surveys Zn, were found to be removed from solution. Manganese, that had been considered to remain fixed to riverborne suspended matter during transport through the estuary and the coastal environment was found to be mobilized into solution. It cannot be used as reference for other elements therefore. Moreover, bottom sediment data cannot be extrapolated to suspended matter as result of the presence of a continuously suspended fraction.

Conclusions

Evidence for desorption of trace metals from riverborne suspended matter upon contact with seawater is very limited. Conservative behaviour and net removal of riverborne dissolved metals has been observed for Fe, Mn,Cd,Cu,Zn in several estuaries. The removal process is more important than any release that might also take place.

Only a very limited part of the river transported load of trace metals may reach the ocean. Only those elements that form very strong anionic complexes may be transported out of the estuary in dissolved form (Turekian, 1977). Particles, through estuarine flocculation and sedimentation processes, play therefore a dominant role in the observed depletion of the ocean in certain trace metals. This may have important consequences for the residence time of trace metals in ocean water (Bewers & Yeats, 1977).

ORGANOCHLORINE COMPOUNDS

Several organochlorine compounds derived from human activities on land are persistent in the marine environment. Their partition over the various biotic and abiotic compartments depend partly on biological and hydrodynamical factors and their relative solubilities in water and lipid material. Lipophilic organochlorines such as polychlorinated biphenyls (PCB) and members of the DDT family have high affinity for lipid tissue of marine organisms.

Most of the work reported on organochlorines in the marine environment apply to their levels in organisms. In the past, specific organochlorines derived from the Meuse-Rhine estuarine region have caused dramatic effects in the populations of some bird species in the Dutch Wadden Sea (Koeman 1971). A strong reduction of the pup production in the population of the harbour seal in the same area and the disappearance of the populations of the harbour porpoise (*Phocoena phocoena*) and the bottle nosed dolphin (*Tursiops truncatus*) from Dutch coastal waters may be directly related to the presence of high concentrations of several organochlorines, in particular PCB's in these mammals. They can be transferred in significant amounts from mother to foetus by transplacental transfer mechanisms (Duinker & Hillebrand, 1979a; Duinker, Hillebrand & Nolting, 1979).

Organochlorines in solution and suspension in an estuary

Literature on their occurrence in seawater solution and suspension is very scarce indeed. The main reason is the large number of problems encountered in their accurate analysis at the extremely low levels in which they occur in seawater. Essentially no data is available to our knowledge on the effect of estuarine processes on the behaviour of riverborne components in solution and suspension. In order to study these processes, observations were made at the three fixed stations mentioned earlier in connection with the investigations on trace metals in December 1974 (Fig. 13). The concentrations in solution and suspension in surface and near-bottom samples at 2-hour intervals during complete tidal cycles are given in Fig. 22 and 23. Variations in dissolved concentrations at each position in the freshwater region occur over small time intervals. The covariation of concentrations in the synoptic and independent surface and near-bottom samples demonstrated that variations are real. Plots of dissolved concentrations versus salinity are given in Fig. 24.

The residence time of fresh water in the Rhine estuary is in the order of a few days. The dissolved concentrations obtained at the fresh water stations during the days preceding the observations in the estuarine mixing zone are proper fresh water end members in the plots therefore. It appears that concentrations in the surface and near bottom layer fit the same linear relationship. This relation includes the fresh water end members, except for dieldrin and endrin. The plots are thus consistent with conservative behaviour of dissolved riverborne pentachlorobenzene, hexachlorobenzene, PCB, α-HCH, γ-HCH and β-HCH during estuarine mixing. (Duinker & Hillebrand 1979b).

The behaviour is markedly different for dieldrin and endrin. For these compounds, a pronounced maximum occurs in the plots at low salinities. Thus, dissolved species are produced in the upper part of the mixing zone. The most probable sources are (1) release from riverborne suspended particles under mixing conditions, (2) interstitial water in estuarine sediments and (3) local pollution. The amount of fluviatile suspended dieldrin and endrin is below the limit of detection in practically all samples studied. Also, interstitial water is another unlikely source, as we have not detected any trace of dissolved dieldrin or endrin in the river and estuarine interstittial waters studied. Also, the range of dissolved concentrations detected in near-bottom more saline water in the estuary does not support the importance of this route. It is more likely that local sources are responsible for the release of these compounds into solution. On the basis of the data of Fig. 24, roughly 2 kg per day of each compound can have been released in that period (1974). Like other compounds, also dieldrin and endrin demonstrate conservative behaviour within the estuary upon further dilution with seawater. One of the harbours near the head of the estuary was traced as a source, its water containing 10 to 15 $ng.L^{-1}$ dieldrin and 8 to 10 $ng.L^{-1}$ endrin (1974). The concentrations in June 1979 were lower: 1.0 and 0.7 $ng.L^{-1}$ for dieldrin and endrin respectively.

Data obtained in 1976 demonstrate that considerably larger variations of river water concentrations can occur over larger time intervals than a few hours as in the 1974 data. The amount of organochlorines in suspension per unit volume depends strongly on the seston concentration. Thus, large variations with time and place can be expected. In the estuary, concentrations in solution are smaller than in suspension (ng.L^{-1}) for pentachlorobenzene, hexachlorobenzene and PCB, both in the surface and near-bottom layers, except in 1976 data because of high concentrations in solution. The α-HCH, γ-HCH and β-HCH have considerably larger concentrations in solution, both in the estuary and in fresh water. It should be mentioned that in the rivers, PCB is roughly equally distributed over dissolved and suspended forms: penta and hexachlorobenzene concentrations in solution usually exceed the amount in suspension. The distribution over these forms in the estuary is a consequence of the trapping mechanism for suspended particles that is associated with estearine circulation and mixing processes (Postma 67, Meade 72). No evidence could be found for exchange of the organochlorines described here between solution and suspension during estuarine mixing.

Organochlorines in seawater

120 litre seawater samples, collected in the Southern Bight in June 1979, were analyzed for organochlorines. Levels in water of Nieuwe Maas (essentially Rhinewater), Dutch coastal water and water from the area of maximum salinity between Hook of Holland and Lowestoft (station 66, Fig. 1) are given in Table 4. The lowest values of all components are detected in water from the central part of the Southern Bight, with minimum direct influence of rivers. The concentrations of PCB is similar to the lower values reported for Mediterranean coastal water (1.3 to 2.8 and 1.5 to 38 ng.L^{-1}) (Elder, 1974, 1976), the North Atlantic (0.8 to 36 ng.L^{-1}) (Harvey, Steinhauer & Miklas, 1974) and the central part of the Southern Bight (0.52 ng.L^{-1}) (Dawson & Riley, 1977). These values are at the very lower end of the large range of concentrations reported for various areas, including the open ocean. This may result from improvements in the complex analytical chemistry involved and also possibly from the reduction in the use of PCB in the Western communities since 1970 as was suggested by Harvey, Steinhauer & Miklas (1974).

The present results suggest the importance of lower chlorinated PCB components in seawater of the Southern Bight. The close similarity of dissolved PCB and Aroclor 1254 (or similarly, Clophen A50) is reported by other authors. It is improbable that the present observations result from analytical errors. This may be derived from a comparison with results for water from other areas obtained by the same methods, e.g. the Danish Wadden Sea (Fig. 25). The importance of atmospheric transport of PCB has been demonstrated by Bidleman & Olney (1974).

These authors reported the presence of lower chlorinated components in air over the Atlantic while Dawson & Riley (1977) found the same result for air over British coastal waters. The contribution could not be quantified however. The present observations of the presence of these lower chlorinated fractions in seawater (in 1979) and their absence in the data for water of the same area obtained by Dawson & Riley in 1974 may reflect variations in deposition from the atmosphere. Also, the application of temperature programmed GLC in the present work has assisted in their detection and quantitation. Although the atmosphere seems a likely source, without further data, river water cannot be excluded. The adoption of Clophen A30 as standard results in an increase in the calculated PCB concentration from 0.7 (Aroclor 1254 or its equivalent (Clophen A50) to 4.1 $ng.L^{-1}$ (Clophen A30). It is difficult to compare these results with findings of other authors reporting their results in terms of Aroclor 1254 as in many cases no chromatograms have been given. (Duinker & Hillebrand 1979b).

Concentrations of all compounds measured in the coastal and Wadden Sea samples are higher than in the central part of the Southern Bight. It is interesting to compare the measured values with those calculated on the assumption of conservative mixing of open seawater and Rhinewater. The samples near the mouth of the estuary (22 $^{o}/oo$ S) and in the Wadden Sea (30 $^{o}/oo$ S) agree reasonably well, with some larger diviations for α-HCH and γ-HCH (Table 4). Previous (unpublished) measurements suggest that the contribution of IJsselmeerwater is not likely to play an important role, as organochlorine concentrations do not deviate significantly from those in its main source, i.e. Rhinewater. The results therefore support the model of conservative behaviour of the compounds reported here, not only in the estuary but also during transport in the coastal marine environment.

Studies of this type may assist to understand in more detail the distribution of organochlorines in organisms in various parts of the world ocean, including the North Sea.

Table 1. Range of elemental contents in pure samples of dinoflagellates and diatoms at stations off the Dutch coast in April 1979, at seston concentrations in the 0.3-1.6 mgl^{-1} range (Duinker 1980a).

Fe	0.3-0.4 %
Mn	15-114 μgg^{-1}
K	0.2-1.2 %
Mg	0.6-2.3 %
Cu	21-100 μgg^{-1}
Zn	85-184 μgg^{-1}

Table 2. Range of interstitial water concentrations of Fe,Mn,Zn and Cu in the five 2-cm slices op the upper 10 cm of the sediment cores taken at stations 3,4,5 and 7. (Fig. 13, from Duinker & Nolting 1978).

Metal	Station			
	3	4	5	7
Fe ($mg.l^{-1}$)	0.2-5	0.7-3.2	10-18	20-50
Mn ($mg.l^{-1}$)	0.6-6	0.7-7	2-8	8-12
Zn ($\mu g.l^{-1}$)	80-180	40-150	120-300	100-700
Cu ($\mu g.l^{-1}$)	40-180	20-120	20-140	4-190

Table 3. Particulate trace metal concentrations calculated from the regressions in metal-salinity plots (Fig. 17) for a salinity of 0.4 $^{o}/oo$ S ("extrapolated") and "average" concentrations for the fresh water samples of the fixed stations 6 and 8, together with their relative standard deviations (%) from Duinker & Nolting 1978.

Metal	Extrapolated to 0.4 $^{o}/oo$ S ($\mu g.g^{-1}$)	Average fresh water suspended ($\mu g.g^{-1}$)	Relative s.d. (%)
Fe	25000	17000	11
Mn	620	870	23
Zn	1400	2100	15
Cr	240	300	6
Cu	250	320	25

Table 4. Concentration of dissolved organochlorines measured in 120-500 litre water samples from the Nieuwe Maas, the coastal area (station 67), the central part of the Southern Bight (station 66) and the Marsdiep area (station 69) in June 1979 (Fig. 1). Dissolved concentrations were calculated (last column) for water composed of water from the Nieuwe Maas and the central part of the Southern Bight in the ratios corresponding to salinities in the coastal and Marsdiep water samples (from Duinker & Hillebrand 1979 b).

Organochlorine	Measured ($ng.L^{-1}$)				Calculated ($ng.L^{-1}$)	
	Nieuwe Maas	Central part Southern Bight	Coast	Mars-diep	Coast	Marsdiep
Salinity (^{o}/oo)	0.3	34.9	22	30.1	22	30.1
Pentachlorobenzene	3.0	0.1	1.2	0.5	2.1	0.4
Hexachlorobenzene	2.8	0.1	1.1	0.1	1.9	0.4
PCB (Aroclor 1254)	8.1	0.7	3.4	1.4	5.7	1.7
α-HCH	10.0	0.9	2.0	1.9	8.0	1.9
γ-HCH	9.9	1.0	4.0	6.2	7.2	2.0
β-HCH	0.9	0.04	0.6	0.1	0.6	0.1
Dieldrin	0.8	0.1	0.7	0.2	0.6	0.2
Endrin	0.5	<0.01	0.3	0.03	0.3	0.05

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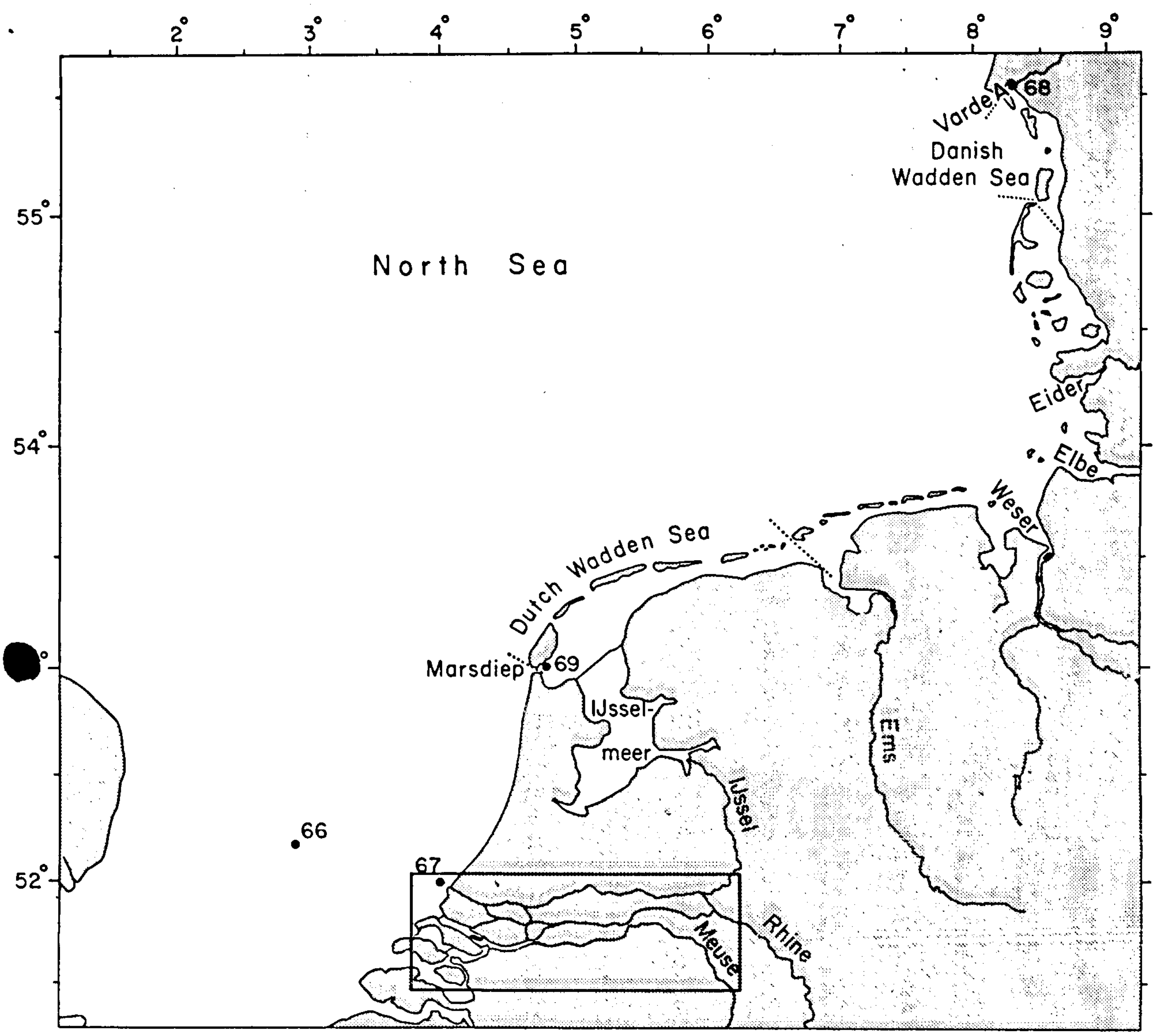


Fig. 1. Representation of area investigated in this paper.

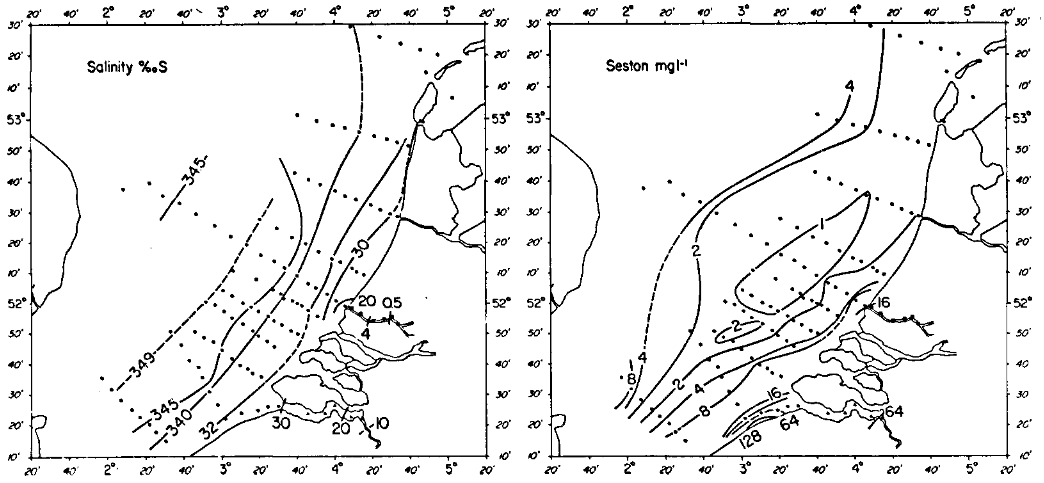


Fig. 2. Distribution of salinity (°/oo) and seston concentration in the surface layer (mg.L^{-1}) in October 1975, from Duinker 1980a.

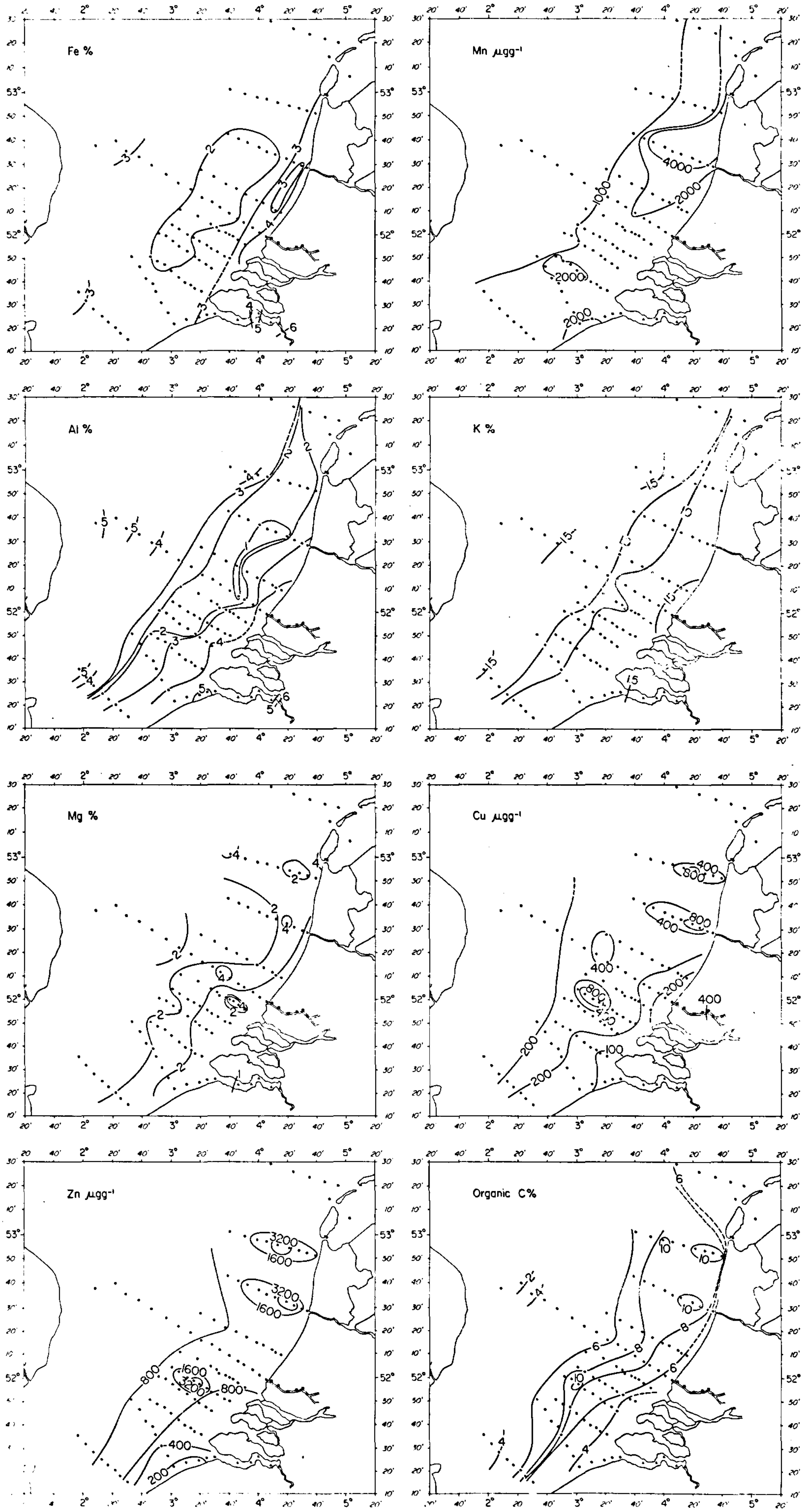


Fig. 3. Distribution of contents of Fe,Mn,Al,K,Mg,Cu,Zn and organic C in suspension matter (Weight per weight, $\mu g g^{-1}$ and %) in October 1975, from Duinker, 1980a.

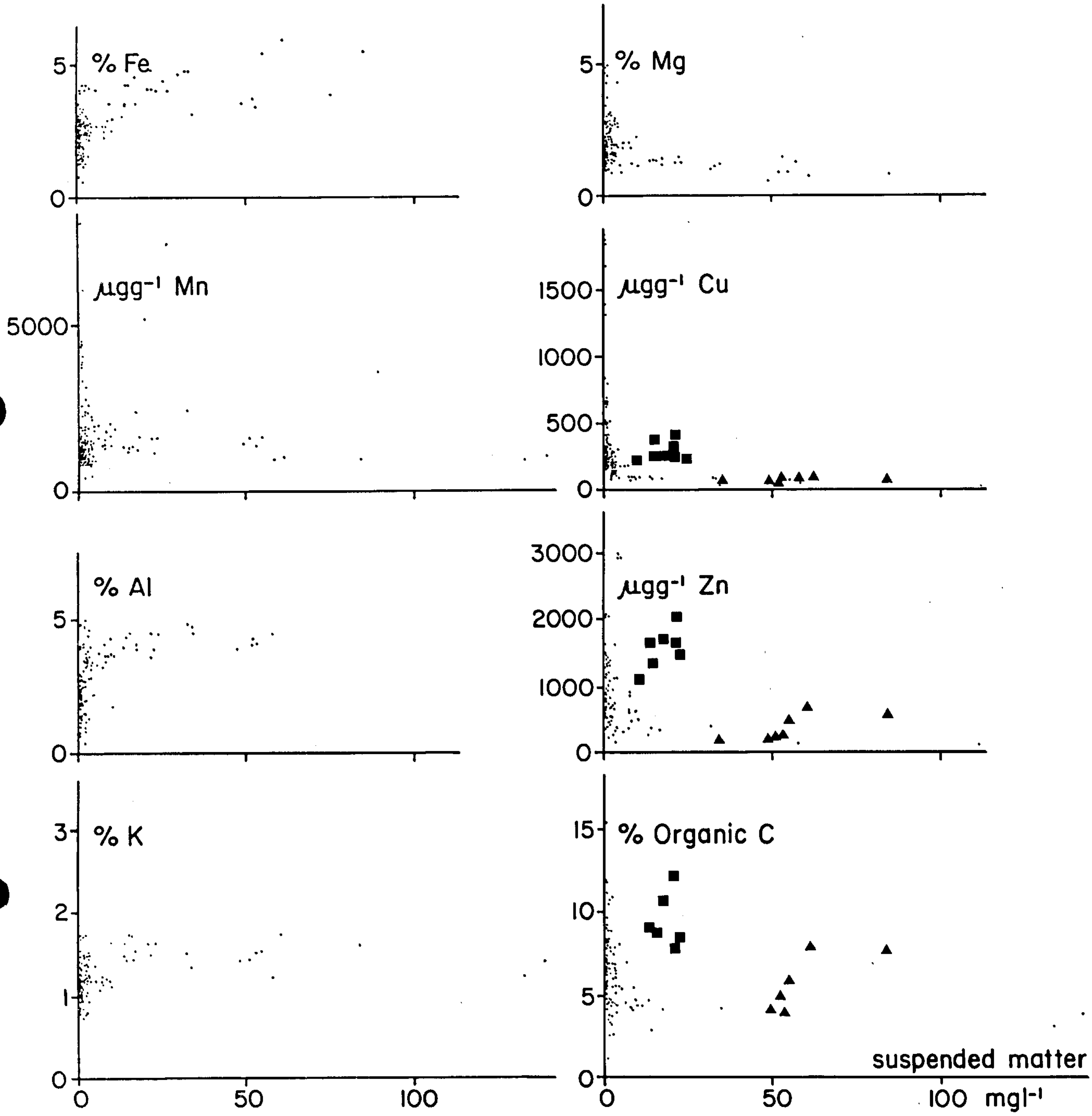


Fig. 4. Elemental contents of Fe,Mn,Al,K,Mg,Cu,Zn and organic C (in µgg^{-1} or %) in relation to total suspended matter concentration (mgL^{-1}) in October 1975, from Duinker, 1980a. ■ : Rhine river, ▲ : Scheldt river.

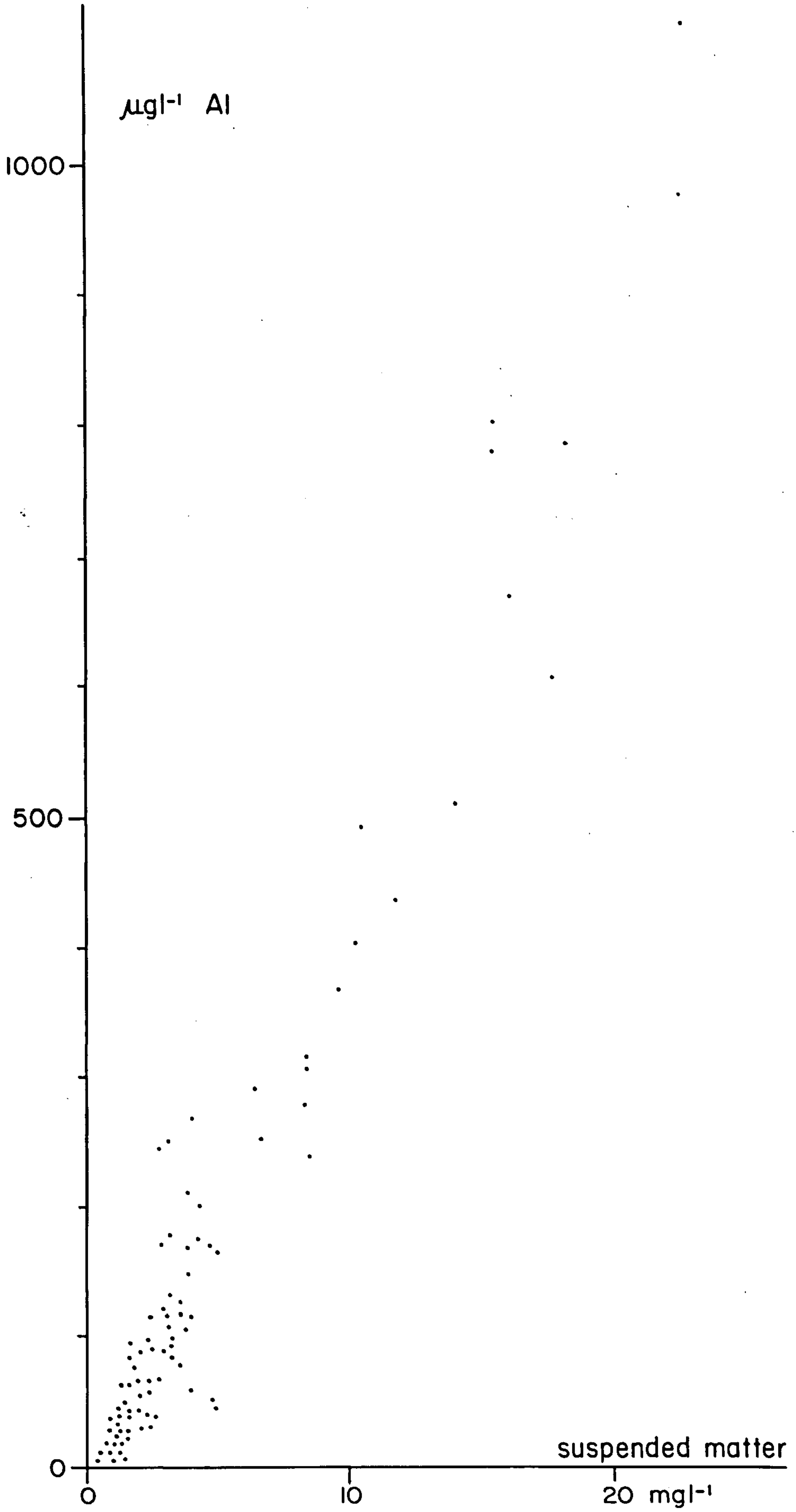


Fig. 5. Concentration of particulate Al (mg.L^{-1}) in relation to the concentration of suspended matter (mg.L^{-1}) in the samples obtained in October 1975. No river data included, from Duinker 1980a.

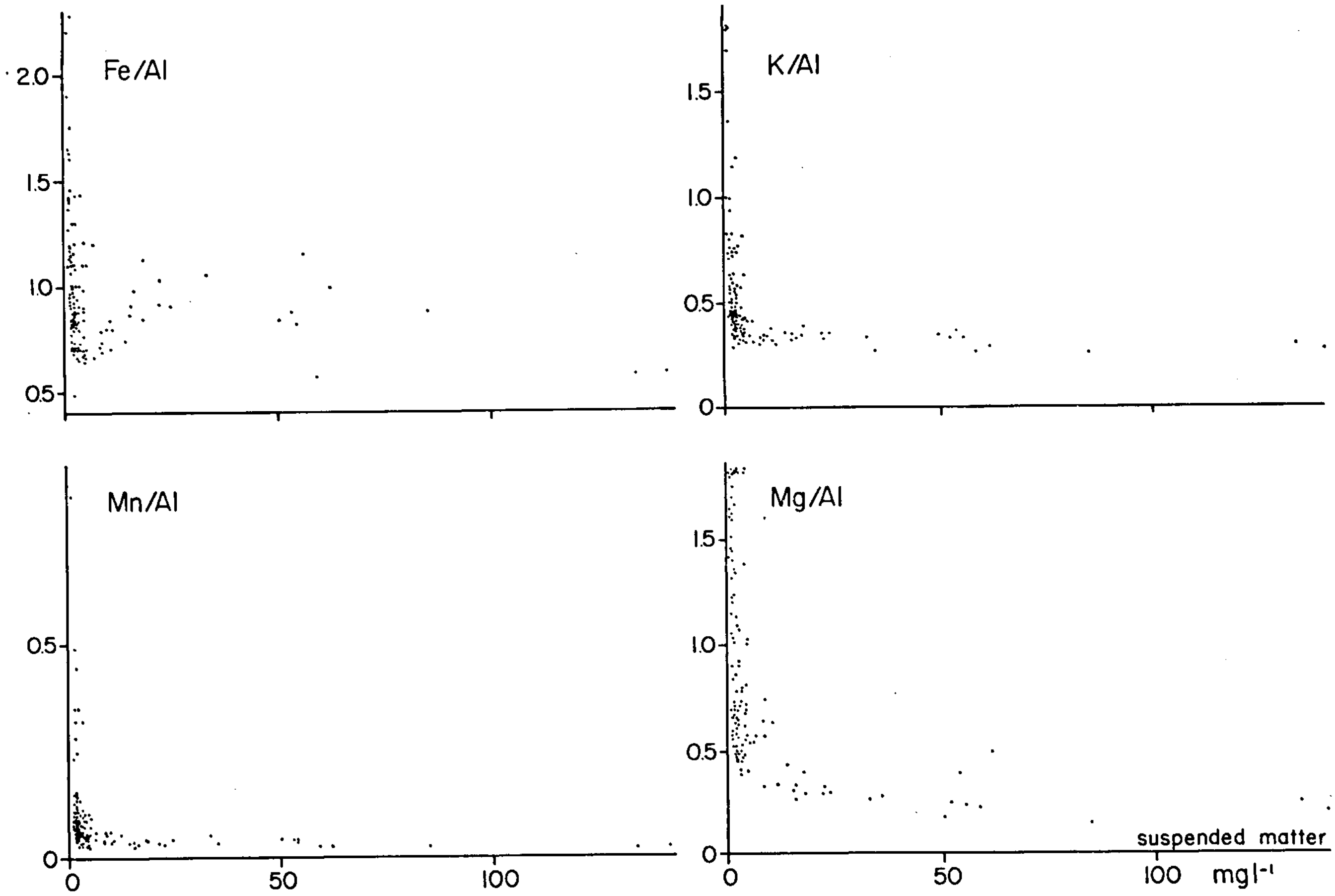


Fig. 6. Elemental/Al ratios for Fe,Mn,K and Mg in suspended matter obtained in October 1975. No river data included, from Duinker, 1980a.

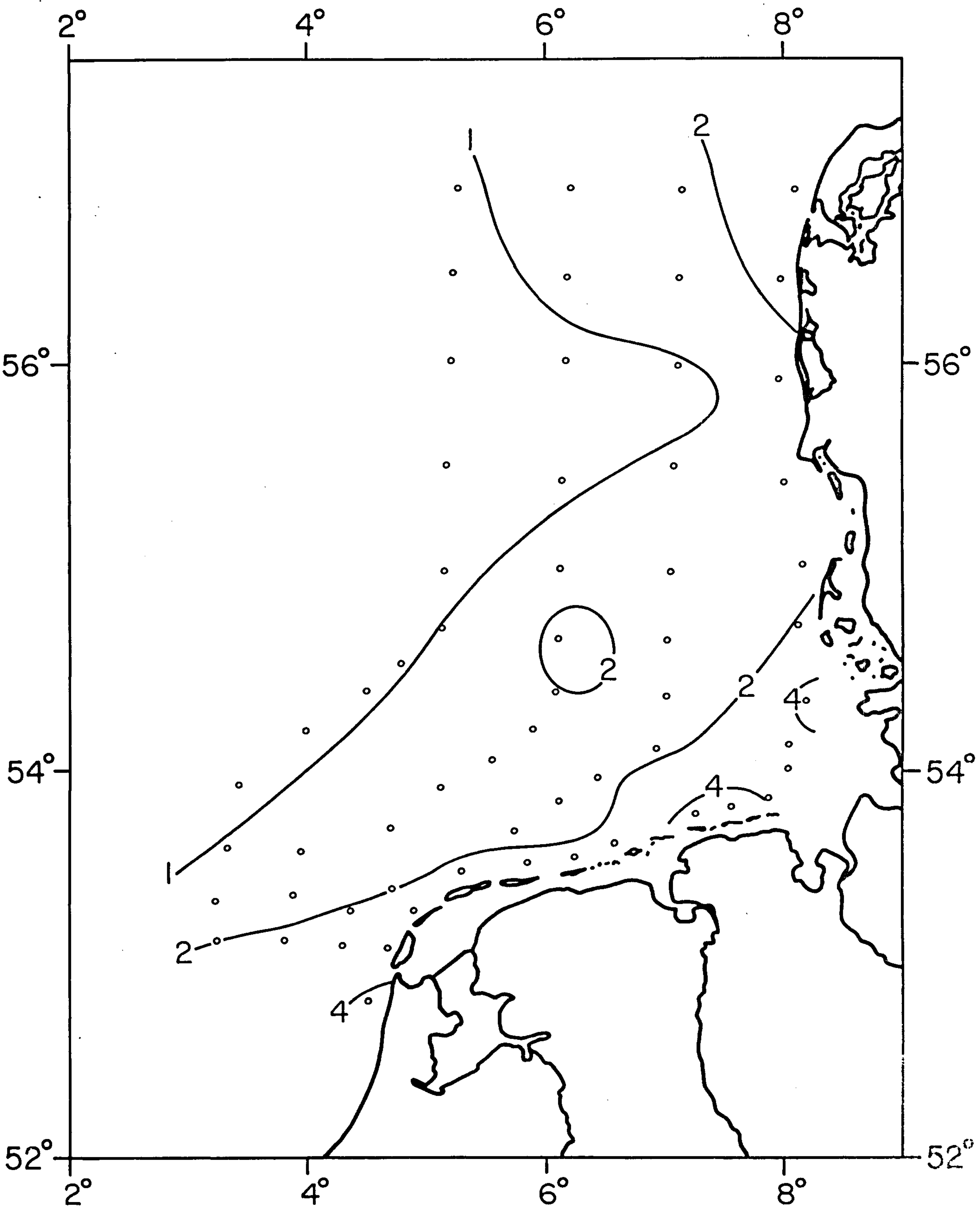


Fig. 7. Distribution of seston concentration (mgL^{-1}) in the surface layer in April-May 1974, from Duinker, 1980a.

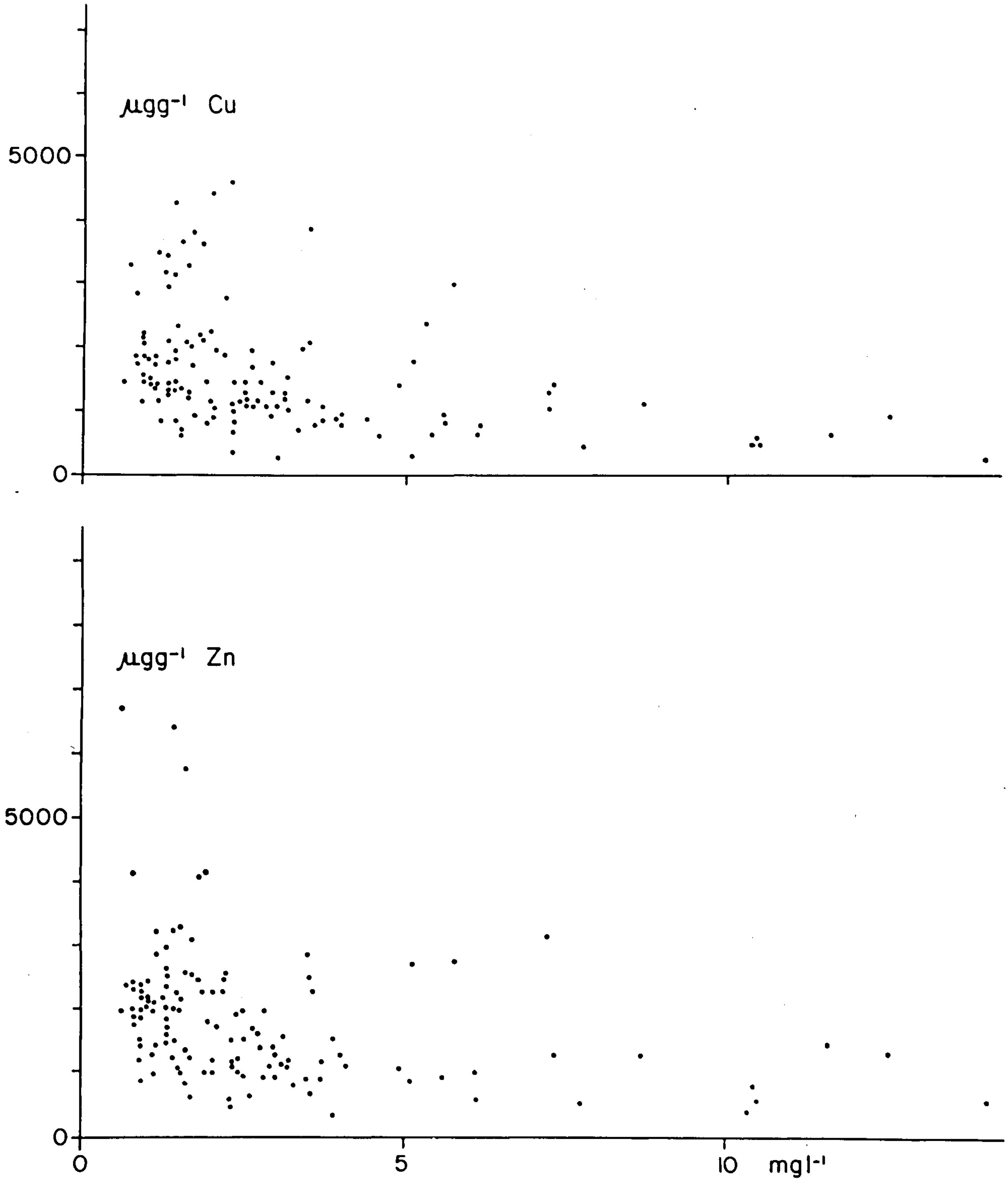
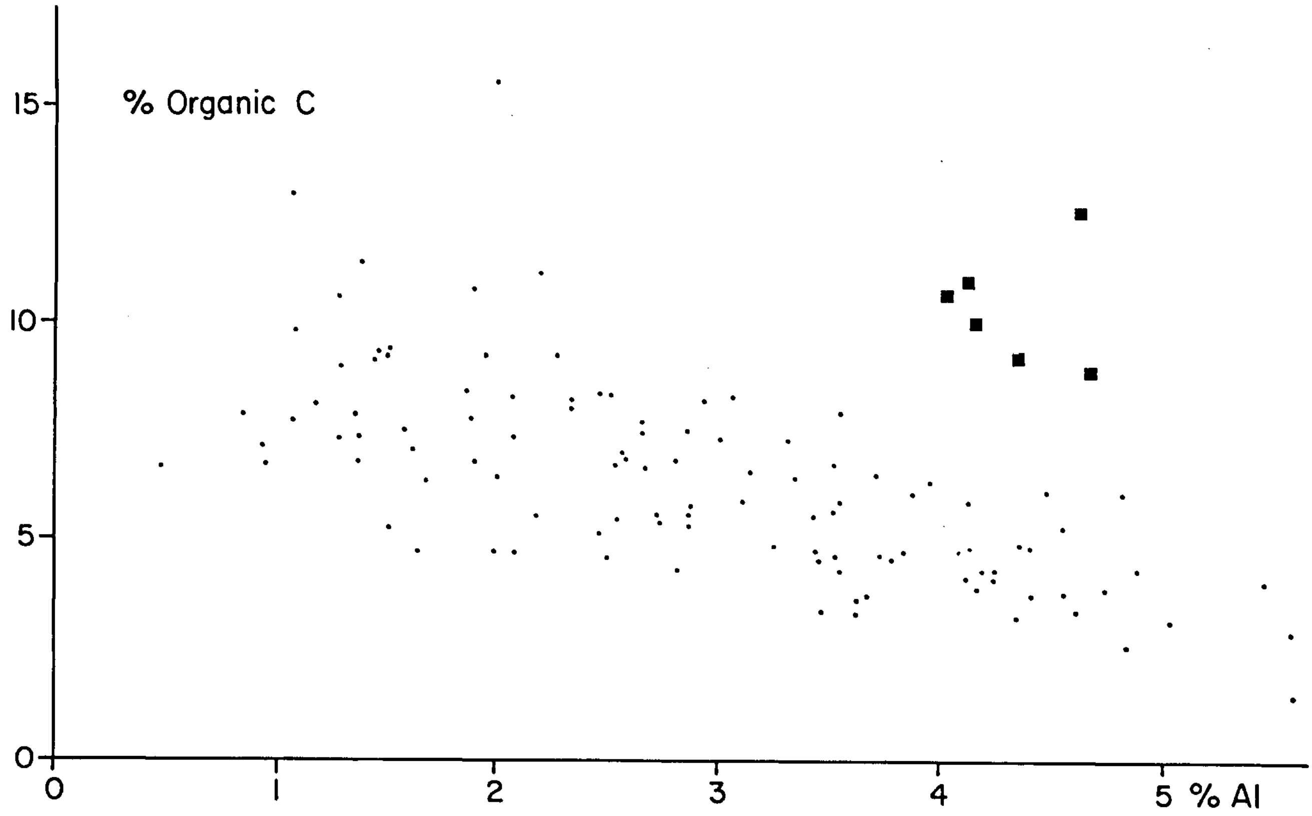


Fig. 8. Elemental content of Cu and Zn ($\mu g.g^{-1}$) in relation to total suspended matter concentration (mgL^{-1}) in April-May 1974, from Duinker, 1980 a.



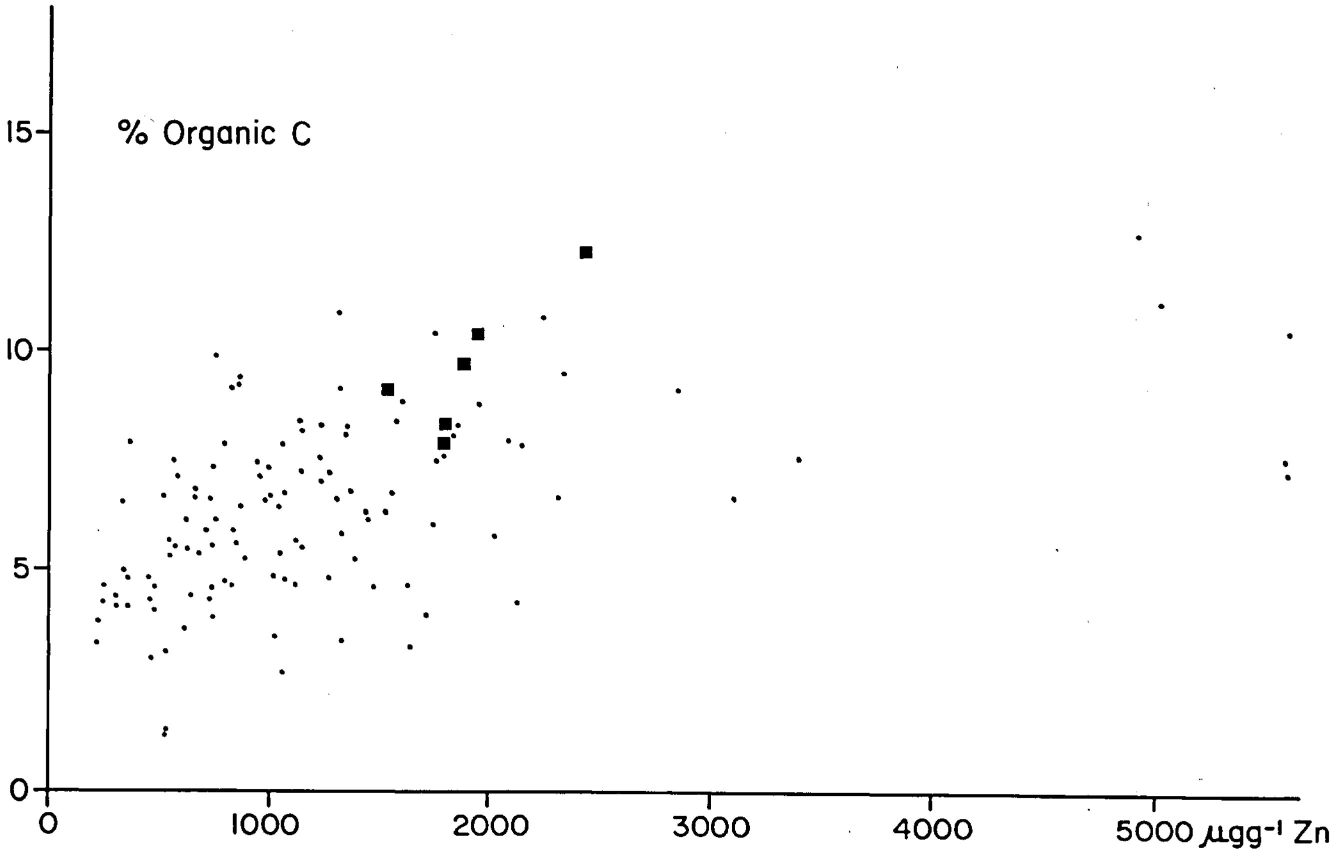


Fig. 9. Relation between contents of Zn and organic C and of Al and organic C in samples obtained in October 1975, Scheldt river values included.

■: Rhine river.

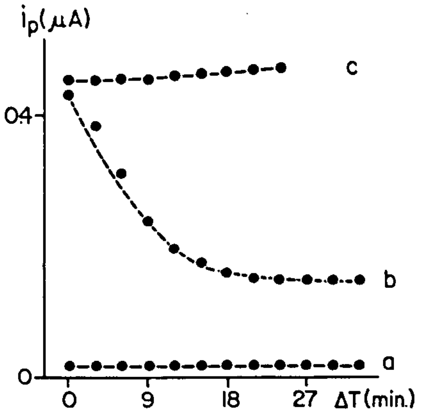


Fig. 10. i_p (Cu) in consecutive runs in the same cell content. T_e = 60 sec., each cycle taking 3 min; a, seawater at pH 8.1;b, seawater after spiking with one standard aliquot, increasing the copper concentration by 16 μgL^{-1}; c, seawater at pH 2.7, spiked as in b, from Duinker & Kramer, 1977.

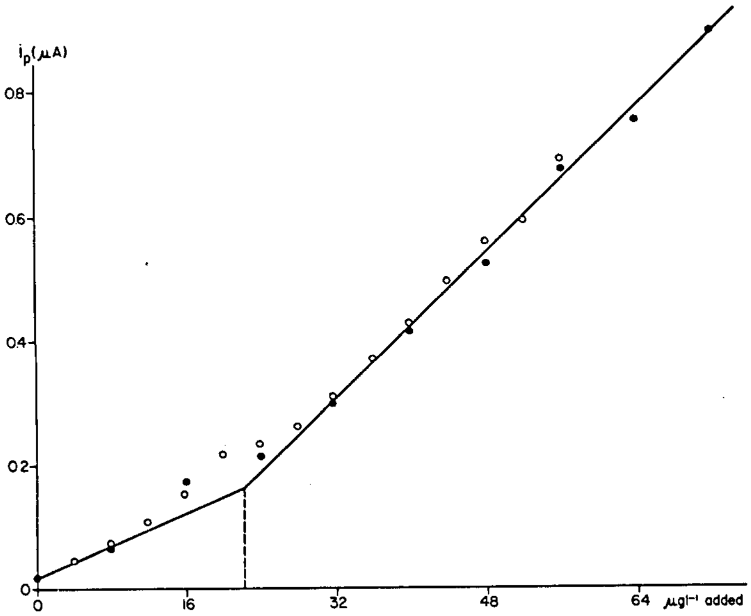


Fig. 11. i_p (Cu) measured immediately after spiking seawater with several aliquots of ionic copper at pH 8.1. Each spike increased copper concentration by 4 μgL^{-1} (experiment with each cycle of measurements taking 210 sec., open symbols) and 8 μgL^{-1} (experiment taking 300 sec., closed symbols). T_e = 60 sec., from Duinker & Kramer, 1977.

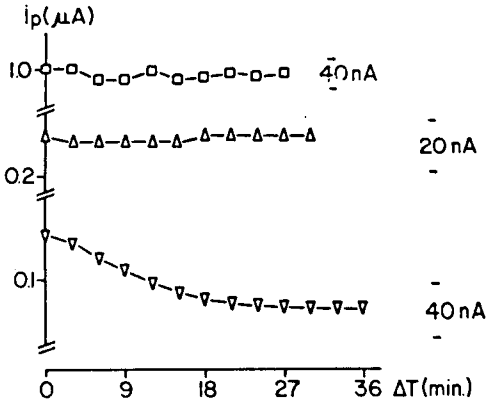


Fig. 12. i_p for Pb (▽), Cd (△), and Zn (□) in consecutive runs in seawater samples at pH 8.1, spiked with 30 μgL^{-1} Pb, 8 μgL^{-1} Cd and 16 μgL^{-1}Zn. Separate series of measurements for each individual element. T_e = 60 sec., each cycle of measurements taking 3 min.

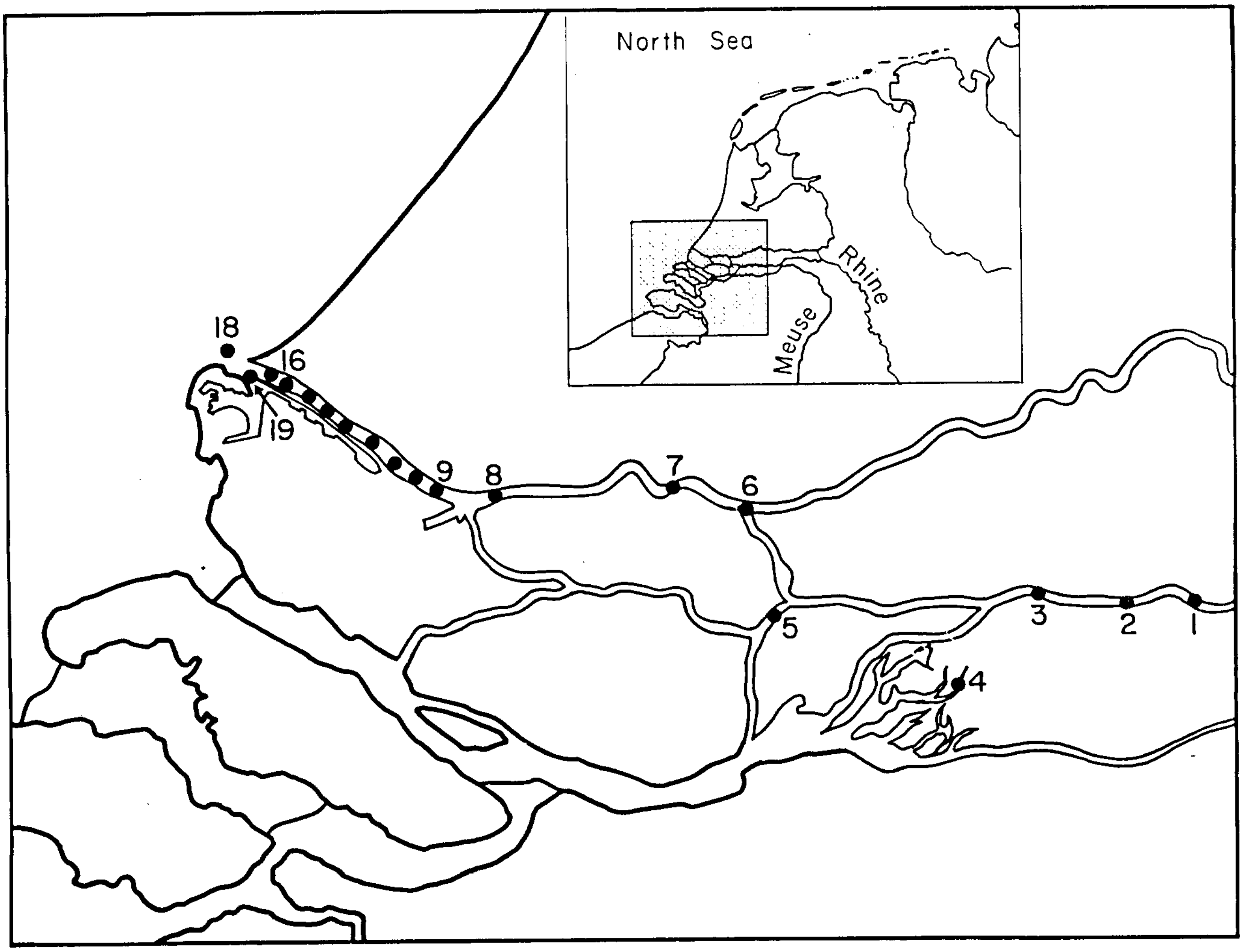


Fig. 13. Sampling stations in the Rhine estuary, for data given in figures 14-18, from Duinker & Nolting 1978.

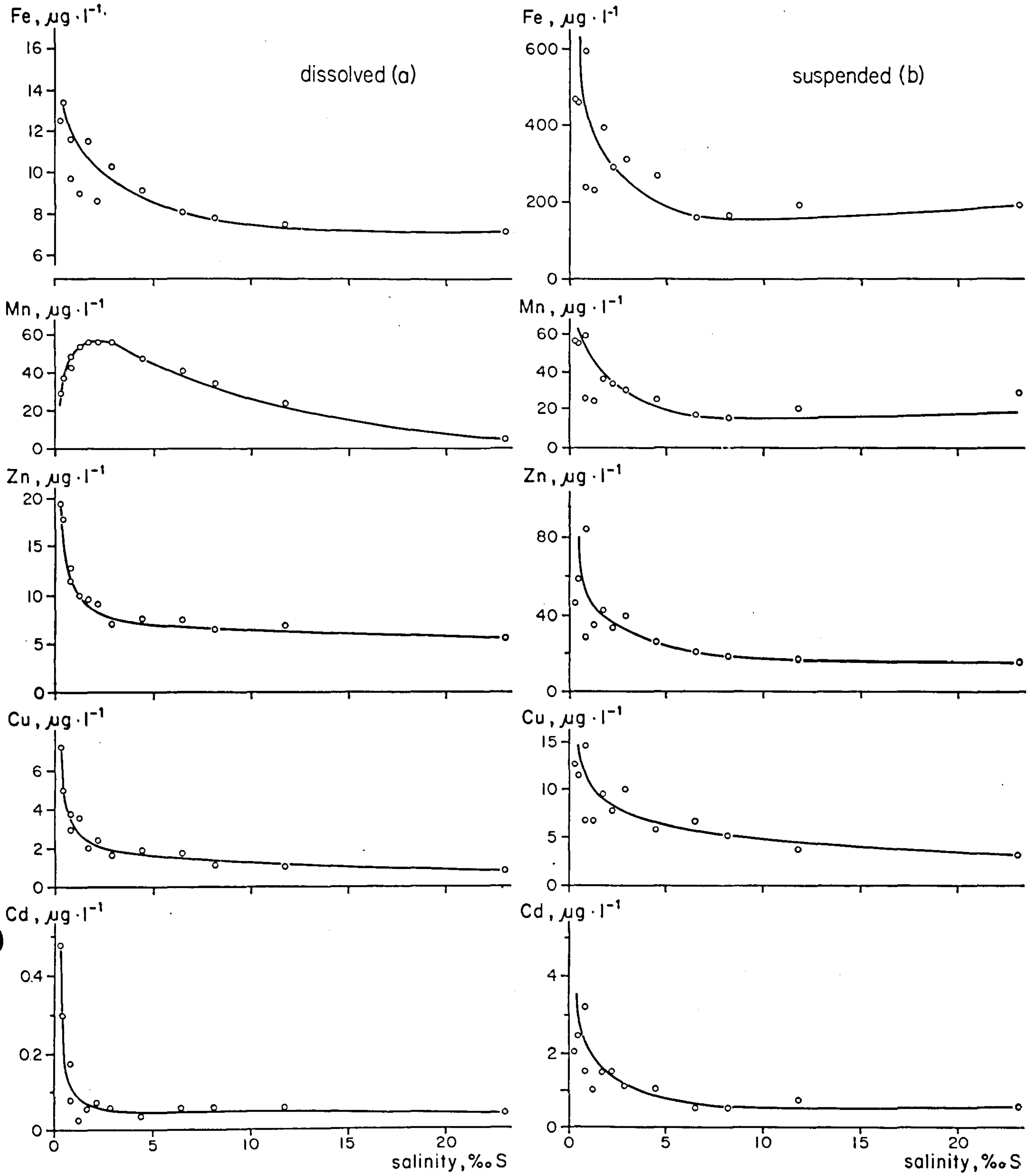


Fig. 14. Dissolved (a) and particulate leacheable (b) metal-salinity plots for the data of the survey in the longitudinal section of the Rhine estuary. Sampling stations 6 to 18 (Fig. 13), from Duinker & Nolting, 1978.

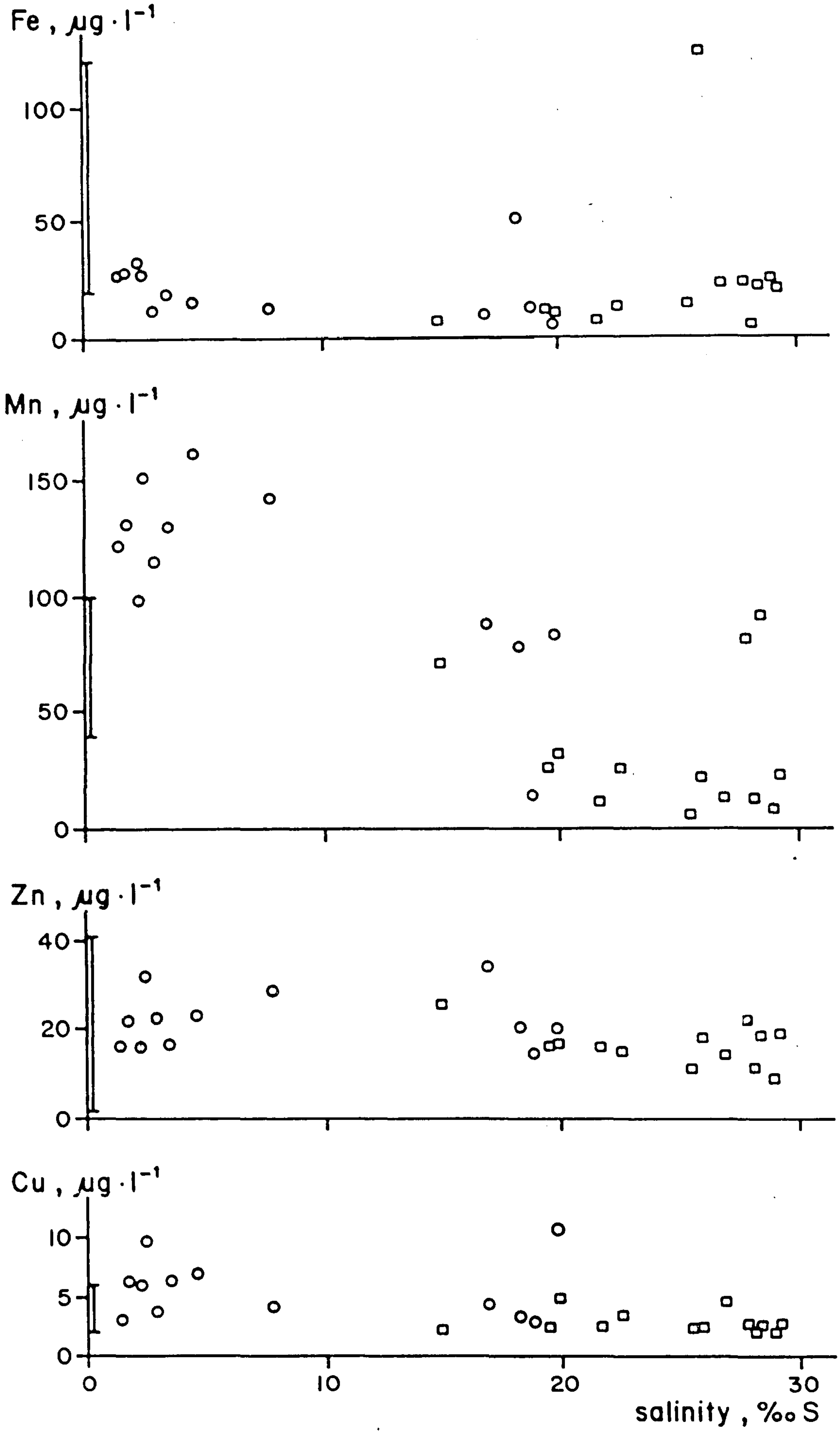


Fig. 15. Dissolved metal-salinity plots for the data of the fixed station 17 in the surface (O) and near-bottom (□) layer and those of the fixed station 6, the latter indicated as a range of values at 0.4 °/ooS (Fig. 13), from Duinker & Nolting 1978.

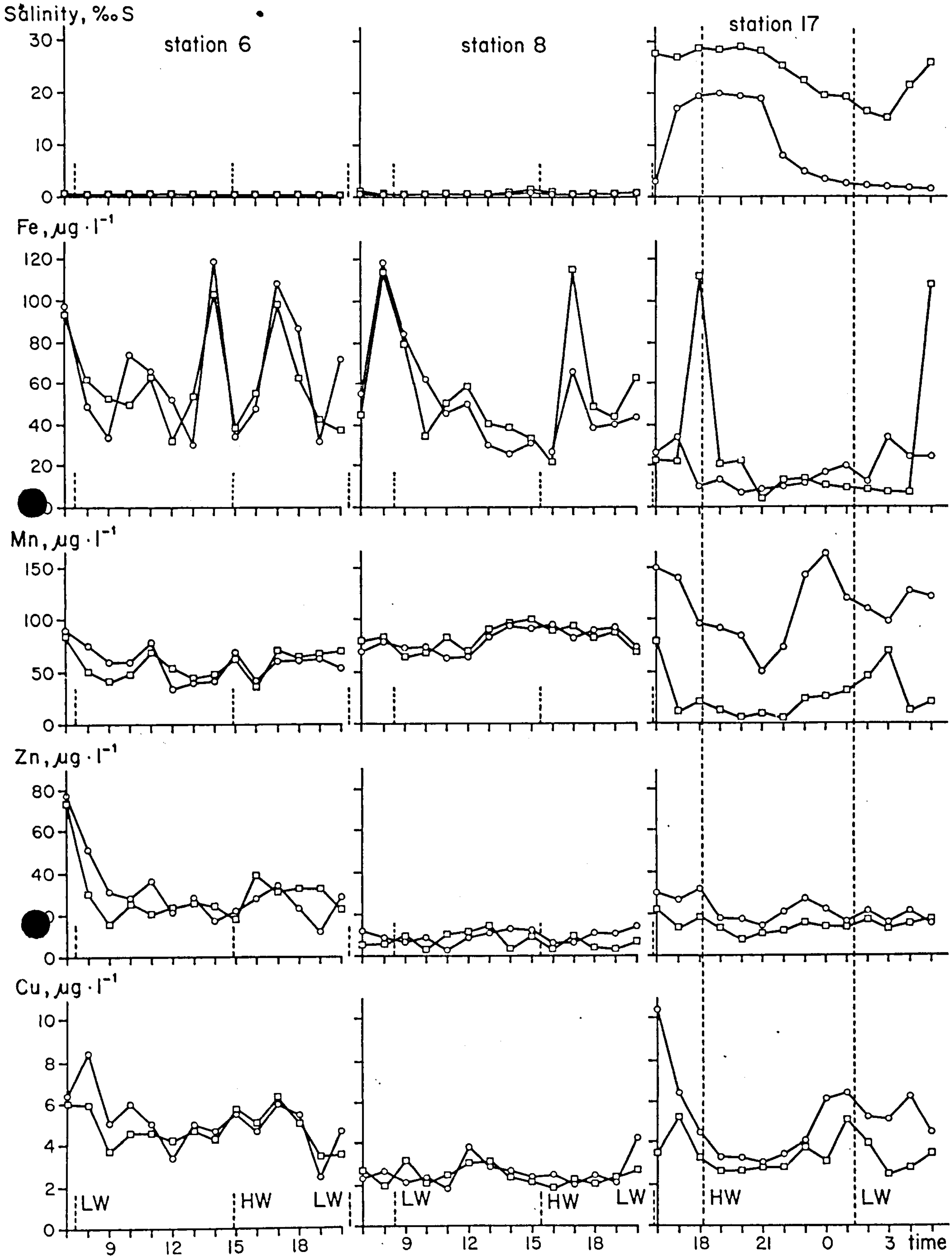


Fig. 16. Salinity and dissolved concentrations of Fe,Mn,Zn and Cu at the fixed stations 6,8 and 17 at 1-hour intervals. Surface (O) and near-bottom layer (□). Times of high and low water indicated (Fig. 13). From Duinker & Nolting, 1978.

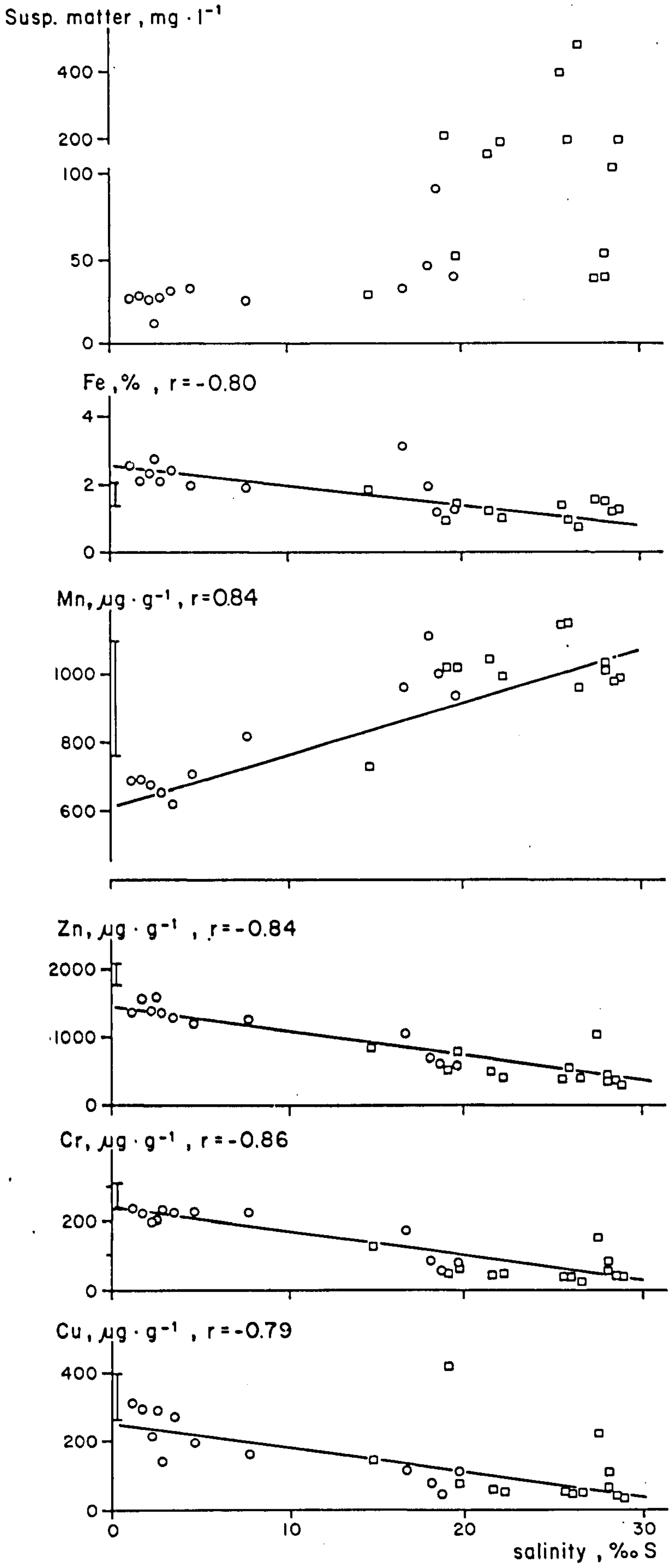


Fig. 17. Relation between salinity and particulate leacheable Fe,Mn,Zn,Cr and Cu concentrations ($\mu g \cdot g^{-1}$,%) in surface (O) and near-bottom (□) samples of station 17. The data of stations 6 and 8 are included as a range of values at 0.4 $^{o}/oo$ S (Fig. 13), from Duinker & Nolting, 1978.

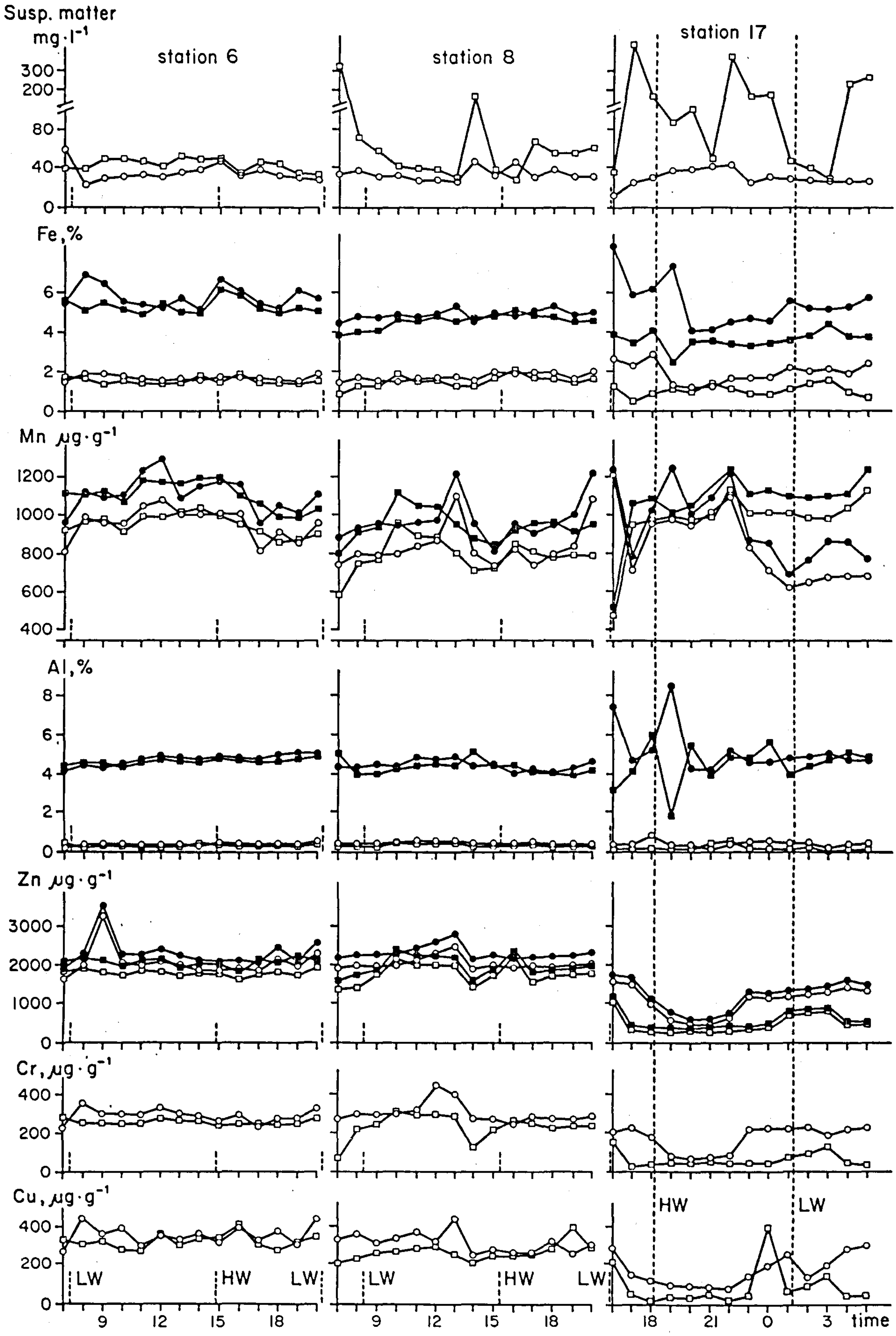


Fig. 18. Concentrations of suspended matter (mg·L^{-1}) and particulate Fe,Mn,Al,Zn, Cr and Cu for the samples of the fixed stations 6,8 and 17 at 1-hour intervals (Fig. 13). Leacheable surface (○) and near-bottom layer (□) concentrations, and total surface (●) and near-bottom (■) concentrations on a weight per sediment dry weight basis (µg·g^{-1},%). Times of high and low water indicated. (Accurate total Cr and Cu concentrations not available: the fractions of the total concentrations that are leached by the method used vary between 60 and 80 % for Cu and between 50 and 70% for Cr.), from Duinker & Nolting, 1978.

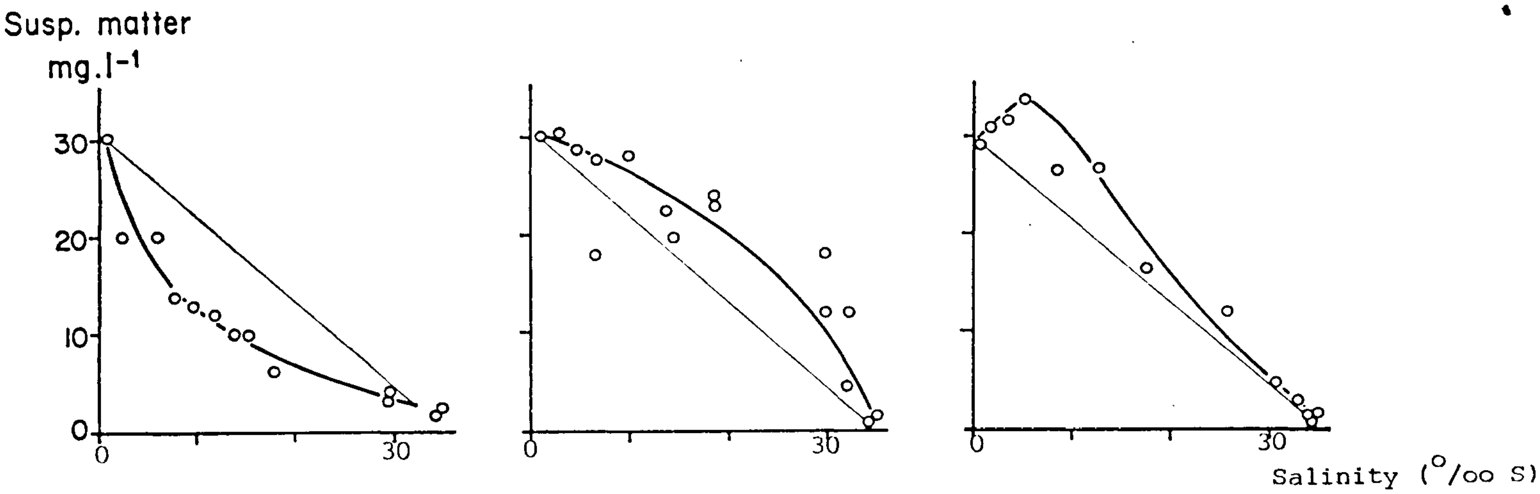


Fig. 19. Suspended matter concentrations in surface samples of a transect off the Rhine river in the Dutch coastal area in September (left), October (middle) and November (right) 1973. From Duinker & Nolting 1976.

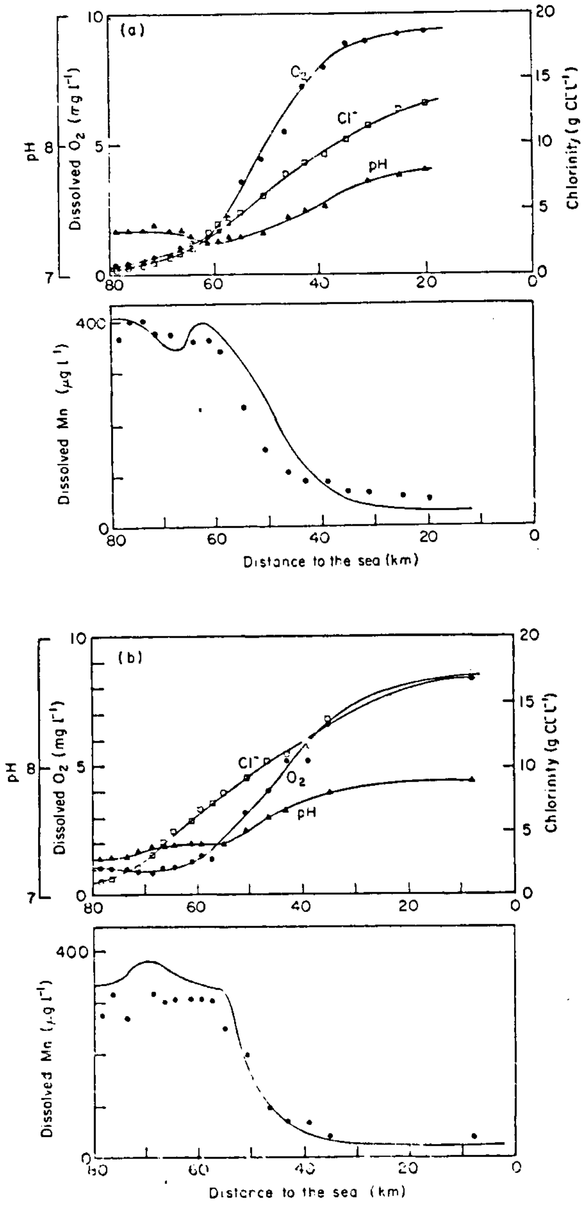


Figure 20. Comparison between experimental profiles of dissolved manganese concentration in the Scheldt estuary (black dots, lower diagram) and profiles computed with the thermodynamic equilibrium model using the experimental profiles of chlorinity, oxygen concentration and pH smoothed as shown in the upper diagram. (a) April-May 1974, (b) July 1974. From Wollast, Billen & Duinker, 1979.

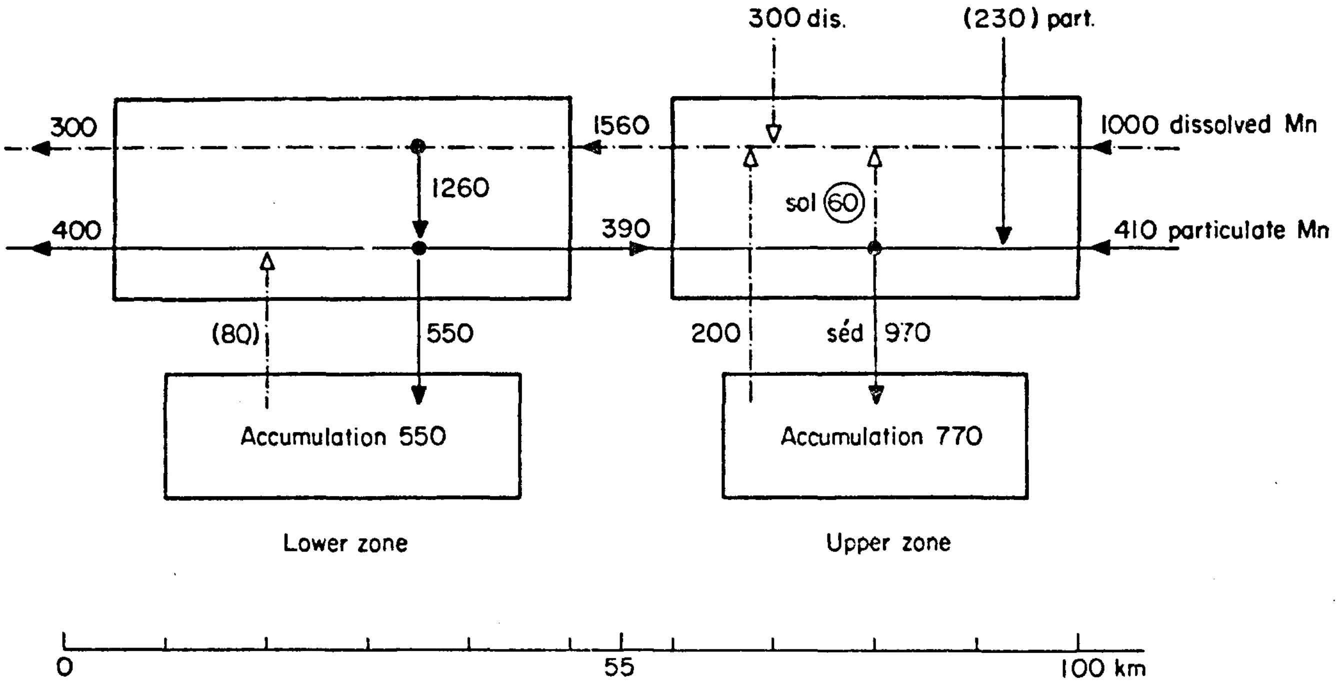


Fig. 21. Tentative mass balance of manganese in the Scheldt estuary. The unit of measurement in tons year^{-1}. From Duinker, Wollast & Billen (1979).

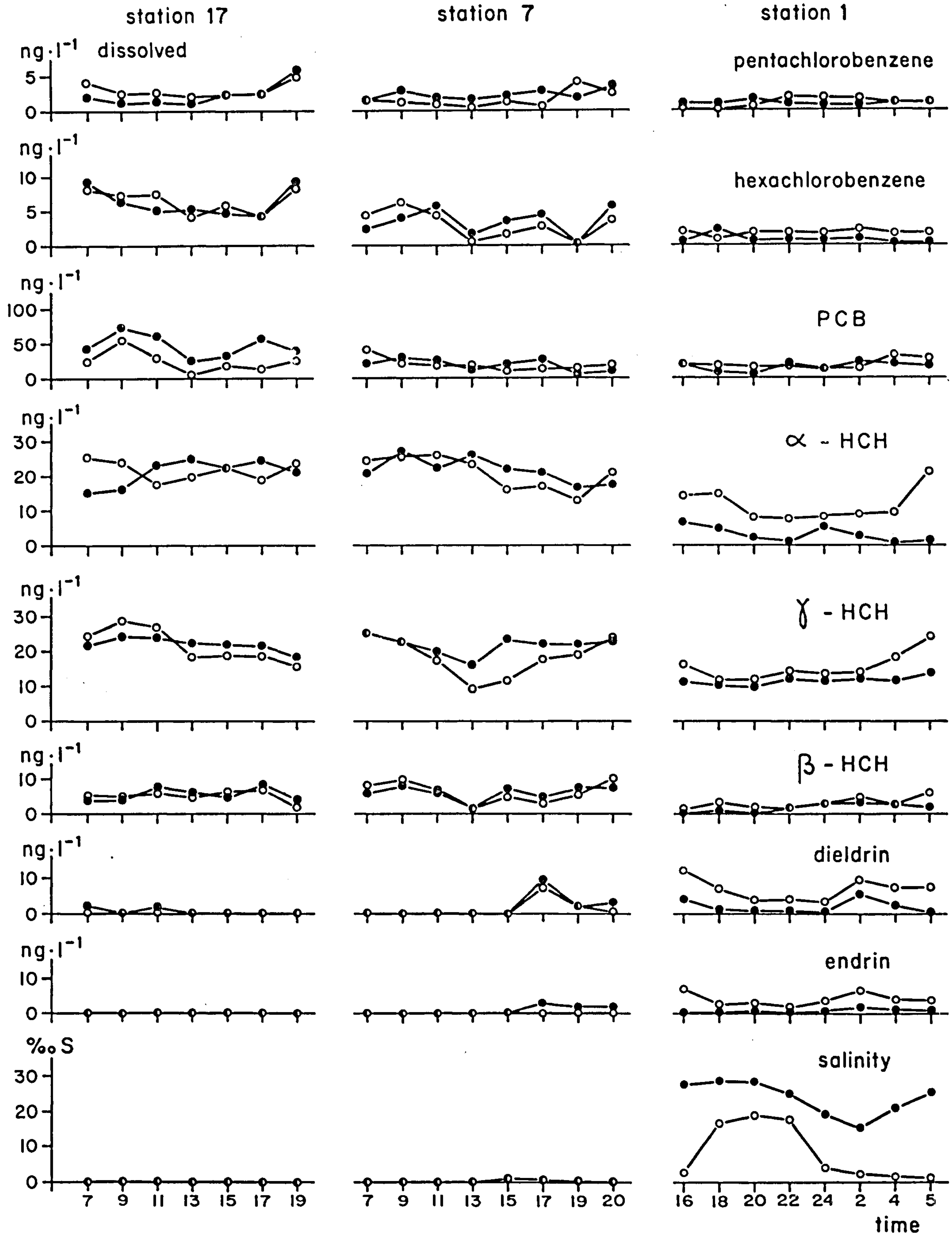


Fig. 22. Concentrations of dissolved organochlorines (ng·L^{-1}) and salinities (^{o}/oo S) in samples obtained at the fixed stations 17, 7 and 1 at surface (O) and near-bottom (●), at 11, 12 and 18 December 1974 (Fig. 13). From Duinker & Hillebrand, 1979b).

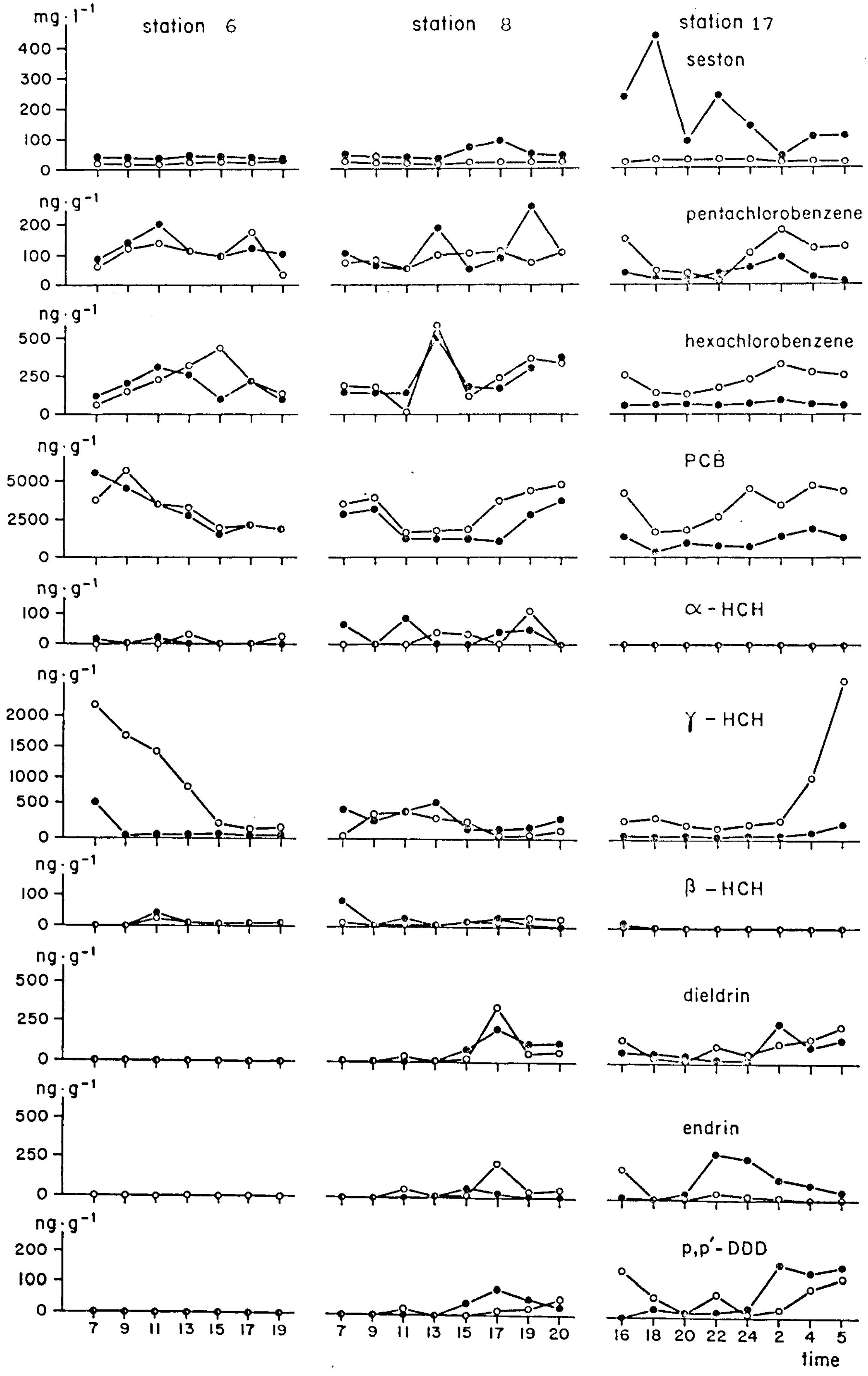


Fig. 23. Concentrations of seston (mg·L^{-1}) and organochlorines in seston (ng·g^{-1} seston dry weight) in samples obtained at the fixed stations 6, 8 and 17 at surface (O) and near-bottom (●), at 11, 12 and 18 December 1974 (Fig. 13). From Duinker & Hillebrand, 1979b.

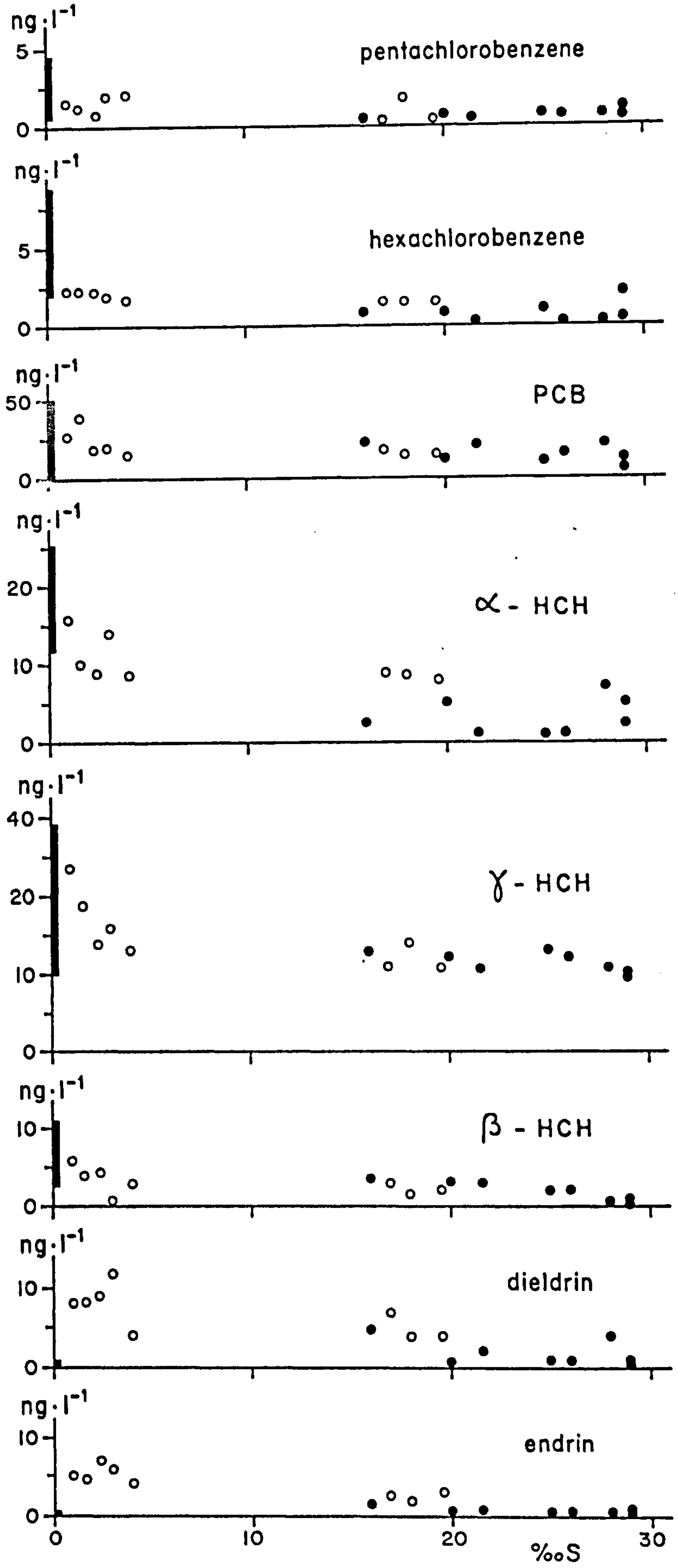


Fig. 24. Dissolved concentrations of organochlorines versus salinity in samples obtained at the fixed stations 6, 8 and 17 at surface (O) and near-bottom (●), at 11, 12 and 18 December 1974. The fresh water data are given as the range observed, represented by vertical bars at river water salinity (Fig. 13). From Duinker & Hillebrand, 1979b.

Fig. 25.

Chromatograms of the first fractions of extracts of water (a) from the central part of the Southern Bight (Station 66, Fig. 1) and (b) from the Danish Wadden Sea (position 68). The peaks corresponding to peaks in Clophen A 30 (c) are indicated by symbol O and those in Aroclor 1254 (d) by symbol ●. Peaks used for quantitation in terms of Clophen A 50 are indicated by ✱ . Chromatograms of blanks obtained by extracting water that had already been extracted twice given in a' and b'. Sample volume 120 litres. Temperature programmed condition $160^{\circ}C$ to $215^{\circ}C$, $4^{\circ}C$ min^{-1}. Column 1.5 % SP2250, 1,9 % SP2401 on 100-120 mesh Supelcon AWDMCS, 1.8 m x 0.64 cm O.D. After Duinker & Hillebrand, 1976b.