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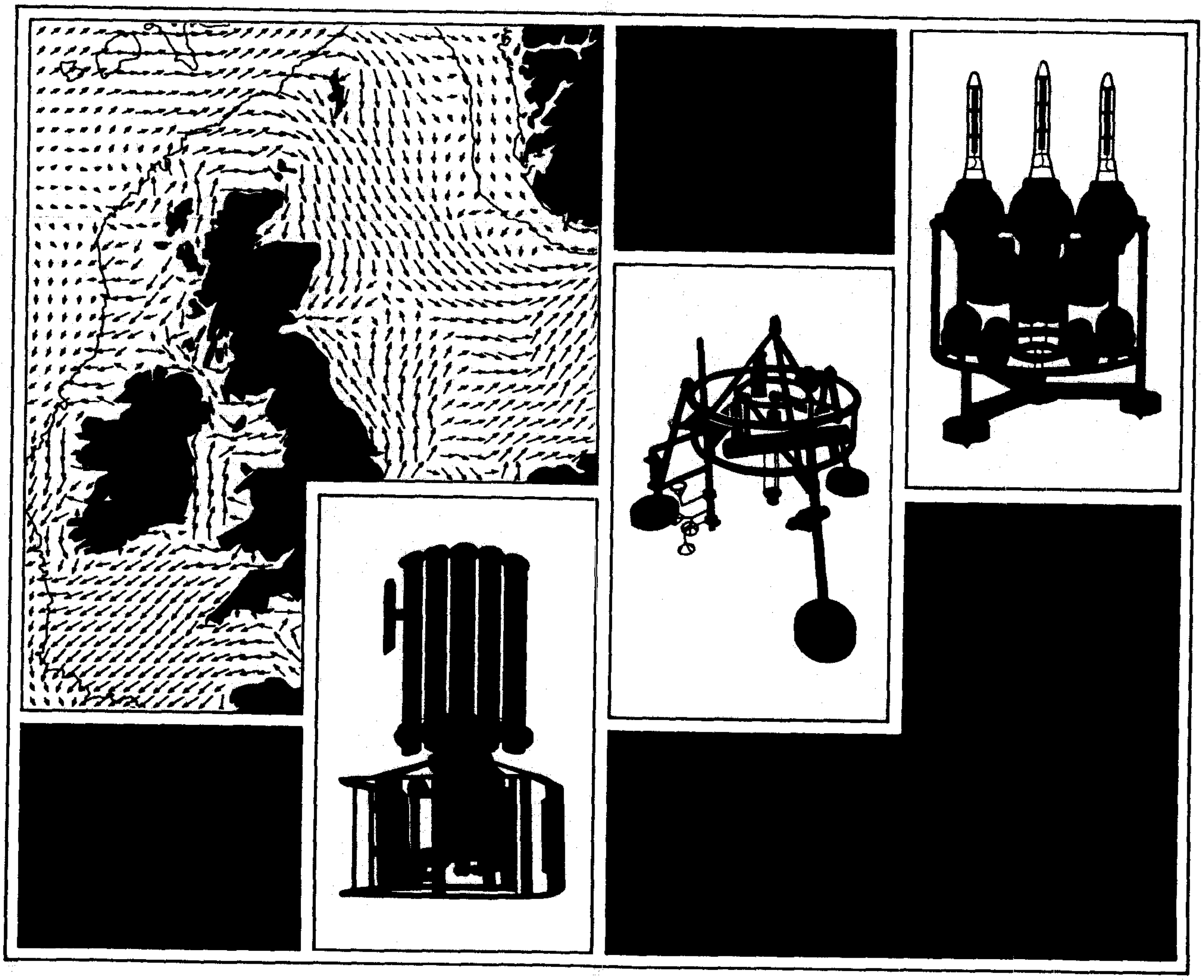
J P McManus
Report No 32 1993



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ABSTRACT

The NERC's North Sea Community Research Project (1987 - 1992) provided an extensive set of synoptic observations recorded on 15 monthly Survey cruises in the southern North Sea. Dissolved trace metal concentrations at over 100 locations were determined on 4 of these cruises. Multiple linear regression is used here to provide quantitative comparisons between these observations and results from numerical model simulations. Source concentrations of the dissolved trace metals Cadmium, Copper, Lead, Zinc and Nickel from rivers, the atmosphere and adjacent sea regions were determined.

For Cadmium, Copper and Nickel, these derived input concentrations are in reasonable agreement with values cited in the 1987 Quality Status Report. In the case of Lead and Zinc, discrepancies between the present results and those from the Quality Status Report are attributed to the affinity of these metals for the particulate phase (this process was not incorporated into the numerical model).

Calculation of correlation coefficients between observed and simulated metal distributions provides a quantitative assessment of their correspondence.

ACKNOWLEDGEMENTS

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CONTENTS

1 INTRODUCTION

The North Sea Project Data Set (BODC/NERC, (1992)) comprises one of the most detailed sets of observations ever undertaken in any shelf sea. Reproduction of these observed contaminant distributions by numerical simulation was one of the major goals of the North Sea Project (NSP). The results of these simulations enable us to both identify and quantify those important non-conservative processes i.e. source and sink terms, that determine the cycling and fate of individual constituents. However, uncertainties in the source concentrations and complex temporal and spatial overlapping of the distributions from each source complicates such simulations.

The approach used here is to simulate, separately, the dispersion patterns for each source using the known volume discharge (of rivers, rainfall and advective transport) but adopting unit concentration. The actual source concentrations are then calculated by means of multiple linear regression between these dispersion model results and the NSP observations. These source concentrations are then compared with values taken from the 1987 Quality Status Report ('87 QSR), International Conference on the Protection of the North Sea, (1987a, 1987b)

The sources considered were: advection across the Northern Boundary of the model (56°N), advection through the Dover Strait, river discharges from the Humber, the Thames, the Rhine (including the Meuse and the Scheldt), the Elbe (including the Ems and the Weser) and precipitation. The dissolved metals considered were Cadmium (Cd), Copper (Cu), Lead (Pb), Zinc (Zn) and Nickel (Ni). Survey data for these metals were taken at some 100 stations on each of four cruises, CH33 (August 1988), CH43 (January 1989), CH51 (May 1989) and CH61 (October 1989). The Survey track which was followed on these cruises is illustrated in Figure 1.1.

The regression technique was also used to estimate source concentrations of Phosphate and Nitrate for the Rhine and the Elbe. The results were compared with observations made during CH72C, i.e. the Rhine plume study of 6 - 19 October, 1990, since no suitable nutrient data was presented in the '87 QSR.

Section 2 describes the mechanism by which the results of the numerical model of dispersion were combined with NSP observations to provide estimates of source concentrations of dissolved trace metals.

Section 3 examines these calculated source concentrations i) for each contaminant and ii) for each source.

The concluding section of this report, Section 4, discusses ways by which certain anomalous results might be improved by the inclusion of relevant inter-related physical, chemical, biological and sedimentological processes into the numerical model.

2 MULTIPLE REGRESSION BETWEEN MODEL AND OBSERVED DATA

2.1 Model Simulations of Dispersion

Simulations of dispersion patterns for tracers introduced via i) the Northern Boundary, ii) the Dover Strait, iii) the atmosphere (via precipitation), iv) the Thames, v) the Humber, vi) the Rhine, Meuse and Scheldt and vii) the Elbe, Ems and Weser were made using the Proudman Oceanographic Laboratory's (POL's) General Purpose Model in dispersion form, see Jones (1991). The model uses a 35km rectangular grid and incorporates vertically averaged (2-D) horizontal advection together with horizontal dispersion.

The calculation domain was restricted to a northern boundary at 56°N, a western boundary at 2°W, a southern boundary at 51°N and an eastern boundary at 9°E. Advective velocities in the model were specified as a sum of i) tidal residuals and ii) steady-state wind driven residuals obtained from a shelf wide version of POL's General Purpose Hydrodynamic Model, Jones (1991). The simulations began in January 1987 i.e. 19 months before the start of the first Survey cruise, with assumed zero concentration. Observed river flow, rainfall and evaporation data were specified in these simulations.

In a series of model simulations, a contaminant with unit concentration was input from a single source into the Southern North Sea, at the observed volume flow rate. Zero contaminant concentration was specified for the remaining sources. The model was run 7 times, once for each of the sources under consideration. The grid utilised in the model, showing the positions of each of the sources, is illustrated in Figure 2.1. Model results, in the form of concentrations for each grid box in units of mol/m^3, were stored for the months of the four Survey cruises for which dissolved metal data was collected, i.e. CH33 (August 1988), CH43 (January 1989), CH51 (May 1989) and CH61 (October 1989). As an example, the computed dispersion patterns for continuous discharges of unit concentration from a) the Thames, b) the Humber, c) the Rhine and d) the Elbe, during CH43, are shown in Figures 2.2a - 2.2d.

2.2 North Sea Project Data

The British Oceanographic Data Centre (BODC) holds all North Sea data sets collected during NERC's North Sea Project (1987 - 1992). It is stored in compact disc format, see BODC/NERC (1992). Data relating to the dissolved metals Cd, Cu, Pb, Zn and Ni were retrieved from this source, via an Oracle relational database, using the SQL command language.

Data for the four NSP Survey cruises (Section 2.1) were reduced to depth and area-averaged values corresponding to the appropriate model grid square. These data were then stored in an array y(i,j,t) where i and j denote the model grid coordinate and t the month of the cruise. Table 1b shows the number of these observations for each metal amounting to an average of 393 values from the four cruises.

2.3 Multiple Linear Regression

The different sources simulated by the model were then related to the observed concentrations of various dissolved trace metals by multiple linear regression. NSP observations for dissolved Cd, Cu, Pb, Zn and Ni and computed concentrations were fitted to an equation of the form,

$$y(i,j,t) = a_1 x_1(i,j,t) + a_2 x_2(i,j,t) + ... + a_n x_n(i,j,t) \tag{2.1}$$

where $x_k(i,j,t)$ is the computed concentration at grid coordinate (i,j) and time,t due to a continuous input of unit concentration from source k. The series x_1 to x_n represents the model simulations from each of the n separate sources (where n=7). The coefficients $a_1, a_2, a_3, ..., a_n$ are the regression coefficients, which provide us with estimates of the input concentrations from the n sources.

Once derived, these input concentrations can be compared with corresponding values taken or derived from the '87 QSR.

The residual advective velocities used in the model simulations were obtained from a hydrodynamic model with no rainfall, evaporation or river flows included. These residuals are therefore based on the assumption that the flows across the Northern Boundary and the Dover Strait are the only sources of water into and out of the model. Since the rivers, rainfall and evaporation all affect the amount of water in the system, the computed concentrations used in the regression calculations were modified to take this into account. This modification involved a scaling of the model results for the Northern Boundary and Dover Strait sources via multiplication by a coefficient, which is defined as follows:

$$\frac{1 - \Sigma_{rain+rivers}\, x(i,j,t)}{x_{nb}(i,j,t) + x_{ds}(i,j,t)} \tag{2.2}$$

where $x_{nb}(i,j,t)$ and $x_{ds}(i,j,t)$ are the model results at location (i,j) and time, t, due to the Northern Boundary and Dover Strait sources respectively, and the summation is taken over the model results for the rain and rivers only.

3 RESULTS

In general, agreement between source concentrations derived from this multiple linear regression approach and values taken from the '87 QSR was very encouraging. For source concentrations along the Northern Boundary and Dover Strait, good agreement was obtained for all five metals considered. Overall, the best agreement occurred for those metals exhibiting the most 'conservative' behaviour, i.e., Cd and Cu. Conversely, the results for Pb (and also Zn, though to a lesser extent) contained a number of anomalies, discussed further in Section 4.

The results are illustrated in Figure 3.1 and listed in Table 1a.

The multiple linear regression (equation 2.1) was used to fit dispersion model results from seven sources (Section 2.1) to NSP observations, in order to determine source concentrations of the dissolved trace metals Cd, Cu, Pb, Zn and Ni.

Problems arose when applying the full expansion (equation 2.1) to the cases of the Rhine and the Elbe estuaries. Possible physical features responsible for this are i) the complex individual coastal circulation patterns of these estuaries, which are not resolved in the model, ii) the approximately equal magnitudes of the two estuarine outflows and iii) the close geographic proximity of these two sources.

In an attempt to overcome these difficulties, equation 2.1 is modified to

$$y(i,j,t) = a\,x(i,j,t) \tag{2.3}$$

where y(i,j,t) are a restricted set of observed (NSP) concentrations lying within a radius of approximately 100 km from the chosen source. These sets comprise 60 observations for the Rhine and 30 for the Elbe. x(i,j,t) are the corresponding model results and 'a' is the regression coefficient, which represents the source concentration of the contaminant.

Similar problems (for the less conservative metals, Pb, Zn and Ni) were encountered for the cases of the Thames and the Humber. Again only observations within about 100 - 175 km of the source were considered, but this time a mean term was also included in the modified regression equation, which is,

$$y(i,j,t) = z + a\,x(i,j,t) \tag{2.4}$$

where z is the mean, or background concentration. These mean terms closely approximate the source concentrations from the Northern Boundary (for the Humber), and the Dover Strait (for the Thames).

3.1 Contaminants

In assessing the levels of agreement, the wide range of concentrations in the North Sea must be considered. The ratio between minimum source concentrations along the Northern Boundary and maximum in the Humber are, ('87 QSR data): Cd - 47, Cu - 110, Pb - 713, Zn - 124, Ni - 79. Thus agreement between computed and observed source concentrations within a factor of 2 is considered good and within a factor of 10 reasonable.

Cadmium

Good agreement with '87 QSR values was obtained for source concentrations derived for the Northern Boundary, the Dover Strait and the Rhine. The agreement for the other sources was considered reasonable, with perhaps slight overestimates of the observed source concentrations from the Humber, the Thames and the Elbe. The computed contribution from the Rain (spatially uniform) appears to underestimate the '87 QSR value. This QSR value itself may be an overestimate of the actual contribution from the Rain since it is derived from 'atmospheric' inputs, which do not necessarily imply wet deposition alone. The R^2 statistic, which indicates the level of agreement between modelled and observed concentrations is 0.85 (see Table 1b)

Copper

For Copper the agreement between '87 QSR values and computed source concentrations was within ±50% for all sources under consideration. The computed values slightly overestimate '87 QSR values in each case except the Rhine, where there is a slight underestimate. (R^2 = 0.33)

Lead

The computed source concentrations for the Northern Boundary, the Dover Strait, the Humber and the Thames were in good agreement with the corresponding values derived from the '87 QSR. The computed concentrations for the Rhine and the Elbe however, were an order of magnitude too small and the value obtained for the Rain showed even wider discrepancy with the corresponding '87 QSR value. ($R^2 = 0.58$)

Zinc

As with Lead, good agreement was obtained between '87 QSR and computed values for the Northern Boundary, the Dover Strait and the Humber. The computed values for the Elbe and the Rhine also showed reasonable agreement with concentrations taken from the '87 QSR. However, the computed source concentrations for the Rain and the Thames are, respectively, gross underestimates and overestimates of the '87 QSR values. ($R^2 = 0.60$)

Nickel

Good agreement between '87 QSR and computed concentrations was obtained for the Northern Boundary, the Dover Strait and the Humber, with reasonable agreement (overestimates) for the Rain and the Thames. ($R^2 = 0.83$)

Nutrients

Data for dissolved Phosphate and Nitrate from NSP cruise CH72C were used to test this regression approach. Only observations in the vicinity of the Rhine were considered and the Rhine was assumed to be the only source. Agreement between computed and observed concentrations was good for Phosphate but the computed source concentration of Nitrate was only one quarter of the observed value.

3.2 Sources

The results for each metal described above are now re-examined from a source perspective.

Northern Boundary and Dover Strait

The source concentrations obtained from the multiple linear regression are in good agreement with the corresponding '87 QSR values for all the trace metals considered in this work.

Precipitation

The input concentration of Cu due to precipitation was estimated quite well by the multiple linear regression. The estimates were not so good for the other metals, with underestimates for Cd (reasonable agreement) and Zn and an overestimate for Ni (reasonable agreement). In the case of Pb, the computed and '87 QSR values differ radically.

Humber

For all the metals considered the source concentration estimates from the linear regression were in good agreement with the '87 QSR values, with slight overestimates for Cd and Cu, and slight underestimates for Pb, Zn and Ni.

Thames

The multiple linear regression gave a source concentration for Cu which agreed well with the '87 QSR value. There was also quite good agreement for the source concentrations of Cd, Pb and Ni.

Rhine

Good agreement was obtained for Cd and Cu source concentrations, with reasonable agreement for Zn but for Pb the regression value was an underestimate (order of magnitude too small) of the '87 QSR value.

Elbe

Good agreement was obtained for the source concentration of Cu, and reasonable agreement for the source concentrations of Cd and Zn. For Pb, the results found for other sources are repeated with the regression value an underestimate (order of magnitude too small) of the '87 QSR value.

4 DISCUSSION AND CONCLUSIONS

North Sea source concentrations of dissolved trace metals were determined from multiple linear regression between concentrations computed from a numerical dispersion model and observations from the NSP Survey cruises. These source concentrations were generally found to be consistent with values derived from the '87 QSR. For the Rhine, concentrations obtained for Cd, Cu and Ni also compared favourably with measurements made by Duinker and Nolting (1977), Duinker and Nolting (1982) and Nolting (1986).

The results presented here illustrate how multiple linear regression can be used to produce a quantitative comparison between dispersion model results and observations.

The volume of sea water in the southern North Sea south of 56°N is primarily related to inflows across the Northern Boundary (80 %) and through the Dover Strait (20 %). The source concentrations derived from the multiple linear regression for these two sources are therefore accurately estimated, even for those metals which produce anomalous results elsewhere, like Pb. Likewise, regression determined source concentrations from the relatively isolated Humber are in good agreement with the '87 QSR values for each of the trace metals studied. However, in the case of the Rhine and the Elbe, whose outflows overlap, the regression technique as described in equation 2.2 was less successful. Considering these sources separately with no mean term (equation 2.3) provided us with better estimates for Cd and Cu input concentrations.

These results are particularly encouraging considering the simplicity of the numerical dispersion model used in this work. Since no attempt was made to simulate some of the complex processes which take place along the continental coast, the source concentrations calculated by multiple linear regression for the Rhine and the Elbe estuaries are subject to some error. Another possible source of error is the fact that the concentrations derived from the '87 QSR assume that all the metals under consideration are to be found predominantly in the dissolved phase - this is obviously not the case for a metal such as Pb.

4.1 Recommendations for Further Work

Although the present dispersion model gives a reasonable first order estimate of input concentrations, improved estimates are possible if the coastal processes mentioned above are incorporated into the model simulations. Additional processes for possible inclusion in the model are:

i) Direct Inputs - i.e. dumping from industry

ii) The uptake of metals by suspended particulate material - this results in metals becoming trapped, by sedimentation, in estuaries and coastal areas.

This process is particularly important in the case of Pb, and has the effect of reducing dissolved concentrations to open ocean levels, even though total (dissolved plus particulate) concentrations remain high.

iii) The release into the dissolved phase of metals adsorbed onto sediments

iv) The simulation of coastal trapping by density 'fronts', which can act as barriers to the offshore transport of contaminants

v) Dry deposition, which is the direct uptake of pollutants by the sea surface. The dispersion model assumes that all atmospheric deposition is wet deposition. This is restricted to particles taken up by cloud droplets, and later precipitated, or to the scavenging of particles by falling raindrops and snowflakes.

Atmospheric deposition is most important for metals whose uses or refining involve an atmospheric release, e.g. Lead, Cadmium and Zinc. The atmospheric input of Lead into the Central North Sea is indicated by higher concentrations in surface waters. Lead concentrations across fronts show no major changes, whereas abrupt concentration changes are observed for the other metals.

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	Northern Boundary	Dover Strait	Rain	Humber	Thames	Rhine[1]	Elbe[2]
Cd	**0.018** 0.017[3]	**0.026** 0.019[3]	**0.48** 0.17[3]	**0.67** 1.58[3]	**0.85** 4.74[3]	**0.21** 0.253[4]	**0.22** 0.520[4]
Cu	**0.177** 0.211[3]	**0.314** 0.277[3]	**3.2** 4.3[3]	**19.5** 24.3[3]	**11.95** 12.84[3]	**5.41** 4.713[4]	**5.19** 8.339[4]
Pb	**0.031** 0.038[3]	**0.029** 0.024[3]	**14.8** -0.4[3]	**20.7** 12.9[5]	**19.32** 12.53[5]	**3.46** 0.291[4]	**4.63** 0.344[4]
Zn	**0.48** 0.62[3]	**0.686** 0.760[3]	**22.0** 1.8[3]	**59.7** 46.4[5]	**27.64** 409.4[6]	**30.89** 7.674[4]	**37.6** 17.91[4]
Ni	**0.263** 0.238[3]	**0.392** 0.336[3]	**1.9** 5.1[3]	**20.9** 16.5[6]	**16.9** 54.5[5]	3.296[4]	10.09[4]
PO_4						0.66[7] 0.599[4]	2.635[4]
NO_3						15.5[7] 3.971[4]	31.88[4]

Table 1a: Input concentrations in µg/l (metals) and mg/l (nutrients), obtained from a multiple linear regression between North Sea Project observations and the output from a numerical model of dispersion. Values shown in **bold** are those taken or derived from the '87 QSR.

[1] - Also includes flows from Meuse and Scheldt
[2] - Also includes flows from Ems and Weser
[3] - Taken from a multiple linear regression using all sources
[4] - Rhine/Elbe considered separately (100 km radius)
[5] - Humber/Thames only plus a mean term (100 km radius)
[6] - Humber/Thames only plus a mean term (175 km radius)
[7] - Taken from CH72C data in the region of the Rhine

Trace Metal	Number of Observations	Mean (Observed) Concentration (μg/l)	Standard Deviation (of Observations) (μg/l)	R^2 [*]
Cd	396	0.025	0.012	0.85
Cu	395	0.355	0.514	0.33
Pb	389	0.034	0.030	0.58
Zn	393	0.757	0.643	0.60
Ni	393	0.375	0.193	0.83

Table 1b: Means and standard deviations of observed dissolved metal concentrations, and R^2 values. R^2 is analogous to a correlation coefficient representing the agreement between modelled and observed concentrations.

[*] R^2 represents the proportion of variation in the dependent variable (y) that is explained by the independent variables (x_n).
R^2 = Regression Sum of Squares / Total Sum of Squares
Total Sum of Squares = TSS = Σy^2, Regression Sum of Squares = TSS - RSS where RSS = Residual Sum of Squares = $\Sigma (y^2 - \hat{y}^2)$,
where $\hat{y}$ represent concentrations predicted by the summation of computed values in equation 2.1

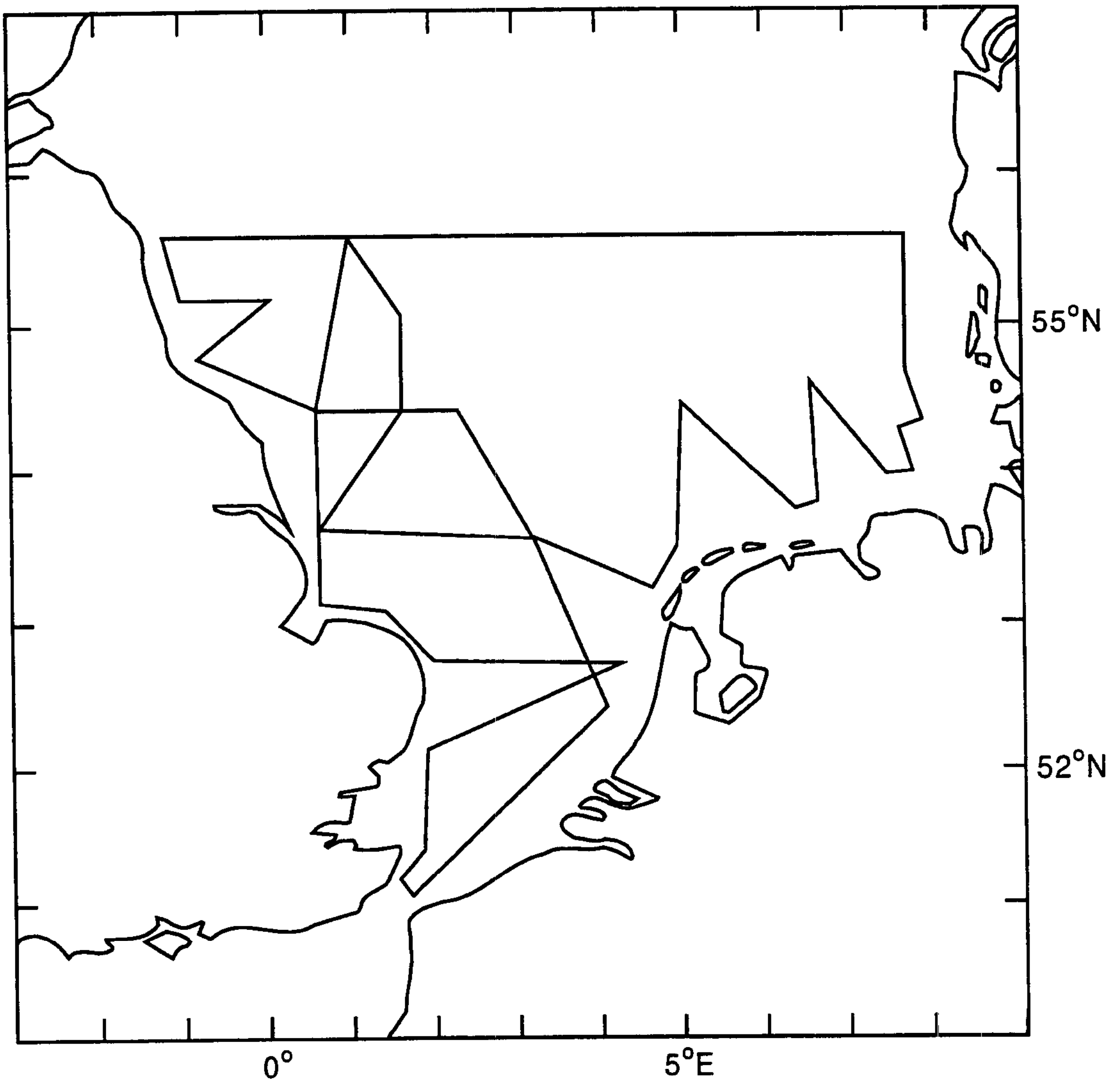

Figure 1.1: North Sea Survey cruise track.

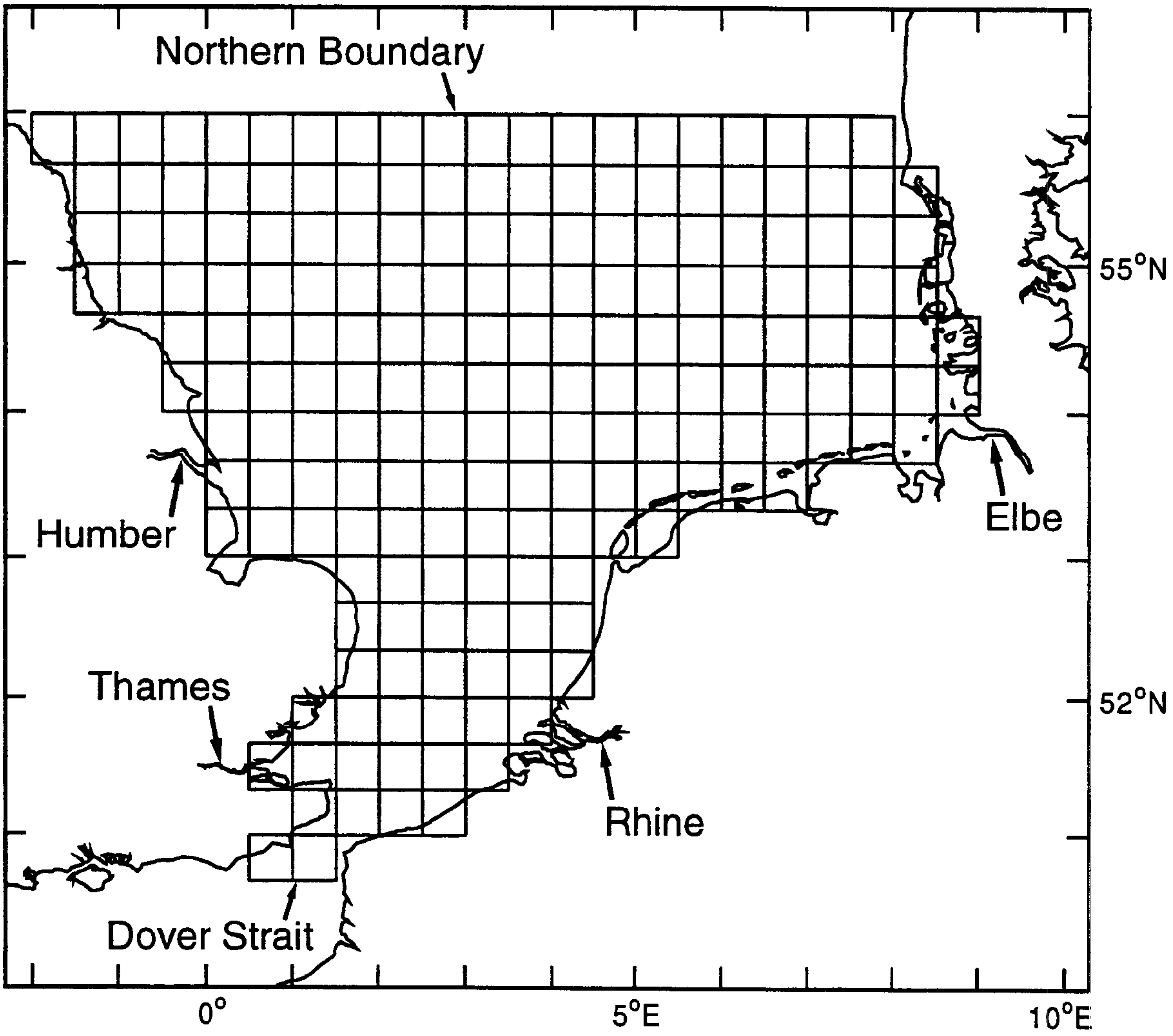

Figure 2.1: 35 km model grid showing positions of sources.

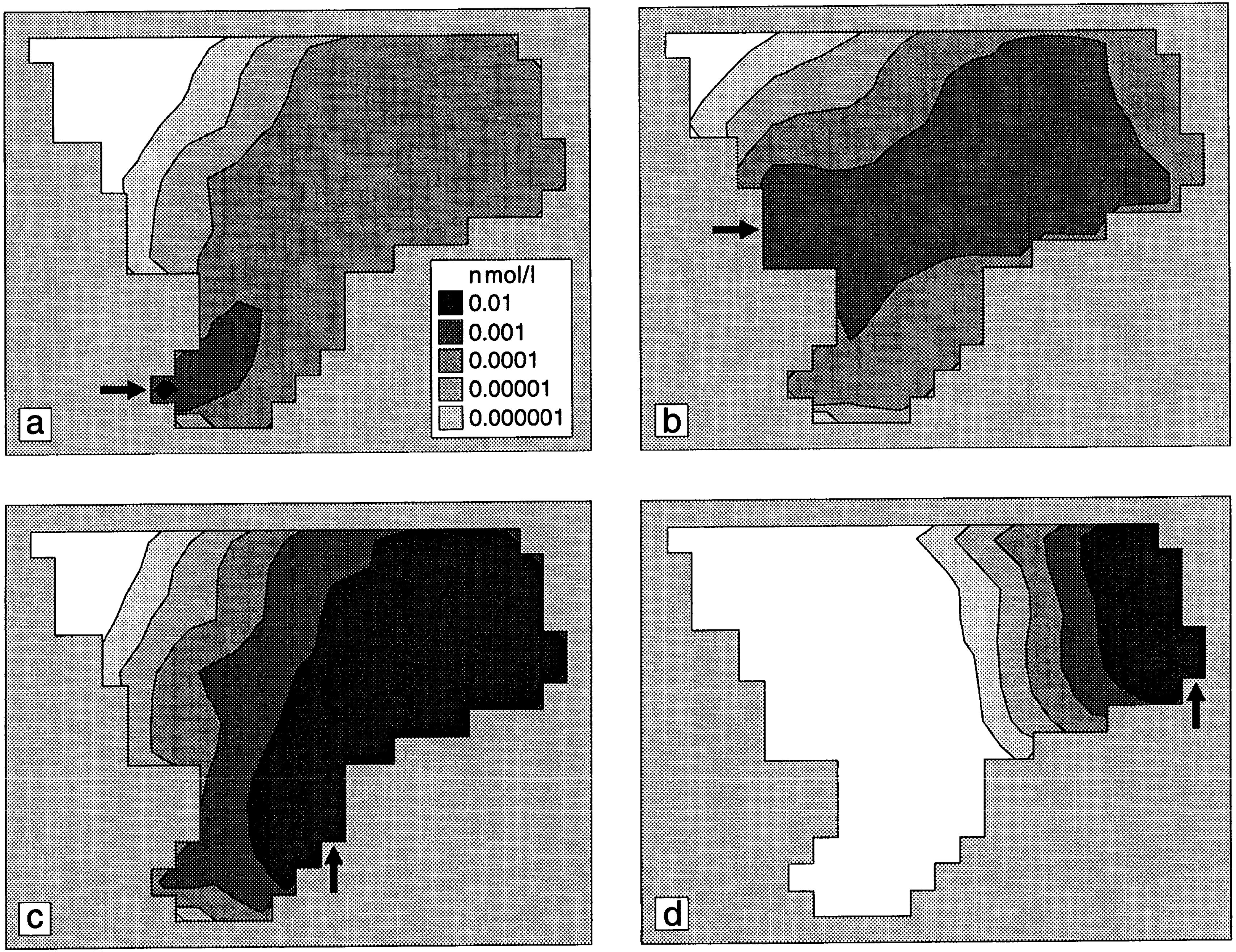

Figure 2.2a - 2.2d: Computed dispersion patterns for discharges from (a) the Thames, (b) the Humber, (c) the Rhine

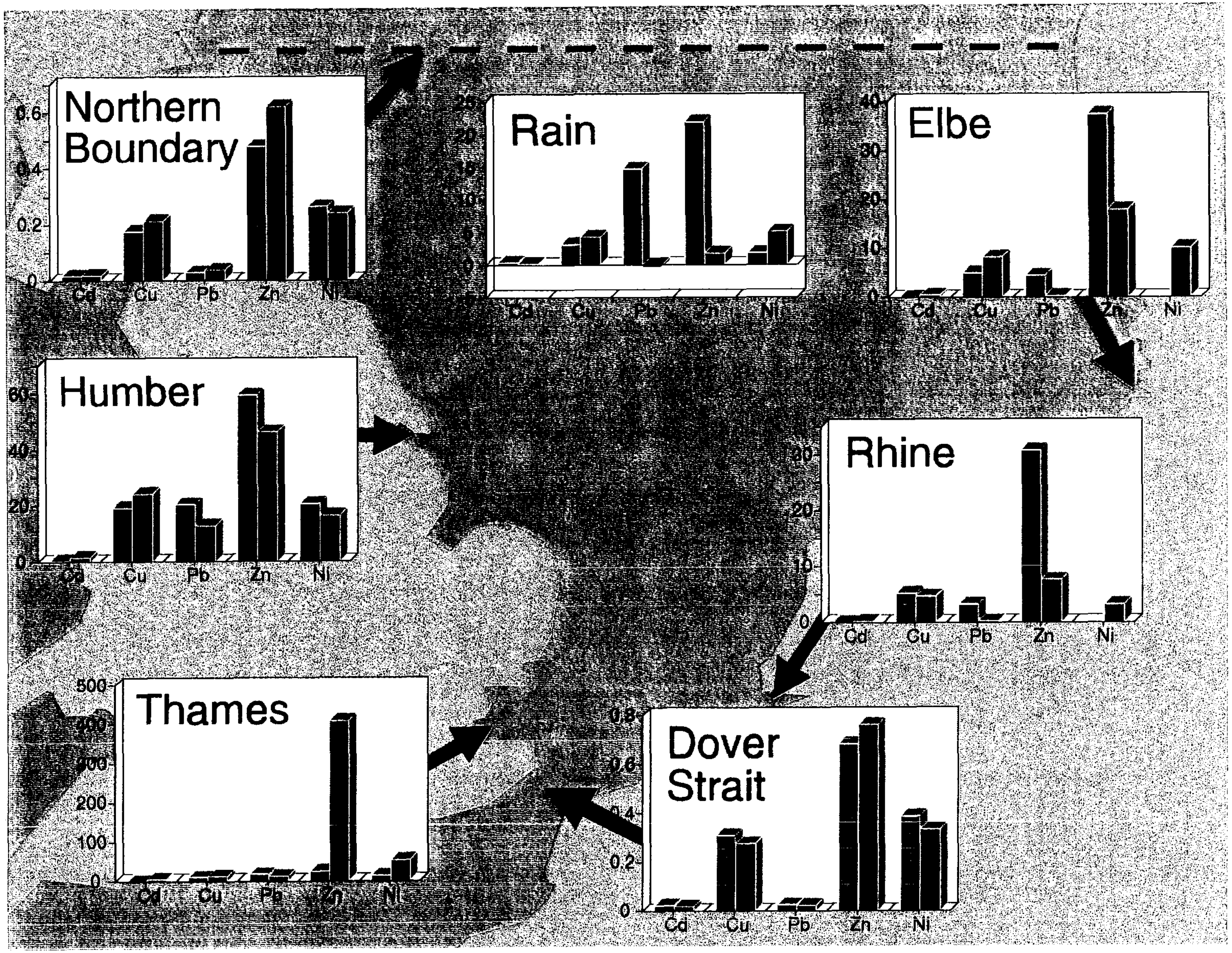

Figure 3.1: Contamination concentrations entering the Southern North Sea from rivers, the atmosphere and adjacent sea regions.

■ '87 QSR values

■ Estimates obtained from a regression of model simulations against '88 - '89 N.S.P. survey data.

Concentrations are in µg/litre