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RAPPORT DES RECHERCHES COLLECTIVES

NO. 208

**RESULTS OF THE 1990/1991 BASELINE STUDY OF CONTAMINANTS
IN NORTH SEA SEDIMENTS**

prepared by

**ICES/NSTF/OSPARCOM *ad hoc* Working Group on Sediment Baseline
Study Data Assessment**

and

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EXECUTIVE SUMMARY

The North Sea Task Force (NSTF) had, as one of its key tasks, the collection of data in a harmonized manner on the concentrations of contaminants in the various compartments of the North Sea. The 1990/1991 Baseline Study on Contaminants in Sediments, conducted by the Joint Monitoring Group of the Oslo and Paris Commissions, was used in the North Sea as an important component of the NSTF monitoring effort, along with work carried out under the NSTF Monitoring Master Plan (MMP).

The assessment of the North Sea component of this Baseline Study and the MMP data, as conducted by the ICES/NSTF/OSPARCOM *ad hoc* Working Group on Sediment Baseline Study Data Assessment (SEDMON) and reported here, provided an important contribution to the *North Sea Quality Status Report*, 1993 (NSTF, 1993). The present report presents details concerning the data submitted, quality control and other checking criteria applied to them, normalization procedures and statistical analyses used, and the ultimate scientific assessment of these data. The overall findings have been summarized as follows:

- a) Aluminium-normalized metal concentrations in whole sediments are generally higher in the coastal areas than in the central North Sea.
- b) The highest aluminium-normalized concentrations of metals occur in areas close to industrial sources (for example, the Norwegian fjords, the Elbe, Scheldt, Seine, Humber, Tyne and Tees) and in areas near zones of mineralized rocks (Norway, Helgoland, southwest England, and northeast England).
- c) The Norwegian Trench and the Skagerrak have high metal concentrations in sediment compared to the central North Sea.
- d) The northern edge of the Dogger Bank has relatively high aluminium-normalized concentrations of cadmium and chromium in sediment.
- e) It is difficult to draw firm conclusions concerning the distribution of organic contaminants (CBs, HCB and PAHs) due to the limited amount of data remaining after the exclusion of unsatisfactory data and data that were not accompanied by organic carbon measurements.
- f) The contaminant data submitted by several laboratories lacked quality assurance (QA) data; the QA data submitted by other laboratories did not meet the criteria adopted for the inclusion of results in the assessment. Contaminant data from these laboratories were, therefore, rejected.
- g) The sediments of the German Bight contain relatively high concentrations of mercury, cadmium and zinc compared to those in the central North Sea. These higher concentrations are not restricted to accumulation areas but also occur in more dispersive sandy zones.
- h) Relatively high concentrations of mercury occur in the fines off the northeast coast of England.
- i) Relatively high concentrations of lead occur in the fines near the northeast coast of England, in the central North Sea, and in the German Bight.
- j) Copper and nickel in the fine sediment fraction are fairly evenly distributed throughout the North Sea.

1 INTRODUCTION

One of the main tasks of the North Sea Task Force (NSTF) was the preparation of the *North Sea Quality Status Report* (QSR), which was published in early 1994. At their joint meeting in June 1991, the Oslo and Paris Commissions (OSPARCOM) agreed that monitoring data to be fed into the preparation of the QSR would be considered in two different data sets:

- 1) the "historical data", mainly from 1985 to 1989, and
- 2) the NSTF Monitoring Master Plan (MMP) data and other relevant data for the years 1990 and 1991.

The OSPARCOM further agreed that the data to be considered on contaminants in marine sediments for 1990–1991 should include MMP data and also data from the Joint Monitoring Programme (JMP) of OSPARCOM. The JMP Baseline Study of Contaminants in Sediments was conducted in 1990 and 1991 in order to assess the spatial distribution (purpose (c) of the JMP) of metals and organic contaminants in marine sediments.

In order to meet the deadline of July 1992 for submissions to be incorporated into the QSR, pre-assessments of the unvalidated data were carried out by national experts in April 1992. A joint ICES/NSTF/OSPARCOM *ad hoc* Working Group on Sediment Baseline Study Data Assessment (SEDMON) was convened in Copenhagen on 27 April to 2 May 1992 in order to assess the data and prepare data products. This document summarizes the findings of that group. In this assessment exercise only data from the NSTF area were taken into account, which included the North Sea proper, the northern North Sea, the Kattegat and Skagerrak, and the English Channel.

The data on contaminants in sediments reviewed here represent a sub-set of the data collected for the OSPARCOM area as a whole (i.e., the Northeast Atlantic); the full data set was assessed at the end of 1992.

Aims of the SEDMON Assessment

The aims of this assessment were as follows:

- a) to describe the variations in metal and organic contaminant concentrations (whether normalized or not) in the North Sea;
- b) to describe the metal and organic contaminant concentrations at the MMP sites;
- c) to relate variations in concentration (whether normalized or not) to known inputs;
- d) to make recommendations for future work.

2 DATA AVAILABLE FOR THE ASSESSMENT

The data assessment concerned the evaluation of data from three main sources:

- a) the NSTF MMP 1990–1991 data on contaminants in sediments;
- b) the North Sea component of the 1990/1991 JMP Baseline Study of Contaminants in Sediments;
- c) additional data sets, e.g., ICES data sets from 1985–1991 that met the requirements for inclusion in the assessment.

Data were available from all eight North Sea countries as follows: Belgium (1990, 1991); Denmark (1990, 1991); France (1987, 1988); Germany (1990, 1991); Netherlands (1990); Norway (1990); Sweden (1990); and the United Kingdom (1990, 1991), with data submitted by both England and Scotland.

In practice, all data included in the assessment related to sampling conducted in 1990 and 1991, with the exception of a limited amount of French data (1987 and 1988) submitted specifically for inclusion in the NSTF assessment. German data for 1985–1989 had been submitted, but with format problems; these data were resubmitted for inclusion in the JMP assessment in December 1992.

Responses to validation requests were received from all countries; however, some of them were not complete and many were received as late as the week prior to the assessment meeting.

Following the incorporation of additional data and corrections notified in the validation responses, four data sets were constructed for the assessment: metals in whole sediment, metals in fines ($<63 \mu\text{m}$ and $<20 \mu\text{m}$), organics in whole sediment, and organics in fines ($<63 \mu\text{m}$ and $<20 \mu\text{m}$).

Metals data covered approximately 30 contaminants. However, for a number of metals (about 20), data were only submitted by one or two laboratories and are therefore not included in the assessments detailed in this report.

Organics data covered approximately 90 contaminants: a range of individual chlorobiphenyls (CBs), polycyclic aromatic hydrocarbons (PAHs), and hexachlorobenzene (HCB), together with several additional compounds included in the voluntary list of parameters in the NSTF monitoring guidelines.

The original data sets comprised approximately 10 000, 6500, 15 000 and 5000 observations for metals in whole

sediment, metals in fines, organics in whole sediment, and organics in fines, respectively, where an observation comprised a value for a given contaminant in a particular size fraction of a sediment sub-sample.

In accordance with procedures specified in advance of the assessment, data were aggregated first by taking mean values for analytical replicates. A second aggregation, applied after computation of normalized values (normalized for %fines, aluminium, and organic carbon), involved computing mean values across sub-samples. The resulting data sets, comprising observations for a given contaminant (for a given extraction method), in a particular size fraction of a sediment sample yielded the following numbers of observations:

metals in whole sediment	ca. 6200 observations
metals in fines	ca. 4400 observations
organics in whole sediment	ca. 11800 observations
organics in fines	ca. 1700 observations

The normalization variables employed (fines, aluminium, and organic carbon) were selected on the basis of the amounts of data available; other potential normalization variables (Li, Fe, etc.) were not consistently available in the data reported by the different countries.

The four aggregated data sets constituted the basic data sets used in the assessments reported here.

Assessments of individual contaminants involved selections from these primary data sets of those data that met specified criteria relating to, for example, extraction methods, treatment of 'less than' qualified values, outliers (high values and low values), and laboratory performance in relation to QA criteria.

3 QUALITY CONTROL OF THE DATA ON METALS AND ORGANIC CONTAMINANTS IN WHOLE SEDIMENTS

3.1 Approach Taken to Quality Control of the Data on Metal Concentrations in Whole Sediment

An initial examination of the files of analytical data and methods held by ICES revealed that 22 laboratories were involved in this programme (listed in Annex 1). It was therefore necessary to devise a scheme for the assessment of the quality and comparability of the data from these laboratories. A recurrent problem encountered in cooperative research or monitoring programmes has been the need to ensure that analytical data derived from different collaborating laboratories can be reliably combined or compared. In designing the present programme, this problem had been addressed through careful definition of the types of sampling and analytical procedures

that should be used (NSTF, 1991). The fundamental requirements were for the determination of the total concentrations of selected metallic contaminants and potential normalization variables in whole sediment. It was recognized that some laboratories have considerable experience in the analysis of separated grain size fractions of sediment, and that these laboratories might, in addition, choose to analyse fractionated sediment.

As was anticipated in the design of the programme, participating laboratories used a range of chemical methods for the extraction and estimation of metal concentrations in the sediment samples. The programme design had clearly stated that determinations should be made of total metal content, to allow the application of certain geochemical normalization techniques. Previous experience in the intercomparison exercise on analysis of trace metals in marine sediments I/TM/MS organized through ICES (Loring, 1987) had demonstrated that strong mineral acid extraction employing concentrated nitric and hydrochloric acids did not extract the total content of many metals. The average percentages of metals extracted by this method in comparison to total digestion methods involving hydrofluoric acid were as follows:

<u>Metal</u>	<u>% Extracted</u>
lead	99.3
zinc	96.0
iron	93.3
copper	91.9
nickel	90.2
manganese	86.9
cadmium	85.0
chromium	53.7
aluminium	33.9

It was clear, therefore, that in the analysis of the whole sediment samples in this intercomparison exercise, nitric and hydrochloric acids extracted lesser amounts than hydrofluoric acid (often used in combination with nitric acid). The differences were particularly marked for aluminium, which occupies mineral lattice positions and is an important potential normalizing element, and chromium which is found in minerals recognized to be insoluble in nitric/hydrochloric acids. The percentages of the other "contaminant" elements listed as mandatory or voluntary determinands in the NSTF programme were somewhat higher, but were not consistently comparable to levels determined by complete digestion.

In the light of these results, and the analytical guidelines for the programme, it was agreed that in the initial assessment only trace metal data obtained by methods which were directed at determining the total concentration of each metal would be considered. These methods included those involving complete dissolution of the

sediment in hydrofluoric acid (HF), proton-induced X-ray emission (PIXE), and a suspension sampling technique (SST). Sediment extraction method codes used in this report are described in Annex 2. It is recognized that other methods with comparable objectives, such as X-ray fluorescence analysis, are available, but they were not used by laboratories in the present study. The codes of the laboratories using methods designed to determine the total concentrations of metals are shown in Annex 3, along with the numbers of samples for which data were submitted for each metal (Table A3.1) and the numbers of samples for which the data were used in the assessment (Table A3.2). Eight laboratories determined aluminium, ten laboratories determined the mandatory NSTF elements (Cd, Cu, Hg, Pb, Zn), and smaller numbers determined the voluntary metals.

Methods for the determination of mercury were not assessed in the same way. Not all complete digestion methods can be recommended for mercury determination, and therefore only some data generated by methods involving HF were included. Extraction with nitric acid or aqua regia has been recommended in previous ICES documents.

Once an initial selection based on the general character of the analytical methods used by participating laboratories had been made, the question of analytical quality control for each element in individual laboratories was addressed. Two types of data were available. Firstly, some laboratories had submitted to ICES the results of their analysis of reference materials, carried out at the same time as the analysis of the field samples. Eight different reference materials had been used by participating laboratories (see Annex 4). In some cases, the certified values were readily available, but in others enquiries were made to the originating laboratories. Some laboratories had not submitted any results of analyses of reference materials to ICES; efforts were made to contact these laboratories, and in several cases they were able to provide appropriate quality assurance data for assessment.

A second possible approach to quality control of the data was to consider the performance of laboratories participating in intercomparison exercises organized primarily by ICES. Reports of both the ICES 1/TM/MS exercise (Loring, 1987) and the intercomparison exercise on sediment analyses for the Baltic Sea (Brügmann and Niemistö, 1987) were consulted, bearing in mind that the information contained in them was six to eight years old. These reports did not contain any additional data that could be used to supplement those obtained by the first approach. In one case, reference was also made to the results of an ICES intercomparison exercise for metals in suspended particulate matter (Hovind and Skei, 1992).

In order to make decisions as to the acceptability of the data from each laboratory for each element, it was necessary to establish criteria by which the data could be assessed. The errors associated with chemical analysis can be either non-random (producing a bias in the results) or random (producing a variance in the results). The former affects the analytical accuracy, and the latter affects the precision. Where possible, the accuracy of the results was expressed by calculating the deviation of the mean of the laboratory analyses of the reference material from the certified value as a percentage of the certified value. The precision was expressed as the relative standard deviation of the laboratory's results (standard deviation as a percentage of the mean). As it is necessary for results to be both accurate and precise, it was agreed that data would be considered unacceptable if either of the expressions of accuracy or precision described above exceeded 20%. The results of the analyses of reference materials for the various metals by participating laboratories are shown in Annex 5; where results do not meet the criteria for accuracy or precision, this is indicated. The number of laboratories from whom analyses of reference materials were not obtained and the number reporting analyses which failed to meet the QA criteria described above are given in Table 3.1.1.

Table 3.1.1 Summary of the conclusions reached from the assessment of the acceptability of data, based on analyses of reference materials for metals.

Metal	Number of laboratories		
	Participating ¹	Lacking QA data	Rejected
Al	8	1	0
Cd	9	1	2
Cu	9	1	0
Hg	9	2	1
Pb	9	1	0
Zn	9	1	0
As	3+1 ²	0	1+1 ²
Cr	5	0	1
Ni	4	0	0
Mn	3	0	1
Fe	4	1	1

¹Omitting those which employed analytical methods not designed to determine the total concentration of metals.

²One laboratory reported two distinct sets of data, one of which was rejected, but the other was accepted.

3.2 Approach Taken to Quality Control of the Data on Chlorinated Biphenyl Concentrations in Sediment

An initial examination of the files of analytical data and methods held by ICES revealed that nine laboratories were involved in this component of the programme (Table 3.2.1). The programme design had specified the analysis of ten mandatory chlorinated biphenyl congeners (CBs), and data were available for all of these compounds (but not from all laboratories), plus data on seven additional congeners from one or more laboratories. Details concerning the CBs reported by each laboratory are shown in Table 3.2.1. Only three laboratories reported data for all ten mandatory congeners.

Although no firm statements can be made with regard to quality assurance from this information, the lack of data from six laboratories on CBs 31 and 105 might bring into question the reliability of the data on the closely eluting CBs 28 and 153.

As in the case of trace metals, it was possible to review the broad basis of the analytical methods used by each laboratory (Table 3.2.2). From this information, it was not possible to identify any methods which could not potentially meet the requirements of the programme, and therefore no data were rejected at this stage.

An important source of information relating to quality assurance arises from the use of reference materials during analysis. Participating laboratories were asked to

report the results of analyses of reference materials with their field sample data. Unfortunately few, if any, appropriate reference sediments, certified for the concentrations of individual CB congeners, are in regular use by laboratories, and so this approach to quality assurance was not available to the Assessment Group, and no comments could be made. A number of laboratories had used internal reference materials (Table 3.2.3), but the results of these analyses could not be used to assess the accuracy of the results for field samples.

A further source of information relevant to quality assurance is the performance of individual laboratories in intercomparison exercises. The most relevant exercise is the ICES/IOC/OSPARCOM Intercomparison Programme on the Analysis of Chlorobiphenyls in Marine Media - Step 2 (1/OC/MS-2), the results of which have been reported by de Boer *et al.* (1995). This exercise included the analysis of a cleaned sediment extract prepared from muddy sediment collected in the Wadden Sea and, therefore, omitted the extraction and clean-up stages. The exercise was thus concerned with the ability of the participating laboratories to operate and calibrate their instrumentation satisfactorily. Laboratories were classified into three groups according to their performance. Most of the laboratories that submitted CB data for this Baseline Study which participated in this intercomparison exercise were placed in Group 1 (good performance) or Group 2 (satisfactory performance).

Table 3.2.1 Chlorinated biphenyl congeners for which data were submitted by participating laboratories, indicating where data on mandatory CBs are missing (□), and where data on other CBs have been submitted.

Analytical Laboratory Code	Mandatory CBs ¹									Other CBs
	31	28	52	101	118	153	105	138	156	180
ALUK										
BLUK										
DGWN									□	
SERI	□						□		□	
IMRN										
BFGG	□						□		□	
LWKG	□						□		□	
ISHG	□						□		□	
IHEB	□				□		□		□	

¹CBs numbered according Ballschmiter and Zell (1980), in order of elution on an apolar column (e.g., CPSil8, SE54, DB₅).

Table 3.2.2 Analytical methodologies used for CB determinations.

Analytical Laboratory Code	Sampling	Extraction	Clean-up	Groups Sep.	GC
ALUK	Grab sampler	Freeze dried Soxhlet	Alumina col.	Silica col.	2 col. ECD
BLUK	Grab sampler	Air dried Soxhlet	Alumina	Silica	1 col. ECD
DGWN	Box corer	Freeze dried Soxhlet	Alumina	Y	2 col. ECD
SERI	Box corer	Fresh sediment Agitation	Alumina	Y	GC-ECD GC-MS
IMRN	Grab sampler	Fresh sediment Ultrasonic agit.	H ₂ SO ₄	Florisil	2 col.
BFGG	Grab sampler	Freeze dried Soxhlet	H ₂ SO ₄ /Cu	Silica	2 col.
LWKG	Grab sampler	Freeze dried	-		
ISHG	Grab sampler	Fresh dried	-		
IHEB	Grab sampler	Freeze dried Extr. polar solvent			

GC = Gas chromatography
ECD = Electron capture detection
MS = Mass spectrometry

Table 3.2.3 Quality assurance procedures used by participating laboratories, and data arising therefrom.

Analytical Laboratory Code	1/OC/MS-2 ¹			Use of reference materials		Detection limit ⁷ ng g ⁻¹
	Code ²	CB153 ³	Group ⁴	IRM ⁵	CRM ⁶	
ALUK	52	2.20	2	☉		0.02
BLUK	51	2.0	2	☉(HS.1)		2
DGWN	37	2.55	1	☉		0.1
SERI						0.04
IMRN	43	1.9	1	☉	CRM.BCR349	0.05
BFGG	27	1.85	2			0.1
LWKG	33	N.R.	3	☉		0.02
ISHG				☉		0.01
IHEB	2	2.5	2			0.1
Mean value		2.43 ⁸				

Notes:

¹Participation in ICES/IOC/OSPARCOM Intercomparison Exercise on the Analysis of CBs in Marine Media - Step 2, reported in de Boer *et al.* (1995).

²Laboratory code number in 1/OC/MS-2.

³Concentrations of CB153 reported in 1/OC/MS-2.

⁴Classification of laboratories in 1/OC/MS-2.

⁵Laboratories reporting the use of an Internal Reference Material (IRM).

⁶Laboratories reporting the use of a Certified Reference Material (CRM).

⁷Estimated "average" detection limit for individual CBs.

⁸Mean value for CB153 in sediment extract used in 1/OC/MS-2.

N.R. = Not reported.

The single laboratory in Group 3 of 1/OC/MS-2 was placed there because it did not submit results to the coordinator of the intercomparison exercise. As one other laboratory had not participated in this exercise, it was decided that these results did not provide sufficient evidence to reject the results from any individual laboratory.

The final type of information used was the typical detection limits reported by each laboratory for individual congeners. Most of these values were between 0.1 and 0.02 ng g⁻¹ sediment, with one laboratory reporting 2.0 ng g⁻¹. This latter laboratory did not report measurable concentrations of CBs in any of the samples it analysed. Data from this laboratory were, therefore, not included in any subsequent discussions.

3.3 Approach Taken to Quality Control of the Data on Polycyclic Aromatic Hydrocarbon Concentrations in Sediment

An initial examination of the files of analytical data and methods held by ICES revealed that seven laboratories

were involved in this component of the programme (Table 3.3.1). The programme design had included polycyclic aromatic hydrocarbons (PAHs) as voluntary contaminants which should be determined as individual compounds. Data were available from participating laboratories for between three and 23 compounds. The compounds selected varied among laboratories. Codes for the PAHs reported are shown in Table 3.3.2. Information on the sampling equipment and analytical methods used is given in Table 3.3.3.

As in the case of the other contaminants, it was possible to review the broad basis of the analytical methods used by each laboratory (Table 3.3.3). It was possible from this information to identify one laboratory which used thin layer chromatography for separation of the PAHs. As this method could not meet the requirements of the programme for the determination of individual compounds, the data from this laboratory were not considered further. Details of analytical procedures were not available from one participating laboratory.

A further source of information relating to quality assurance arises from the use of reference materials during analysis. Participating laboratories were asked to report the results of analyses of reference materials with their field sample data. All laboratories reported the use of either internal reference materials or materials certified for other compounds (e.g., HS-3, and HS-4), but only one laboratory provided analytical data. There are few, if any, appropriate reference sediments certified for the concentrations of individual PAHs in regular use by laboratories, and data on internal reference materials cannot on their own be used to assess the accuracy of analyses. It was therefore not possible to use the data on reference materials as a criterion for admitting or rejecting data for field samples.

A further source of information relevant to quality assurance is the performance of the individual laboratories in

intercomparison exercises. The most relevant exercise was organized through ICES, as reported by Law and Nicholson (1995). This exercise consisted of the circulation of standard solutions containing known concentrations of ten individual PAH compounds, and another solution containing undeclared concentrations of the same compounds. The exercise therefore was concerned with the ability of the laboratories to separate and quantify ten compounds in "clean" solutions only.

Three of the six laboratories that submitted data for this Baseline Study also successfully took part in this intercomparison exercise. As half the laboratories had not taken part in the intercomparison exercise, it was decided that these results did not provide an adequate basis for rejection of the data from any individual laboratory.

Table 3.3.1 Overview of laboratories analysing PAHs, including the number of compounds for which data were submitted.

Laboratory	Country	No. of compounds	Total sediment	Fines
ALUK	UK	13*	X	
DGWN	Netherlands	13*		X
BFGG	Germany	3	X	
ECCB	Belgium	14*	X	
IHEB	Belgium	7*	X	
SERI	Sweden	13	X	
IMRN	Norway	23	X	

*Borneff series of PAHs included.

Table 3.3.2 List of codes for polycyclic aromatic hydrocarbons.

Code	Name
ANT	anthracene
BAA	benz[<i>a</i>]anthracene
BAP	benzo[<i>a</i>]pyrene
BBF	benzo[<i>b</i>]fluoranthene
BBKF	benzo[<i>b+k</i>]fluoranthene
BEP	benzo[<i>e</i>]pyrene
BGHIP	benzo[<i>ghi</i>]perylene
BKF	benzo[<i>k</i>]fluoranthene
CHR	chrysene
CHTR	chrysene + triphenylene
DBAHA	dibenz[<i>a,h</i>]anthracene
DBT	dibenzothiophene
DBTC1	C ₁ -dibenzothiophenes
DBTC2	C ₂ -dibenzothiophenes
DBTC3	C ₃ -dibenzothiophenes
FLE	fluorene
FLU	fluoranthene
ICDP	indeno[1,2,3- <i>cd</i>]pyrene
NACL8	octachloronaphthalenes
NAP	naphthalene
NAPC1	C ₁ -naphthalenes
NAPC2	C ₂ -naphthalenes
NAPC3	C ₃ -naphthalenes
PA	phenanthrene
PAC1	C ₁ -phenanthrenes
PAC2	C ₂ -phenanthrenes
PER	perylene
PYR	pyrene
SPAH	Sum of PAHs (total)
SPAH5	Sum of 5 PAH compounds

Table 3.3.3 Overview of methods used in the determination of PAHs.

Laboratory code	Fraction	Sampling	Extraction	Clean-up	Fractionation	Detection	Det. limit ng g ⁻¹	Inter-comparison exercise
ALUK	<2 mm	Grab sampler	Continuous pentane	Alumina and silica pentane/dichloromethane	GC	MS	15	X
DGWN	<63 μ m	Box corer	Continuous acetone/hexane	A1203 hexane	HPLC Vyde 201TP	UVF	1 DBAH A 5	X
IMRN	<2 mm	Grab sampler mix of 2 samples	Continuous	Silica	GC (SE-54)	MS	1	X
IHEB	<2 mm	Grab sampler					1	
BFGG	<2 mm	Grab sampler	Continuous acetone/dichloromethane		Thin layer chromatography		100 NAPC8 1	
SERI	<2 mm				Volatile: GC heavy: HPLC	FID UVF	5	

GC = Gas chromatography

HPLC=High-performance liquid chromatography

MS =Mass spectrometry

UVF =Ultra-violet fluorescence

FID =Flame-ionization detection

4 DATA HANDLING PROCEDURES FOR DATA ON WHOLE SEDIMENTS

4.1 Approach to Normalization of Data on Metals in Sediment

The geographical distribution of metals in sediment is usually found to reflect strongly the distribution of fine-grained material. The need for normalization of whole sediment analytical data to reduce or eliminate the influence of differences in grain size between samples has been clearly established within ICES and the Joint Monitoring Group (JMG). It was, therefore, necessary at a very early stage in the assessment of the data available to decide upon the most appropriate approach to be taken to normalization.

H. Albrecht described his extensive investigations of relationships within the data set between metal concentrations and potential normalizing parameters, such as the proportion of material less than 63 μ m, and organic carbon, aluminium, and iron concentrations. He had also employed multivariate statistical techniques, including

factor analysis. He reported that the pattern of correlations, and the composition of main factors, in the data varied with both area and laboratory. In general, correlations with the proportion of fine-grained material, or a factor strongly influenced by this variable, appeared most consistently to show good correlations with metal concentrations, and therefore might be recommended for normalization. However, he noted that not all laboratories had reported the results of grain size measurements, which would limit the applicability of the technique.

S. Rowlett had carried out some exploratory analysis of the data from the English coast. He had concentrated on normalization using aluminium as a marker for fine-grained material, and reported that there were good correlations between some metals and aluminium. He concluded that aluminium was an appropriate normalizer for the present task. In response to some recent suggestions, he had also investigated the use of lithium. He found broad geographical trends in aluminium to lithium ratios, with higher values in the north than in the south. These patterns could also be seen in the distributions of

the ratios of some other metals to lithium. He therefore concluded that normalization to aluminium was preferable for this data set.

The Assessment Group agreed, in view of the above discussion and the lack of data on some normalization variables in some data sets, that the initial normalization procedure to be used on the trace metal data would be normalization to aluminium.

4.2 Partitioning of the Data During Normalization/Compensation

4.2.1 Metals

In exploring the data, and in the light of other experience and publications, it became apparent that the primary method chosen for the normalization of results to remove the influence of grain size variations on the observed concentrations of metals presented some difficulties in sediments with very low proportions of fine-grained material. These difficulties arose for a number of reasons:

- a) The sediments concerned normally contained only low concentrations of metals. At such low concentrations, the imprecisions and inaccuracies of the analytical methods used could have a strong influence on the results. These uncertainties in the analysis could cause reported concentrations to be significantly larger than the true concentrations.
- b) Studies of the $<20\ \mu\text{m}$ fraction of the sediments in the North Sea, reported by Germany, indicated strongly that the concentrations of metals in the fine fraction of sediment containing about 1% or less of fines were strongly influenced by diagenetic recycling processes. Maxima in, among others, iron and manganese concentrations in fines were found in sediment containing 1% fines or less (see Figures 4.2.1 and 4.2.2), suggesting that dissolution and reprecipitation processes associated with the redox boundary were greatly affecting the composition of the fine fraction in these sediments.
- c) Studies of the concentrations of copper, zinc, cadmium, and lead in material $<63\ \mu\text{m}$ in size in sediments of the southern North Sea, carried out in the Netherlands, showed similar effects. The concentrations of these elements in fine material in sediments containing less than 1% fines were much greater than those found in fines from other sediments.
- d) As indicated above, the primary normalization method selected was the calculation of metal to aluminium ratios. In some cases, e.g., cadmium, the regression of metal concentrations on aluminium concentrations showed a positive intercept on the metal axis. If ratios were then calculated, the ratios increased rapidly at low aluminium concentrations as a consequence of the intercept of the regression line. This could lead to a misleading assessment of many of the coarse sediments in the study area as being heavily contaminated.

In view of these observations, it was agreed that data on coarse sediments containing less than about 1% of material $<63\ \mu\text{m}$ should be separated from the rest of the data and assessed independently. It was clear that normalization to aluminium could not sensibly be applied, and that data on these samples should be separated from the rest of the data set. Unfortunately, in several of the data sets, grain size measurements had not been reported, and so a partitioning at 1% fines could not readily be made. However, regression analysis (see Figure 4.2.3) revealed that the mean aluminium concentration found in sediment with 1% fines is 1% aluminium, although there is considerable variance in the data. It was, therefore, agreed that the data should be partitioned at 1% aluminium, bearing in mind the considerable variance in this relationship. As an additional observation, it was noted that it was unreasonable for sediment containing 1% fines to contain 1% aluminium, if all the aluminium is associated with fine-grained material. The low concentration of aluminium in the coarser material in such sediment must be sufficient to strongly influence the observed concentrations of aluminium in the whole sediment, suggesting that aluminium does not act as a good marker for fine-grained material in sediments containing very small amounts of fine-grained material.

4.2.2 Organic contaminants

From the experience gained in the assessment of the data on trace metals, attention was given to compensation of the concentrations of organic contaminants for variation in organic carbon levels. In calculating ratios between contaminants and total organic carbon, by analogy with the manipulation of trace metals, it was found necessary to partition the data at 0.3% organic carbon.

4.3 General Procedure for Manipulation of Data on Metal Concentrations

A general procedure was established for the initial selection and manipulation of data on metals in sediment, and this was applied to all elements. Following this initial processing and presentation, it was found appropriate for

some elements to undertake further manipulations, as described in Sections 5.4.1 to 5.5.3, below. The general procedure adopted was as follows:

- a) Identification of laboratories not using appropriate analytical techniques, i.e., not using techniques designed to determine total concentrations, and elimination of their data (see Section 3.1, above).
- b) Identification and elimination of data from laboratories not meeting the quality control criteria (see Section 3.1, above).
- c) Identification and elimination of data on samples taken below 5 cm depth in sediment cores.
- d) Identification and elimination of concentrations reported as "less than detection limit" by laboratories using methods with rather high detection limits. This was necessary as it was found that these data disturbed subsequent regression analyses.
- e) The identification and removal from the data set of particularly high, but reliable, concentrations of metals, which tended to have undue influence on subsequent regression analyses. These data were eliminated from the regressions, but were retained for discussion in the text and presentation in tables and charts.
- f) Graphical presentation of the distribution of the reliable data in charts and other products together with descriptive univariate statistics.
- g) Examination of the regressions of metal concentrations on aluminium, with and without partitioning at 1% aluminium.
- h) Calculation of metal to aluminium ratios for samples containing more than 1% aluminium.
- i) Presentation and discussion of the distribution of non-normalized data for samples containing less than 1% aluminium.
- j) Presentation and discussion of the distribution of metal to aluminium ratios in samples containing more than 1% aluminium.

4.4 General Procedure for Manipulation of Data on CB and PAH Concentrations

A general procedure was established for the initial selection and manipulation of data on CBs and PAHs in sediment. This procedure took account of the need to

reduce the complexity of the data, which included varying amounts of information on at least 40 compounds. Both of these classes of compounds are strongly associated with organic material in the sediment, and therefore particular attention was paid to the use of organic carbon measurements in making comparisons between samples and areas. Following this initial processing and presentation, it was found appropriate to make some further manipulations, as described in the sections below dealing with these groups of compounds.

The general procedure adopted was as follows:

- a) Identification of laboratories not using appropriate analytical techniques, i.e., which did not have the potential to meet the requirements of the programme for separation and determination of individual compounds, and elimination of their data (see Sections 3.2 and 3.3, above).
- b) Assessment of the information provided by laboratories concerning the analysis of reference materials. The lack of appropriate reference materials greatly limited the usefulness of this procedure and, in contrast to the data on metals, no quantitative quality control criteria were applied.
- c) Identification and elimination of data on samples taken below 5 cm depth in sediment cores.
- d) Identification and elimination of concentrations reported as "less than detection limit" by laboratories using methods with unacceptably high detection limits.
- e) Tabulation and graphical presentation of the distribution of the reliable data in charts and other products, together with descriptive univariate statistics.
- f) Multivariate statistical analysis of the data, together with potential normalization variables such as grain size, aluminium, and organic carbon, with a view to the selection of a limited number of compounds that could be used as representative of a wider range of compounds. These were chosen on the basis of being prominent in factors which accounted for a high proportion of the variance in the data, and also were among those compounds showing the higher concentrations.
- g) Examination of regressions of the concentrations of selected compounds on organic carbon, and

calculation of ratios between selected compounds and organic carbon.

- h) Presentation and discussion of the distribution of compound to carbon ratios.

5 CONCENTRATIONS OF METALS AND NORMALIZING VARIABLES IN WHOLE SEDIMENTS

5.1 Introduction

This section describes the distribution of metals measured by total sediment analysis techniques (HF digestion, PIXE or SST) in whole (<2 mm) sediment. The geographical distribution of samples for which data were submitted by the various laboratories is shown in Figure 5.1.1. It should be noted that not all determinands were analysed in all samples.

Heavy metals, including mercury, cadmium, zinc, lead and copper, have been discharged into the Sörfjord in Norway for more than 60 years. The main source is a zinc plant situated at the head of the fjord. The area may be considered a "hot spot"; the sediments contain levels of trace metals orders of magnitudes higher than sediments from other areas covered by the NSTF Monitoring Master Plan (MMP) stations, including other more typical fjords. Sörfjord, therefore, is recognized as an exceptional area and should not be considered representative of any other areas. For presentational reasons, data from the Sörfjord have commonly been omitted from the figures.

5.2 Contaminant Concentrations at MMP Stations

Under the NSTF programme, data on mandatory metals and organic contaminants were required for the MMP stations. However, not all submissions to ICES included references to NSTF monitoring stations. Therefore, it was not possible to retrieve the data easily on the basis of MMP station from the ICES computer and no separate assessment by station was made.

However, the sample grids submitted generally included the North Sea Task Force MMP stations. Figure 5.2.1 shows the location of the MMP stations and should be referred to when considering the chemical data.

5.3 Distributions of Potential Normalizing Factors and Elements

5.3.1 Concentrations of fine-grained material

The distribution of material <63 μm in size in sediments of the North Sea is shown in Figure 5.3.1.1. Data points are quite well distributed, with the exception of the English Channel area.

Sediments containing the highest proportions of fine material are found in the Skagerrak and Norwegian Trench areas, and at the Fladen Ground east of the Moray Firth. Coastal sediments of the northern and eastern North Sea, outside the Wadden Sea, contain little fine material. The English Channel sediments are also known from other data to be predominantly coarse grained.

5.3.2 Concentrations of aluminium

A) Data

Data on aluminium concentrations in whole sediments were submitted by most laboratories for normalization purposes in relation to trace metals. No data sets were rejected.

B) Distribution

The distribution of aluminium is shown in Figure 5.3.2.1. Higher concentrations were found in the Norwegian fjords, the Skagerrak, off the northeast coast of England and the Humber. The lowest concentrations were found in the Southern Bight and, particularly, in the English Channel.

C) Discussion

The aluminium content of sediments is a reflection of the clay mineral content. The observation that the highest values are found in muddy areas and the lowest in carbonate-rich sediments is, therefore, to be expected.

5.3.3 Concentrations of organic carbon

A) Data

Data on organic carbon concentrations were submitted by several laboratories, particularly in relation to measurements of organic contaminants. The analytical methods used were sometimes not clear, and quality assurance data were rare. No quality control assessment was possible, so no data sets were rejected.

B) Distribution

The distribution of organic carbon is shown in Figure 5.3.3.1. The highest values were found in muddy sediments, e.g., in the Skagerrak area, in areas west of Norway, and in some estuarine areas. Few data were available for the southern North Sea and the English Channel.

C) Discussion

No organic carbon values were available for many of the samples in the programme (see Table 5.3.3.1). This was a limitation on investigations of the potential of using organic carbon as a normalizing variable, as an alternative to aluminium or grain size.

Table 5.3.3.1 Laboratories that reported data on organic contaminants, including those that also reported data on organic carbon.

Laboratory	CBs	PAHs	Others	Organic carbon	TOC method	det. limit (g g ⁻¹)
ALUK	X	X	X			
BFGG	X	X	X	X	X	0.001
BLUK	X		X			
SERI	X	X	X			
ICNF			X	X	?	?
IMRN/NIVA	X	X	X	X	X	0.002
LWKG	X		X			
ECCB		X	X			
IHEB	X	X	X			
ISHG	X		X	X	X	0.001

5.3.4 Concentrations of iron

A) Data

Data on iron were submitted by six laboratories, of which only four used an appropriate analytical method.

B) Distribution

The distribution of concentrations of iron is shown in Figure 5.3.4.1. Relatively high concentrations of iron occur in the sediments off the northeast coast of England and in the northern North Sea.

C) Discussion

Few firm conclusions can be drawn as the data only cover part of the North Sea, but it does appear that iron concentrations near the English coast are higher than those further offshore.

5.3.5 Concentrations of manganese

A) Data

Data on manganese concentrations in sediments were submitted by four laboratories, of which only two used the appropriate analytical methodology. Data on only 22 samples were acceptable.

B) Distribution

The distribution of concentrations of manganese is shown in Figure 5.3.5.1. The samples were widely distributed and show little variability. No conclusions can be drawn from these data.

5.4 Distributions of NSTF Mandatory Metals

5.4.1 Cadmium

A) Data

Eight countries submitted data on cadmium. Some of the data sets from France (3), Belgium (7), and Germany (45), and all the data sets from Denmark (33) and Sweden (9) were rejected, because only data obtained using an extraction method based on either HF or another procedure regarded as a total method were included in the assessment. The rest of the data from Germany (9) and all data from Norway (255) were rejected due to the fact that the quality assurance data gave doubts about the quality of these data. This left 417 samples for assessment.

Valid but very high cadmium concentrations, $>0.5 \text{ mg kg}^{-1}$, were excluded from the statistical runs, etc., but

they have been discussed in the text. The detection limits varied between 1 and $31 \text{ } \mu\text{g kg}^{-1}$ for the different laboratories. No data were excluded due to the use of methods with high detection limits.

Only data sets from the United Kingdom, the Netherlands, Belgium, and a small data set from France (two samples) were assessed. Where appropriate, some of the rejected data are discussed in the text.

B) Univariate Statistics

The mean, quartiles, standard deviation, and other relevant statistical parameters for the whole data set are given in Table 5.4.1.1, below. The data set was partitioned at 1% Al, and relevant statistical parameters for the divided data are also given in Table 5.4.1.1.

Table 5.4.1.1 Characteristics of the data set on cadmium.

Variable	N	Range ($\mu\text{g kg}^{-1}$)	Mean ($\mu\text{g kg}^{-1}$)	S.D.	Quartiles		
					25 %	50 %	75 %
Cd	417	<10–380	50	54	<20	30	53
Cd ($\geq 1\%$ Al)	317	<10–320	48	50	<20	28	50
Cd ($< 1\%$ Al)	100	<20–380	58	64	<20	39	67

A plot of the ratio of Cd/Al vs. Al concentration is shown in Figure 5.4.1.1.

The equations of the regressions of Cd and Al, shown in Figures 5.4.1.2 and 5.4.1.3, are as follows:

- 1) $\text{Cd (in } \mu\text{g kg}^{-1}) = 35 + 969 \text{ Al (in g g}^{-1}); r=0.177 \text{ (all Al values).}$
- 2) $\text{Cd (in } \mu\text{g kg}^{-1}) = 11 + 1866 \text{ Al (in g g}^{-1}); r=0.338 \text{ (Al values } > 1\%).$

The natural background concentration of cadmium is relatively low compared, for example, to copper and other more abundant metals. It is therefore reasonable to believe that a Cd-Al regression equation is more sensitive to the "disturbance" of contamination than such an equation for most of the other metals. A good correlation can thus only be expected in an area with a constant level of contamination.

C) Distribution of Concentrations

a) Very high cadmium concentrations ($>0.5 \text{ mg kg}^{-1}$)

Three high values of cadmium were found in the English Channel, one of which was close to the English coast (0.678 mg kg^{-1}) and two in the Baie de Seine (1.0 and 4.0 mg kg^{-1}). Four high concentrations of cadmium were found in the Western Scheldt estuary, three from the Belgian coast (0.52 – 8.69 mg kg^{-1}) and one from the Netherlands (1.02 mg kg^{-1}).

Three very high cadmium values were also reported by Norway from the Sörfjord (5.5 – 12.2 mg kg^{-1}). These values can only be regarded as minimum values, however, as the quality assurance data indicated that all the Norwegian data on cadmium might be too low.

b) Overall distribution

The correlation between Cd and Al was not very strong ($r = 0.338$). The likely reason for this was discussed earlier. The distribution of Cd was, therefore, plotted both using actual concentrations and also using Al-normalized values. The total concentration distribution of the whole data set is shown in Figure 5.4.1.4, and the data set on $Al < 1\%$ is presented in Figure 5.4.1.5. The Al-normalized data set is given in Figure 5.4.1.6.

The coverage of the North Sea is very uneven, as several data sets were rejected. It is therefore not possible, in a comprehensive and adequate manner, to compare different coastal areas around the North Sea, nor large parts of more open sea areas.

The patterns of the absolute and normalized data are largely the same. The highest concentrations are mainly found in the coastal areas, especially in the Western Scheldt, the Humber, and the northeast coast of England. The Dogger Bank also contains some areas with elevated concentrations of cadmium.

The enrichment factors of trace metal concentrations in the Belt Sea surface sediments, compared to the pre-1850 level, have been calculated in an ICES review of Baltic Sea sediments (Pertilä and Brüggemann, 1992). This is found to be 1.1–3.7 for Cd, and the concentrations of Cd in the surface sediments (0–1 cm) in the same area are 280–600 $\mu\text{g kg}^{-1}$. The pre-industrial sediment concentration would accordingly be 280/3.7 or 76 $\mu\text{g kg}^{-1}$. These "background values" can be compared with the 75% quartile for Cd in this Baseline Study of 53 $\mu\text{g kg}^{-1}$. This predominance of low values reflects the high proportion of sandy sediment analysed in the present survey.

Even though some countries did not use a total analysis method, their quality control data for Cd were acceptable. Other investigations have shown that, for example, a nitric acid dissolution usually gives almost 100% recovery for cadmium in most reliable standard sediments. Results from these non-total methods suggest that most of the cadmium concentrations along the Danish west coast are quite low ($< 20 \mu\text{g kg}^{-1}$), although there are some higher values north of the German Bight (50–137 $\mu\text{g kg}^{-1}$). The low values are to be expected, as the sediment in this area is mostly rather sandy and there are no accumulation areas. In the accumulation sites in the Kattegat, the concentrations were also quite low (42–137 $\mu\text{g kg}^{-1}$) compared to the high estuarine values shown in Figure 5.4.1.4.

D) Conclusions

The limited data set prevented complete interpretation although it was possible to identify the Scheldt, the

Humber, the northeast coast of England, and the Dogger Bank as areas of elevated cadmium concentrations.

5.4.2 Mercury

Mercury is one of the high priority contaminants on the hazardous substances list and is, therefore, of great concern. For this reason, it is of importance to identify areas in the North Sea showing elevated levels of mercury in the sediments, and to consider potential sources and effects.

A) Data

Data were reported for more than 600 sediment samples, analysed by nine laboratories for total mercury in whole sediment. The quality control of the data eliminated results from one laboratory, representing 8 values. Another laboratory reported Hg values on a wet weight basis and these data were also eliminated.

Most laboratories reported a detection limit of 0.001 mg kg^{-1} , and the lowest mercury value reported was 0.003 mg kg^{-1} .

B) Univariate Statistics

The statistical analysis included 594 samples, excluding concentrations exceeding 0.5 mg kg^{-1} (19 samples, 11 from Norwegian fjords). This gave the following results:

Mean: 0.057 mg kg^{-1}
Std. dev.: 0.08

75% of the data were at or below a level of 0.025 mg kg^{-1} . This implies that most of the data were well below 0.1 mg kg^{-1} , an upper concentration found in fjord sediments not known to be contaminated by point sources.

Organic carbon was measured in 202 samples:

Mean: 0.97 %
Std. dev.: 0.8
Range: 0.03–3.3 %

The concentration of aluminium was measured in 532 samples:

Mean: 2.2 %
Std. dev.: 1.6
Range: 0.1–9.29 %.

The correlation analyses showed the following ($p = 0.0001$):

	<u>Org. C</u>	<u>Al</u>
Hg	0.48	0.23
	n = 202	n = 532

The strong correlation with organic carbon rather than aluminium is consistent with the known geochemical behaviour of mercury.

A plot of the ratio of Hg/Al vs. Al concentration in sediments with an Al content $\geq 1\%$ shows a negative slope (Figure 5.4.2.1).

Figure 5.4.2.2 shows the correlation between Hg in total sediment and Al. A removal of data for samples with $< 1\%$ Al (Figure 5.4.2.3) did not change the slope significantly. Both figures indicate little covariation between Hg and Al.

In contrast, Figure 5.4.2.4 shows a strong correlation between mercury and total organic carbon, based on the data from the German Bight.

C) Distribution of Concentrations

The concentrations of mercury are generally low and below what may be considered an upper "background" level. This implies that most of the sediments in the North Sea may be considered uncontaminated with respect to mercury.

Figure 5.4.2.5 shows the distribution of mercury in surface sediments without any normalization. All values higher than 0.5 mg kg^{-1} have been omitted; these higher values were found in Norwegian fjords and the Tyne and

Thames estuaries. Figure 5.4.2.5 indicates elevated concentrations of mercury on the south and east coasts of England, the mouth of the river Seine, the Scheldt-Rhine area, the German Bight, the inner Skagerrak, and the Dogger Bank area.

Figure 5.4.2.6 shows the distribution of sediments with mercury concentrations between 0.1 and 0.5 mg kg^{-1} . Figure 5.4.2.7 shows the Hg/Al ratio for stations with an Al content $\geq 1\%$ and a Hg content $< 0.5 \text{ mg kg}^{-1}$. No change in distribution pattern occurs compared to non-normalized values. Data on Hg/Al ratios from the German estuaries and the German Bight are not shown, because of the low concentrations of aluminium in these sediments.

D) Discussion

The distribution of mercury in sediments in the NSTF region shows that some coastal, estuarine, and fjord sediments are contaminated. The central part of the North Sea shows levels in the sediments within natural variations. This implies that most of the mercury discharged into the North Sea is trapped in estuaries and near-coastal areas. Additionally, some elevated levels occur in the inner Skagerrak and the Norwegian Trench as well as to the north of the Dogger Bank, where muddy sediments are deposited.

Based on the report on land-based inputs of contaminants to the waters of the Paris Convention in 1990 (OSPAR-COM, 1992), the following direct and riverine inputs of mercury are estimated for the North Sea:

Country	Input of Mercury (tonnes)
Belgium	3.1
Denmark	0.13
France (Channel, North Sea)	3.6
Germany	11
Netherlands	3.3
Norway (Skagerrak, North Sea)	0.5
Sweden	0.1
United Kingdom (Channel, North Sea)	1.8
Total	23.5

In addition to areas of permanent sediment accumulation (fjords, estuaries, deep basins, and trenches), fine particulate matter with high levels of contaminants may be trapped temporarily in areas with coarse sediments. This will not be demonstrated unless analyses of the fine fraction ($< 63\mu\text{m}$ or $< 20\mu\text{m}$) are performed or the

results of total sediment analysis are normalized to grain size.

The average concentration of total organic carbon in the sediment samples from the North Sea was 1% ($0.03\text{--}3.3\%$). Organic carbon shows small variations

except in the estuaries, where considerable gradients may occur. The strong correlation between mercury and organic carbon in total sediment in the German Bight is shown in Figure 5.4.2.4.

E) Conclusions

The results of analyses of mercury and normalizing elements in sediments of the NSTF region may be summarized by the following conclusions:

- 1) The central parts of the North Sea contain sediments with normal concentrations of mercury, except for an area to the north of the Dogger Bank.
- 2) Norwegian fjords, the Swedish coastline, and some estuaries in England, France, the Netherlands and Germany show elevated mercury concentrations in sediments, indicating local sources.

5.4.3 Copper

A) Data

Copper concentrations were reported for 693 whole sediment samples. Data for 278 samples were excluded from the assessment, as the analytical methods employed did not match the requirements of the programme for the

determination of total concentrations of metals. The remaining 415 values ranged between 3 mg kg⁻¹ and 87mg kg⁻¹, and the detection limits of the methods used ranged from 0.01 to 3 mg kg⁻¹. The relatively high detection limit of the method used in England necessitated the truncation of the BLUK data set, so all values at or below 6 mg kg⁻¹ were eliminated. Data on three samples were omitted from the statistical analyses because they contained very high concentrations of copper; all came from the Sørkjord and they contained 169, 178, and 368 mg kg⁻¹, respectively.

B) Univariate Statistics

Descriptive univariate statistics (means, standard deviations, quartiles, etc.) for both the whole data set and the data set partitioned at 1% aluminium are given in Table 5.4.3.1.

Correlation coefficients of copper with aluminium, fines, and organic carbon are listed in Table 5.4.3.2.

The plot of the ratio of Cu/Al against Al is given in Figure 5.4.3.1, which clearly supports the need to partition the data set at 1% aluminium. The regression lines for the relationships between Cu and Al (total and $\geq 1\%$) are shown in Figures 5.4.3.2 and 5.4.3.3.

Table 5.4.3.1 Characteristics of the data set on copper.

Variable	N	Range (mg kg ⁻¹)	Mean (mg kg ⁻¹)	S.D.	Quartiles		
					25 %	50 %	75 %
Cu	291	0.1–87	14	16	3.2	7.5	22
Cu ($\geq 1\%$ Al)	268	0.8–87	15	16	3.4	8	23
Cu (<1% Al)	14	1.4–27	5.8	6.6	3	3.4	7

Table 5.4.3.2 Correlation coefficients (R) of copper with aluminium, fines and organic carbon, probability (P) of a higher value of R under $H_0: \rho = 0$, and number of samples (N).

Variable		All samples	Al $\geq 1\%$	Al $< 1\%$
Al	R	0.459	0.446	0.181
	P	0.0001	0.0001	0.535
	N	282	268	14
Fines	R	0.609	0.620	0.012
	P	0.0001	0.0001	0.974
	N	91	72	10
Organic carbon	R	0.582	0.575	0.952
	P	0.0001	0.0001	0.048
	N	202	198	4

C) Distributions of Concentrations

Copper concentrations in whole sediment, not normalized for grain size variations, were relatively high in Norwegian fjords, off the west coast of Norway, in the Skagerrak area, in the Scheldt and Seine estuaries, and at occasional other locations, such as the Tyne and Tees estuaries in northeast England (see Figure 5.4.3.4).

There is little discernable pattern in the distribution of copper in sediment containing less than 1% aluminium (see Figure 5.4.3.5), except for a single high value in the Scheldt estuary, which is consistent with observations in sediment with higher aluminium concentrations from the same area.

Copper to aluminium ratios for samples containing more than 1% aluminium are shown in Figure 5.4.3.6. The highest ratios are associated with sediments in Norwegian fjords and in the Scheldt estuary. Other areas of consistently high values occur off the Norwegian and Swedish coasts, including depositional areas in the Skagerrak, off the English coast around the Tyne, Tees, and Humber estuaries and east Anglia, and in a few samples off the southern part of the west coast of Denmark.

D) Conclusions

High copper concentrations can arise from naturally mineralized areas and also from waste discharges. In areas where these two sources coincide (e.g., the north

east coast of England and Helgoland), it is difficult to assess their relative importance. The highest copper concentrations were found in contaminated fjords and estuaries, and enhanced concentrations were found in depositional areas such as the Skagerrak.

5.4.4 Lead

A) Data

Only data produced by total analysis procedures were included in the assessment. No data were rejected on the basis of quality control review. Samples with lead concentrations greater than 1000 mg kg⁻¹ were excluded from the statistical analyses as they would dominate the distribution and unduly influence any calculated parameters. Exclusion of these data was also required for the production of distribution charts, as their presence would have compressed the lower value symbols and obscured variations. Only three samples were excluded for these reasons; all were from the Sörfjord and contained lead concentrations of 3150, 1330, and 1250 mg kg⁻¹, respectively.

B) Statistical Analysis

The characteristics of the data set, excluding the three above-mentioned samples, are shown in Table 5.4.4.1.

The correlation coefficients of lead with aluminium, fines and organic carbon are listed in Table 5.4.4.2.

Table 5.4.4.1 Characteristics of the data set on lead.

Variable	N	Range(mg kg ⁻¹)	Mean (mg kg ⁻¹)	S.D.	Quartiles		
					25 %	50 %	75 %
Pb	601	1.7-288	21	27	7.8	12	21
Pb ($\geq 1\%$ Al)	489	1.9-288	23	29	9	14	27
Pb ($< 1\%$ Al)	112	1.7-13	9.5	13	5	7	10

Table 5.4.4.2 Correlation coefficients (R) of lead with aluminium, fines and organic carbon, probability (P) of a higher value of R under Ho:Rho = 0, and number of samples (N).

Variable		All samples	Al $\geq 1\%$	Al $< 1\%$
Al	R	0.60399	0.60	0.22
	P	0.0001	0.0001	0.02
	N	592	489	103
Fines	R	0.54	0.57	0.07
	P	0.0001	0.0001	0.80
	N	83	67	16
Organic carbon	R	0.51	0.51	0.51
	P	0.0001	0.0001	0.07
	N	197	194	3

Both the data set for all samples, and that for samples containing greater than 1% aluminium, show highly significant correlations with aluminium, fines and organic carbon. The samples containing less than 1% aluminium were not significantly correlated with these variables.

The regression of Pb/Al vs. Al is shown in Figure 5.4.4.1. Regressions of the relationships between lead and aluminium in all samples and in only those samples containing more than 1% Al are shown in Figures 5.4.4.2 and 5.4.4.3, respectively. In the complete, and $\geq 1\%$ aluminium, data sets there is little scatter around the regression lines, and the lines are similar to each other.

C) Distribution of Concentrations

Figure 5.4.4.4 shows the distribution of total lead in all sediments. The most notable areas exhibiting higher concentrations are the Hardanger Fjord, the Scheldt estuary, the Baie de Seine, and the northeast coast of

England. The Norwegian Trench and the Skagerrak also showed slightly higher concentrations compared to the general North Sea. No data were available from the Elbe, a major river flowing into the North Sea and draining an industrialized area.

Figures 5.4.4.5 and 5.4.4.6 show the distribution of concentrations of Pb in sediments containing less than 1% aluminium and the distribution of lead normalized to aluminium (Pb/Al ratio) in sediments containing more than 1% aluminium.

The low-concentration aluminium samples in the English Channel and the Southern Bight contain low concentrations of lead compared to the Scheldt estuary and show little variation in concentration.

The Pb/Al ratios in the North Sea are more uniform than the absolute Pb values, although the Hardanger Fjord, the Scheldt, and the northeast coast of England show relatively high values.

The area off the southwest coast of England shows only limited elevation of lead concentrations compared to other areas. However, after normalization the elevations became more apparent. It must be remembered that the southwest area of England is heavily mineralized, and the aluminium concentrations in English Channel sediments are very low due to the presence of shelly material; consequently, the metal/Al ratios are high.

D) Discussion

Lead concentrations and Pb/Al ratios are relatively high in only a few areas: some Norwegian fjords, the Scheldt estuary, and off the northeast and southwest coasts of England. The Norwegian Trench and the Humber and Thames estuaries also show slightly elevated concentrations and Pb/Al ratios. No data were available for the Elbe. The concentrations and ratios are low in the central North Sea. The higher concentrations are therefore found in coastal areas, and particularly in areas associated with rivers which drain industrialized catchments. By contrast, the southwest area of England has only limited industry but is heavily mineralized and has a history of mining, particularly in the nineteenth century.

The Pennine hills in northern England are also heavily mineralized, causing elevated concentrations and ratios in the sediments off the northeast coast where erosion products are deposited. However, unlike the southwest, there is considerable industry, particularly around the rivers Tyne and Tees.

Thus, it may be deduced that there are two primary causes of the elevated lead concentrations: variations in geological setting, and industrialization. The present data set does not allow these two factors to be separated.

E) Conclusions

Normalized lead values are high in some Norwegian fjords, the Scheldt estuary, and off the northeast and southwest coasts of England. The Norwegian Trench and the Humber and Thames estuaries also show slightly elevated concentrations and normalized values.

5.4.5 Zinc

A) Data

Only data produced by total analysis procedures were included in the assessment. No data were rejected on the basis of quality control review. Three samples with concentrations greater than 1000 mg kg⁻¹ were excluded from the statistical analyses and the plotting procedures. All three were from the Sörfjord and had concentrations of 4240, 1980, and 1970 mg kg⁻¹, respectively.

B) Statistical Analysis

The characteristics of the data set are shown in Table 5.4.5.1.

The correlation coefficients of zinc with aluminium, fines and organic carbon are given in Table 5.4.5.2.

Table 5.4.5.1 Characteristics of the data set on zinc.

Variable	N	Range (mg kg ⁻¹)	Mean (mg kg ⁻¹)	S.D.	Quartiles		
					25 %	50 %	75 %
Zn	610	3-510	39	57	10	19	39
Zn (≥ 1 % Al)	494	3-510	45	61	11	20	50
Zn (< 1 % Al)	116	3-208	15	21	7	10	16

Table 5.4.5.2 Correlation coefficients (R) of zinc with aluminium, fines and organic carbon, probability (P) of a higher value of R under $H_0: \rho = 0$, and number of samples (N).

Variable		All samples	Al $\geq 1\%$	Al $< 1\%$
Al	R	0.71	0.71	0.26
	P	0.0001	0.0001	0.007
	N	601	494	107
Fines	R	0.63	0.64	0.31
	P	0.0001	0.0001	0.18
	N	92	72	20
Organic carbon	R	0.72	0.72	0.84
	P	0.0001	0.0001	0.02
	N	206	199	7

Both the data set for all samples, and that for sediments containing greater than 1% aluminium, show highly significant correlations with aluminium, fines and organic carbon. On the whole, the sediments containing less than 1% aluminium were not significantly correlated with these variables.

A plot of the regression of Zn/Al vs. Al is shown in Figure 5.4.5.1. Regressions of the relationships between zinc and aluminium in all sediments, and in only those sediments containing more than 1% Al are shown in Figures 5.4.5.2 and 5.4.5.3, respectively. In the total and $\geq 1\%$ aluminium data sets, there is only limited scatter around the regression lines and the regression lines are similar.

C) Distribution of Concentrations

Figure 5.4.5.4 shows the distribution of total zinc concentrations in all sediments. The most notable areas with high concentrations are the Hardanger fjord, the Norwegian Trench and the Skagerrak, the Oslo fjord, the Baie de Seine, the Scheldt estuary, and the Humber, Tyne and Tees estuaries of northeast England. No data were available for the Elbe estuary.

Figures 5.4.5.5 and 5.4.5.6 show the distribution of absolute zinc concentrations in sediments containing less than 1% aluminium and the distribution of zinc concentrations normalized to aluminium (Zn/Al ratio) in sediments containing more than 1% aluminium.

The low aluminium-content sediments in the English Channel and the Southern Bight show little consistent variability and have low zinc concentrations compared to the Scheldt estuary.

Zn/Al ratios in sediments of the North Sea are more uniform than the absolute zinc concentrations, although these ratios in the Hardanger fjord, the Scheldt estuary, and off the northeast coast of England are still higher than those in the central North Sea. The area off the southwest coast of England is also seen as an area of higher ratios, although absolute concentrations are low.

D) Discussion

Zinc concentrations and Zn/Al ratios are relatively high in coastal areas and particularly at the mouths of rivers: the Hardanger fjord, Oslo fjord, Scheldt, Seine, Humber, Tyne and Tees. Unfortunately, no data were available for the Elbe, another major industrial river. As with lead, the southwest coast of England is an area of relatively elevated zinc when ratios to aluminium are considered. This is not apparent in the absolute zinc concentrations. Areas of mineralization in the southwest of England contribute particulates with high zinc concentrations to the coastal sediments, and account for a proportion of the relatively elevated values. A similar situation applies to the northeast coast of England, the Humber estuary, and the Oslo and Hardanger fjords, although in all these areas there is also an industrial input of zinc to the marine environment. The present data do not allow the relative contributions of industrial and natural background values to be assessed.

E) Conclusions

The highest zinc concentrations reported were found in the Sør fjord. Compared to the central North Sea, the coastal area generally contains elevated concentrations of zinc although sediments around most large estuaries contain particularly elevated concentrations.

Sediments of the northeast and southwest coasts of England contain elevated zinc concentrations. The former area receives river flow from industrial and naturally mineralized areas, while the latter only receives drainage from natural zones. The relative importance of natural and anthropogenic inputs to these areas cannot be determined from the data.

5.5 Distributions of NSTF Voluntary Metals

5.5.1 Arsenic

A) Data

Data were submitted from four countries: Belgium, Denmark, Germany, and Norway. The Belgian data (7 samples) were not included in the assessment because a non-total extraction method had been used. Some of the Norwegian data (61 samples) and all the data from Germany (9 samples) were also rejected because the quality

assurance information gave rise to doubts about the quality of the data submitted. No data were excluded due to a high detection limit.

Only data for 45 samples from Denmark and 70 from Norway were assessed further. No samples were excluded from the presentation on the basis of extremely high values.

B) Univariate Statistics

The mean, quartiles, standard deviation, and other relevant statistical parameters for the data accepted are given in Table 5.5.1.1. The data set was partitioned at 1% Al, and the relevant statistical parameters for the Al $\geq 1\%$ data set are also given in Table 5.5.1.1. Only two samples had Al concentrations less than 1%; both were from the west coast of Denmark. Only some of the statistical variables are therefore given in the table below and no charts are presented for the Al $< 1\%$ data set.

Table 5.5.1.1 Characteristics of the data set on arsenic.

Variable	N	Range (mg kg ⁻¹)	Mean (mg kg ⁻¹)	S.D.	Quartiles		
					25%	50%	75%
As	81	<1.2–33	11	8.1	3.2	7.7	18
As ($\geq 1\%$ Al)	79	<1.2–33	11	8.1	3.0	7.7	18
As ($< 1\%$ Al)	2	3.2–12	7.5	-	-	-	-

A plot of the regression of As/Al vs. Al is shown in Figure 5.5.1.1.

The equations of the regressions of As on Al (shown in Figures 5.5.1.2 and 5.5.1.3) are as follows:

- 1) $\text{As (in mg kg}^{-1}\text{)} = -4.4 + 383 \text{ Al (in g g}^{-1}\text{)}$;
 $r=0.823$ (all Al values).
- 2) $\text{As (in mg kg}^{-1}\text{)} = -5.5 + 406 \text{ Al (in g g}^{-1}\text{)}$;
 $r=0.843$ (Al $\geq 1\%$).

C) Distribution of Concentrations

There were no extreme arsenic values. The highest total arsenic concentrations were found in the sediment accumulation areas in the Skagerrak (see Figure 5.5.1.4). The concentrations were lower in the more open areas of the North Sea, along the west coast of Denmark, and also in the southern and western parts of the Kattegat.

The distribution of the Al-normalized arsenic concentrations (Figure 5.5.1.5) gives a slightly different picture. The Al-normalized arsenic concentrations from the more sandy areas off the Danish west coast north of the German Bight, and at the two stations close to the Norwegian west coast outside the Sogne fjord, have values similar to those found in the accumulation areas in the Skagerrak. The normalized arsenic concentrations are low in the western and southern parts of the Kattegat, as are the concentrations in the open North Sea areas.

The upper normal level of arsenic in aerobic Norwegian fjord sediments, not affected as far as is known by any point sources, has been set at 20 mg kg⁻¹ in a Norwegian suggestion for water quality criteria (Jon Knutzen, Vannkvalitetskriterier for Marin Områder, Miljøgifter). This may be compared with the 75% quartile of 18 mg kg⁻¹ and the maximum value of 32.5 mg kg⁻¹ in the current data set.

D) Conclusions

The distribution of sampling points for arsenic is very poor, being confined to the Danish, Norwegian, and Swedish coasts and the northern North Sea. Little can be concluded from the data except that the concentrations in the Skagerrak and Kattegat are higher than those in the central North Sea.

5.5.2 Chromium

A) Data

All Danish (HFLD) data on chromium were rejected because of imprecision in the quality assurance data. All samples with concentrations below the detection limit ($<5 \text{ mg kg}^{-1}$) were also rejected (46 from BLUK).

Samples containing more than 140 mg kg^{-1} were excluded from the data set to prevent their exerting undue influence on the statistical procedures. This also avoided compression of the small symbols on the charts. Nine samples, ranging from $149\text{--}221 \text{ mg kg}^{-1}$, were excluded in this manner. All were from the northern North Sea.

B) Statistics

Table 5.5.2.1 gives a list of the characteristics of the data sets used to produce the graphs and charts.

Table 5.5.2.2 gives the correlation coefficients of chromium with aluminium, fines and organic carbon in the three data sets used.

Table 5.5.2.1 Characteristics of the data set on chromium.

Variable	N	Range (mg kg^{-1})	Mean (mg kg^{-1})	S.D.	Quartiles		
					25%	50%	75%
Cr	458	3–117	30	27	10	20	36
Cr ($\geq 1\% \text{ Al}$)	391	4–117	33	28	12	23	40
Cr ($< 1\% \text{ Al}$)	67	3–41	11	6.5	7	10	12

Table 5.5.2.2 Correlation coefficients (R) of chromium with aluminium, fines and organic carbon with the probability (P) of a higher value of R under $H_0: \rho = 0$, and the number of observations (N).

		All samples	Al $\geq 1\%$	Al $< 1\%$
Al	R	0.90	0.90	0.35
	P	0.0001	0.0001	0.008
	N	183	125	58
Fines	R	0.53	0.009	0.94
	P	0.011	0.98	0.0001
	N	22	10	12
Organic carbon	R	0.95	0.95	-
	P	0.0001	0.0001	-
	N	127	125	2

The correlations between chromium and aluminium and between chromium and organic carbon are significant in the complete and in the Al $\geq 1\%$ data sets, and also in the Al $< 1\%$ data set.

The regressions of Cr/Al vs. Al, Cr vs. Al (whole data set), and Cr vs. Al (Al $\geq 1\%$) are shown in Figures 5.5.2.1, 5.5.2.2, and 5.5.2.3, respectively.

C) Distribution of Concentrations

The distribution of chromium concentrations in whole sediments is shown in Figure 5.5.2.4, and concentrations of chromium in sediments containing less than 1% Al are illustrated in Figure 5.5.2.5. Figure 5.5.2.6 shows the distribution of Cr/Al ratios in whole sediments with Al $\geq 1\%$.

Chromium concentrations are higher near the English coast, in the Skagerrak, and in the Norwegian Trench. This is due largely to the presence of fine material in these sediments. After normalization with aluminium, these variations are less apparent. By contrast, the Dogger Bank is more clearly an area of high values in the map of normalized values than it is in the map of total chromium concentrations.

D) Conclusions

Normalized chromium concentrations are fairly uniform throughout the North Sea, however, there is evidence of elevated Cr/Al ratios in the Dogger Bank area.

5.5.3 Nickel

A) Data

Only data produced by total analysis procedures were included in the assessment. It was not necessary to exclude any particularly high values from the data set prior to statistical analysis and graphical presentation.

B) Statistical Analysis

The characteristics of the data set are shown in Table 5.5.3.1.

The correlation coefficients for regressions of nickel on aluminium, fines, and organic carbon are shown in Table 5.5.3.2.

Table 5.5.3.1 Characteristics of the data set on nickel.

Variable	N	Range (mg kg ⁻¹)	Mean (mg kg ⁻¹)	S.D.	Quartiles		
					25%	50%	75%
Ni	153	1.5–113	23	22	5.3	20	33
Ni (≥ 1% Al)	143	1.5–113	24	23	5.8	21	34
Ni (< 1% Al)	1	-	6	-	-	-	-

Table 5.5.3.2 Correlation coefficients (R) of nickel with aluminium, fines and organic carbon with the probability (P) of a higher value of R under Ho:Rho = 0, and the number of samples (N).

Variable		All samples	Al ≥ 1%	Al < 1%
Al	R	0.832	0.834	
	P	0.0001	0.0001	
	N	144	143	1
Fines	R	0.661	-0.253	
	P	0.0053	0.0001	
	N	16	6	1
Organic carbon	R	0.552	0.552	
	P	0.0001	0.0001	
	N	137	137	1

The nickel concentrations were well correlated with aluminium and organic carbon. There were few data pairs of nickel and the proportion of fines.

The regressions of nickel against aluminium for all samples, and for samples containing greater than 1% aluminium, are shown in Figures 5.5.3.1 and 5.5.3.2, respectively.

C) Distribution of Concentrations

The distribution of nickel in whole sediments (see Figure 5.5.3.3) indicates that, apart from certain Norwegian fjords, the highest concentrations of nickel occur in the Skagerrak area and west of Norway. A consideration of the distribution of Ni/Al ratios shows a similar pattern (Figure 5.5.3.4).

However, if the data are normalized to organic carbon (see Figures 5.5.3.5 and 5.5.3.6), the Skagerrak no longer appears to have enhanced levels of nickel in relation to other areas.

The distribution of nickel data is not extensive. No data were assessed from the English coast, nor from coastal areas of France, Belgium, the Netherlands, or Germany north of the Elbe. It is not possible to make a complete assessment of the North Sea from these data, and there are no clear indications of areas contaminated by nickel.

D) Conclusions

The distribution of the samples was limited and prevented any firm conclusions from being drawn.

6 CONCENTRATIONS OF METALS AND NORMALIZING VARIABLES IN THE FINE GRAIN SIZE SEDIMENT FRACTIONS

6.1 Distribution of Fine Sediments

Large areas of the North Sea floor are covered by sands. These areas are considered to be dispersive, that is, there is in general no net sediment accumulation. It can be seen, however, that contaminants may (and do) accumulate in the sediments of dispersive areas. This is due

to the fact that sedimentation, to a varying degree, occurs in almost all areas of the North Sea. In dispersive areas, however, sedimentation is balanced, in the long run, by resuspension. Mixing of deposited material into the sediment by bioturbation, wave or current action, or fishing activities leads sediments to respond to changes in the composition of suspended matter; this occurs in dispersive areas, as well as in areas of sediment accumulation.

Figure 5.3.1.1 shows the distribution of fines ($<63 \mu\text{m}$) in sediments of the North Sea. Data submitted by BSHG and, in addition, data obtained by the Technische Universität Hamburg-Harburg (Michael Kersten) are shown.

The diameter of the circles plotted is proportional to the proportion of fines. The largest circles in the Skagerrak area correspond to almost 100% fine material. Large areas of the southern and eastern North Sea are covered by sands containing very small amounts of fines, in many cases less than 1%.

6.2 Metals in the Fine Sediments

Several laboratories reported data on metals in the fine sediment fraction ("fines"). Some laboratories analysed the $<20 \mu\text{m}$ fraction and others the $<63 \mu\text{m}$ fraction. Few laboratories analysed both size fractions (and, in addition, the whole sediment) (see Table 6.2.1).

Table 6.2.1 Numbers of samples analysed for metals in fine sediment fractions according to laboratory.

$<20 \mu\text{m}$														
Lab	Al	TOC	Fe	fra20	Hg	Cd	Pb	Zn	Cu	Cr	Ni	Mn	As	Ti
BFGG				5	5	5	5	5	5	5	5		5	
BSHG	131	162	175	175	175	175	175	175	175	157	148	175	144	132
ISHG		13	13	13	13	13	13	13	13	13	13		13	
LWKG			7	9	7	7	7	7	7	7	7		7	
NLWG			32	49	32	32	32	31	32	32	31	32		
$<63 \mu\text{m}$														
Lab	Al	TOC	Fe	fra63	Hg	Cd	Pb	Zn	Cu	Cr	Ni	Mn	As	Ti
ALUK		16		16										
BFGG				4										
BSHG			14	157	14	14	10	10	14	14	12	14		
DGWN		19		19	19	19	19	19	19	19	19			
FRUK		1		1	1	1	1	1	1	1	1			
HFLD	7	7	7		7	7	7	7	7	7	7	7	7	7
ICNF	6	6		9	8	9	9	9	9					
ISOB	32			32	32	32	32	32	32	7	7			
LWKG			1	9	1	1	1	1	1	1	1			
NIVA	6	6		19	6	6	6	6	6					
NLWG			4	13	4	4	4	4	4	4	4	4		1

It appears that few laboratories measured more than one covariate. Only one laboratory measured aluminium, organic carbon (TOC), and iron in the fines. No data on the content of carbonates were available, although some laboratories, e.g., BSHG, reported corresponding data. According to BSHG data, the content of carbonates in the fines of North Sea sediments varies between less than 2% and more than 70% (expressed as CaCO_3).

Summary statistics for data on concentrations of metals and covariates in the $<20\ \mu\text{m}$ fraction and in the $<63\ \mu\text{m}$ fraction are given in Annex 6. The range of variation is also illustrated by frequency histograms (see Figure 6.2.1).

The large range of variation for some metals in the $<63\ \mu\text{m}$ fraction is in part due to the inclusion of samples from some contaminated Norwegian fjords. These sampling positions are located far from the open coastline, and cannot be considered as representing North Sea sediments.

Additional variation in the $<63\ \mu\text{m}$ fraction is caused by the inclusion of data from a few laboratories that reported exceptionally high metal values, for example, for copper (including offshore stations).

Separating and analysing the fines is one way of normalizing metal data in sediments of varying grain size. Figures 6.2.2 to 6.2.4 show plots of metal values *versus* values of potential normalizers, as far as available, in the $<63\ \mu\text{m}$ fraction. After inspection of these plots, it was decided to make no attempt to further normalize metal data in the $<63\ \mu\text{m}$ fraction.

6.3 Spatial Distributions of Metals in the $<63\ \mu\text{m}$ Fraction

Figures 6.3.1 to 6.3.8 show the spatial distributions of metal concentrations in the $<63\ \mu\text{m}$ fraction.

The spatial coverage of metal data in the $<63\ \mu\text{m}$ fraction is poor and not sufficient to provide a full perspective of the distribution of contamination throughout the North Sea area.

For some metals, e.g., mercury, cadmium and zinc, higher levels are found at nearshore stations compared to offshore stations. The scatter of data, however, is large.

6.4 Spatial Distributions of Metals in the $<20\ \mu\text{m}$ Fraction

Figures 6.4.1 to 6.4.9 show the spatial distributions of metal concentrations in the $<20\ \mu\text{m}$ fraction.

The spatial coverage of these data in the 1990/1991 Baseline Survey is poor and not sufficient to describe the distribution of metal contamination of North Sea sediments in the entire North Sea. Some spatial variations, however, are clearly visible:

- 1) Mercury, cadmium, and zinc show elevated values in the German Bight compared to stations in the central North Sea. High concentrations of these metals in the fines of German Bight sediments are not restricted to accumulating areas, such as the muddy area southeast of Helgoland, but also occur in the sandy areas of the German Bight, which are considered to be dispersive.
- 2) Some elevated concentrations of mercury also occur close to the northeast coast of England.
- 3) Copper and nickel are more or less uniformly distributed throughout the area investigated.
- 4) Relatively high concentrations of lead are found near the east coast of England, in the central North Sea, and in the German Bight. The high concentrations of lead in the central North Sea are accompanied by high levels of TOC, as shown in Figures 6.4.7 and 6.4.8.
- 5) Chromium concentrations are highest in the central North Sea. High chromium concentrations in these areas are also associated with high levels of TOC.
- 6) Aluminium, a potential normalizer, is rather uniformly distributed in the $<20\ \mu\text{m}$ fraction. Low values in the English Channel area, and in the northwestern North Sea, are associated with high concentrations of carbonates.

6.5 Additional Information

The data discussed so far refer to the 1990/1991 survey. Some laboratories also reported data from earlier years. These data, however, still have to be processed. Nonetheless, in the case of one laboratory (BSHG), the entire data set (653 samples for the $<20\ \mu\text{m}$ fraction) could be used because the data were readily available in separate PC files. It was decided to make use of these data and Figure 6.5.1 shows the sampling locations covered by BSHG.

Using this set of data, an attempt was made to determine whether metal data in the $<20\ \mu\text{m}$ fraction needed further geochemical normalization. To this end, factor analysis was carried out for data obtained on samples from three different sub-areas of the North Sea.

- 1) Samples from NSTF Areas 1, 2B, 7A, and 6 were combined into one set. These areas are considered to

be more or less remote from contaminant sources and are not suspected to be seriously contaminated with metals.

- 2) Samples from NSTF Area 7B were used for the second run. Area 7B is considered a transition area, extending from less contaminated to more heavily contaminated locations.
- 3) Samples from NSTF Area 5 were used for the final run. Most of the samples in Area 5, however, originate from the southern part of that area, e.g., from the German Bight. This area is considered to be heavily contaminated, at least with mercury, cadmium, and zinc.

Tables 6.5.1 to 6.5.3 show the results of the analyses. Four factors were extracted. These four factors account for 77% to 80% of the overall variation of the data. For all sub-areas, an iron factor, an organic factor and an aluminium factor could be separated, the iron factor being the most important one.

After inspection of the results, it was decided that additional normalization of metal concentrations in the $<20 \mu\text{m}$ fraction is, in general, not needed. Only in the cases

of lead and chromium was it felt that high concentrations of these metals in the central North Sea might be associated with high concentrations of organic carbon (TOC).

Some examples of metal distributions over the investigated area were plotted. As the station grid in the German Bight is rather dense, average values over appropriate sub-areas were used in order to allow plotting of circles of reasonable size. These results are shown in Figures 6.5.2 to 6.5.10. The distribution of lead includes data obtained by M. Kersten. Two plots for mercury are shown. The first one includes data from samples taken in 1976. The second one includes only data from samples taken in 1985 or later.

Notched box-and-whisker plots are given showing the quartiles and the range of values for metals and the main components in different NSTF areas in Figures 6.5.11 to 6.5.27 (on the x-axis of these plots, Area 2B is designated 2.2; Areas 3A and 3B are designated 3.1 and 3.2, respectively; and Areas 7A and 7B are designated 7.1 and 7.2, respectively). In addition, plots of chromium/TOC ratios and lead/TOC ratios are shown in Figures 6.5.16 and 6.5.23, respectively.

Table 6.5.1 The results of factor analysis of data from NSTF Areas 1, 2B, 7A, and 6 for the $<20 \mu\text{m}$ fraction (BSHG data).

VARIMAX ROTATED FACTOR MATRIX				
Variable/Factor	1	2	3	4
TOC	0.01367	0.96662	0.10468	0.08968
N	0.05300	0.95536	0.06830	0.18009
P	0.78703	0.50217	0.02002	0.14594
CaCO ₃	-0.38490	-0.52466	-0.67767	-0.08226
Al	0.02564	0.36455	0.83387	0.00171
Ti	0.02947	-0.04423	0.82097	0.34412
Fe	0.97439	0.03034	0.04414	-0.02159
Mn	0.75589	-0.11931	0.11409	0.19133
Hg	0.27067	-0.01589	0.19029	0.74846
Cd	-0.05972	0.38505	-0.39088	0.32249
Pb	0.73234	0.45898	0.15763	0.32076
Zn	0.78089	0.11965	0.28666	0.26317
Cu	0.06228	0.26412	0.05550	0.74530
Cr	0.47552	0.70422	0.19210	0.19950
Ni	-0.03854	0.61914	0.41484	-0.38775
V	0.96649	0.05874	-0.03452	-0.01572
As	0.95394	-0.00075	-0.05149	-0.00076
	Fe	TOC	Al	Hg
109 samples, 80%				

Table 6.5.2 The results of factor analysis of data from NSTF Area 7B for the <20 μm fraction (BSHG data).

VARIMAX ROTATED FACTOR MATRIX				
Variable/Factor	1	2	3	4
TOC	0.09760	0.95164	0.17888	0.15798
N	0.09718	0.94528	0.19489	0.15960
P	0.52041	0.80041	0.07132	0.10600
CaCO ₃	-0.15827	-0.09813	0.37127	-0.68824
Al	-0.10779	-0.24022	-0.24842	0.62538
Ti	-0.26294	-0.33854	-0.57294	0.32322
Fe	0.86907	0.01329	0.21893	0.34059
Mn	0.82783	0.28017	0.15981	-0.18631
Hg	-0.03656	-0.04303	0.76270	-0.31900
Cd	0.01612	0.47787	0.77200	0.02912
Pb	0.61173	0.64061	0.21315	0.11427
Zn	0.31977	0.16817	0.84006	0.09184
Cu	0.26734	0.46334	0.10729	-0.27986
Cr	0.19976	0.33146	0.46501	0.66742
Ni	0.16877	0.28191	0.03834	0.63945
V	0.88229	0.16678	0.14771	0.25963
As	0.93589	0.21151	-0.10320	-0.04561
	Fe	TOC	Zn	Al
176 samples, 77%				

Table 6.5.3 The results of factor analysis of data from NSTF Area 5 for the <20 μm fraction (BSHG data).

VARIMAX ROTATED FACTOR MATRIX				
Variable/Factor	1	2	3	4
TOC	0.32438	0.86419	0.15113	-0.04729
N	0.27201	0.89275	0.10598	0.01928
P	0.65686	0.61942	-0.00579	0.04339
CaCO ₃	-0.63684	-0.41499	-0.23515	0.13285
Al	0.18040	-0.19660	0.78205	0.17353
Ti	0.73927	-0.12359	-0.20073	-0.31633
Fe	0.94779	0.06520	0.07609	0.18261
Mn	0.18671	0.54107	-0.45582	0.40700
Hg	-0.12318	0.22718	0.05450	-0.68474
Cd	-0.10631	0.30384	0.74649	-0.13537
Pb	0.51905	0.53235	0.11455	0.52399
Zn	0.79269	0.28237	0.02261	0.21841
Cu	0.06937	0.81878	-0.14778	-0.03041
Cr	0.74258	0.06291	0.51410	0.13480
Ni	-0.00942	0.56458	0.15519	0.65826
V	0.87882	0.30115	0.09091	0.23328
As	0.83739	0.33534	-0.21240	0.13561
	Fe	TOC	Al	Hg
257 samples, 77%				

6.6 Conclusions

Inspection of these plots, also taking into account data from the 1990/1991 survey alone, leads to the following conclusions:

- 1) Metal contamination clearly occurs in various coastal areas of the North Sea;
- 2) Mercury, cadmium and zinc concentrations are elevated in the German Bight;
- 3) Elevated concentrations of mercury have been identified in some coastal areas of eastern England, the Netherlands, and Denmark;
- 4) Higher concentrations of lead are found in some coastal areas of eastern England, at Dogger Tails End, and at the Great Fisher Bank than elsewhere in the open North Sea;
- 5) Lead/TOC ratios at the Great Fisher Bank are not higher than those in the southern North Sea;
- 6) Low concentrations of lead in the northwestern North Sea may indicate a large-scale contamination of the fines of North Sea sediments with lead, the contamination being less pronounced in the northwestern areas;
- 7) Higher concentrations of chromium in the central North Sea are associated with high concentrations of TOC and probably do not indicate contamination;
- 8) Copper and nickel are rather uniformly distributed in the fines of North Sea sediments;
- 9) Despite rather uniform distribution over the North Sea, high concentrations of copper are detected from time to time in sediments from the eastern North Sea. These patches may originate from ship cleaning operations;
- 10) High concentrations of arsenic and vanadium in the fines of surficial sediments are always associated with high concentrations of iron and do not reflect contamination (cf. Figure 6.6.1).

6.7 Temporal Trends

It is most unlikely that any temporal trends in contaminant concentrations will be detectable by a comparison of the 1990 and the 1991 data. Detection of changes requires many years of observation and frequent sampling. In most areas of the North Sea, both the period of observations and the sampling frequency are not adequate for the detection of trends over time.

In one sub-area of the German Bight, namely, the muddy area southeast of Helgoland, sampling was started as early as 1975. In this area, a decrease in mercury concentrations in the $<20\ \mu\text{m}$ fraction is detectable (see Figure 6.7.1).

7 CONCENTRATIONS OF ORGANIC CONTAMINANTS IN WHOLE SEDIMENTS

7.1 Distributions of NSTF Mandatory Organic Contaminants

7.1.1 Chlorinated biphenyl compounds

A) Background

Chlorinated biphenyl (CB) compounds (congeners) are included in the NSTF list of mandatory determinands, with sediment identified as the primary matrix for analysis. This group of compounds is of anthropogenic origin, and concentrations in completely uncontaminated areas should therefore be zero. However, these compounds are now ubiquitous in distribution, and it could be predicted that areas of greater contamination (usually close to sources) might be identifiable above a general "background" degree of contamination. The group contains a large number of compounds and, therefore, ICES/NSTF identified ten individual congeners to be considered as mandatory for determination. These were congener numbers 28, 31, 52, 101, 105, 118, 138, 153, 156 and 180 (according to the IUPAC system).

B) Quality Assurance and Scope of the Data

The number of data submitted for each CB, according to laboratory and extraction method (see Annex 2), is listed in Table 7.1.1.1. As discussed in Section 3.2, above, quality assurance data for CBs did not provide an adequate basis for the assessment of the comparability of the data from the eight laboratories involved, beyond the need to disregard all data from one laboratory. The lack of data on four of the mandatory congeners from some laboratories reduced the assessed data set to information on six congeners (CBs 28, 52, 101, 138, 153 and 180) obtained from the analysis of whole sediment. Of the 216 data sets assessed (Table 7.1.1.2), 144 originated from one laboratory (IMRN/NIVA). The areas surveyed by this laboratory tended to display low degrees of contamination and, therefore, data on these less contaminated samples tended to dominate the data set.

C) Univariate Statistics

Descriptive univariate statistics of the results for the six major congeners selected are shown in Table 7.1.1.3. The number of determinations varies between 183 and 217. Mean values are in the range $0.212\text{--}0.636\ \mu\text{g kg}^{-1}$.

Standard deviations are mainly 150–200% of the means, and the distributions are skewed towards low values, with a few high values making large contributions to the

variances. The concentrations of CBs 101, 138 and 153 are usually greater than those of CBs 28, 52 and 180.

Table 7.1.1.1 Number of data submitted for chlorinated biphenyl compounds.

Analytical Laboratory	Extraction Method Code	Parameters														
		CB 101	CB 105	CB 118	CB 128	CB 138	CB 149	CB 153	CB 156	CB 170	CB 180	CB 194	CB 109	CB 28	CB 31	CB 52
		N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
ALUK	EXC	17	17	17		17		17	17		17			17	17	17
BFGG	EXC	5		5		5	5	5		5	5	5	5	5		5
BLUK	EXC	32	32	32		32		32	30		32			32	32	32
IHEB	EXP	33		33		33		33			33			32		33
IMRN	EXP	144	144	144	144	144	144	144	144	144	144			144	144	144
ISHG	EXN	28				28		28			28			28		28
LWKG	EXO	9		8		7		7			4			4		6
SERI	EXP	9		9		9		9			9			9		9
ALL	EXC	54	49	54		54	5	54	47	5	54	5	5	54	49	54
	EXN	28				28		28			28			28		28
	EXO	9		8		7		7			4			4		6
	EXP	186	144	186	144	186	144	186	144	144	186			185	144	186

Table 7.1.1.2 Number of data used in the assessment of CB concentrations.

Analytical Laboratory	Extraction Method Code	Parameters					
		CB 101	CB 138	CB 153	CB 180	CB 28	CB 52
		N	N	N	N	N	N
ALUK	EXC	13	13	12	6	15	9
BFGG	EXC	5	5	5	3	3	1
BLUK	EXC		1				
IHEB	EXP	11	17	17	11	8	6
IMRN	EXP	142	144	142	138	116	135
ISHG	EXN	28	28	28	27	28	28
LWKG	EXO	9	7	7	4	4	6
SERI	EXP	9	9	9	9	9	9
ALL	EXC	18	19	17	9	18	10
	EXN	28	28	28	27	28	28
	EXO	9	7	7	4	4	6
	EXP	162	170	168	158	133	150

Table 7.1.1.3 Univariate statistics for the six CBs assessed.

	Concentration ($\mu\text{g kg}^{-1}$ dry weight)					
	CB28	CB52	CB101	CB138	CB153	CB180
Mean	0.257	0.212 ¹	0.407	0.636	0.574	0.275
S.D.	0.394	0.510	0.747	1.114	1.095	0.525
Minimum	0.010	0.010	0.010	0.01	0.01	0.01
Maximum	3	3 ¹	5.5	9	11	5.9
Number of data	183	194	217	224	220	198

¹Excluding one outlying value of $20 \mu\text{g kg}^{-1}$.

D) Factor Analysis and the Distribution of CB Concentrations

Rather than attempt to display and discuss the distributions of all six selected CB congeners, the data were subjected to factor analysis to explore the underlying patterns within the data with a view to simplifying the presentation. The first analysis was carried out on the accepted data set of 231 observations of the six selected CB congeners, with accompanying measurements of organic carbon and aluminium concentrations, and the percentage of material less than $63 \mu\text{m}$. The results are shown graphically in Figure 7.1.1.1 (a), together with a covariance matrix in Table 7.1.1.4. The close correlations of concentrations of CBs 101, 138, 153 and 180 with each other and, to a lesser degree, with the proportion of fines, organic carbon, and aluminium may be noted. By contrast, CB52 correlates poorly with the potential compensation variables. The lack of strong correlations between concentrations of CBs and organic carbon levels was unexpected. The two principal factors identified accounted for 70.1% and 16.5% (total 86.6%) of the variance. Organic carbon and aluminium grouped together, with CBs 180, 138 and 153, in the same area. CBs 101 and 28 also grouped together, but CB52 appeared distinct from the others. As a consequence, maps are presented of the concentrations of CB153 and CB52 (Figures 7.1.1.2 and 7.1.1.3) to represent extremes of the distribution. Concentrations of CB153 (Figure 7.1.1.2) are highest in coastal regions of the southeastern part of the North Sea (Belgium, southern Netherlands, Germany), in the Skagerrak and, to a lesser extent, off the west coast of Norway and possibly the

east coast of Scotland. It is necessary to be aware that there are large areas (e.g., off England and the Netherlands) for which data are not available. The listing of areas of higher concentrations may therefore be misleading, as it is not known whether the large areas for which there are no data should also be included on the list. The distribution of CB52 (Figure 7.1.1.3) appears broadly similar to that of CB153, with the exception of the area near Belgium, which seems to have relatively low CB52 levels.

A second covariance matrix was prepared using data from samples showing the highest concentrations of CBs, i.e., CBs 28, 52, 101 with concentrations $> 0.5 \mu\text{g kg}^{-1}$, and CBs 153, 138, 180 with concentrations $> 1 \mu\text{g kg}^{-1}$ (8 observations, see Table 7.1.1.5). CBs 138, 153 and 180 are again well correlated, and the correlations between CB52 and the other congeners are much stronger than those in Table 7.1.1.4. Missing data prevented the calculation of some correlation coefficients.

A factor analysis was carried out on these data, omitting the data on normalizing variables. The first two factors account for 98.8% of the variance. The first factor appears to be a "contamination level" factor, whilst the second is related to the behaviour of the compounds. The congeners appear arranged in order (right to left) of increasing chlorination, decreasing solubility, and increasing octanol/water partition coefficients (Figure 7.1.1.1 (b)). CB52 no longer appears as an "outlier", but is within the continuum of the other congeners. There is, therefore, a detectable influence of the physico-chemical properties of individual CB congeners on their distribution in sediment.

Table 7.1.1.4 Matrix of covariance for all data on CB concentrations in sediment.

CB28	1								
CB52	0.84	1							
CB101	0.75	0.17	1						
CB138	0.78	0.16	0.96	1					
CB153	0.66	0.14	0.94	0.96	1				
CB180	0.53	0.59	0.86	0.90	0.97	1			
Org. C	0.36	0.09	0.34	0.39	0.33	0.24	1		
Fines	0.60	-0.10	0.61	0.63	0.63	0.44	0.46	1	
Al	0.57	0.16	0.59	0.62	0.70	0.56	0.83	0.56	1
	CB28	CB52	CB101	CB138	CB153	CB180	Org. C	Fines	Al

Table 7.1.1.5 Matrix of covariance for samples contaminated with CBs (CBs 28, 52, 101 with concentrations $>0.5 \mu\text{g kg}^{-1}$, and CBs 153, 138, 180 with concentrations $>1 \mu\text{g kg}^{-1}$).

CB28	1								
CB52	0.83	1							
CB101	0.61	0.56	1						
CB138	0.63	0.67	0.94	1					
CB153	0.35	0.51	0.89	0.91	1				
CB180	-0.06	0.30	0.70	0.75	0.94	1			
Org. C	0.54	-0.02	0.18	0.20	0.24	-0.24	1		
Fines	0.85	-0.25	0.78	0.87	0.84	0.72	0.35	1	
Al	-0.69	0.92	-0.28	-0.76	x	x	x	x	1
	CB28	CB52	CB101	CB138	CB153	CB180	Org. C	Fines	Al

E) Compensation for Organic Carbon Variations

As discussed in Section 4.2.2, above, the data on CB concentrations were compensated for organic carbon variations (in samples with organic carbon levels greater than 0.3%). The correlation with organic carbon is not particularly good, with notably high values being found in the estuaries of the Elbe, Ems, and Scheldt. The ratios of CBs 153 and 52 to organic carbon are presented in Figures 7.1.1.4 and 7.1.1.5, respectively, to represent the range of the selected CBs.

The compensation procedure resulted in elimination of data from several areas, further reducing the geographical coverage of the data. The remaining data are very limited, although higher CB to organic carbon ratios

occur in data from some estuaries than in data from some other parts of the North Sea. It is not possible to reliably interpret the information available to provide assessments of the distribution of CBs in the North Sea or the relative contamination levels of different areas, nor to identify "hot spots".

F) Discussion

In general, the data on CBs are difficult to assess, partially due to limitations on the quality of the data (e.g., data for CB52, and a lack of complete data on four other mandatory congeners). Many of the data assessed were from offshore areas (see Figure 7.1.1.6), where concentrations fell near the detection limits of the methods used.

It has been reported that the distribution of CBs depends on physico-chemical properties such as hydrophilicity and relative persistence. Some indication of this was seen in the factor analyses. Recent information suggests that areas close to sources may be recognized by high concentrations of all CBs and/or relatively high contributions from less persistent compounds such as CBs 28, 52, 101 (and 138). CBs 153 and 180 are rather more persistent, and would be predicted to dominate in areas distant from inputs. The present data set did not show such differences between samples of high and low concentrations.

7.1.2 Hexachlorobenzene

The time and expertise available to the Assessment Group permitted only limited discussion of the data on hexachlorobenzene (HCB), an NSTF mandatory determinand (see Tables 7.1.2.1 and 7.1.2.2). Two particularly high values from Norway were omitted from the regression analyses, which are shown for the ratio of HCB/TOC against TOC in Figure 7.1.2.1 and for HCB against total TOC and TOC $\geq 0.3\%$ in Figures 7.1.2.2 and 7.1.2.3, respectively. The same conclusions can be drawn as for CBs. The geographical distribution of the sampling stations does not allow a complete North Sea assessment. However, as shown in the distribution of HCB concentrations in Figure 7.1.2.4, it can be stated that some estuaries and fjords exhibit high values, and that the concentrations in the Skagerrak are higher than those in the northern North Sea. Figure 7.1.2.5 shows the distribution of HCB/TOC ratios for sediments with TOC concentrations $\geq 0.3\%$.

Table 7.1.2.1 Number of samples for which data were submitted for HCB in sediment.

Analytical Laboratory	Extraction Method Code	HCB
		N
ALUK	EXC	17
BFGG	EXC	5
BLUK	EXC	32
IHEB	EXP	26
IMRN	EXP	143
ISHG	EXN	28
LWKG	EXO	9
SERI	EXP	9
ALL	EXC	54
	EXN	28
	EXO	9
	EXP	178

Table 7.1.2.2 Number of samples used in the assessment of HCB concentrations.

Analytical Laboratory	Extraction Method Code	HCB
		N
ALUK	EXC	14
BFGG	EXC	3
IHEB	EXP	11
IMRN	EXP	139
ISHG	EXN	27
LWKG	EXO	9
SERI	EXP	9
ALL	EXC	17
	EXN	27
	EXO	9
	EXP	159

7.2 Distributions of NSTF Voluntary Organic Contaminants

7.2.1 Polycyclic aromatic hydrocarbons

A) Data

Data on polycyclic aromatic hydrocarbons (PAHs) were submitted from six countries (Table 7.2.1.1). They covered 29 compounds or groups of compounds, as listed in Table 7.2.1.2 (see Table 3.3.2 for the full names of the compounds associated with the codes). Data from BFGG were rejected because the method used did not provide adequate separation of PAHs. The number of observations used in the assessment is given in Table 7.2.1.3, and the sampling locations are shown in Figure 7.2.1.1.

B) Investigation of Patterns of Different PAH Compounds

In an attempt to simplify the data, factor analysis was used to determine whether PAH compounds would group on different factors; for example, compounds from combustion sources might group together, and compounds from oil sources group separately. Possible explanatory factors such as organic carbon, aluminium and fraction of fines ($< 63 \mu\text{m}$) were also included in the factor analyses, provided that sufficient data were available.

(i) Data on the fine sediment fraction ($< 63 \mu\text{m}$)

Factor analyses of the data for fine sediment yielded two factors explaining more than 1% of the variance each. The first factor explained 88% of the variance, and all thirteen PAH compounds considered loaded highly on it.

Table 7.2.1.1 Overview of number of data submitted.

Laboratory	Country	Number of variables	Total sediment	Fines
ALUK	UK	13*	X	
DGWN	Netherlands	13*		X
BFGG	Germany	3	X	
ECCB	Belgium	14*	X	
IHEB	Belgium	7*	X	
SERI	Sweden	13	X	
IMRN	Norway	23	X	

* Borneff series of PAHs included.

Table 7.2.1.2 Number of samples for which data were submitted on PAH concentrations.

Analytical Laboratory	Extraction Method Code	Variables																
		ANT	BAA	BAP	BBF	BBKF	BEP	BGH-IP	BKF	CHR	CHR-TR	DBT	DBT-C1	DBT-C2	DBT-C3	FLE	FLU	ICDP
ALUK	EXC	6	6	6	6		6	6	6		6						6	6
BFGG	EXC																5	
ECCB	EXC	7	7	7	7			7	7	7							7	7
IHEB	EXC			7	7			7	7								7	7
IMRN	EXP	145	145	145		145	145	145		145		145	145	144	144	144	145	145
SERI	EXC	9	9	9	9			9	9	9							9	9
ALL	EXC	22	22	29	29		6	29	29	16	6						34	29
	EXP	145	145	145		145	245	145		145		145	145	144	144	144	145	145

Table 7.2.1.2 (continued)

Analytical Laboratory	Extraction Method Code	Variables												
		NA-P	NAP-C1	NAP-C2	NAP-C3	NAC-L8	PA	PAC1	PAC2	PER	PYR	SPA-H	SPA-H5	
ALUK	EXC						6			6	6			
BFGG	EXC					5							5	
ECCB	EXC	7					7				7			
IHEB	EXC													
IMRN	EXP	144	144	144	144		145	145	145	145	145	145		
SERI	EXC	9					9				9	9		
ALL	EXC	16				5	22			6	22	9	5	
	EXP	144	144	144	144		145	145	145	145	145	145		

Organic carbon loaded separately on the other factor, which explained 7% of the variance.

This information was confirmed by the correlation matrix; all PAH compounds correlated very well with each other, but none correlated with organic carbon. One should bear in mind that the small number of data analysed (n=19) were derived from only one laboratory.

(ii) Data on total sediment (<2 mm)

Factor analyses (n=92) yielded two factors explaining more than 1% of the variance each. The first factor explained 81% of the variance, and the second 11%. Organic carbon and all but three PAHs (BGHIP, DBAHA, ICDP) loaded highly on the first factor. BGHIP, DBAHA and ICDP and organic carbon loaded highly on the second factor.

Table 7.2.1.3 Number of samples used in the assessment of PAH concentrations.

Analytical Laboratory	Extraction Method Code	Variables			
		BAP	NAP	NAP-C1	PA
		N	N	N	N
ALUK	EXC	2			1
ECCB	EXC	4	4		6
IHEB	EXC	7			
IMRN	EXP	138	107	132	134
SERI	EXC	9			9
ALL	EXC	22	4		16
	EXP	138	107	132	134

This information was partly confirmed by the results of the correlation matrix. All PAHs, except the three mentioned above, correlated very well with each other. All PAHs, including DBAHA and ICDP, correlated well with organic carbon content, but BGHIP did not.

Results were mainly produced by one laboratory (Table 7.2.1.3) and, therefore, the results of the factor analyses might reflect analytical features, rather than any fundamental environmental factors or processes.

C) Regression of Some PAH Compounds and Organic Carbon

Organic carbon has been considered an important co-factor in concentrations of organic contaminants in sediment. To investigate the possibility of compensating the concentrations of PAHs using organic carbon content, a regression analysis was undertaken. As the results of the correlation table and factor analyses had already shown that PAH compounds in the fine sediment do not correlate at all with organic carbon, this regression was only done for data on total sediment. The compounds chosen were: benzo[a]pyrene (BAP), a high molecular weight PAH mainly produced by combustion; phenanthrene (PA) and naphthalene (NAP) of lower molecular weight and arising from combustion and oil sources; and mono-alkyl naphthalenes (NAPC1) as representative of oil sources. Regressions were carried out for values of organic carbon higher than and lower than 0.3%. The results of the regression analyses are presented in Annex 7 and in Figures 7.2.1.2 to 7.2.1.4 for benzo[a]pyrene, Figures 7.2.1.7 to 7.2.1.9 for phenanthrene, Figures 7.2.1.12 to 7.2.1.14 for naphthalene, and Figures 7.2.1.17 to 7.2.1.19 for mono-alkyl naphthalenes.

D) Discussion of the Distribution Plots

Locations sampled for PAHs are shown in Figure 7.2.1.1. In samples with organic carbon concentrations larger than 0.3%, organic carbon was used to normalize the concentrations of the PAH compounds by calculating the ratio of the PAH compound to the organic carbon content. The distribution of the sampling stations for BAP does not cover the North Sea well (Figure 7.2.1.5). Information on the Southern Bight, the English Channel, and the British, Dutch and Danish coasts is missing. High concentrations were found in the western Scheldt, the fjords, and the Skagerrak. When the data are normalized, the distribution (shown in Figure 7.2.1.6) does not appear significantly different for the Skagerrak and the Norwegian coast, but ratios are somewhat more pronounced in the open sea, especially in the area around 55.5°N and 0°E, near the Dogger Bank.

The distributions for PA (Figures 7.2.1.10 and 7.2.1.11), NAP (Figures 7.2.1.15 and 7.2.1.16) and NAPC1 (Figures 7.2.1.20 and 7.2.1.21) concentrations and their normalized values are similar to those for BAP.

The distribution of the sampling stations does not allow a complete North Sea assessment for polycyclic aromatic hydrocarbons. Since normalizing with organic carbon is not considered appropriate for very low organic carbon concentrations, this would not allow normalization of data on organic compounds for most of the southern part of the North Sea. For a reliable assessment, it is necessary to have a much more complete distribution of data throughout the North Sea area. Partitioning of the data at 0.3% organic carbon is particularly limiting, and other compensation/normalization procedures should be considered for PAHs.

7.2.2 Other organic compounds

Annex 8 gives an overview of all other organic compounds for which data were submitted. The number of observations is given, along with the number of observa-

tions containing information on the organic carbon content. For a selected series of contaminants, the analytical laboratories are listed in Table 7.2.2.1 together with the number of values below and above the detection limit, and the minimum and maximum concentrations.

Table 7.2.2.1 Number of observations submitted for DDEPP, DDTPP, DIELD, HCB, HCHA and HCHG below and above the detection limit and the minimum and maximum concentrations, for each laboratory. Concentrations are given in g g^{-1} in scientific notation, with the number after the letter E indicating the exponent (power of 10). For example, 1.4 E-11 is $1.4 \times 10^{-11} \text{ g g}^{-1}$ (14 ng kg^{-1}).

		ALUK	BFGG	BLUK	ICNF	IHEB	IMRN	LWKG	ISHG	SERI
DDEPP	< d.l.	3	5	-	3	19	2		4	-
	> d.l.	14	-	-	-	7	141		24	9
	min	1.4E-11				1E-10	1E-11		1E-10	3.2E-10
	max	8.6E-10				3E-10	2.9E-9		8E-10	8.4E-10
DDTPP	< d.l.	7	5	-	3	23	9		6	
	> d.l.	10	-	-	-	3	134		22	
	min	5.5E-12				1E-10	1E-10		1E-10	
	max	1.5E-10				2E-10	9.5E-9		11.8E-9	
DIELD	< d.l.	3		29	3	21	21			9
	> d.l.	14		3	-	4	105			-
	min	8.5E-12		2E-9		1E-10	1E-11			
	max	3.1E-10		8.8E-9		5E-10	2.7E-10			
HCB	< d.l.	3	2	32		15	4	-	1	9
	> d.l.	14	3	-		11	139	9	27	9
	min	8.4E-12	1E-9			1E-10	1E-11	1E-11	2E-10	6.1E-11
	max	2.0E-10	3E-9			3E-10	6.4E-8	1.7E-10	4E-9	2.8E-10
HCHA	< d.l.	9	5		3	19	23	-	11	2
	> d.l.	-	-		-	13	120	3	17	7
	min					1E-10	1E-10	3E-11	1E-10	1.4E-10
	max					5E-10	2.2E-10	5E-11	6E-10	3.8E-10
HCHG	< d.l.	3	-		3	10	49	-	-	1
	> d.l.	14	5		-	22	93	9	28	8
	min	1.4E-11	1E-9			1E-10	1E-11	5.1E-10	1E-10	6.4E-11
	max	3.0E-10	2E-9			6.8E-9	2.9E-10	1.5E-9	1.5E-9	1.5E-10

8 CONCLUSIONS

The main conclusions of this assessment are listed below, with reference to the corresponding sections in the text.

Data Available for Assessment (Section 2)

The data set available to the Assessment Group was large, but the density of sampling points varied greatly in terms of both areas and contaminants.

Quality Assurance (Section 3)

Using several sources of information, it was possible to construct quantitative criteria for the acceptance or rejection of data on metals in whole sediments. Of those laboratories using methods designed to determine total concentrations, most reported acceptable quality assurance information.

The lack of consistent use of certified reference materials, or participation in intercomparison exercises using whole sediment samples, greatly limited the possibility to conduct a quality control assessment of the data on organic contaminants.

Some laboratories used methods with unacceptably high detection limits for metals or organic contaminants.

Data Handling Procedures (Section 4)

In order to prepare a coherent document in the time available, standard procedures for data analyses and presentations were defined, which were supplemented by conducting additional work on particular contaminants as was found necessary.

The lack of consistent reporting of data on normalizing/compensating variables limited both the scope of the interpretive techniques that could be used and the value of the data on contaminant concentrations.

Data Interpretation (Sections 5, 6, and 7)

After review of the data submitted, application of quality control and other checking criteria to them, and employment of normalization procedures and statistical analyses, the overall findings of the ultimate scientific assessment of these data can be summarized as follows:

- a) Aluminium-normalized metal concentrations in whole sediments are generally higher in the coastal areas than in the central North Sea.
- b) The highest aluminium-normalized concentrations of metals occur in areas close to industrial sources (for example, the Norwegian fjords, the Elbe,

Scheldt, Seine, Humber, Tyne and Tees) and in areas near zones of mineralized rocks (Norway, Helgoland, southwest England, and northeast England).

- c) The Norwegian Trench and the Skagerrak have high metal concentrations in sediment compared to the central North Sea.
- d) The northern edge of the Dogger Bank has relatively high aluminium-normalized concentrations of cadmium and chromium in sediment.
- e) It is difficult to draw firm conclusions concerning the distribution of organic contaminants (CBs, HCB and PAHs) due to the limited amount of data remaining after the exclusion of unsatisfactory data and data that were not accompanied by organic carbon measurements.
- f) The contaminant data submitted by several laboratories lacked quality assurance (QA) data; the QA data submitted by other laboratories did not meet the criteria adopted for the inclusion of results in the assessment. Contaminant data from these laboratories were, therefore, rejected.
- g) The sediments of the German Bight contain relatively high concentrations of mercury, cadmium and zinc compared to those in the central North Sea. These higher concentrations are not restricted to accumulation areas but also occur in more dispersive sandy zones.
- h) Relatively high concentrations of mercury occur in the fines off the northeast coast of England.
- i) Relatively high concentrations of lead occur in the fines near the northeast coast of England, in the central North Sea, and in the German Bight.
- j) Copper and nickel in the fine sediment fraction are fairly evenly distributed throughout the North Sea.

9 RECOMMENDATIONS

The following recommendations were made:

- 1) Laboratories should use analytical techniques that are in accord with the requirements of the programme (e.g., capable of the determination of total concentrations).
- 2) Laboratories should select methods with sufficiently low detection limits to provide quantitative data for most samples.

- 3) More Certified Reference Materials (CRMs) should urgently be prepared for organic contaminants in sediment.
- 4) Data on contaminants not accompanied by data on supporting normalizing variables are of very limited value, and participating laboratories should therefore ensure that supporting data are reported.
- 5) Consideration should be given to quality assurance procedures for measurements of normalizing variables, particularly grain size measurements.
- 6) Future programme designs should include the recommendation of appropriate reference materials. An appropriate authority, such as the ICES Marine Chemistry Working Group or the EC Measurement and Testing Programme, should consider the possibility of the certification of reference materials with chemical characteristics similar to those of North Sea sediments.
- 7) CRM data must be submitted to the coordinating data centre by all participating laboratories.
- 8) The CRM data submitted should preferably have been obtained at the same time as the analyses of the field samples were carried out.
- 9) All data should be submitted to the coordinating data centre on time and in the correct format.
- 10) Future programme designs should include clearer definition of the variables to be measured, particularly normalizing variables, and of the number of replicate samples or sub-samples to be analysed for each station.
- 11) Assessment groups should include scientists with experience concerning all contaminants considered, particularly organic contaminants.
- 12) In defining the objectives of new programmes, the organizers should consider the relative importance of areas of sediment accumulation and dispersive areas (the latter predominate in the North Sea).
- 13) The method of interpretation of data to be produced in any future programme should be considered during the design of the programme, to allow identification of the required variables.
- 14) The assessment of data on contaminants in sediments to be made by the OSPARCOM working group in December 1992 should build upon the experience of the SEDMON Group. There should

be a significant element of common membership. A small sub-group should meet at ICES Headquarters prior to the main assessment meeting to prepare summaries of the data, identify particular difficulties, and undertake initial data manipulations.

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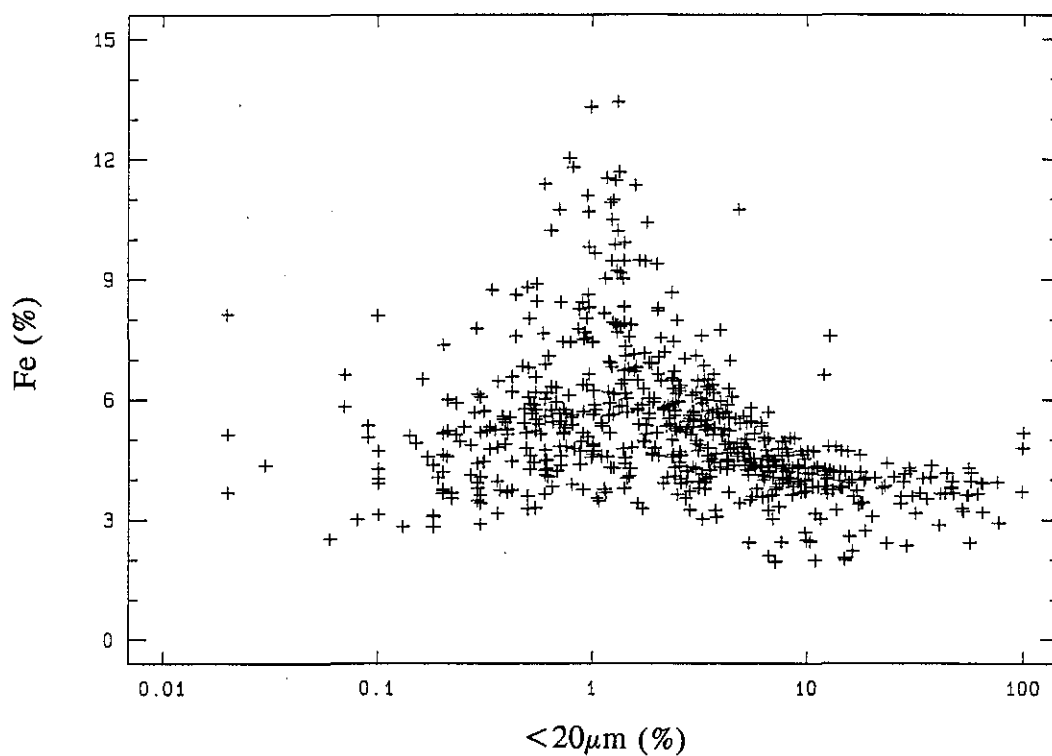


Figure 4.2.1 Fe vs proportion fines <20 μm.

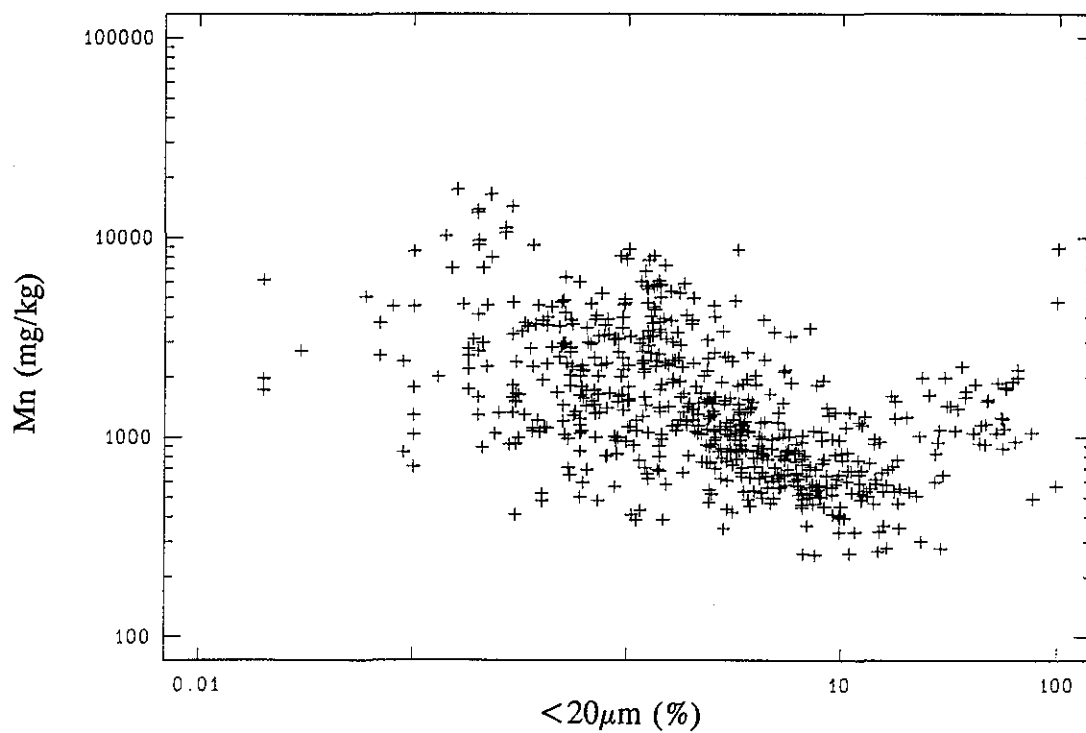


Figure 4.2.2 Mn vs proportion fines <20 μm.

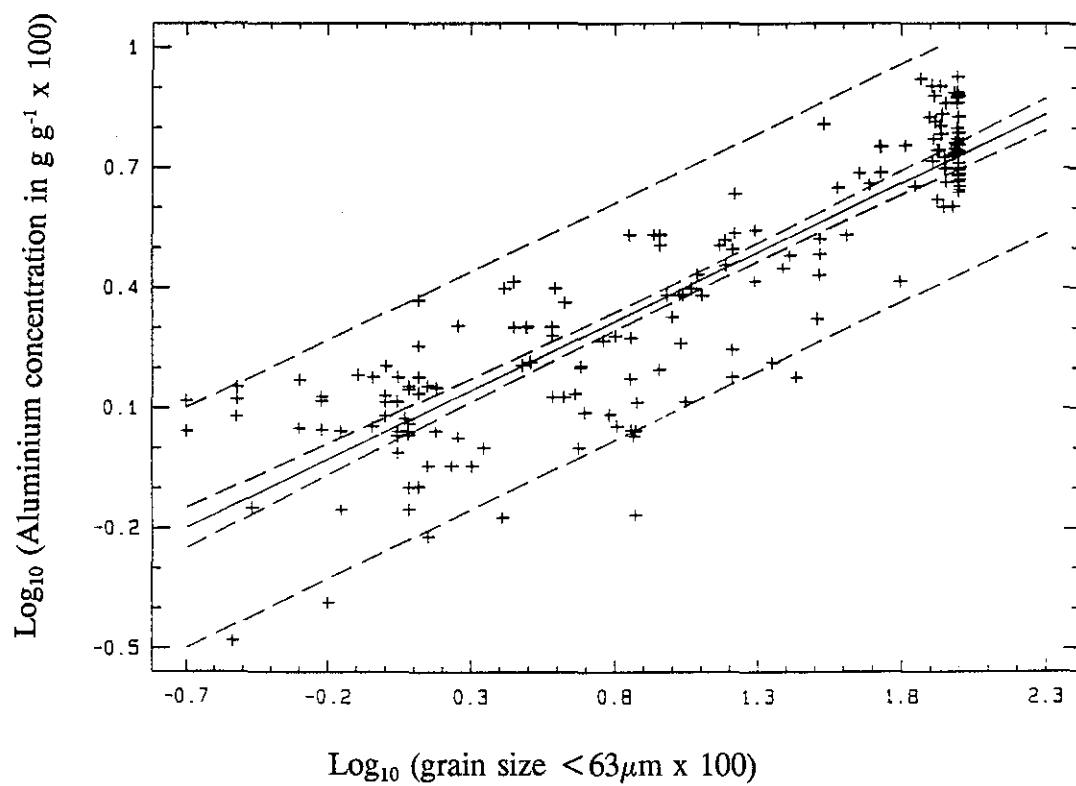


Figure 4.2.3 Regression of log Al vs. log fines $< 63 \mu\text{m}$.

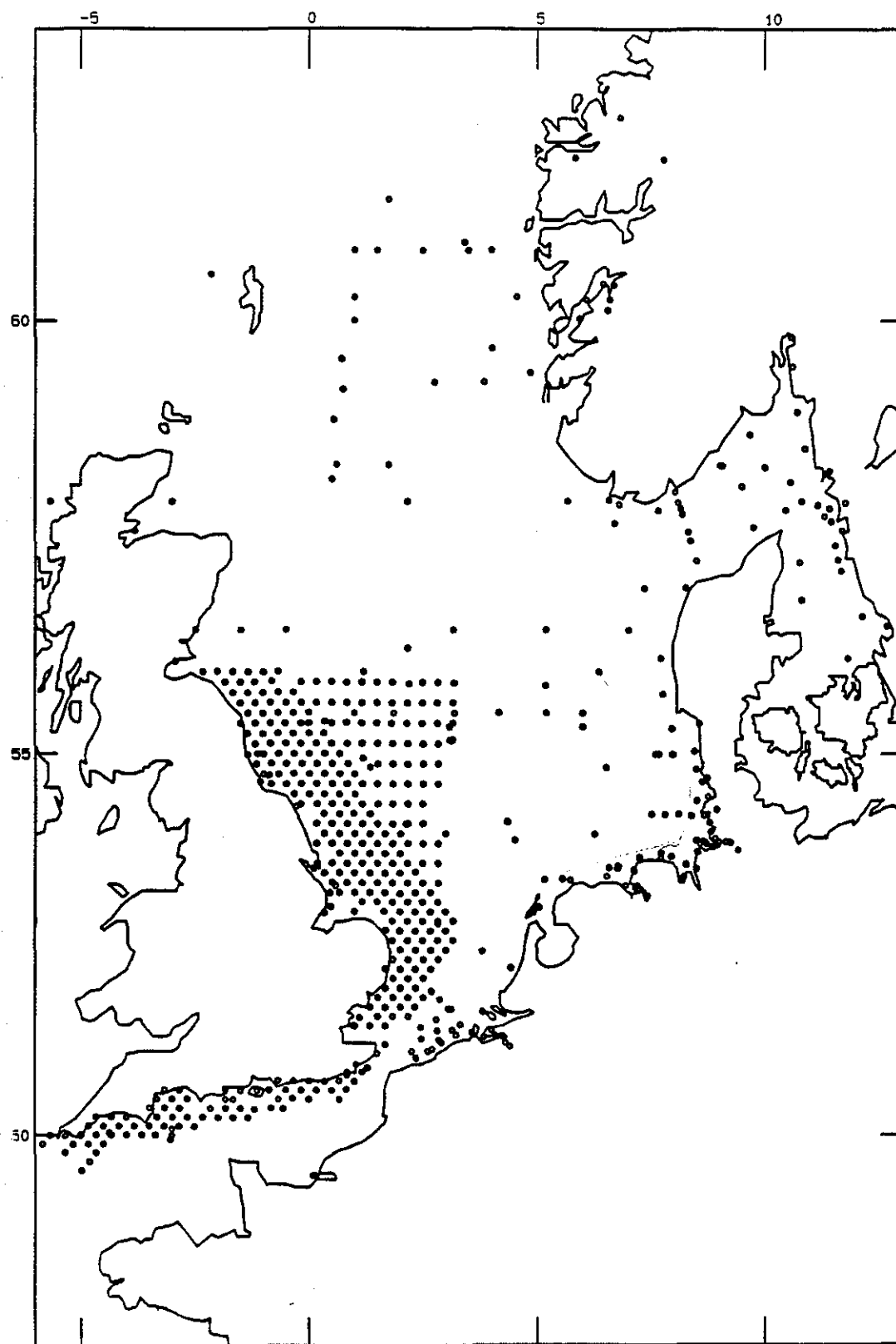


Figure 5.1.1 Map of sampling locations for the determination of metals in the Baseline Study of Contaminants in North Sea Sediments.

North Sea Task Force Stations

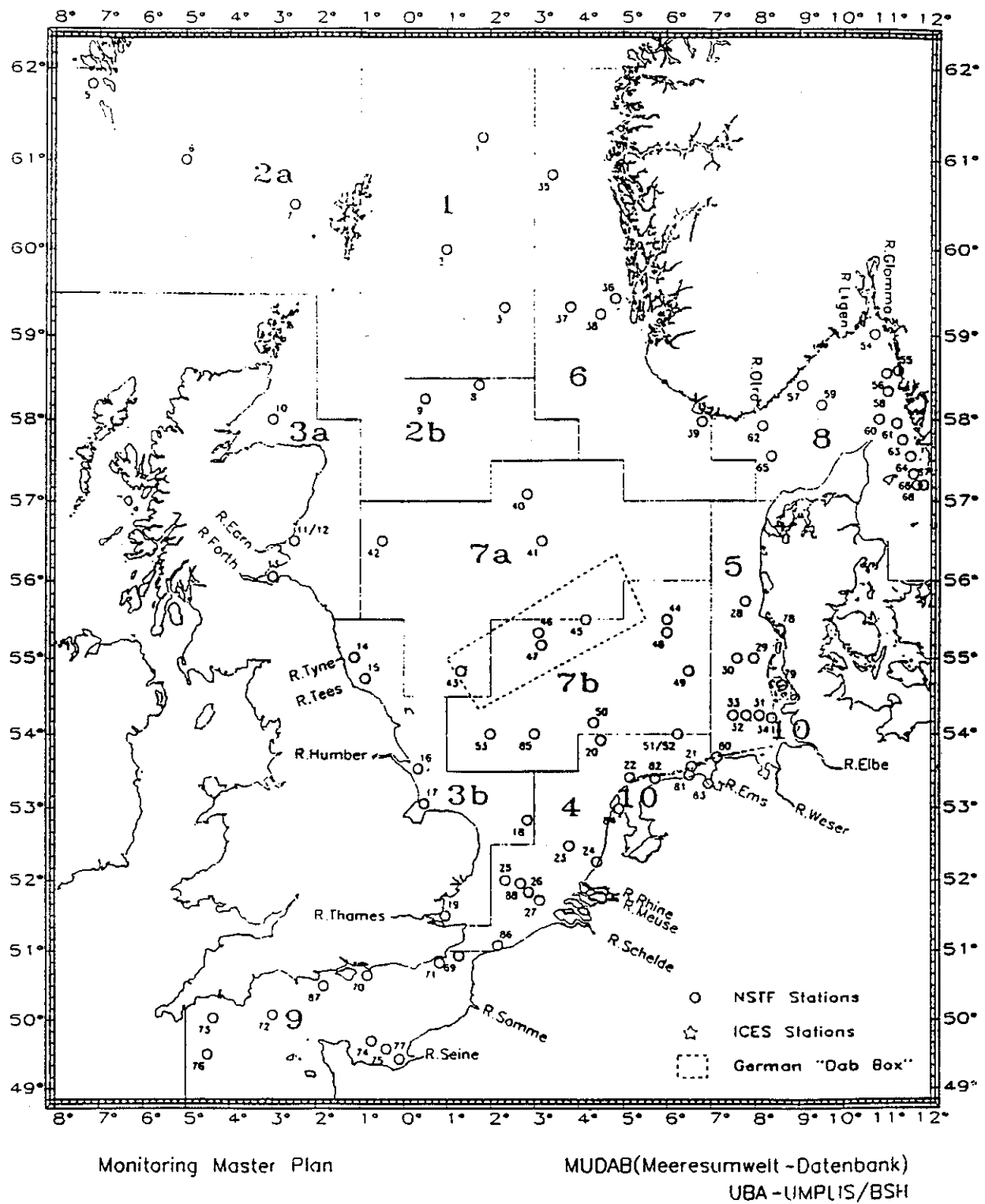


Figure 5.2.1 Map showing NSTF sub-regions and monitoring stations under the Monitoring Master Plan (1990-1991).

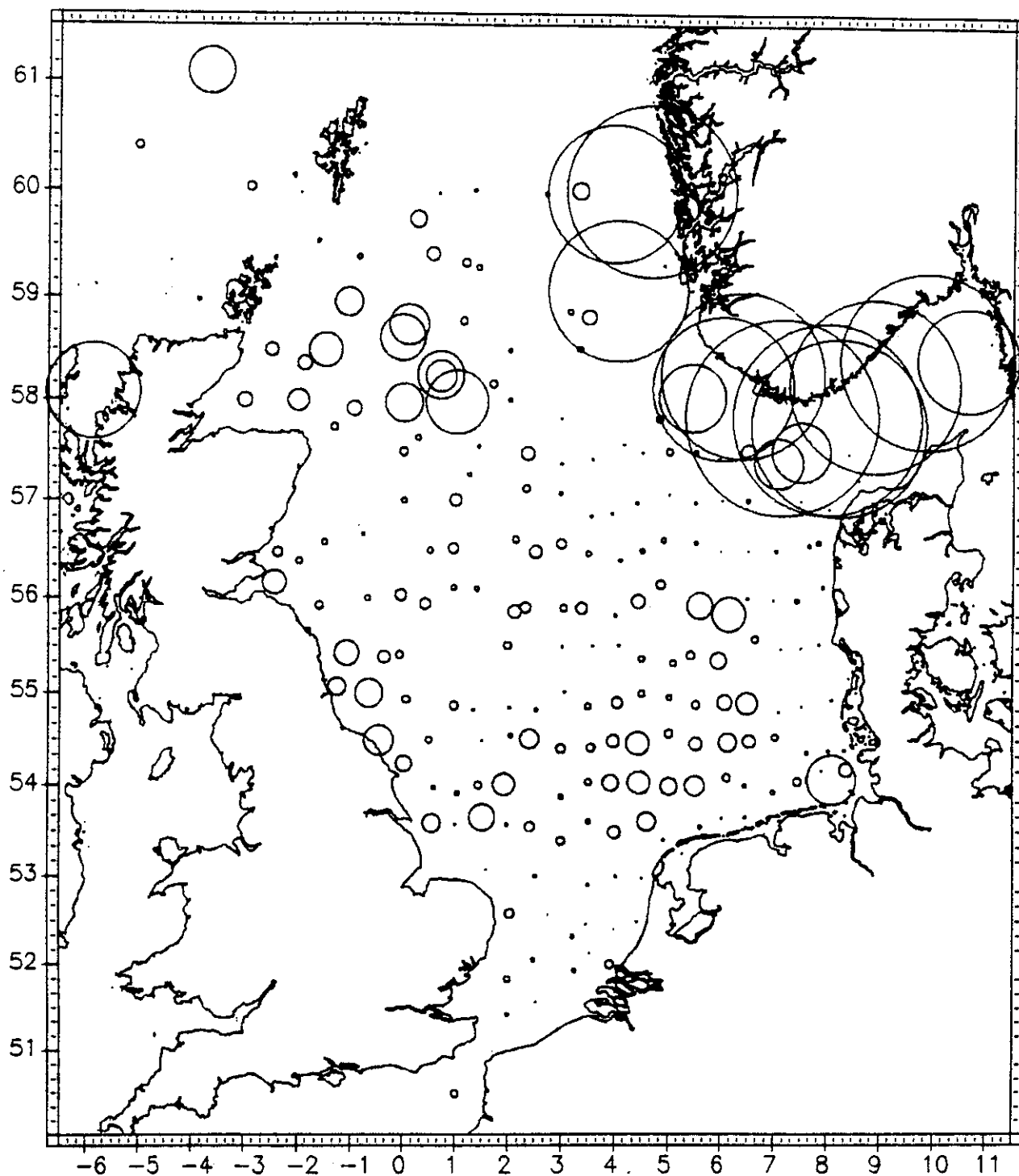


Figure 5.3.1.1 The distribution of mud (grain size <63 μm) in North Sea sediments (circle diameter is proportional to mud content).

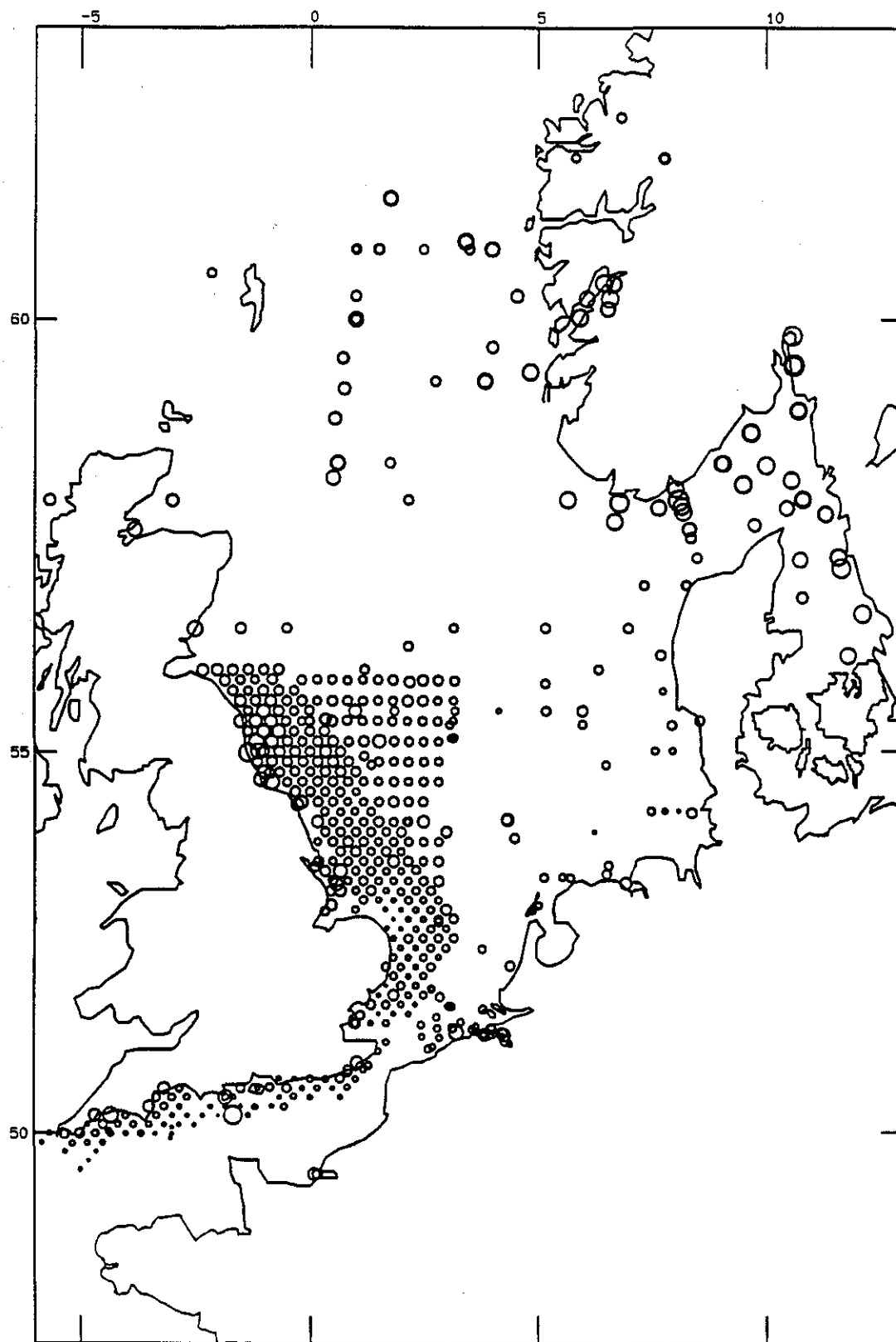


Figure 5.3.2.1 The distribution of aluminium concentrations in North Sea sediments $<2000 \mu\text{m}$ (circle area is proportional to Al concentration). The maximum concentration is 9.3%.

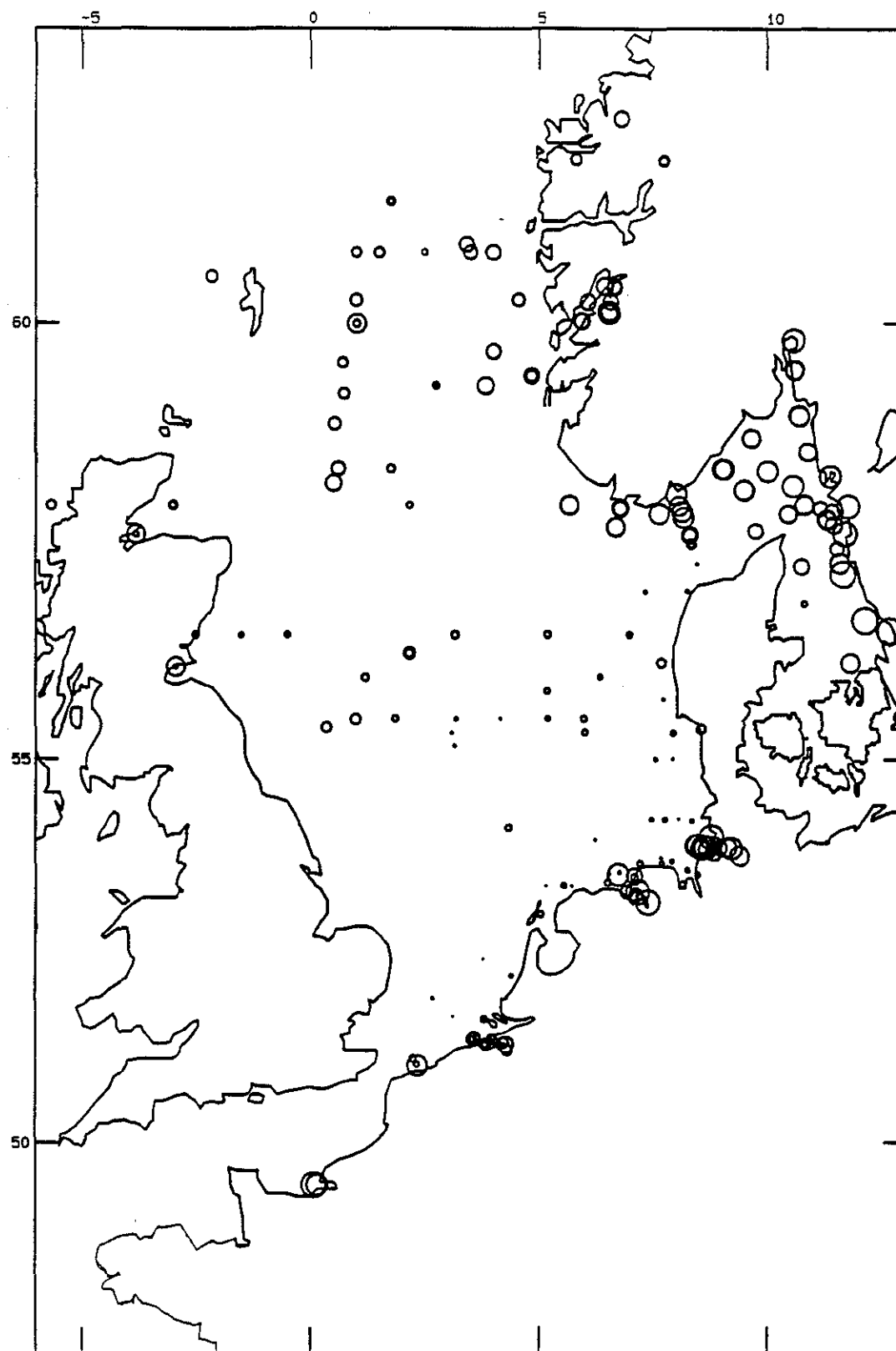


Figure 5.3.3.1 The distribution of total organic carbon (TOC) content in North Sea sediments $< 2000 \mu\text{m}$ (circle area proportional to TOC content).

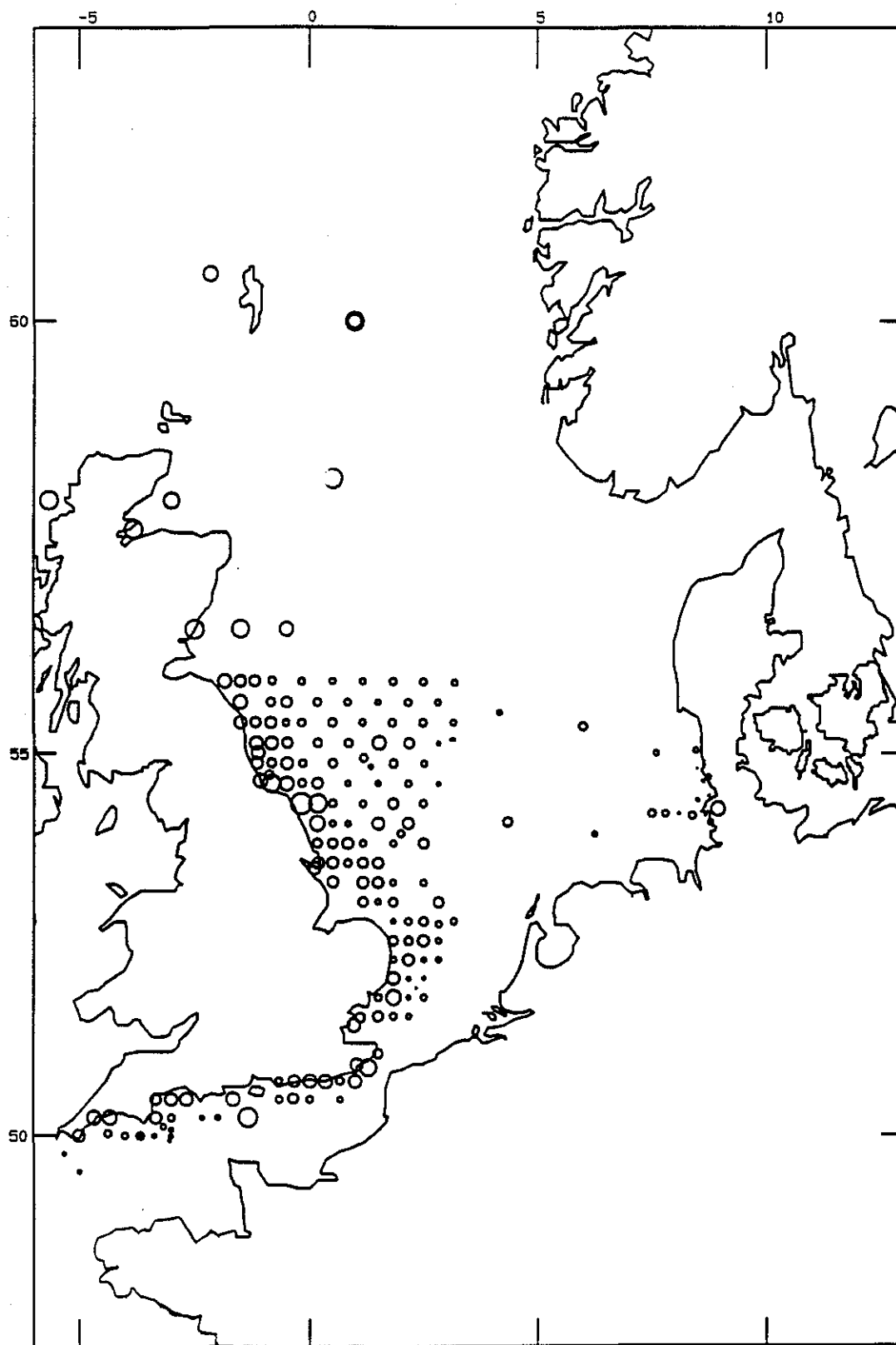


Figure 5.3.4.1 The distribution of iron concentrations in North Sea sediments $< 2000 \mu\text{m}$ (circle area is proportional to Fe concentration). The maximum concentration is 5.1 %.

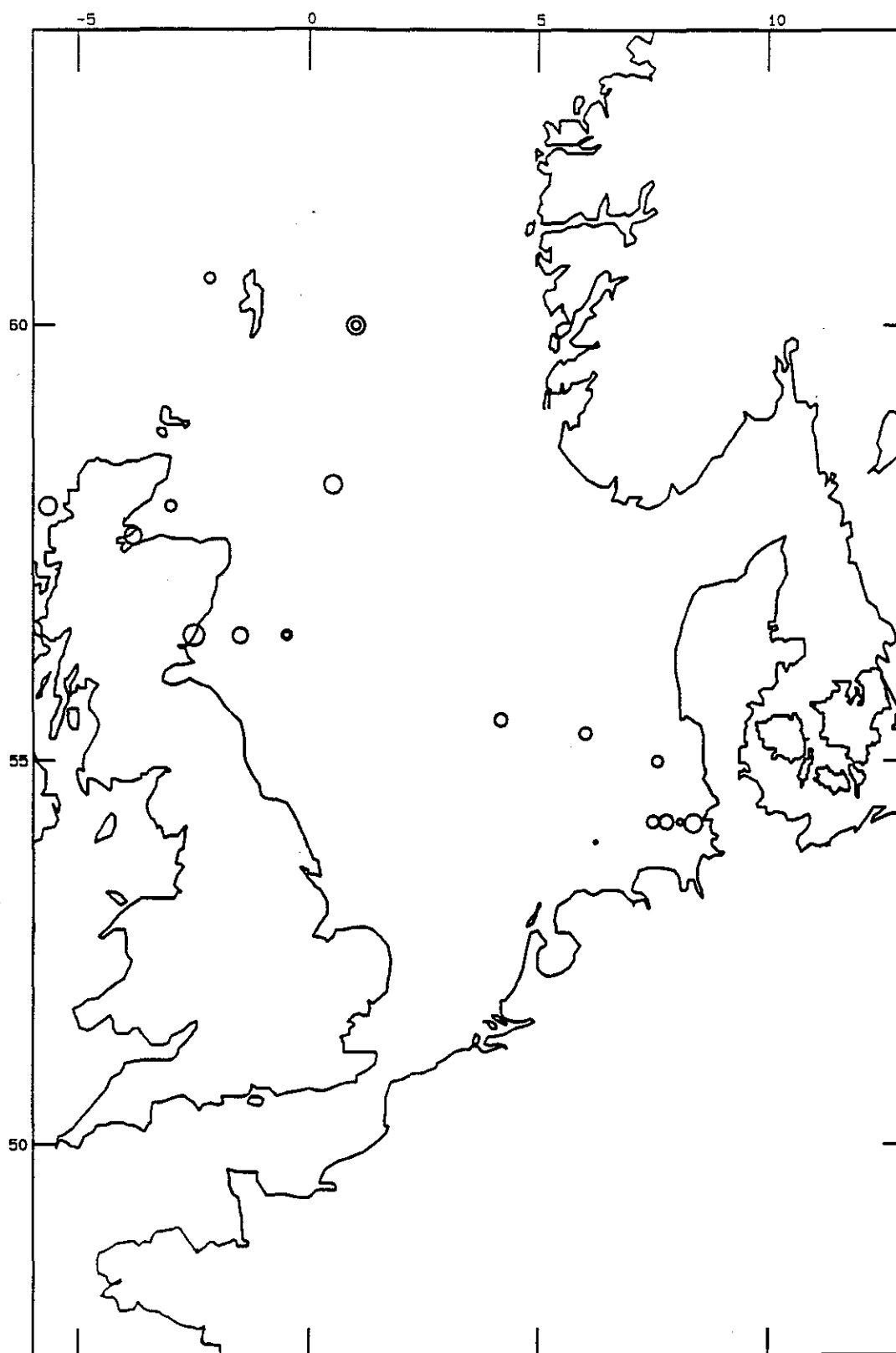


Figure 5.3.5.1 The distribution of manganese concentrations in North Sea sediments $< 2000 \mu\text{m}$ (circle area is proportional to Mn content). The maximum concentration is 332 mg kg^{-1} .

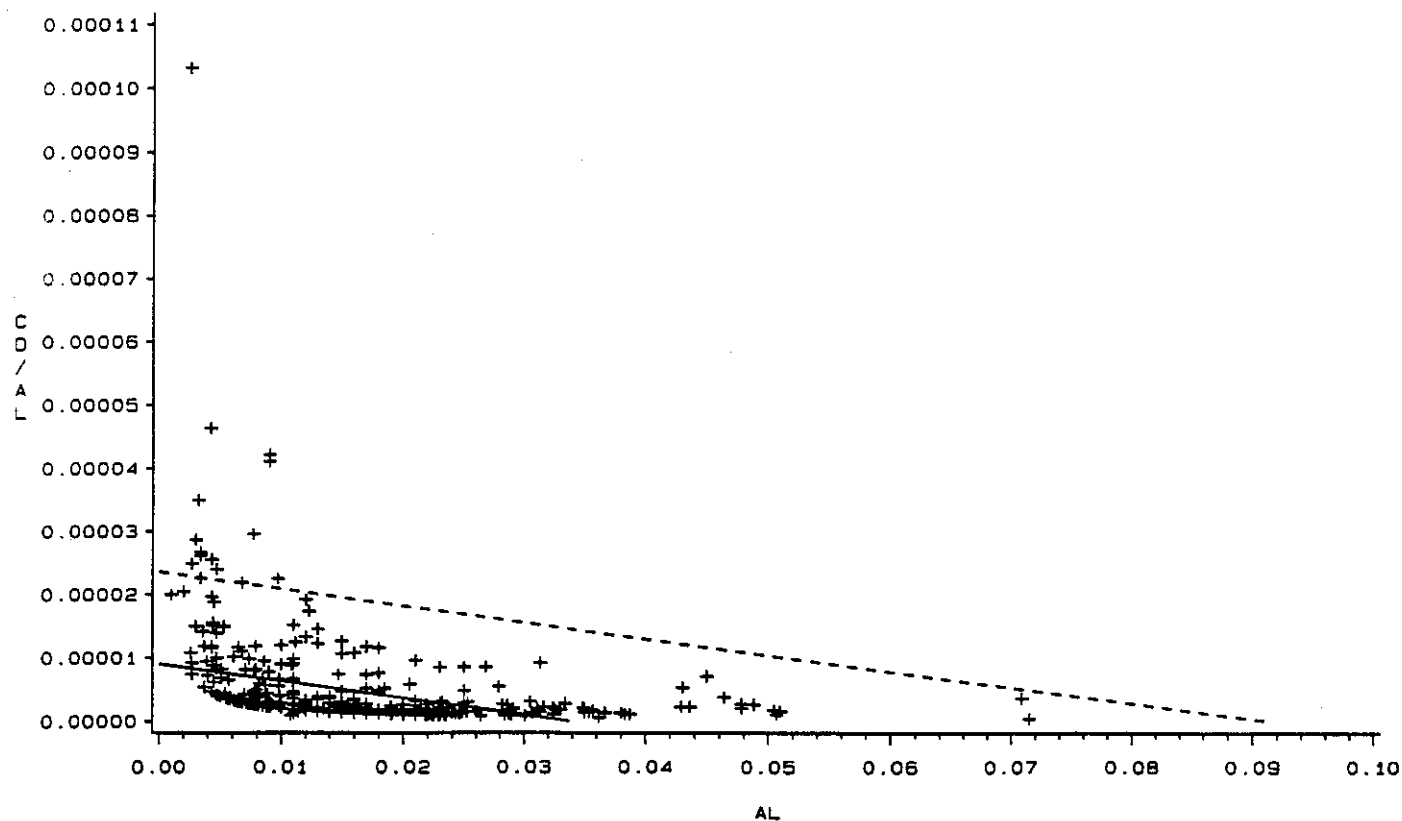


Figure 5.4.1.1 Regression of Cd/Al vs. Al (in g g^{-1}).

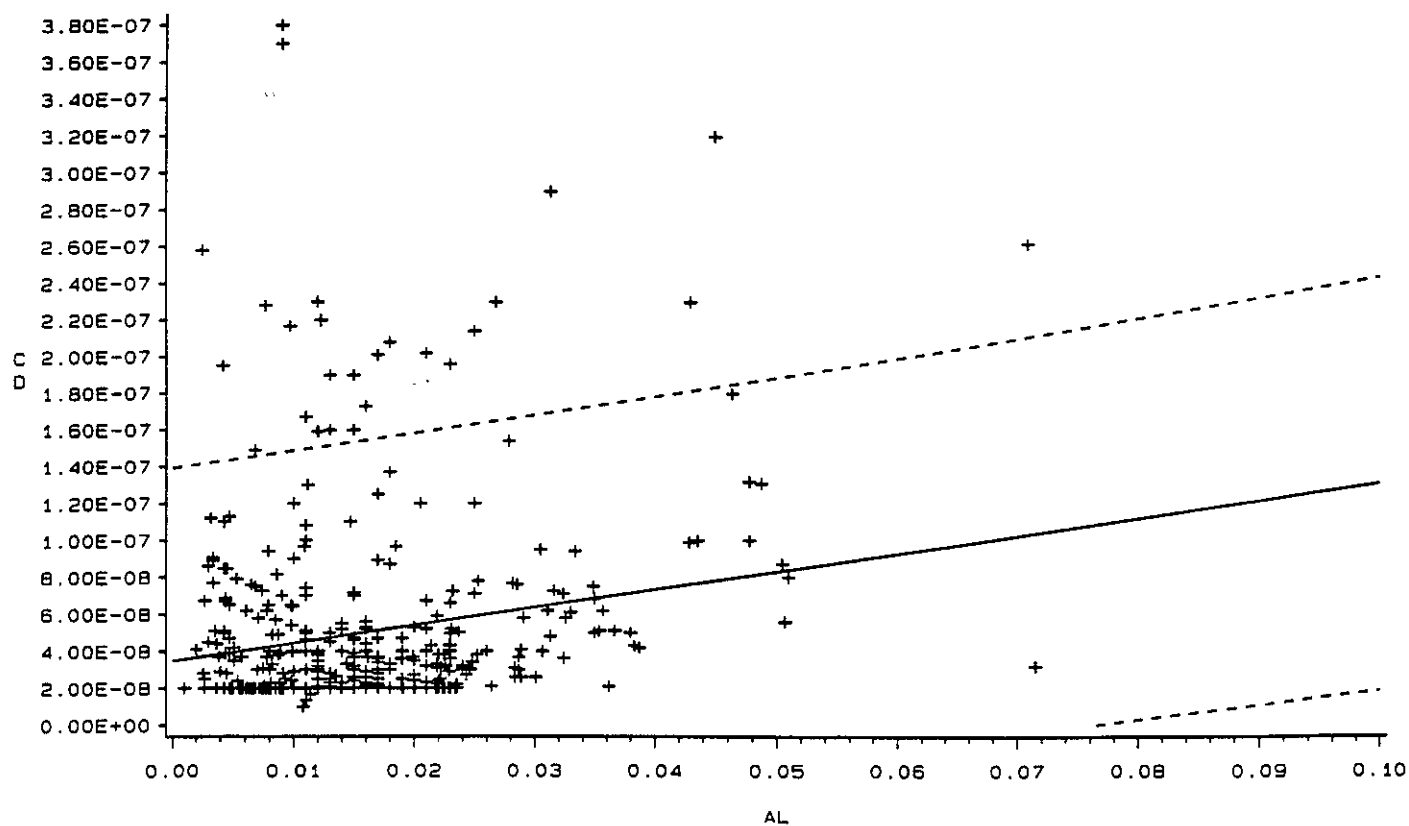


Figure 5.4.1.2 Regression of Cd vs. Al (both in g g^{-1}).

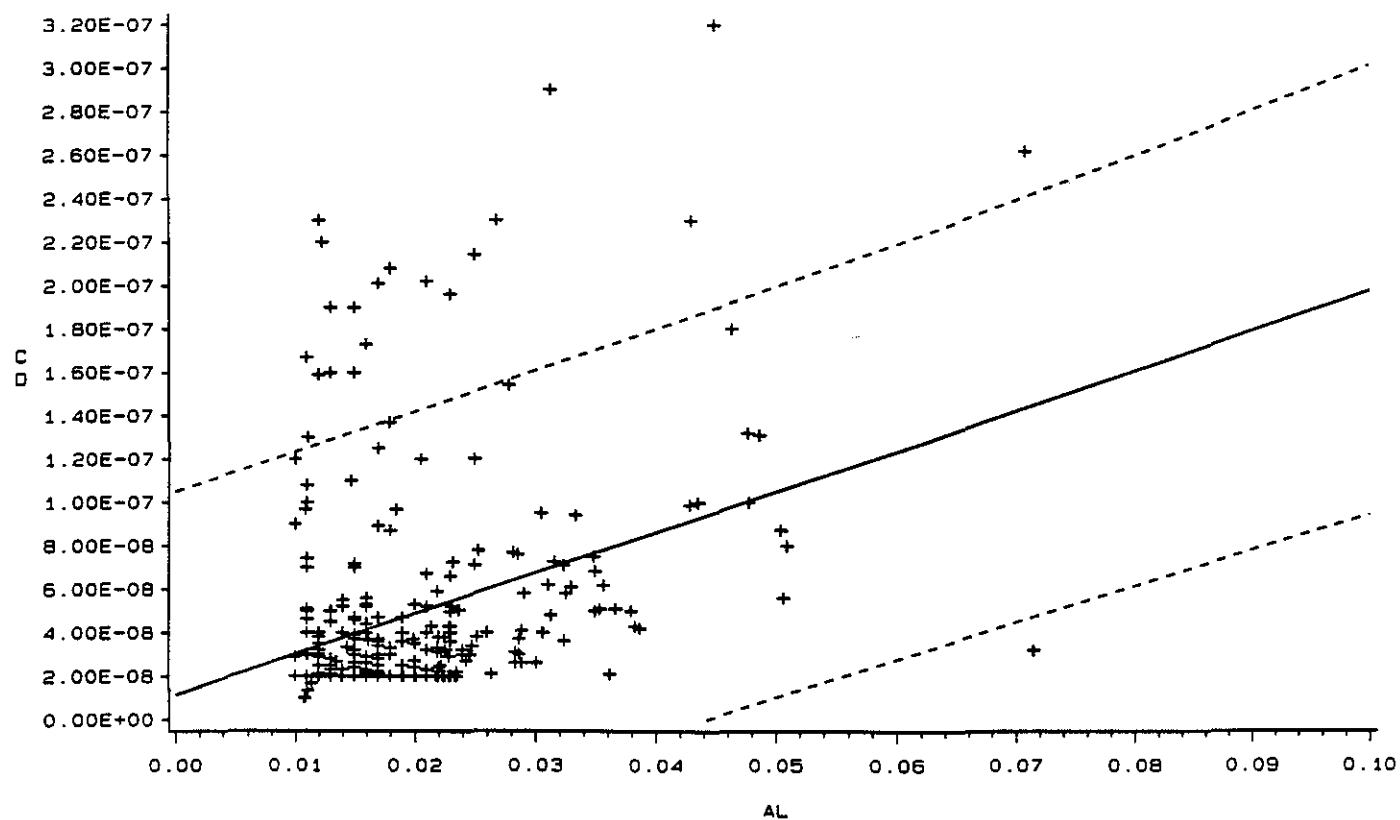


Figure 5.4.1.3 Regression of Cd vs. Al (both in g g^{-1}) for $\text{Al} \geq 1\%$.

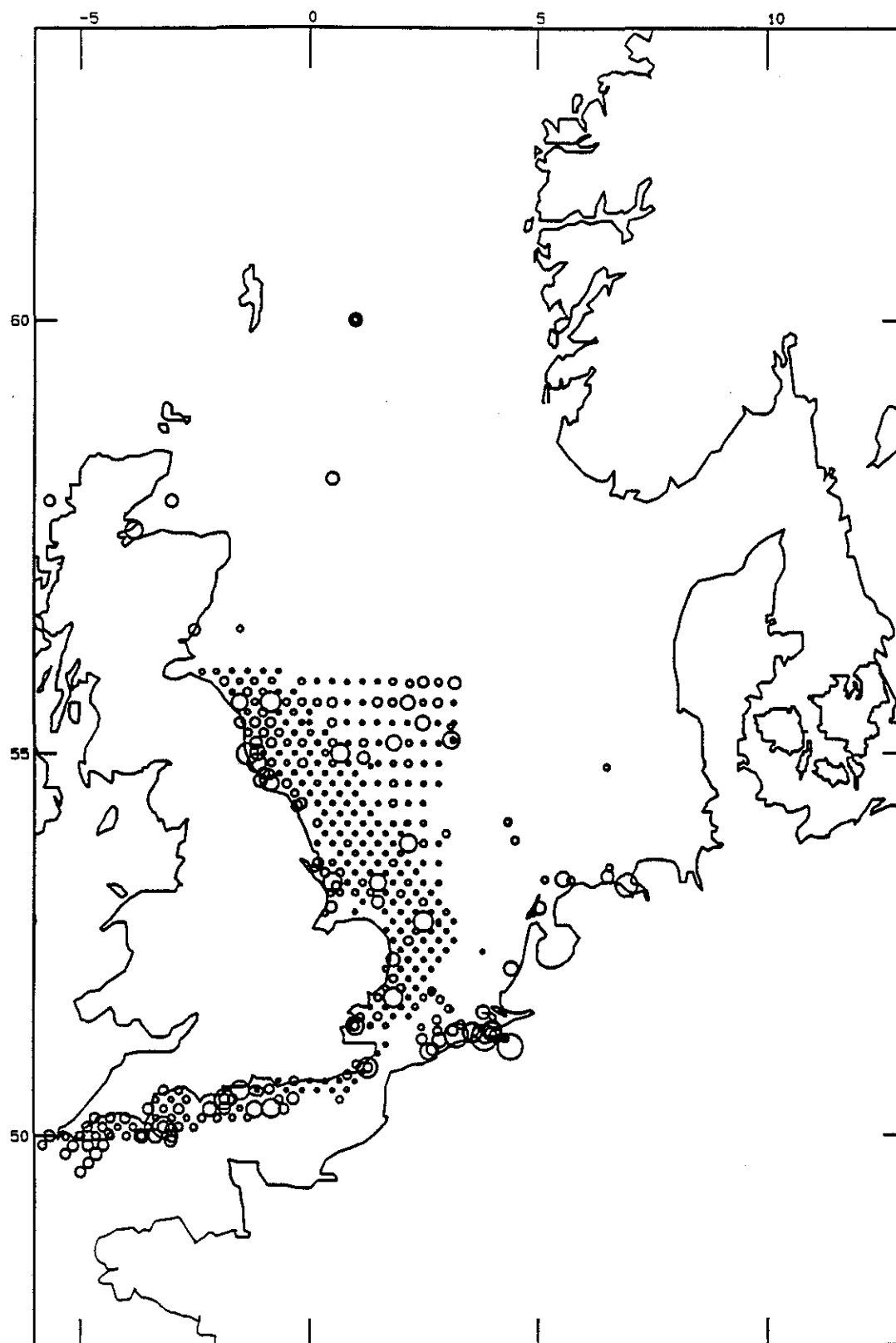


Figure 5.4.1.4 The distribution of cadmium concentrations in North Sea sediments $<2000 \mu\text{m}$ (circle area is proportional to value). The maximum concentration is $380 \mu\text{g kg}^{-1}$.

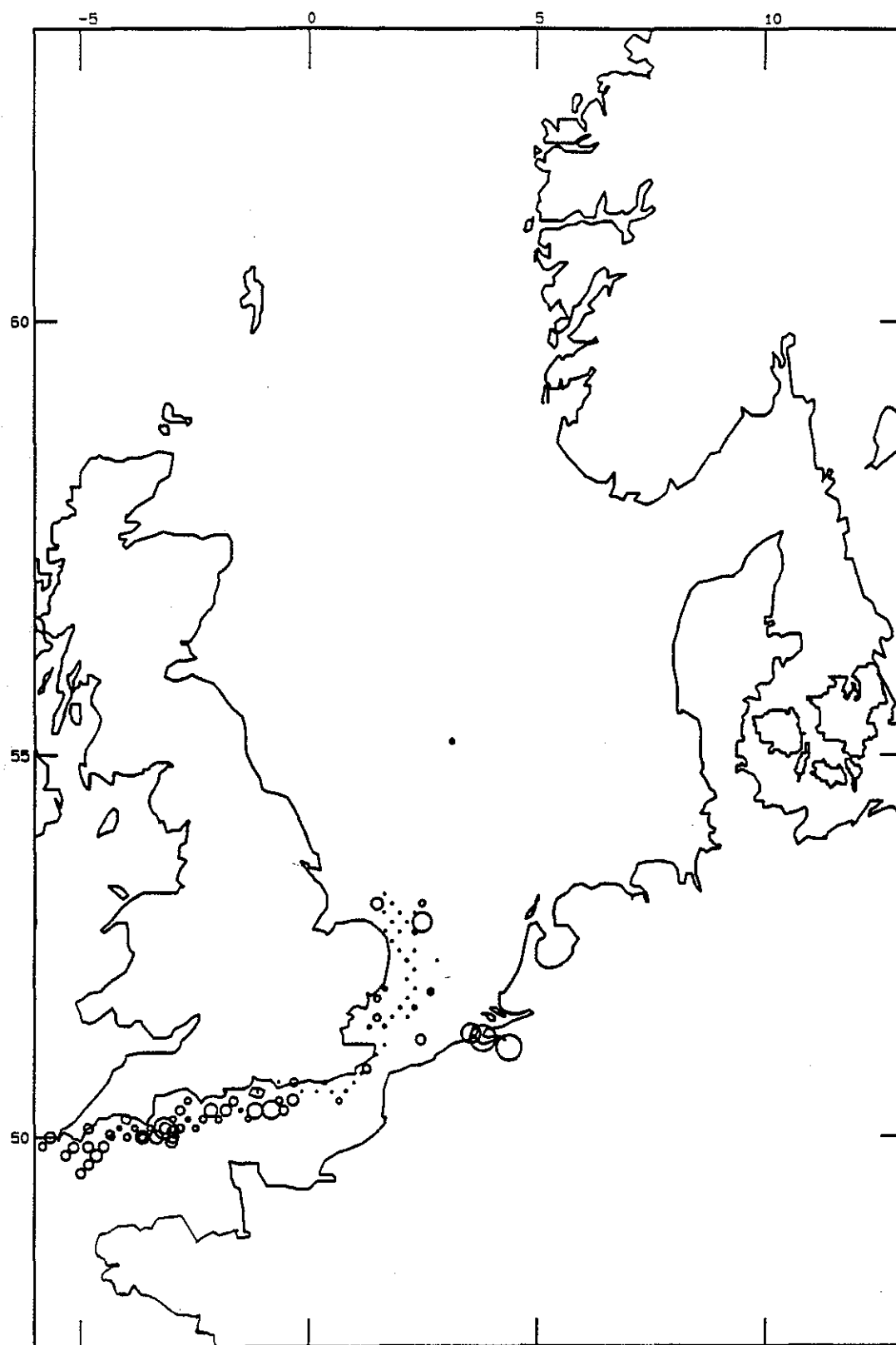


Figure 5.4.1.5 The distribution of cadmium concentrations in North Sea sediments $<2000\ \mu\text{m}$, with aluminium $<1\%$ (circle area is proportional to value). The maximum concentration is $380\ \mu\text{g kg}^{-1}$.

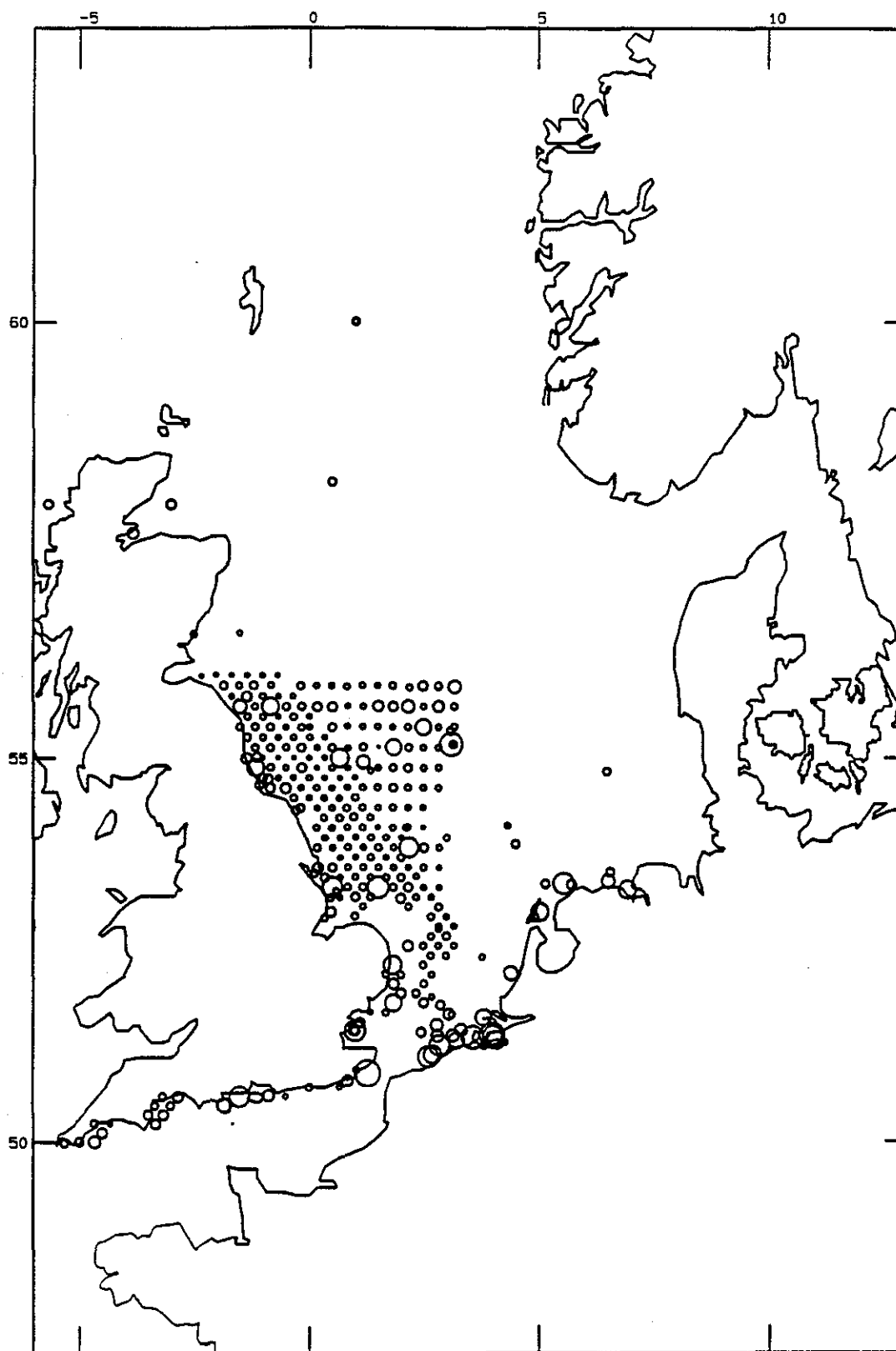


Figure 5.4.1.6 The distribution of cadmium/aluminium ratios in North Sea sediments $< 2000 \mu\text{m}$, with aluminium $\geq 1\%$ (circle area is proportional to value).

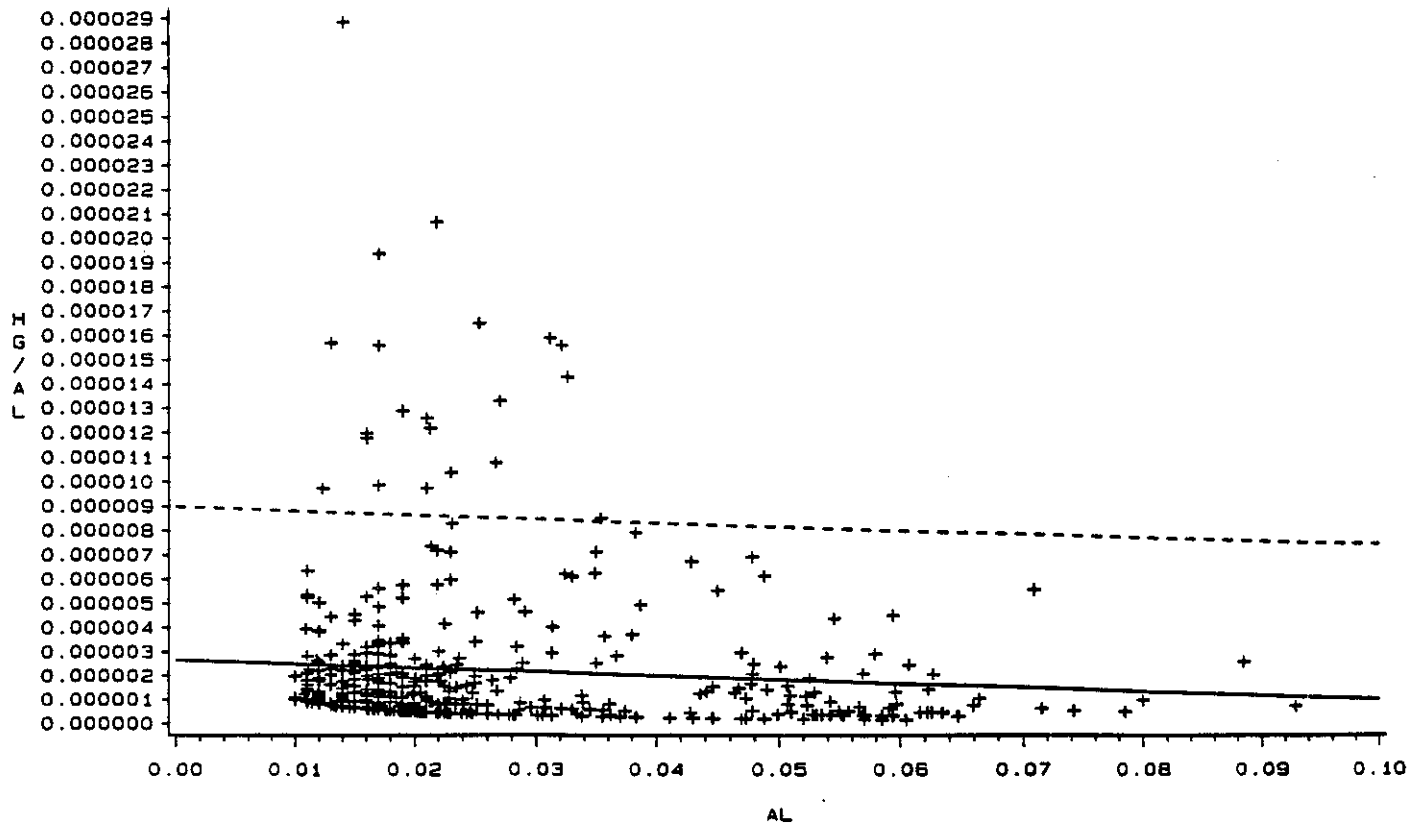


Figure 5.4.2.1 Regression of Hg/Al vs. Al (in g g^{-1}), for samples with Al $\geq 1\%$.

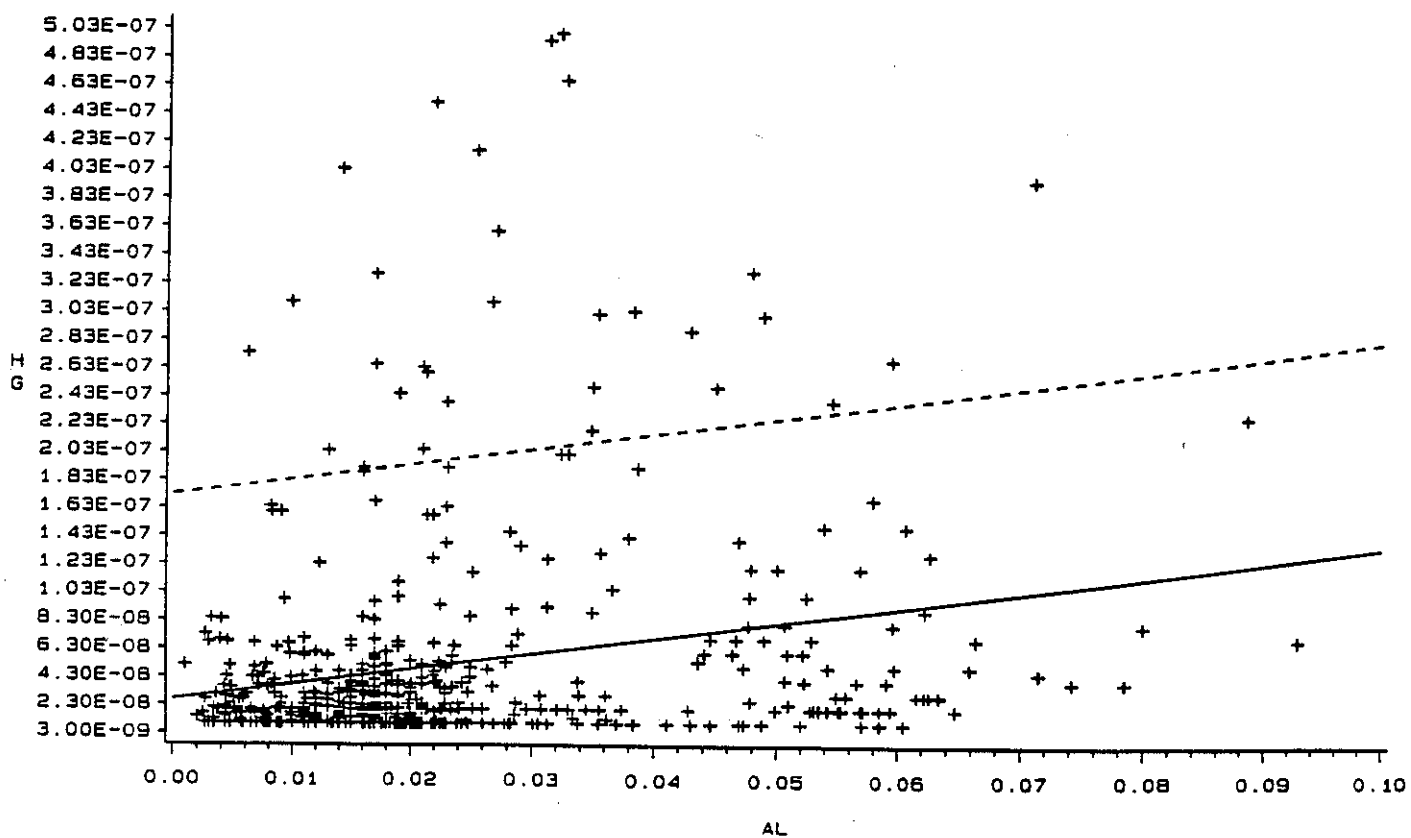


Figure 5.4.2.2 Regression of Hg vs. Al (both in g g^{-1}).

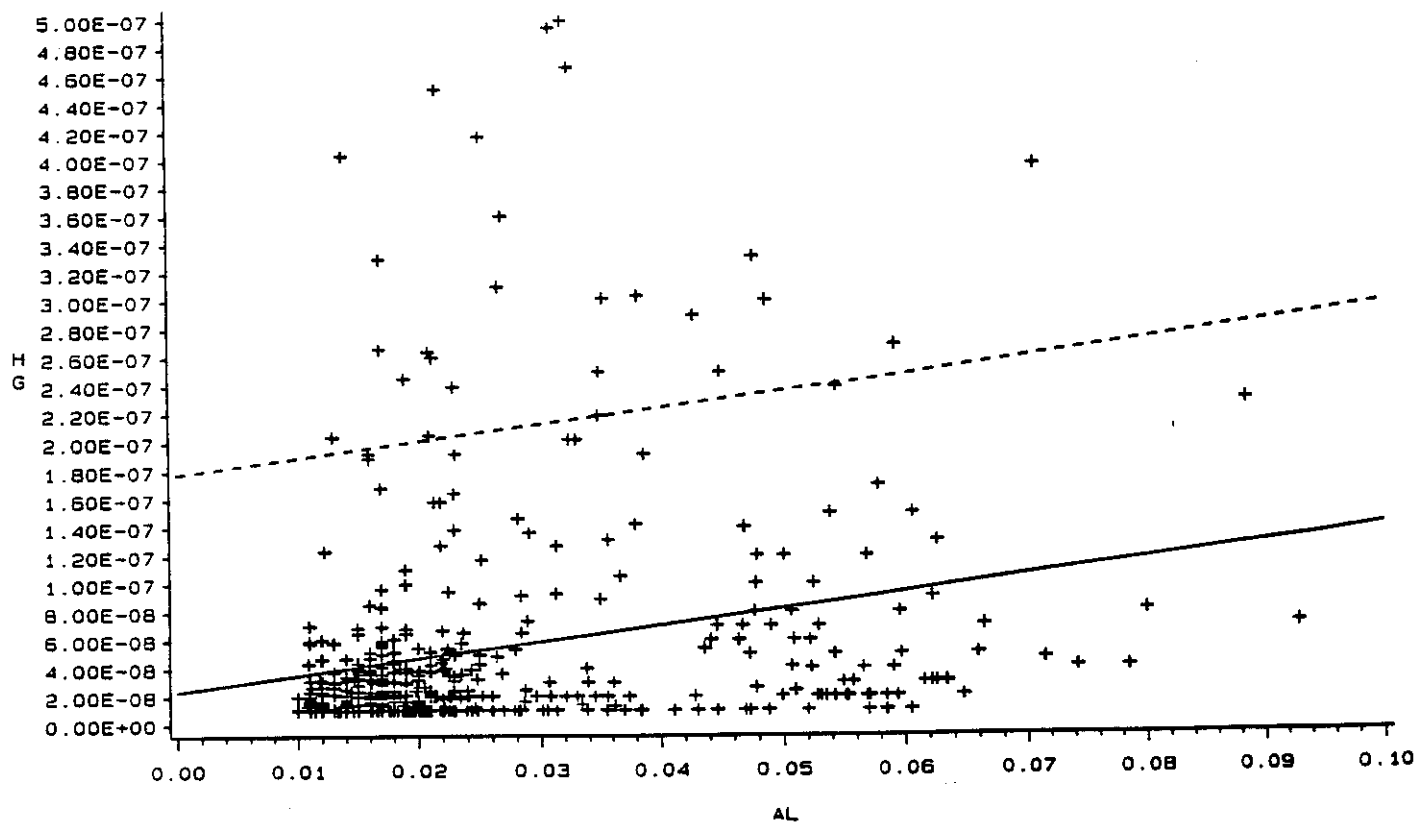


Figure 5.4.2.3 Regression of Hg vs. Al (both in g g^{-1}), for $\text{Al} \geq 1\%$.

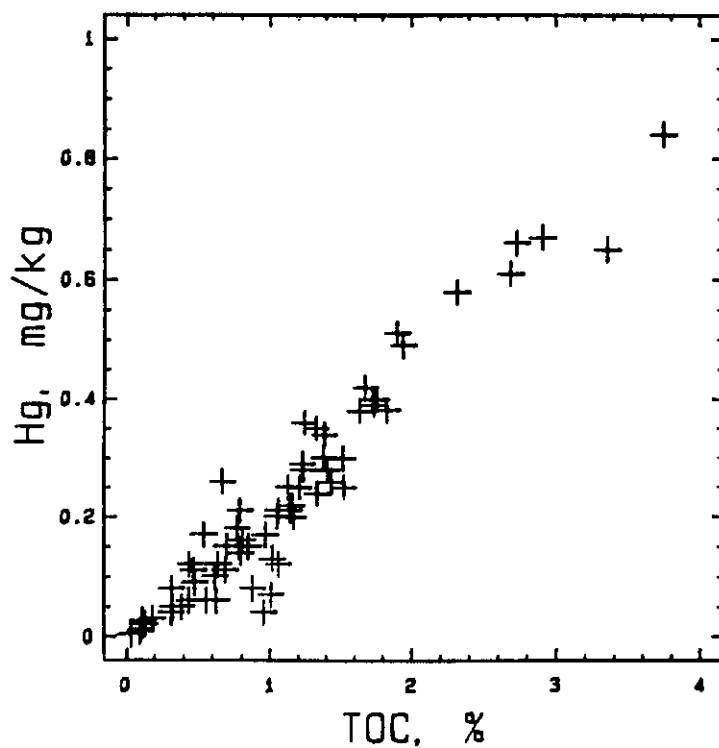


Figure 5.4.2.4 Hg vs. TOC in whole sediments of the German Bight.

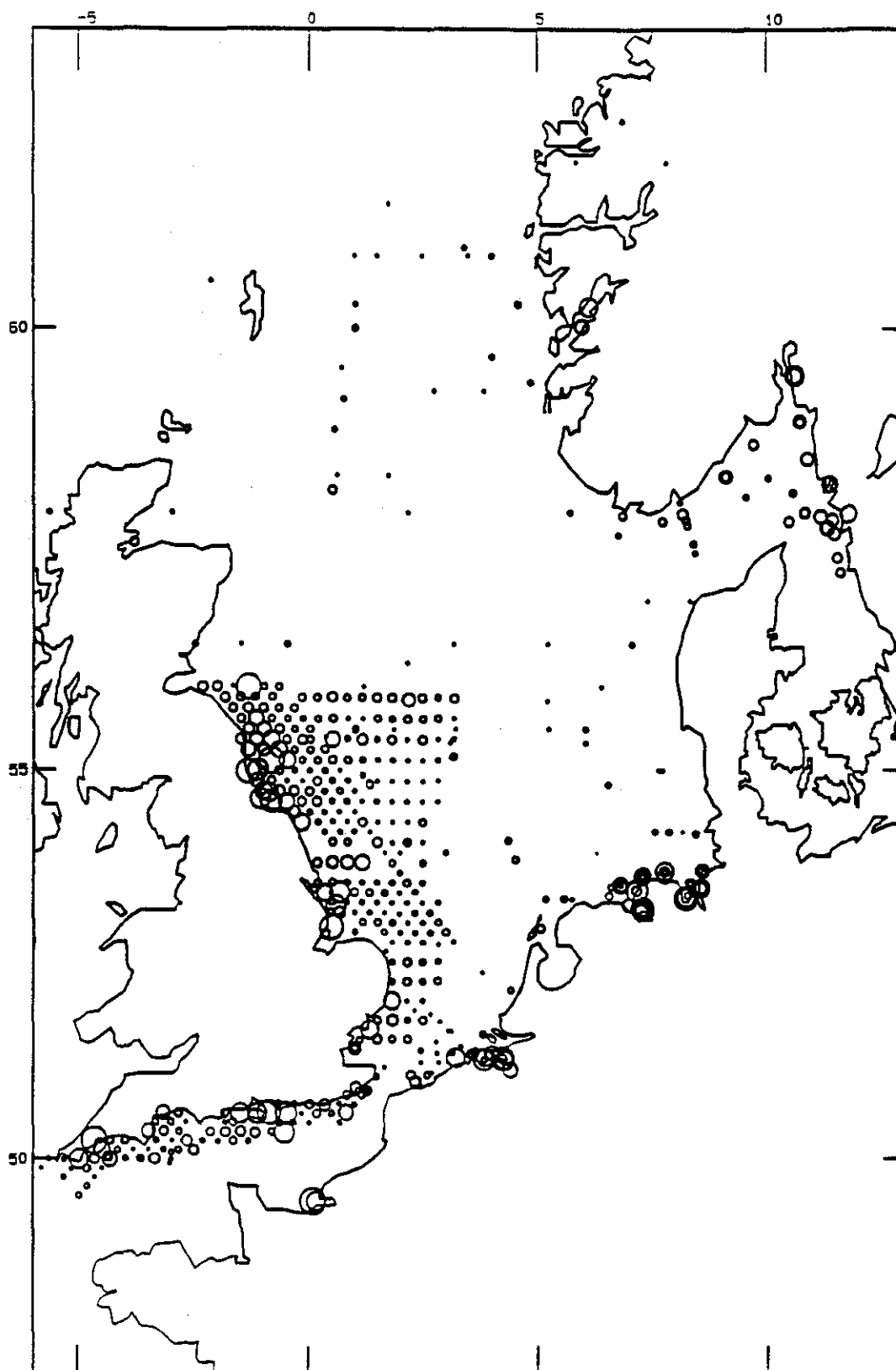


Figure 5.4.2.5 The distribution of mercury concentrations in North Sea sediments $<2000 \mu\text{m}$ (circle area is proportional to value). The maximum concentration is 0.5 mg kg^{-1} .

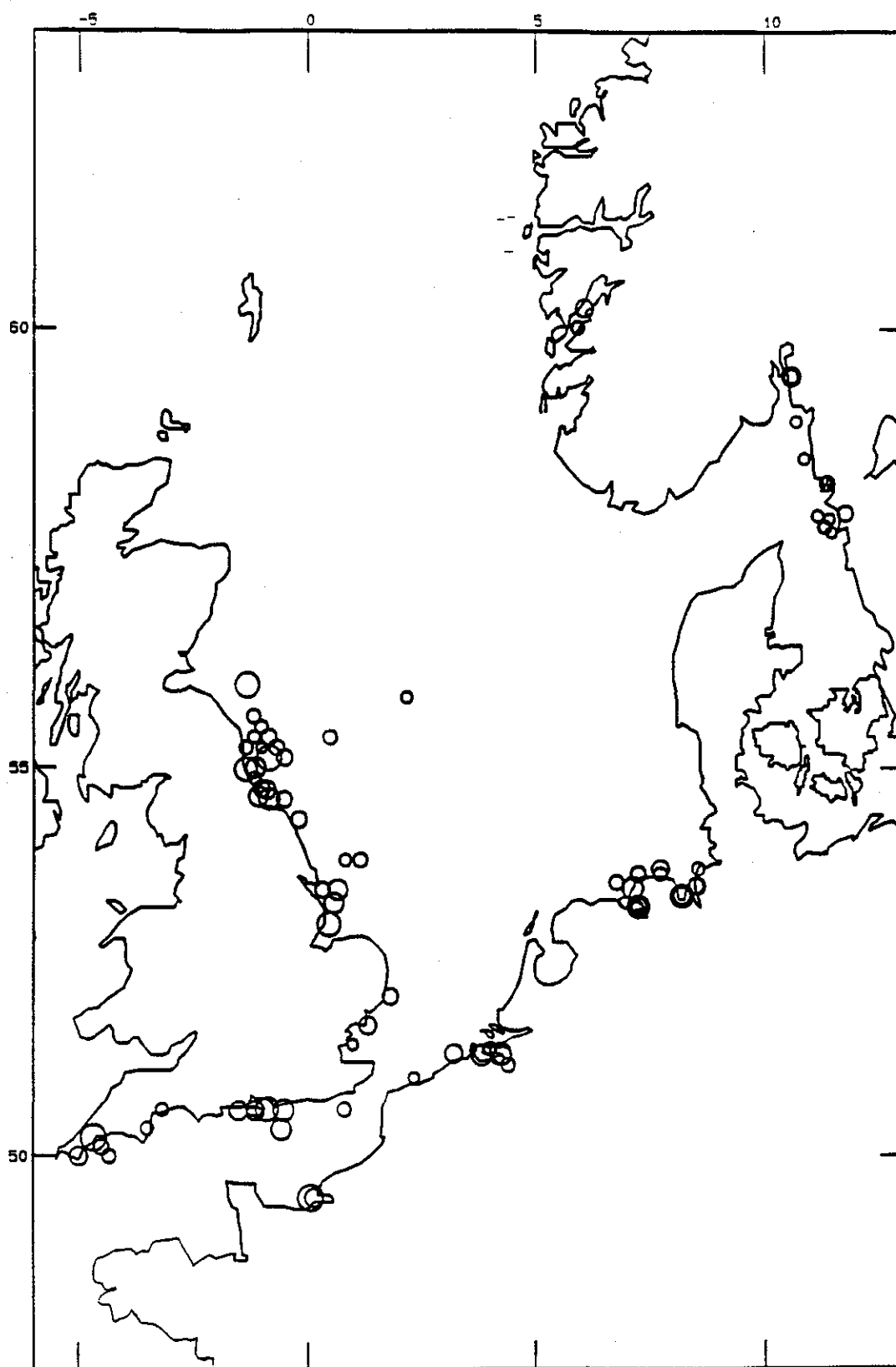


Figure 5.4.2.6 The distribution of mercury concentrations in North Sea sediments $<2000\ \mu\text{m}$, for samples with Hg concentrations between 0.1 and $0.5\ \text{mg kg}^{-1}$ (circle area is proportional to value).

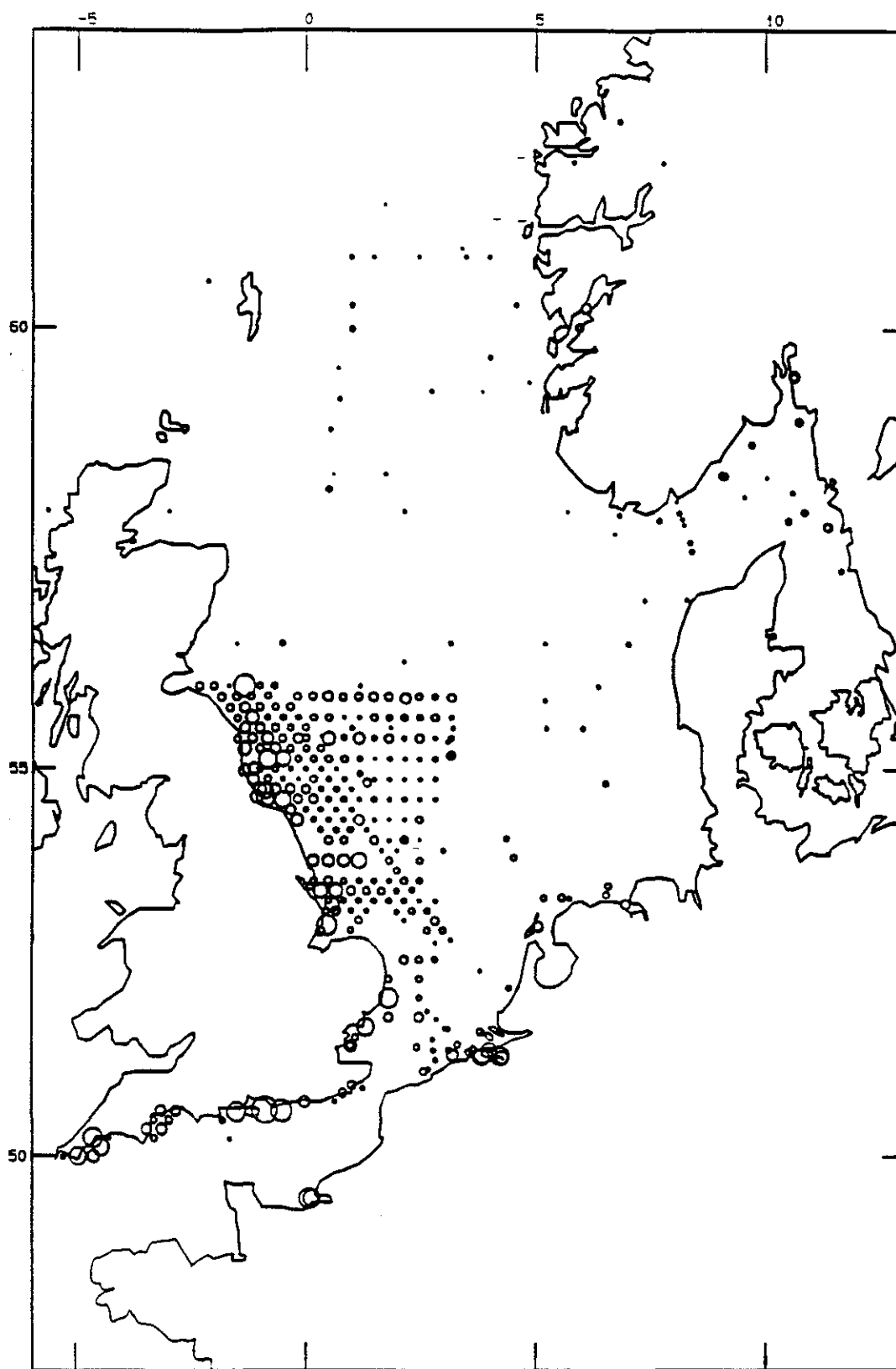


Figure 5.4.2.7 The distribution of mercury/aluminium ratios in North Sea sediments $< 2000 \mu\text{m}$, with aluminium $\geq 1\%$.

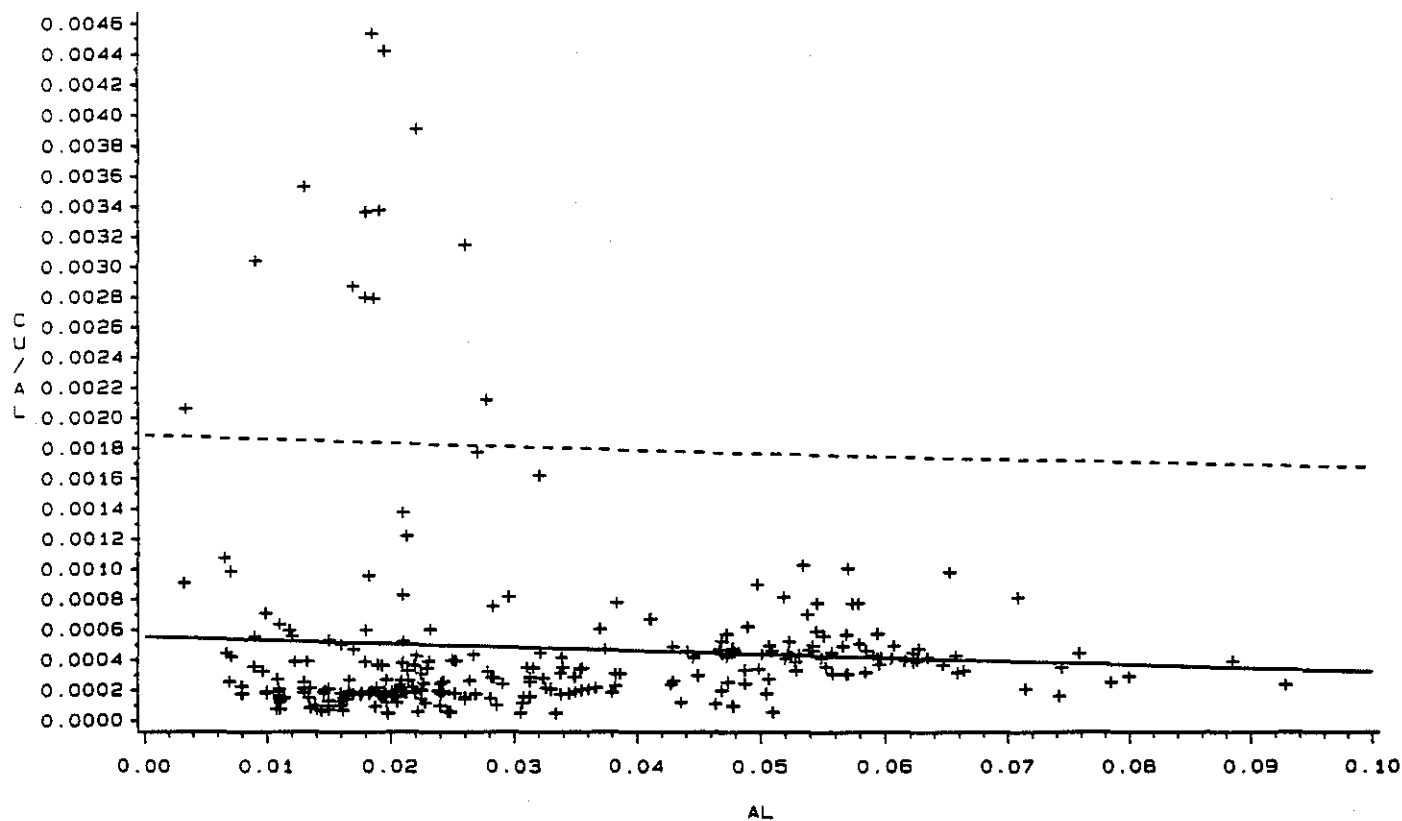


Figure 5.4.3.1 Regression of Cu/Al vs. Al (in g g⁻¹).

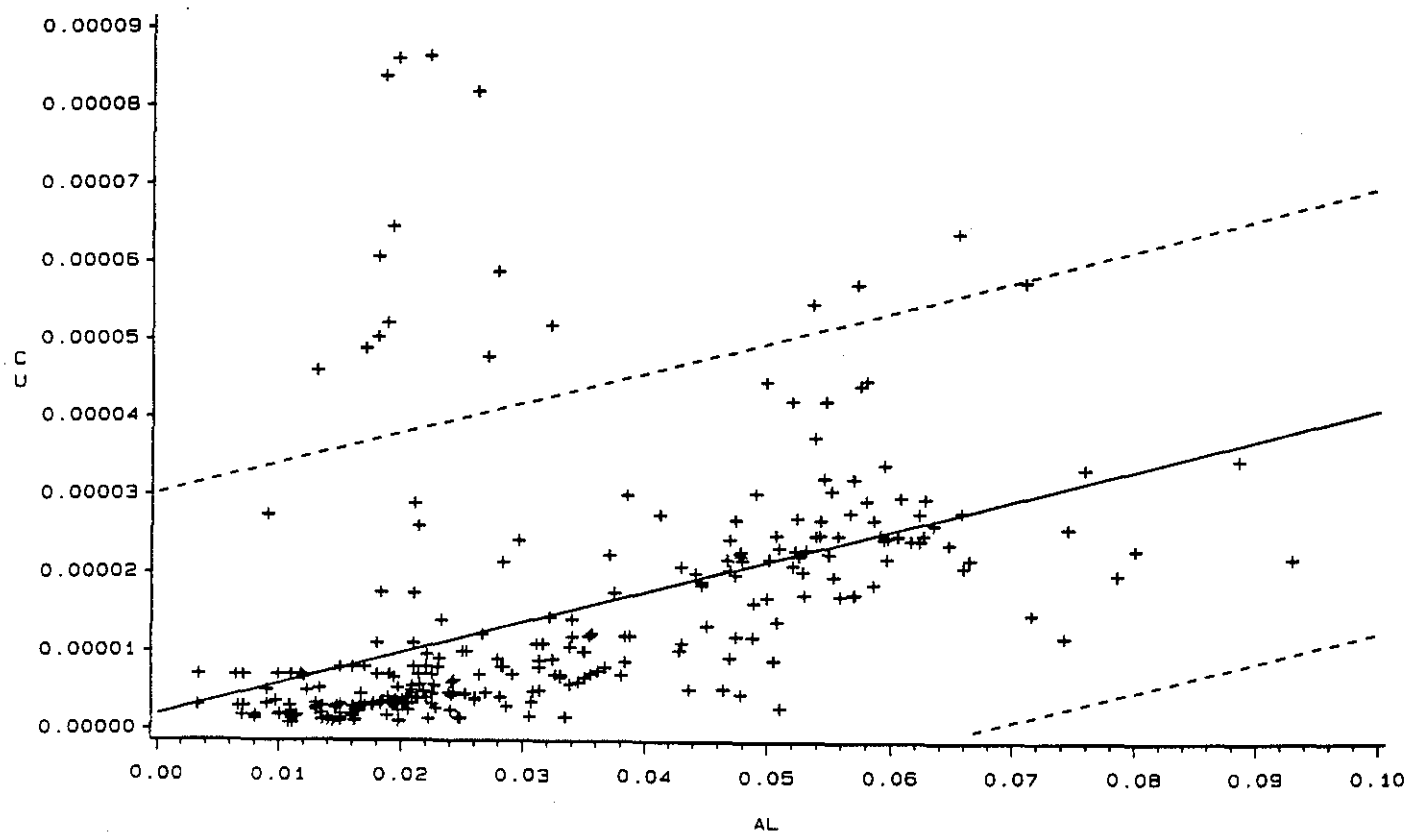


Figure 5.4.3.2 Regression of Cu vs. Al (both in g g⁻¹).

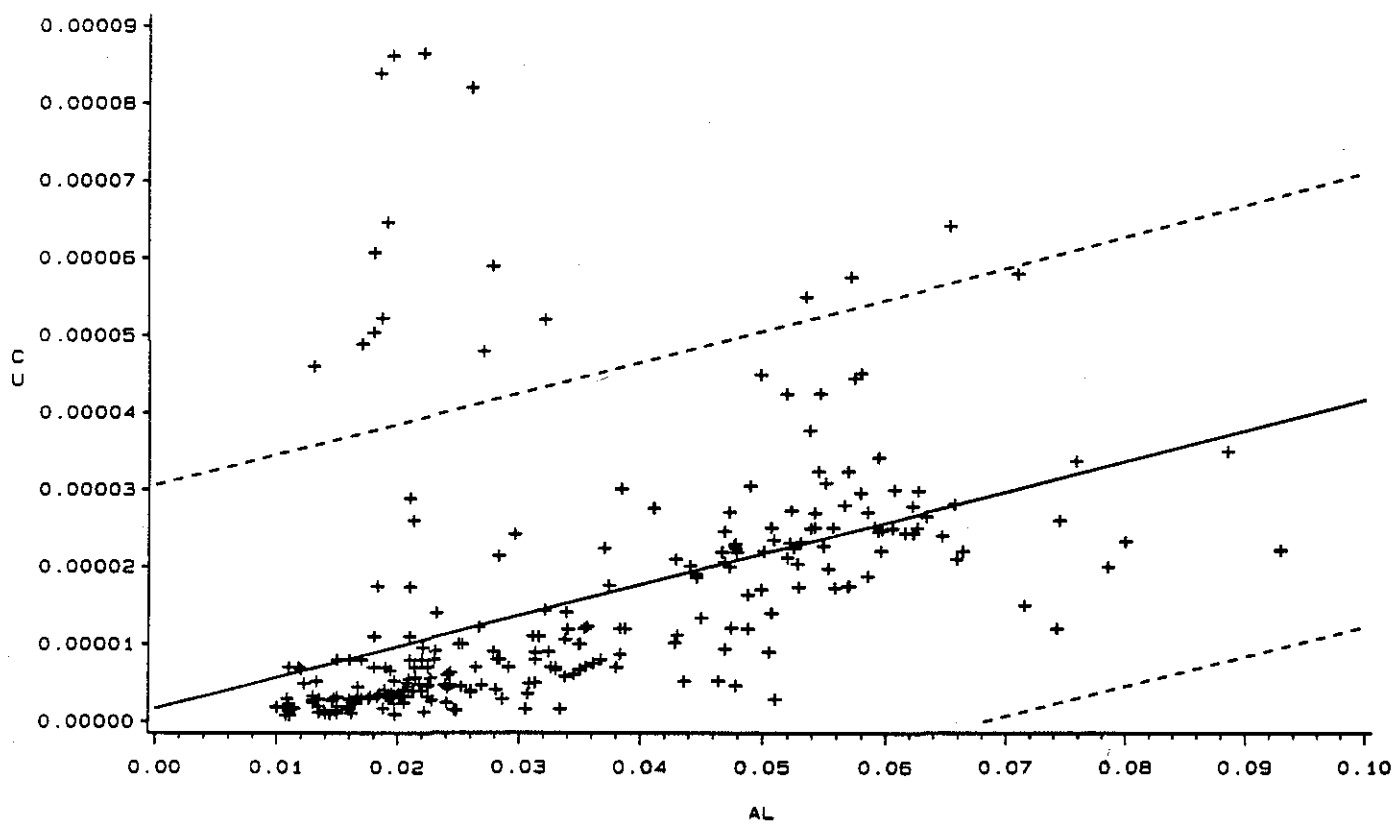


Figure 5.4.3.3 Regression of Cu vs. Al (both in g g^{-1}), for $\text{Al} \geq 1\%$.

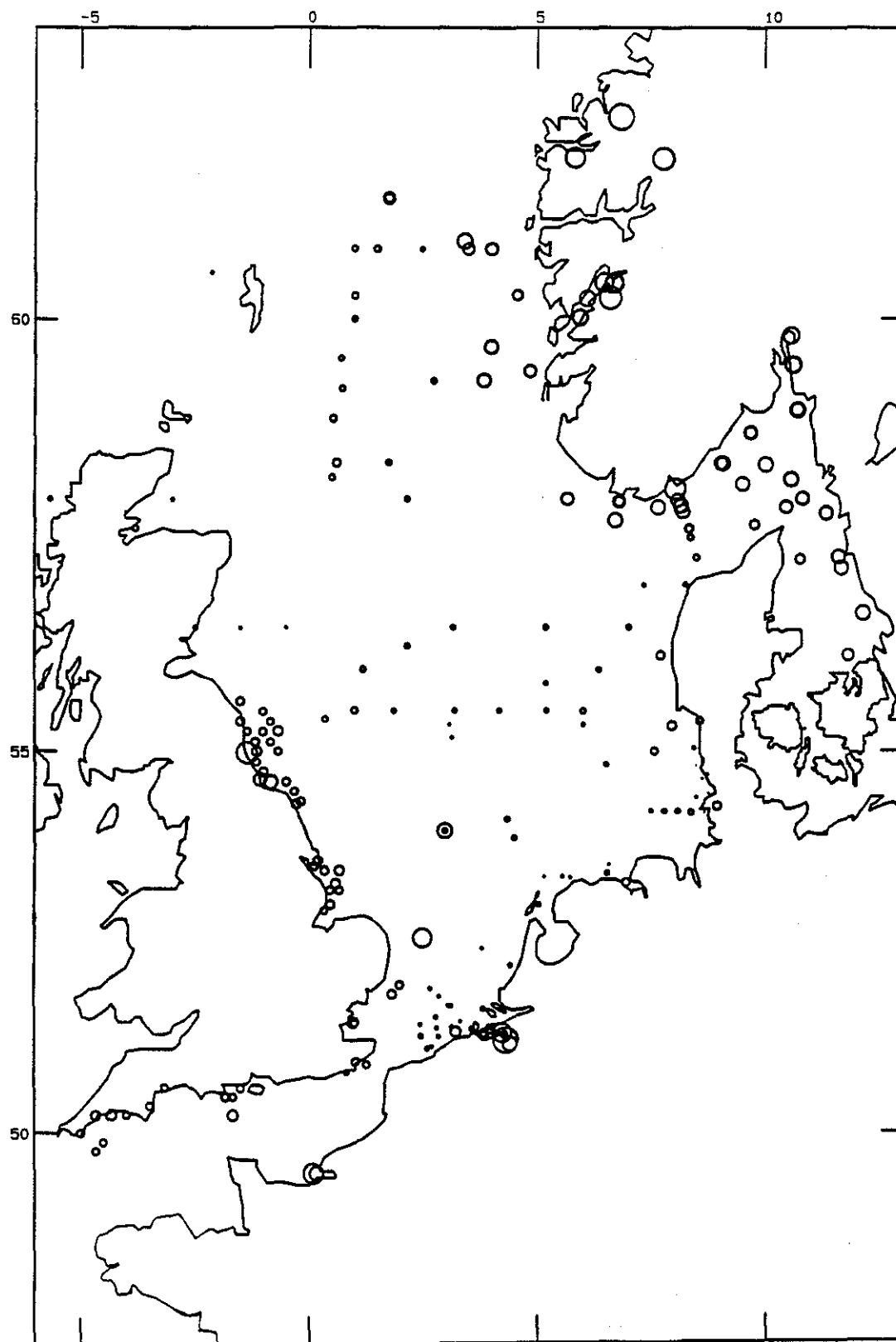


Figure 5.4.3.4 The distribution of copper concentrations in North Sea sediments $<2000 \mu\text{m}$ (circle area is proportional to value). The maximum concentration is 86.5 mg kg^{-1} .

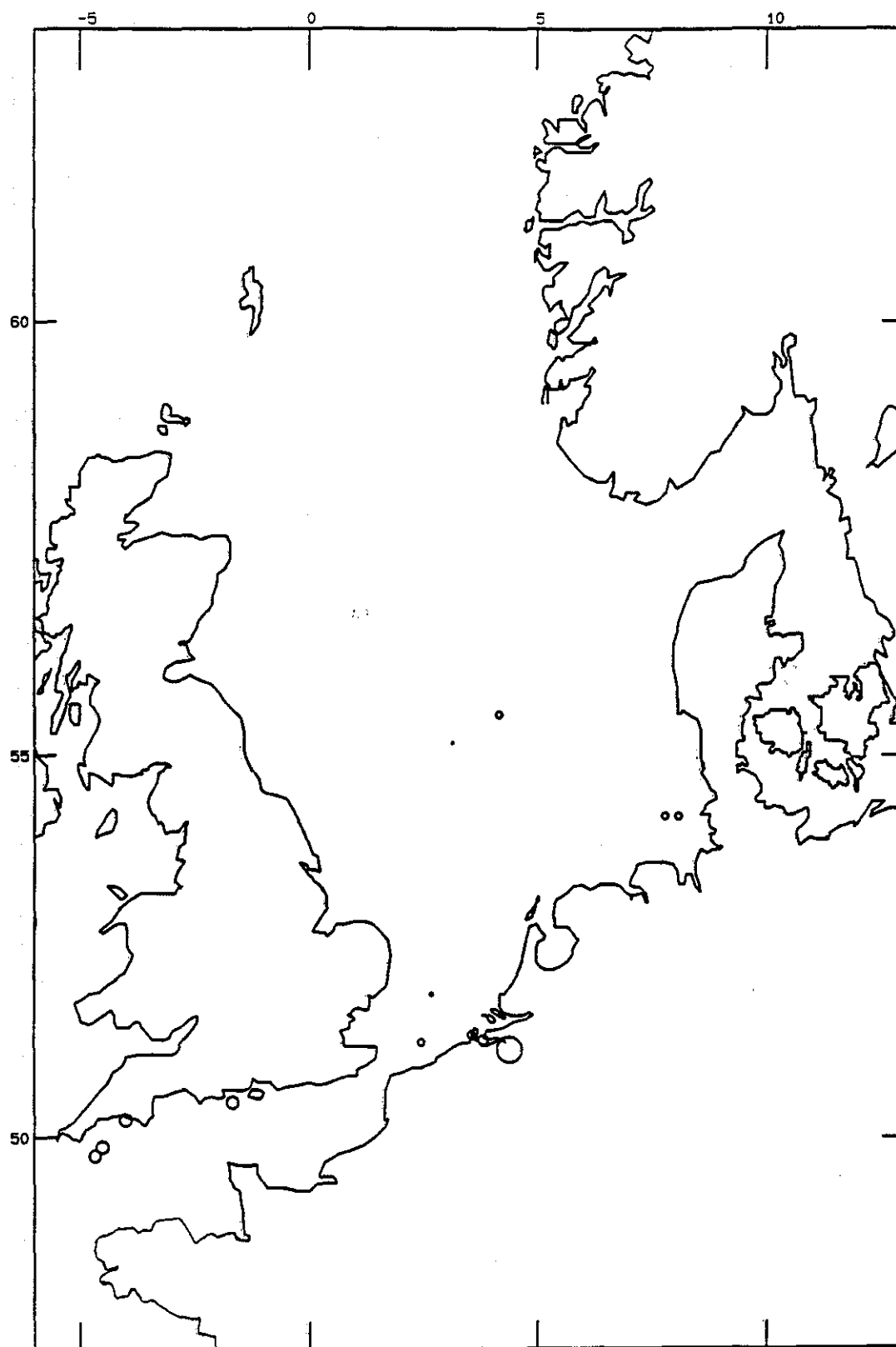


Figure 5.4.3.5 The distribution of copper concentrations in North Sea sediments $<2000 \mu\text{m}$, with aluminium $<1\%$ (circle area is proportional to value). The maximum concentration is 27.4 mg kg^{-1} .

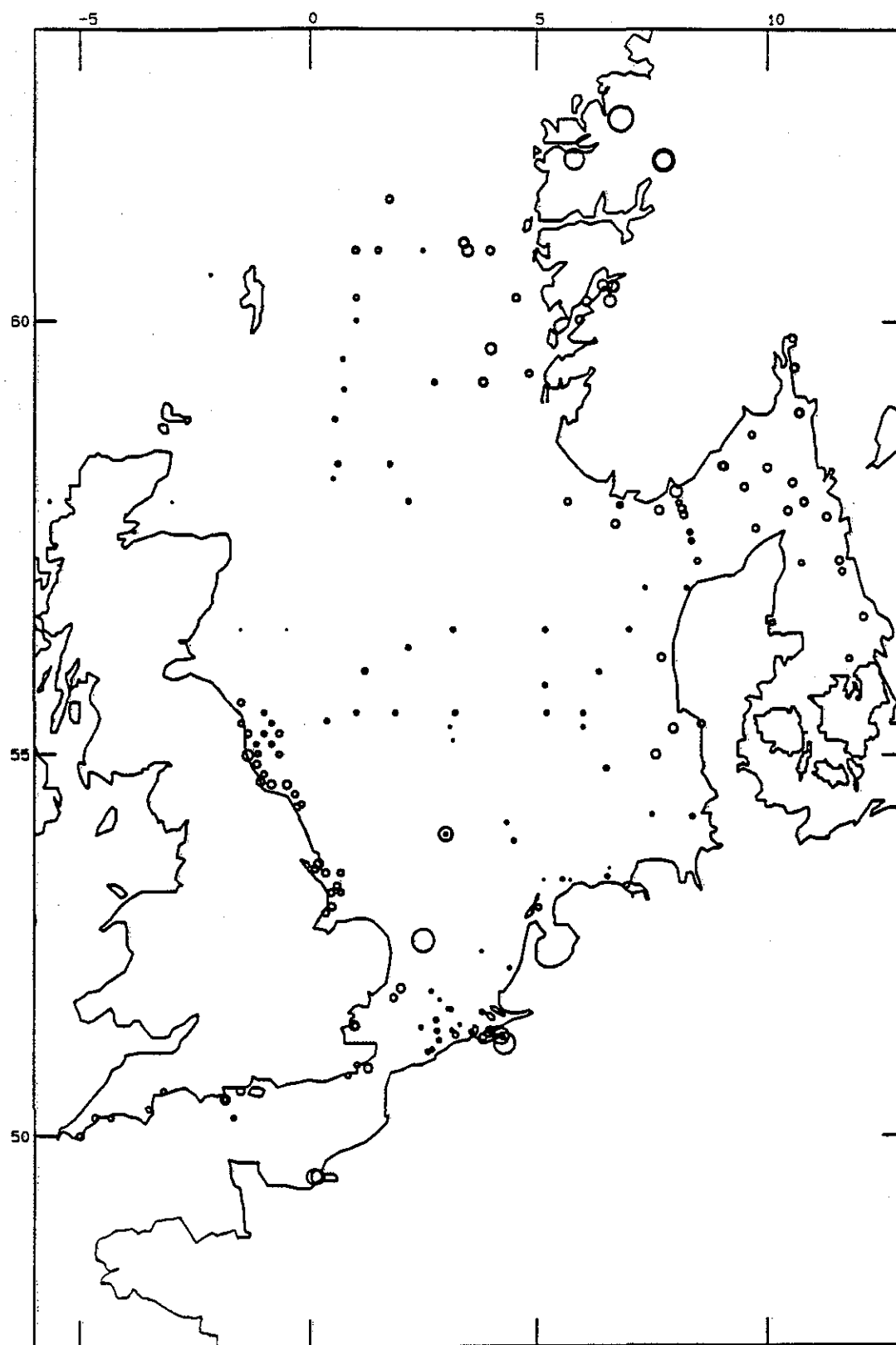


Figure 5.4.3.6 The distribution of copper/aluminium ratios in North Sea sediments $<2000 \mu\text{m}$, with aluminium $\geq 1\%$ (circle area is proportional to value).

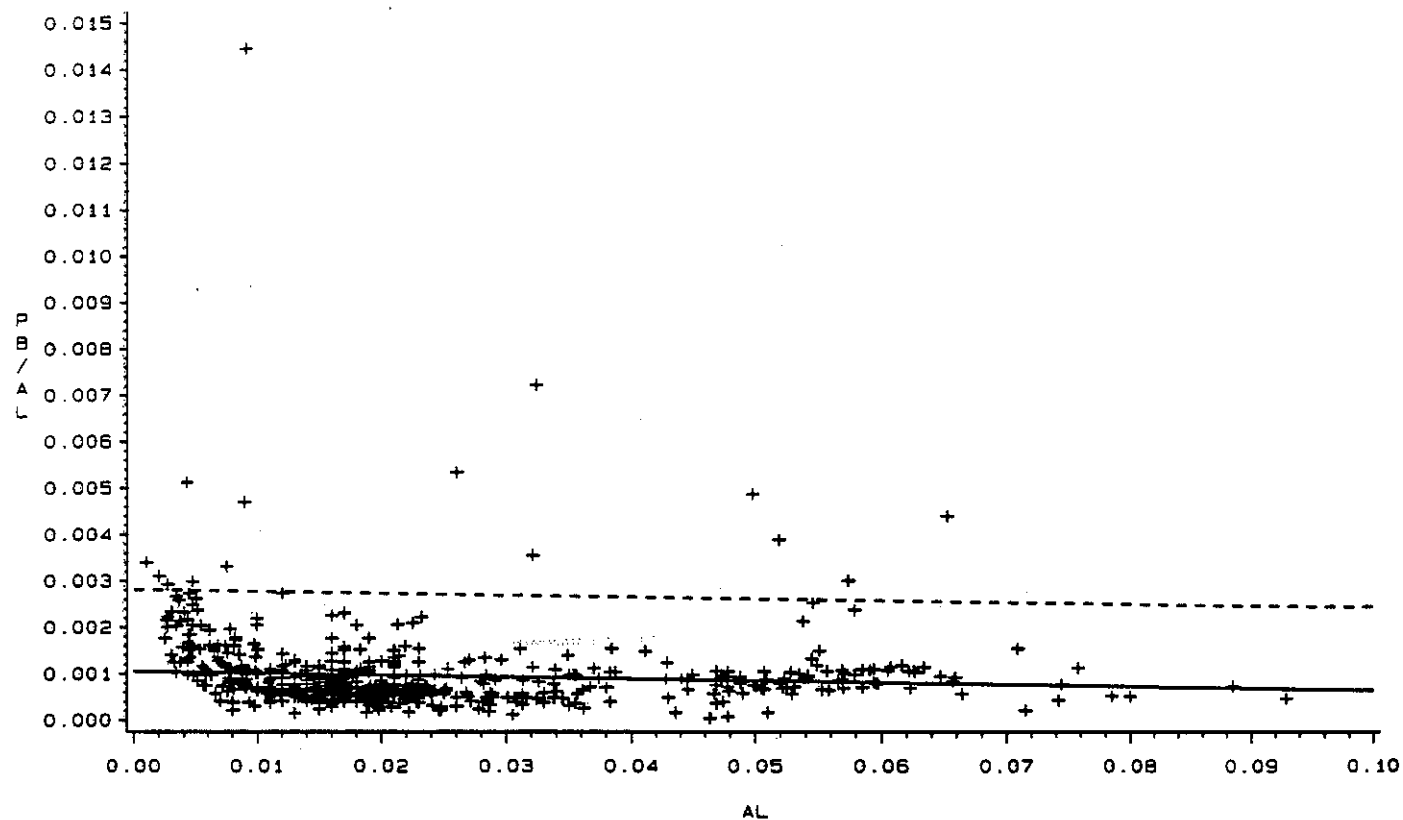


Figure 5.4.4.1 Regression of Pb/Al vs. Al (in g g⁻¹).

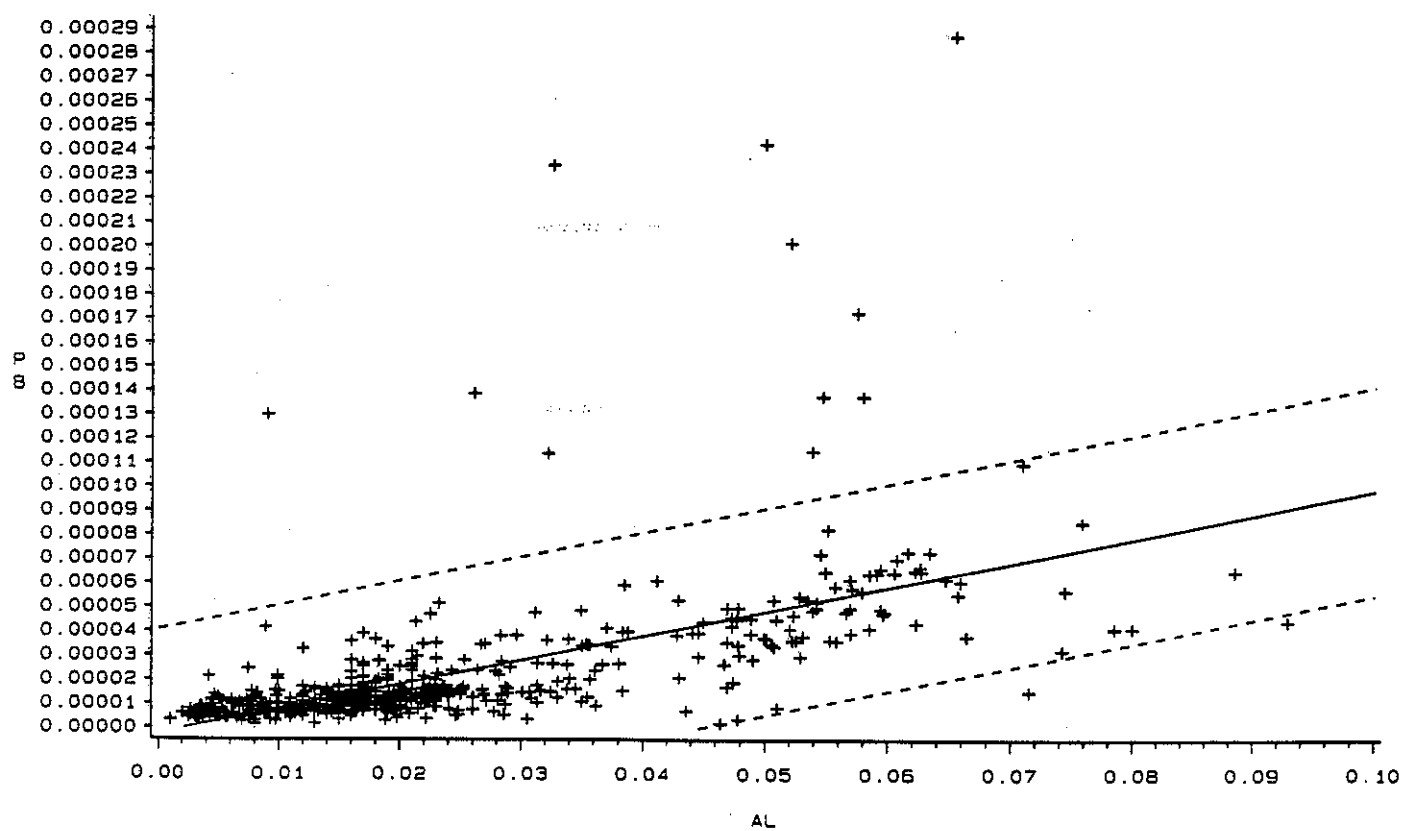


Figure 5.4.4.2 Regression of Pb vs. Al (both in g g⁻¹).

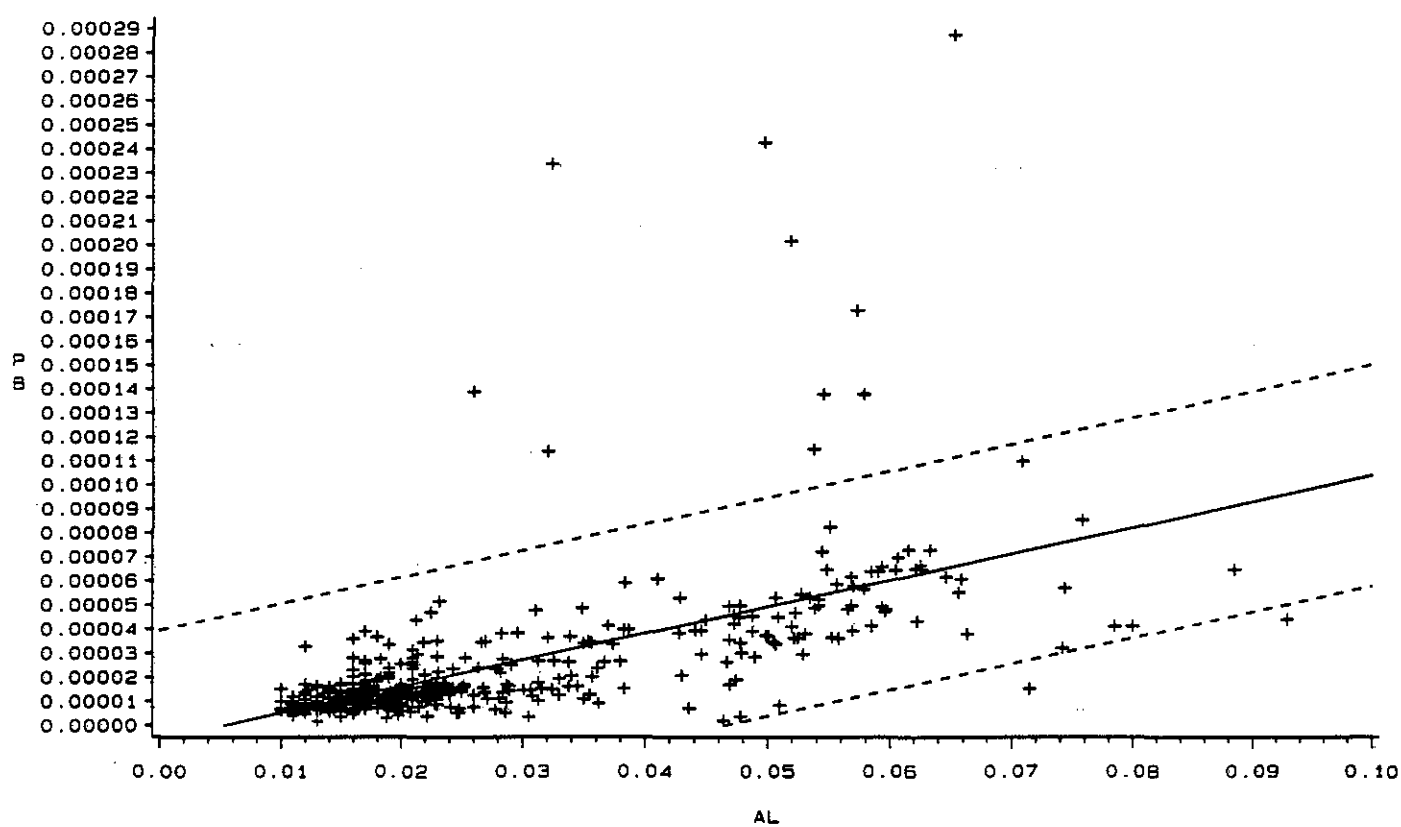


Figure 5.4.4.3 Regression of Pb vs. Al (both in g g^{-1}), for $\text{Al} \geq 1\%$.

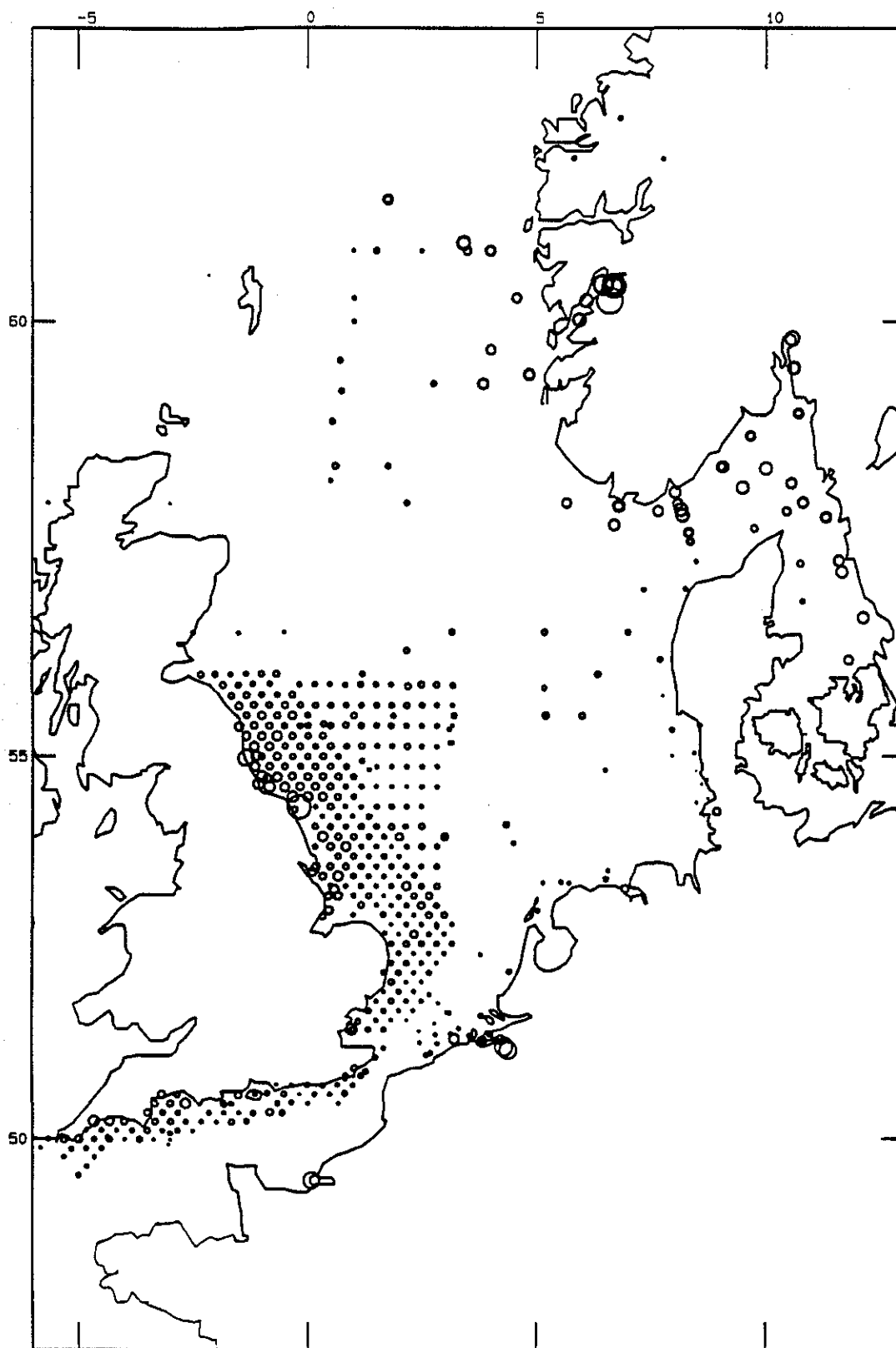


Figure 5.4.4.4 The distribution of lead concentrations in North Sea sediments $< 2000 \mu\text{m}$ (circle area is proportional to value). The maximum concentration is 288 mg kg^{-1} .

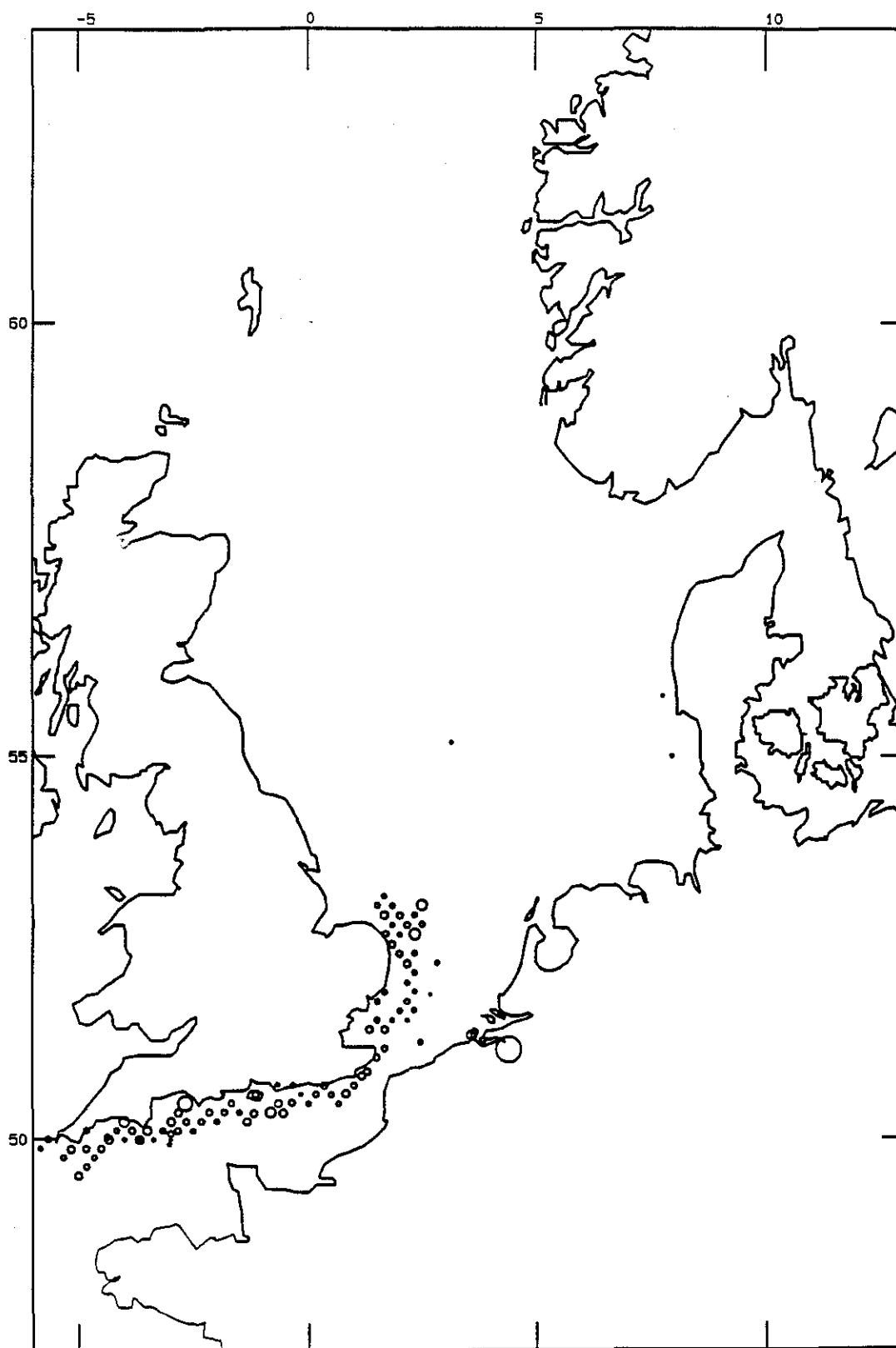


Figure 5.4.4.5 The distribution of lead concentrations in North Sea sediments $<2000\ \mu\text{m}$, with aluminium $<1\%$ (circle area is proportional to value). The maximum concentration is $13\ \text{mg kg}^{-1}$.

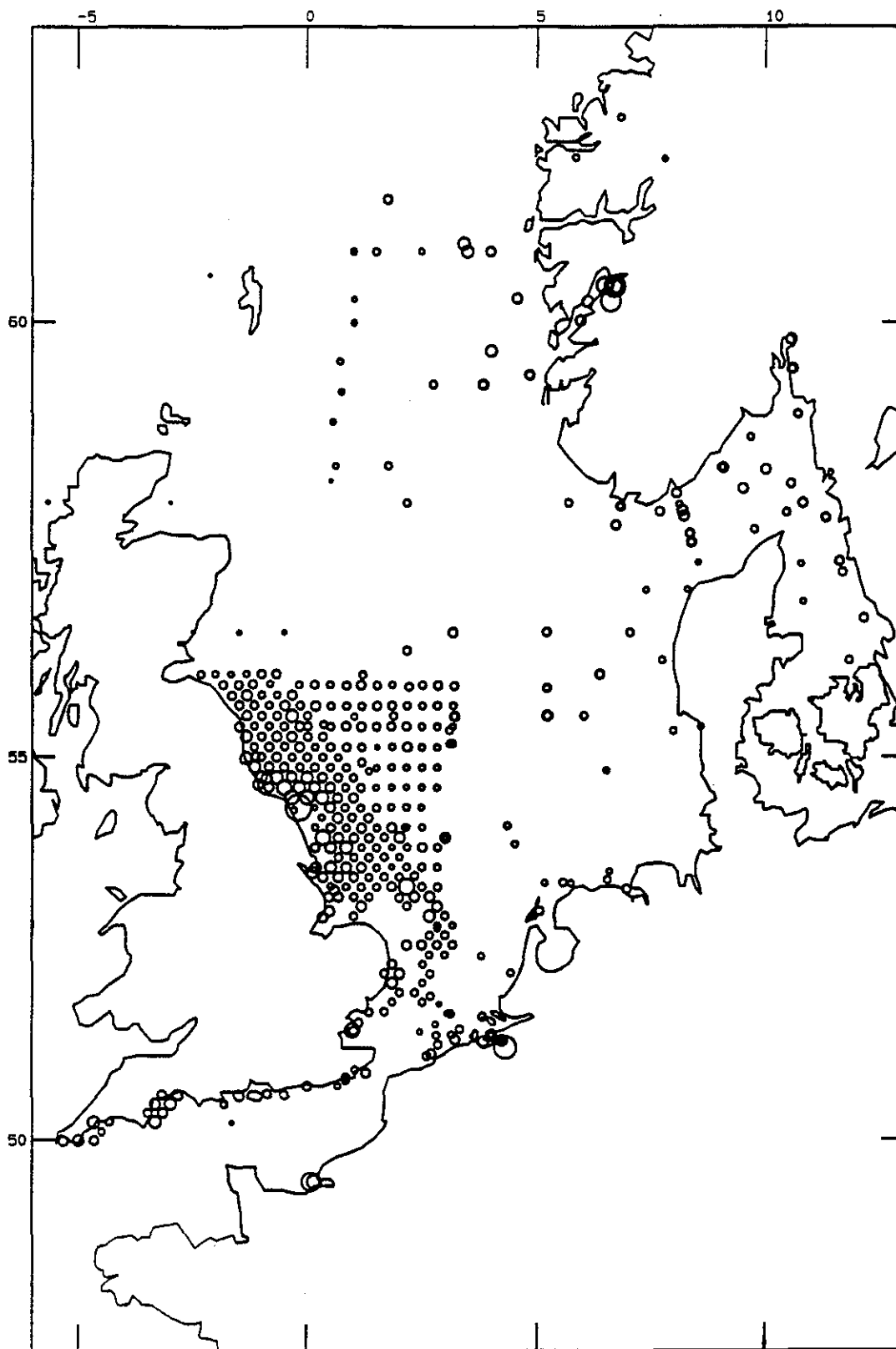


Figure 5.4.4.6 The distribution of lead/aluminium ratios in North Sea sediments $< 2000 \mu\text{m}$, with aluminium $\geq 1\%$ (circle area is proportional to value).

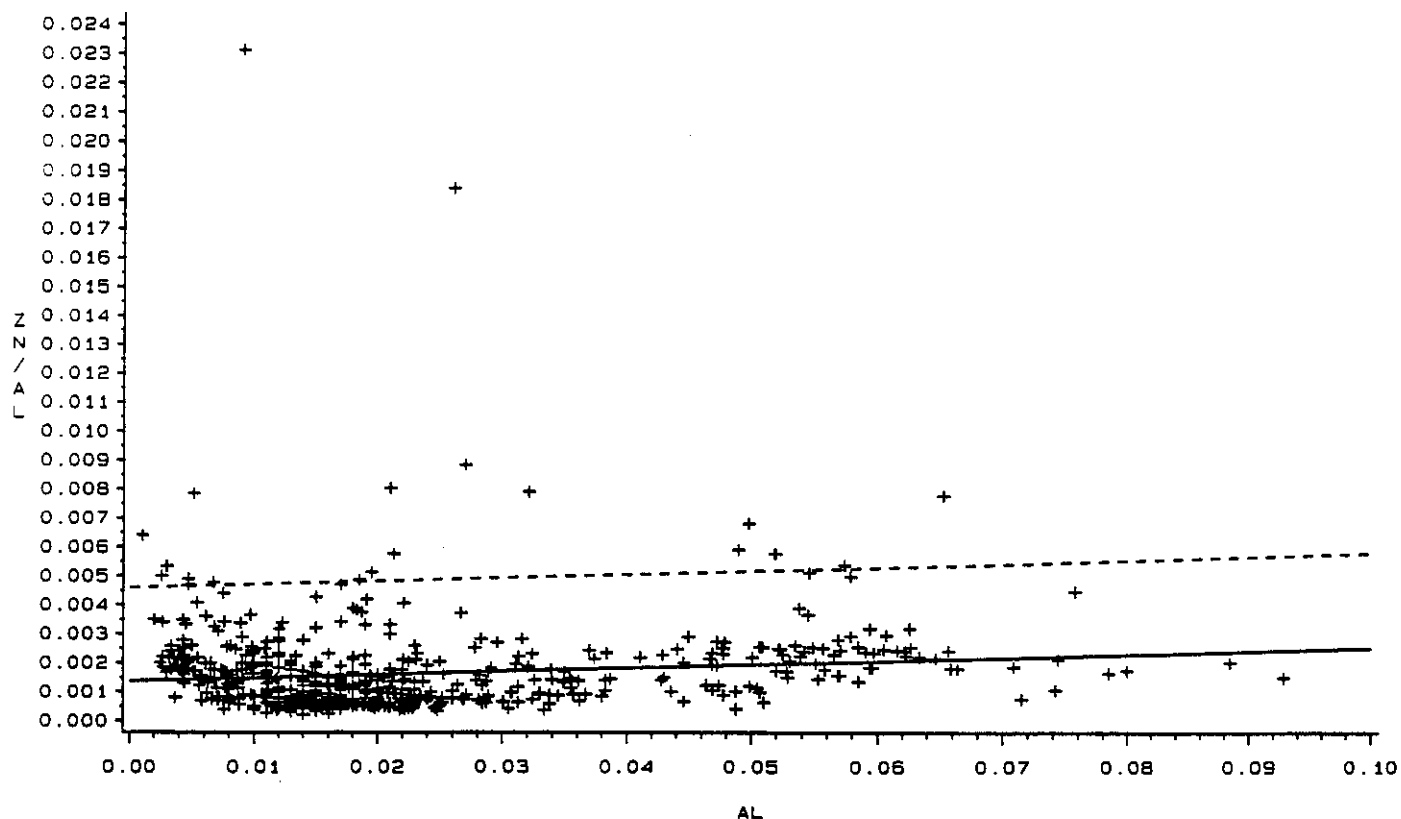


Figure 5.4.5.1 Regression of Zn/Al vs. Al (in g g^{-1}).

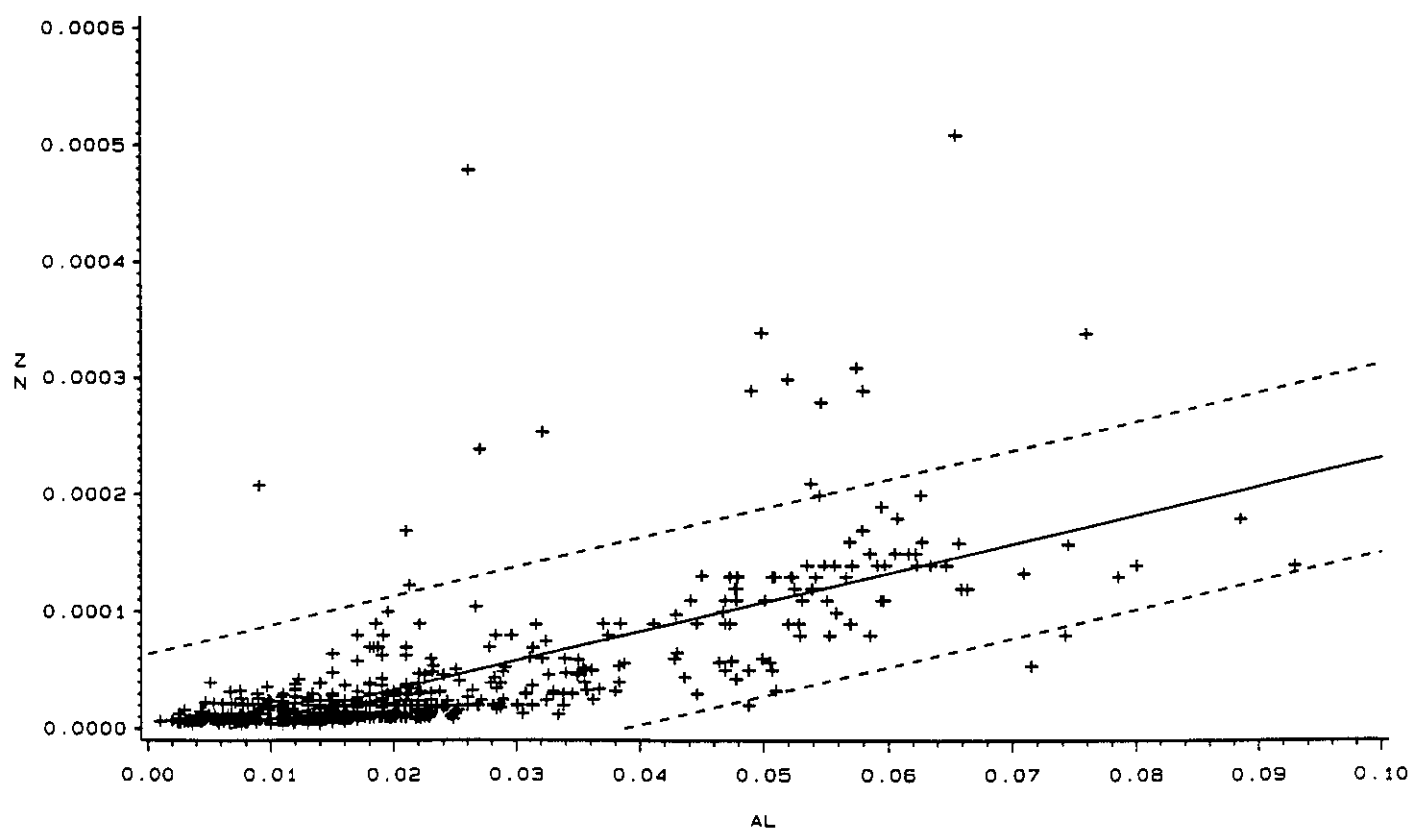


Figure 5.4.5.2 Regression of Zn vs. Al (both in g g^{-1}).

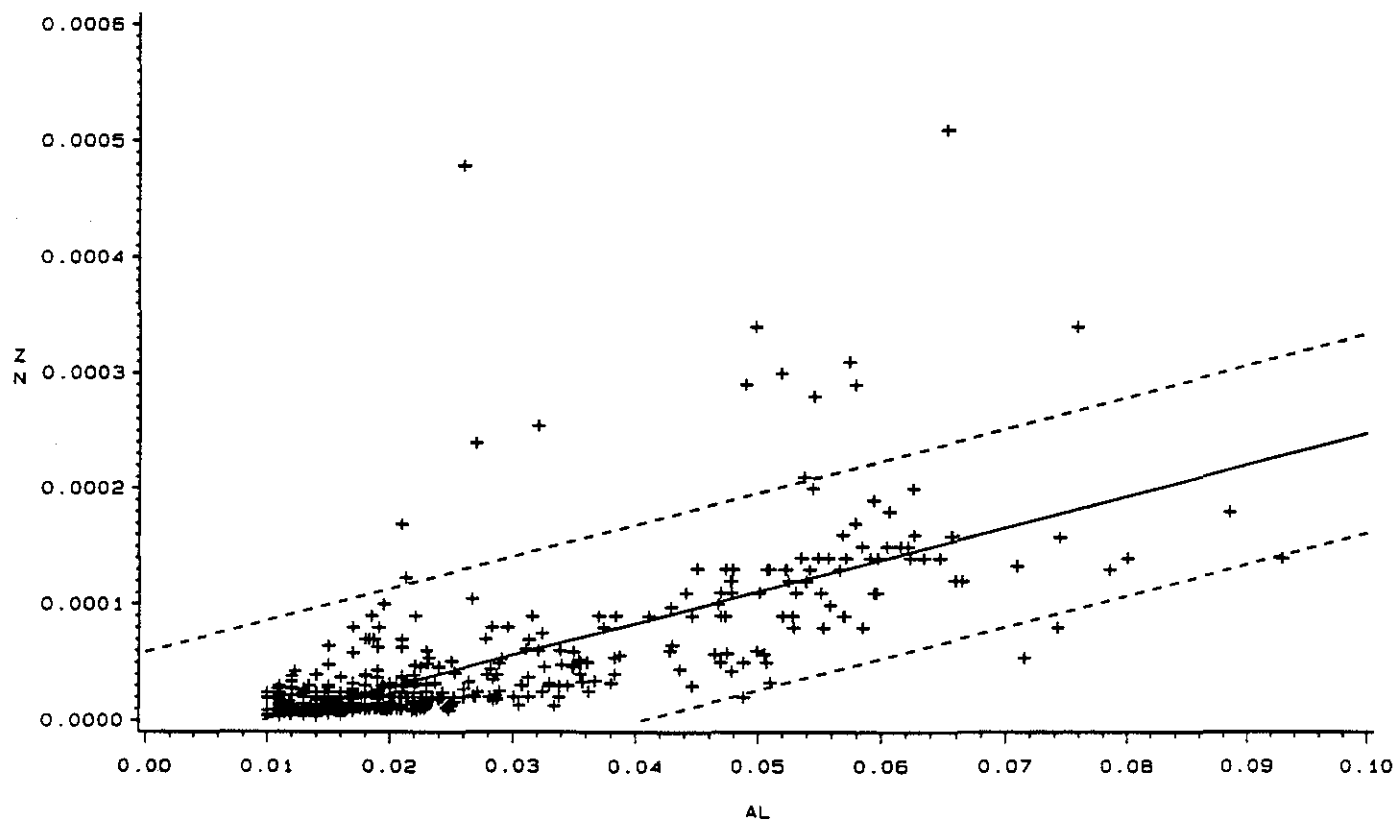


Figure 5.4.5.3 Regression of Zn vs. Al (both in g g^{-1}), for $\text{Al} \geq 1\%$.

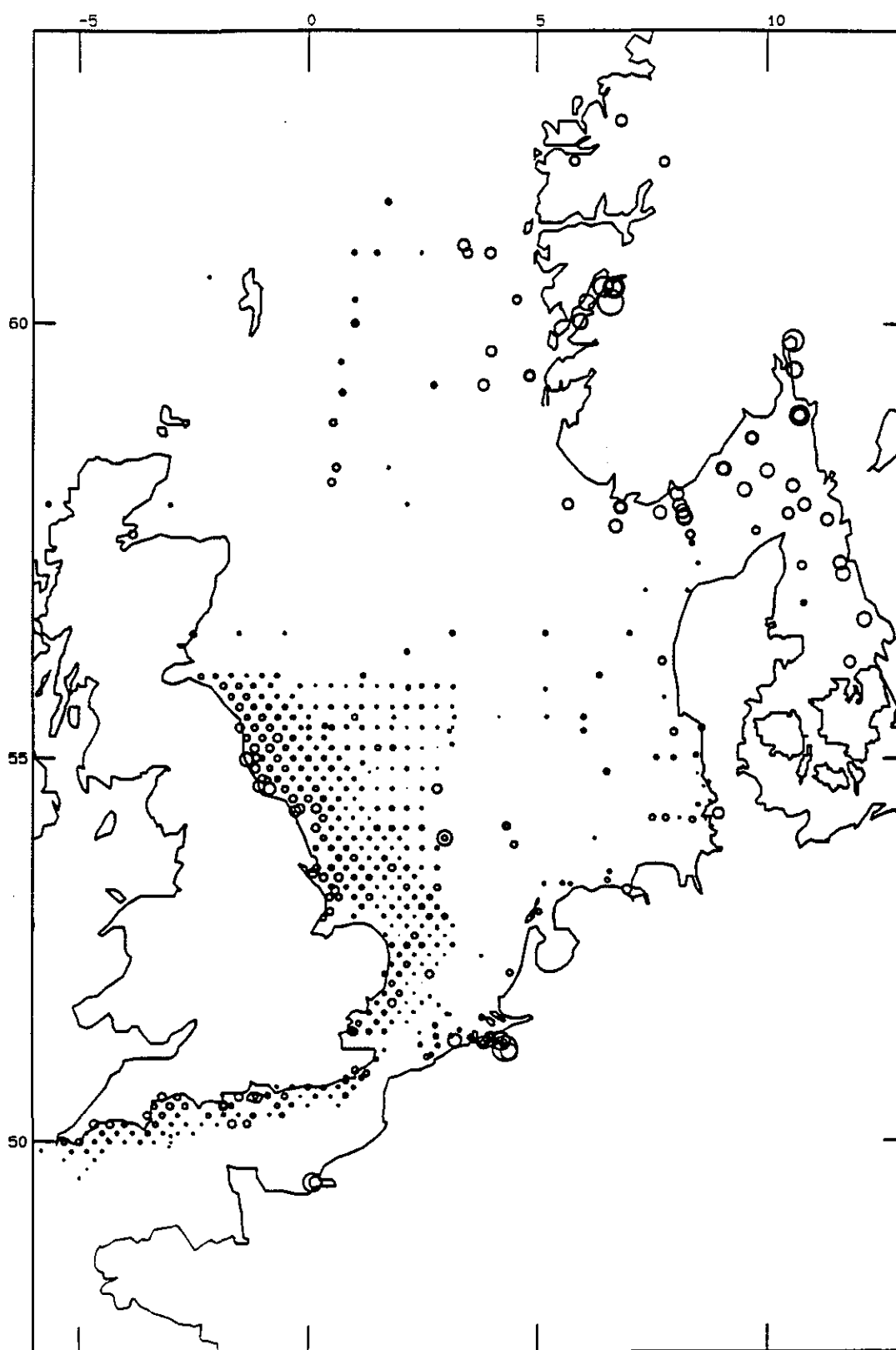


Figure 5.4.5.4 The distribution of zinc concentrations in North Sea sediments $< 2000 \mu\text{m}$ (circle area is proportional to value). The maximum concentration is 510 mg kg^{-1} .

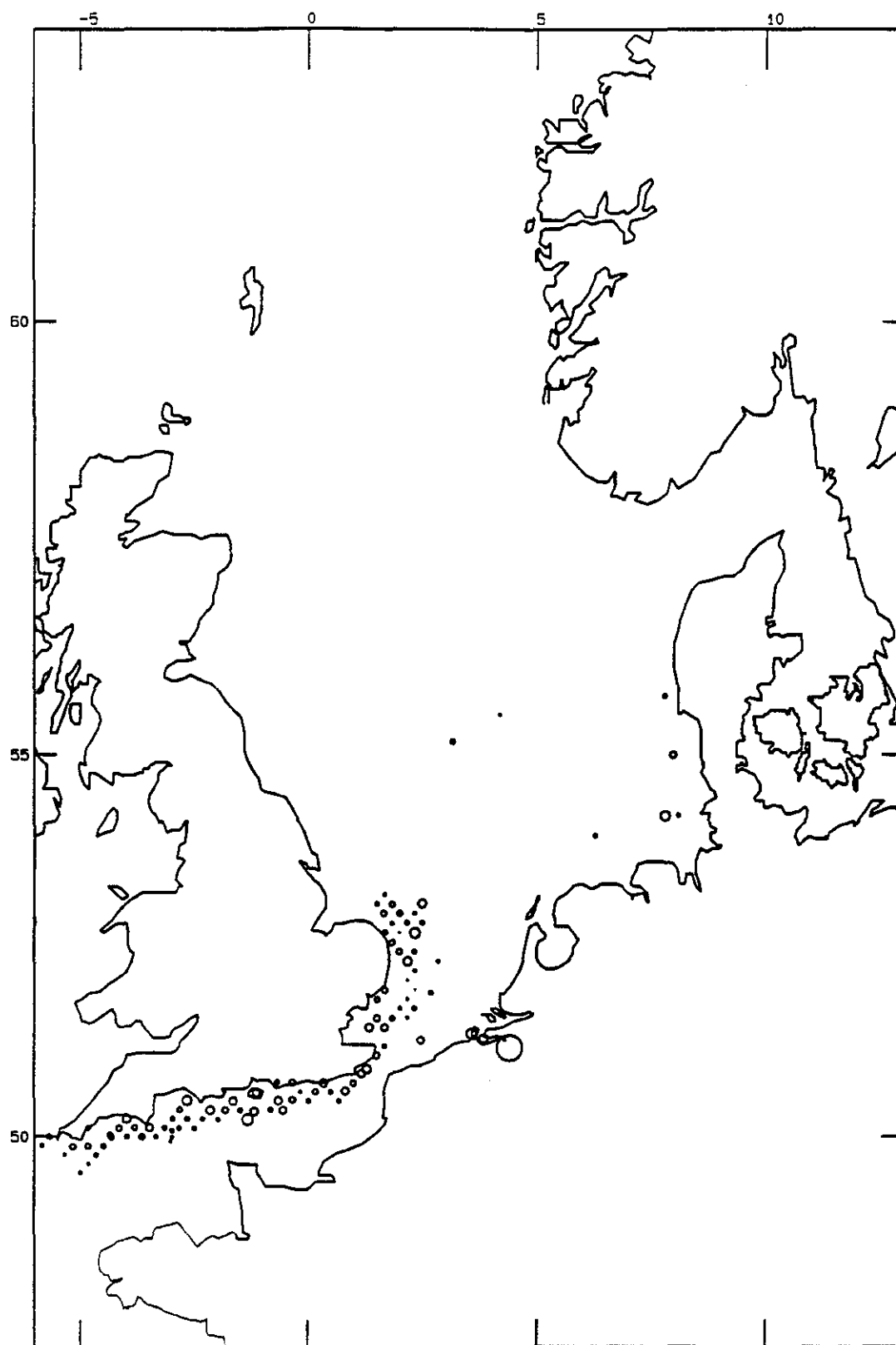


Figure 5.4.5.5 The distribution of zinc concentrations in North Sea sediments $<2000\ \mu\text{m}$, with aluminium $<1\%$ (circle area is proportional to value). The maximum concentration is $208\ \text{mg kg}^{-1}$.

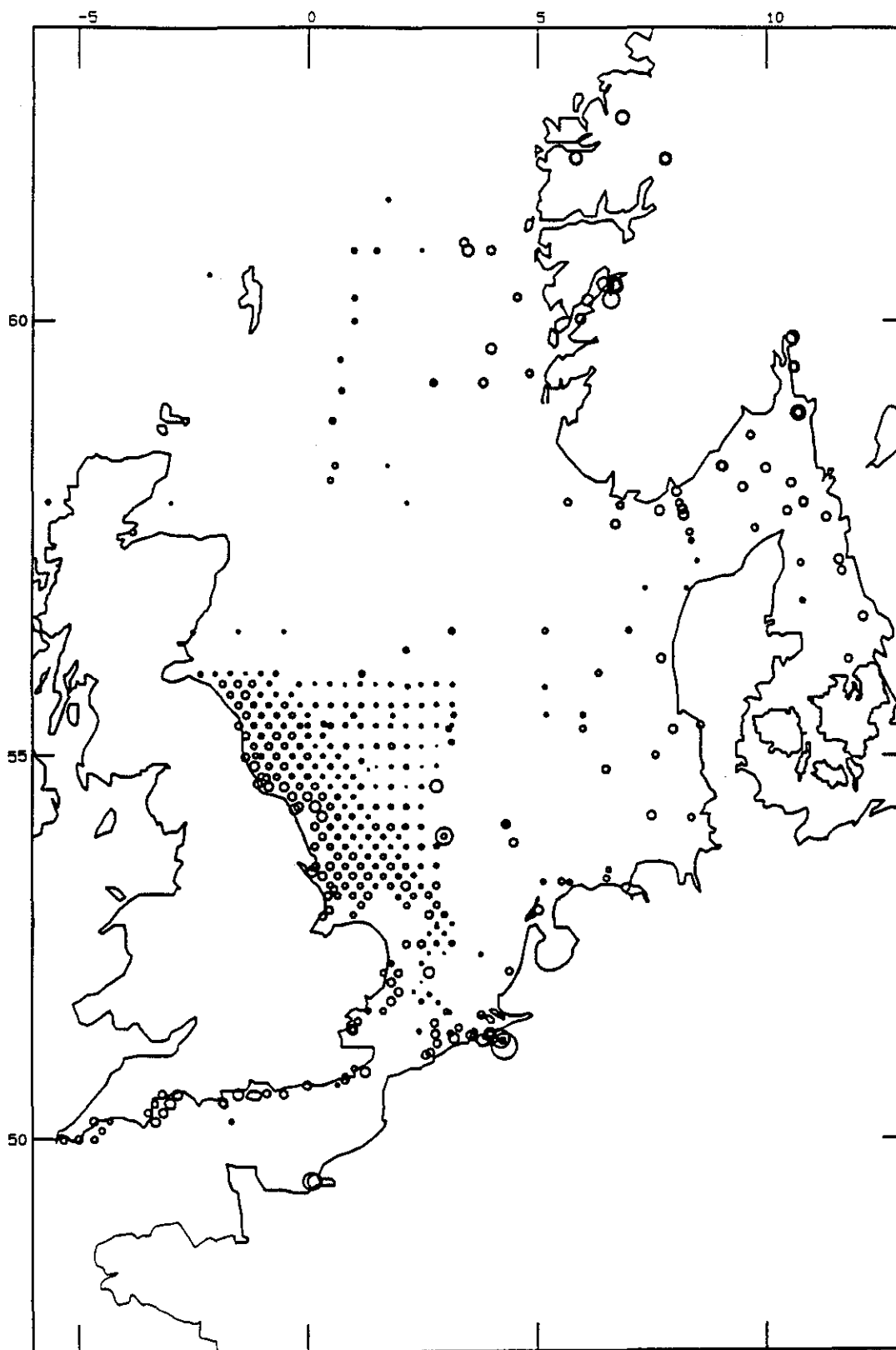


Figure 5.4.5.6 The distribution of zinc/aluminium ratios in North Sea sediments $< 2000 \mu\text{m}$, with aluminium $\geq 1\%$ (circle area is proportional to value).

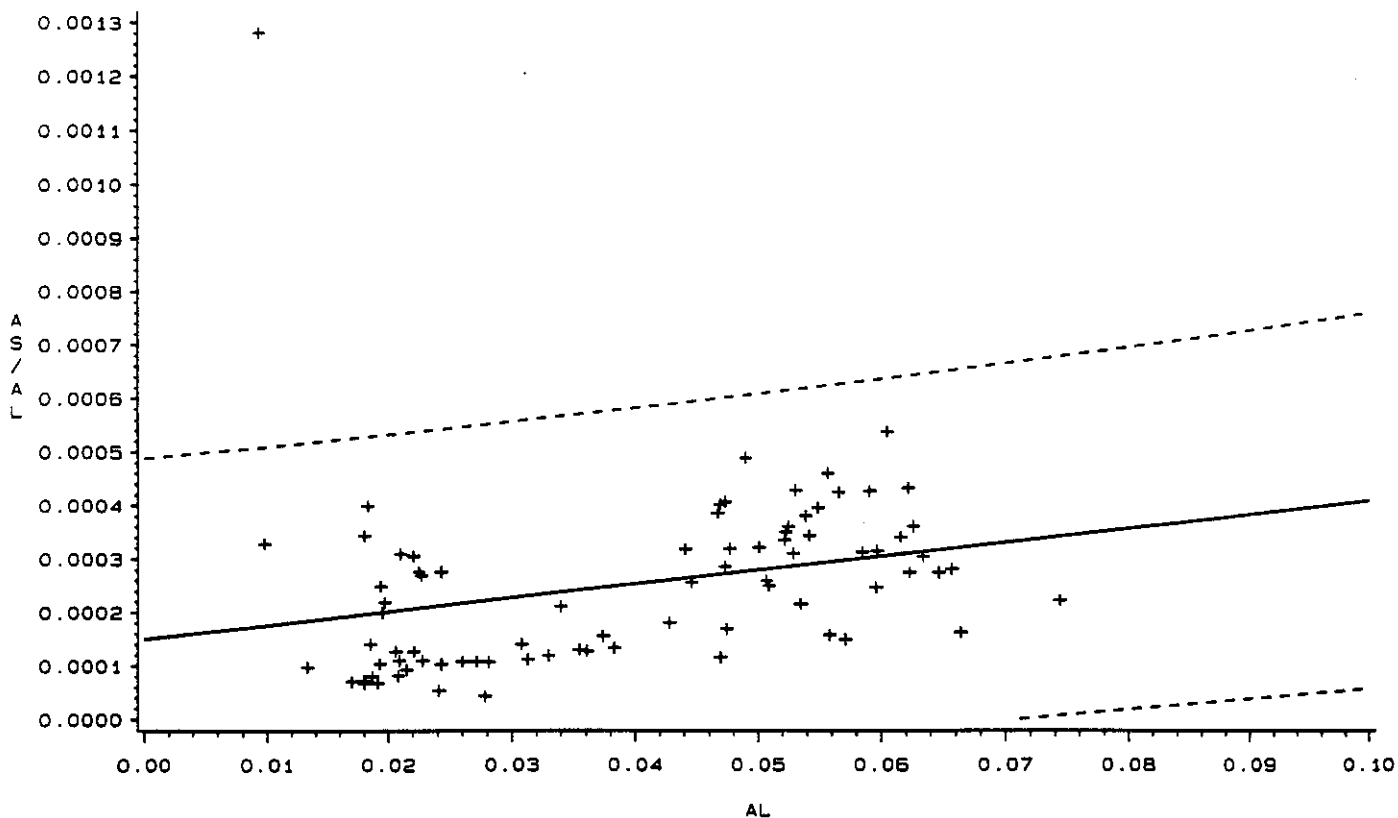


Figure 5.5.1.1 Regression of As/Al vs. Al (in g g⁻¹).

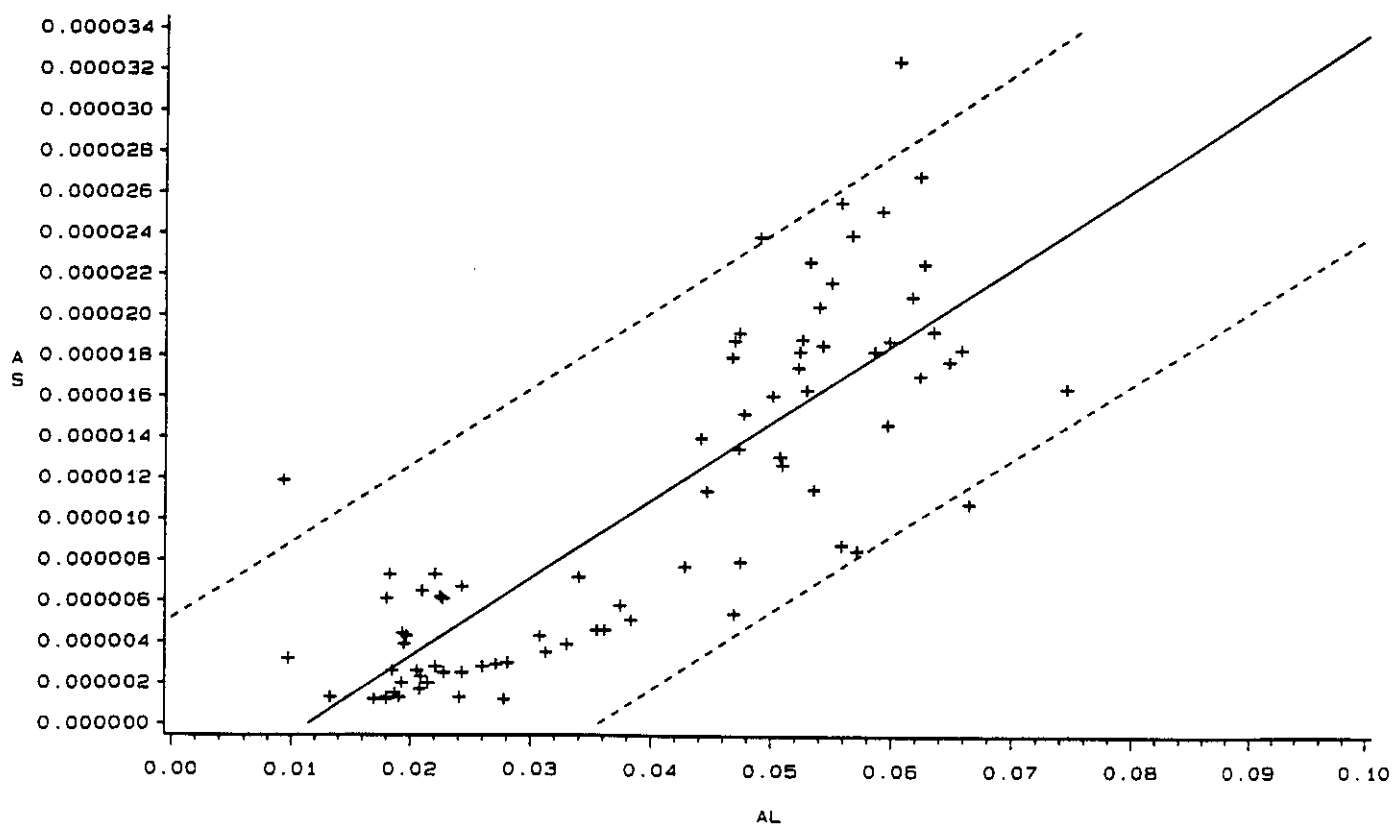


Figure 5.5.1.2 Regression of As vs. Al (both in g g⁻¹).

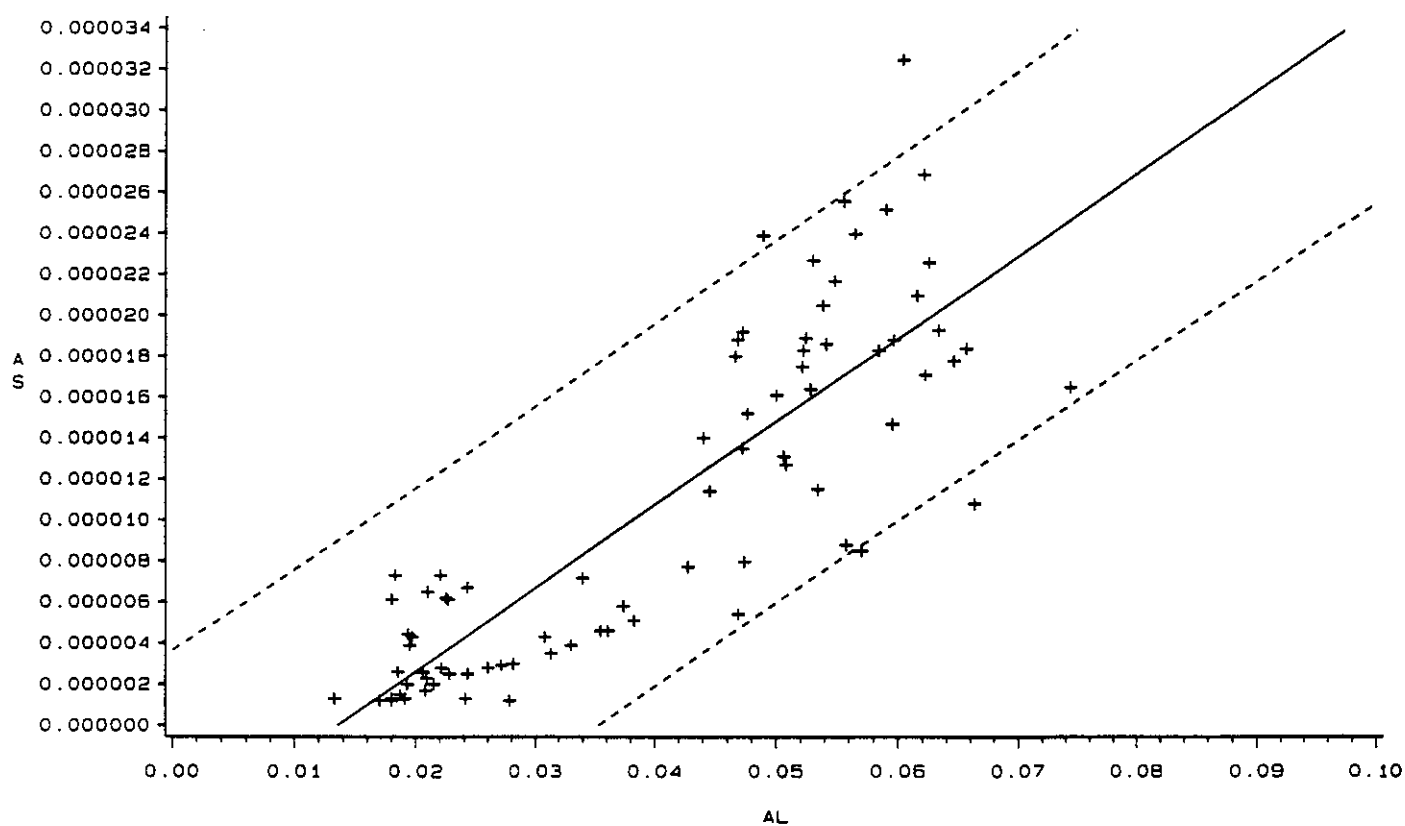


Figure 5.5.1.3 Regression of As vs. Al (both in g g⁻¹), for Al ≥ 1%.

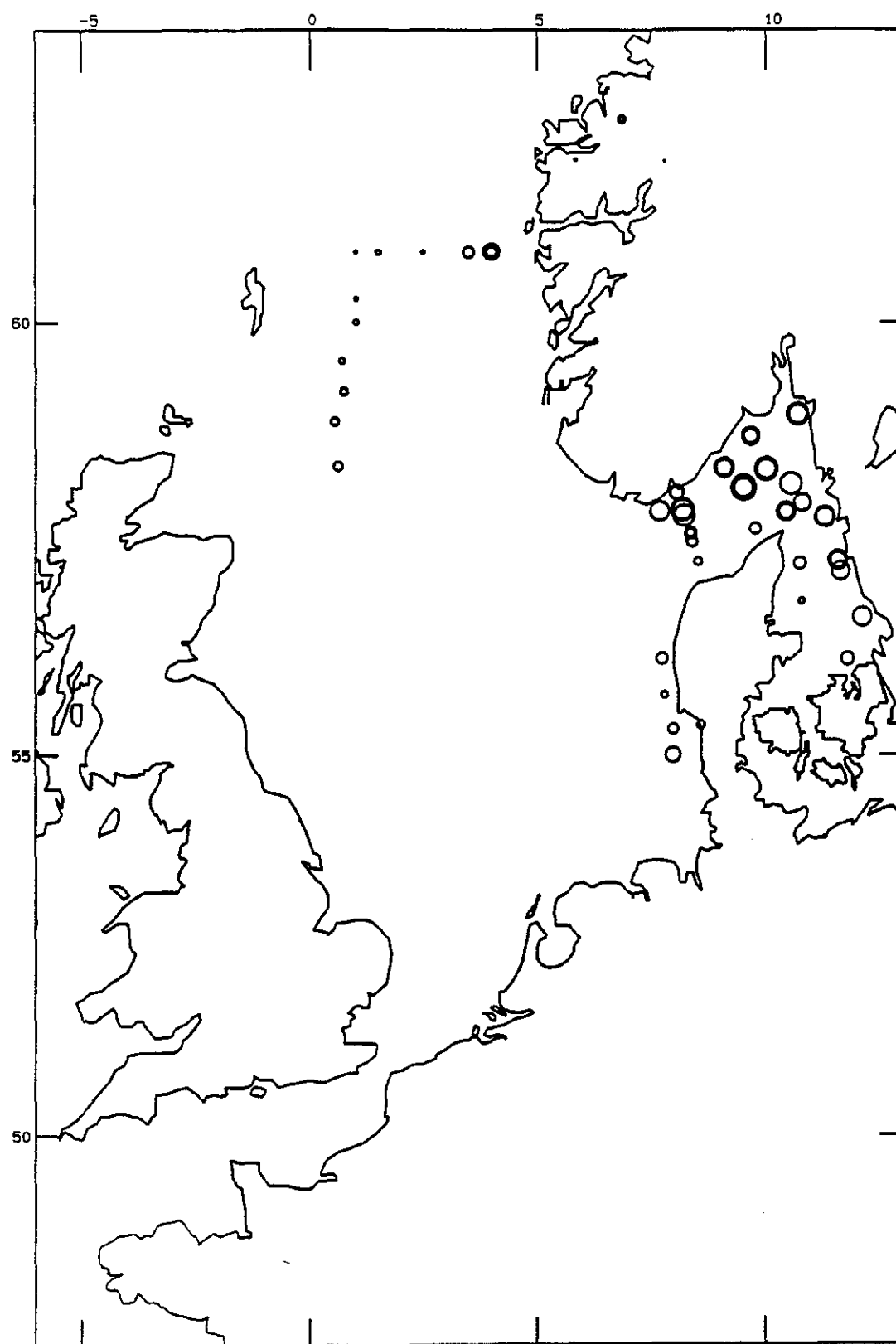


Figure 5.5.1.4 The distribution of arsenic concentrations in North Sea sediments $< 2000 \mu\text{m}$ (circle is proportional to value). The maximum concentration is 32.5 mg kg^{-1} .

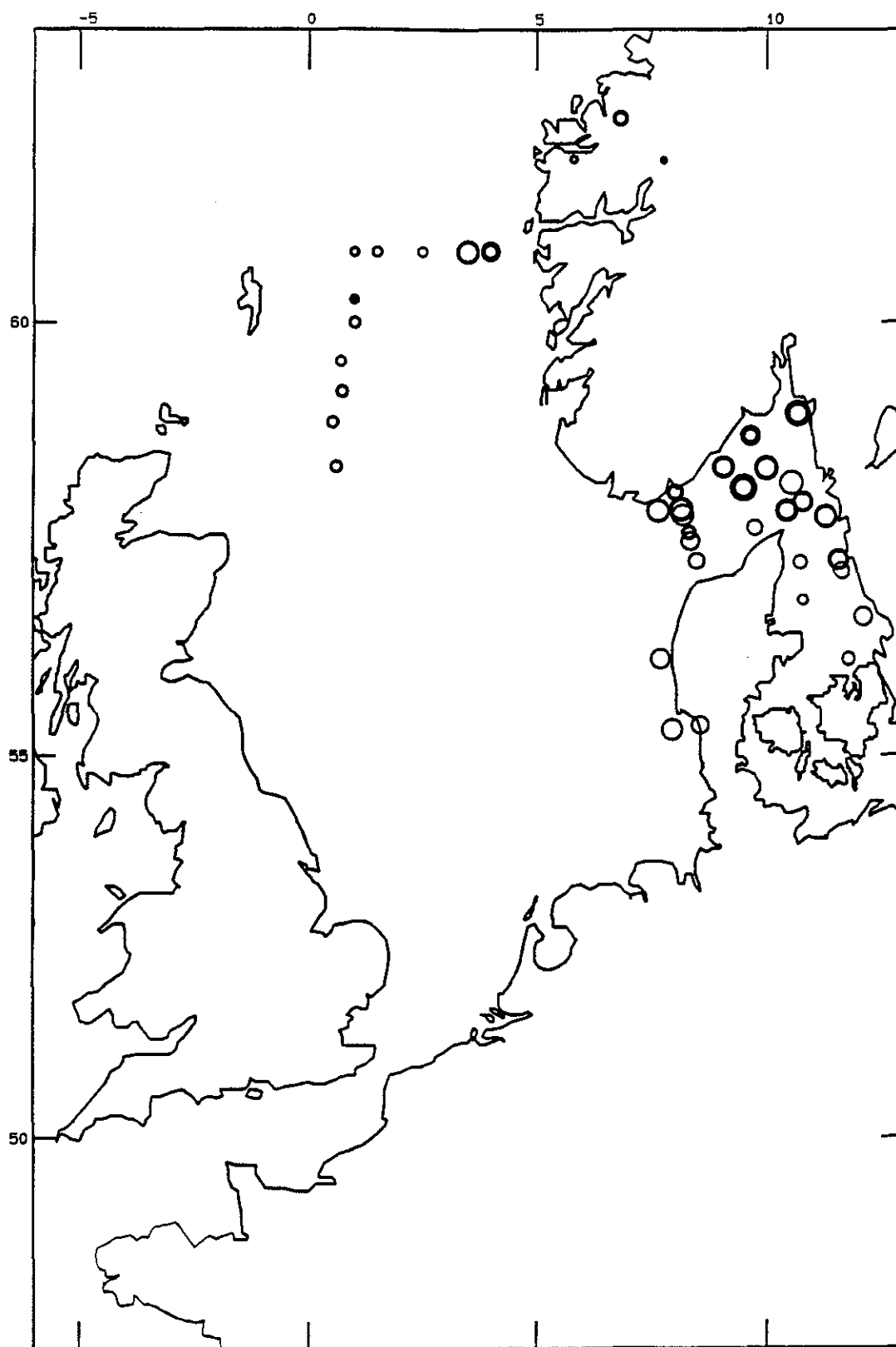


Figure 5.5.1.5 The distribution of arsenic/aluminium ratios in North Sea sediments $< 2000 \mu\text{m}$, with aluminium $\geq 1\%$ (circle area is proportional to value).

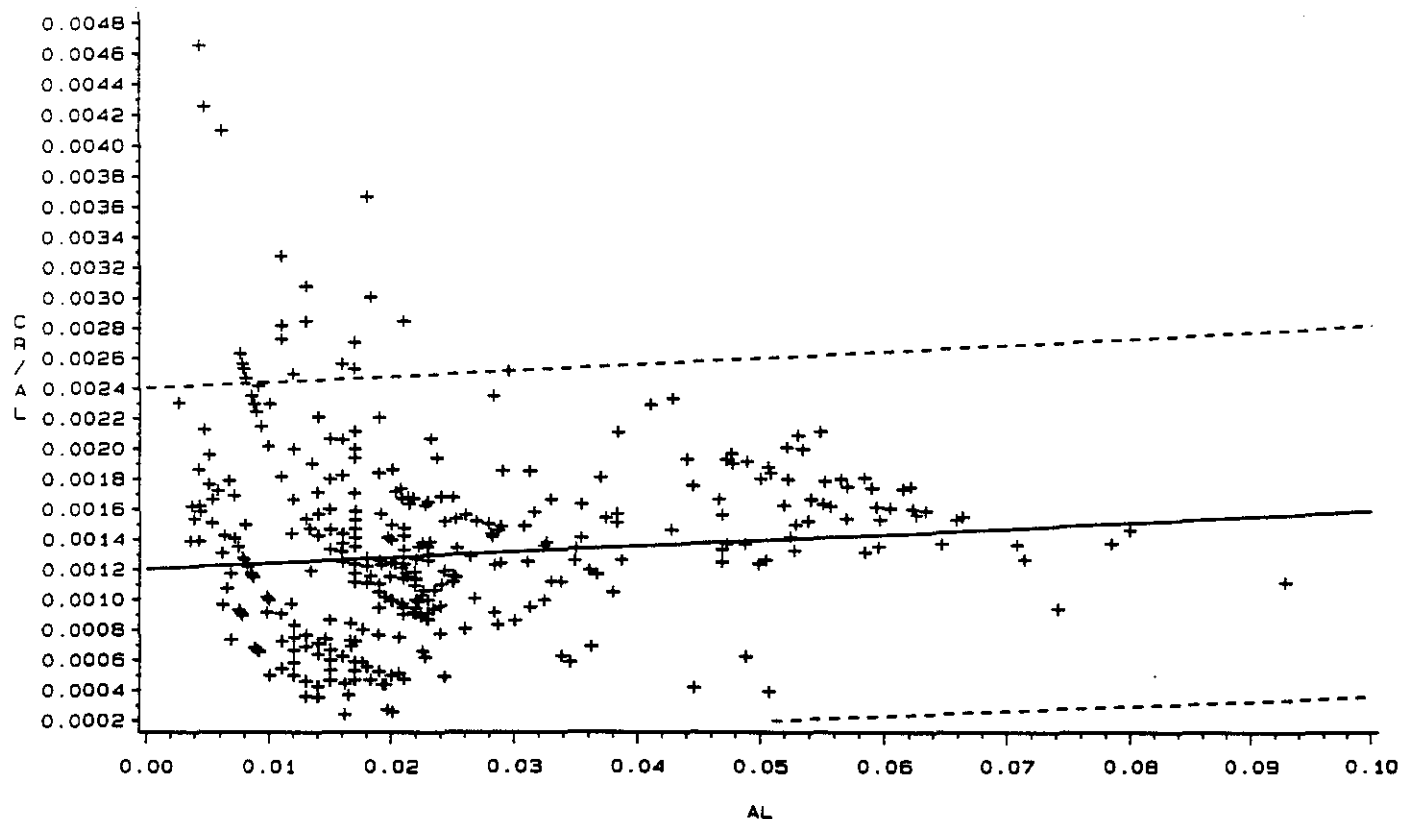


Figure 5.5.2.1 Regression of Cr/Al vs. Al (in g g⁻¹).

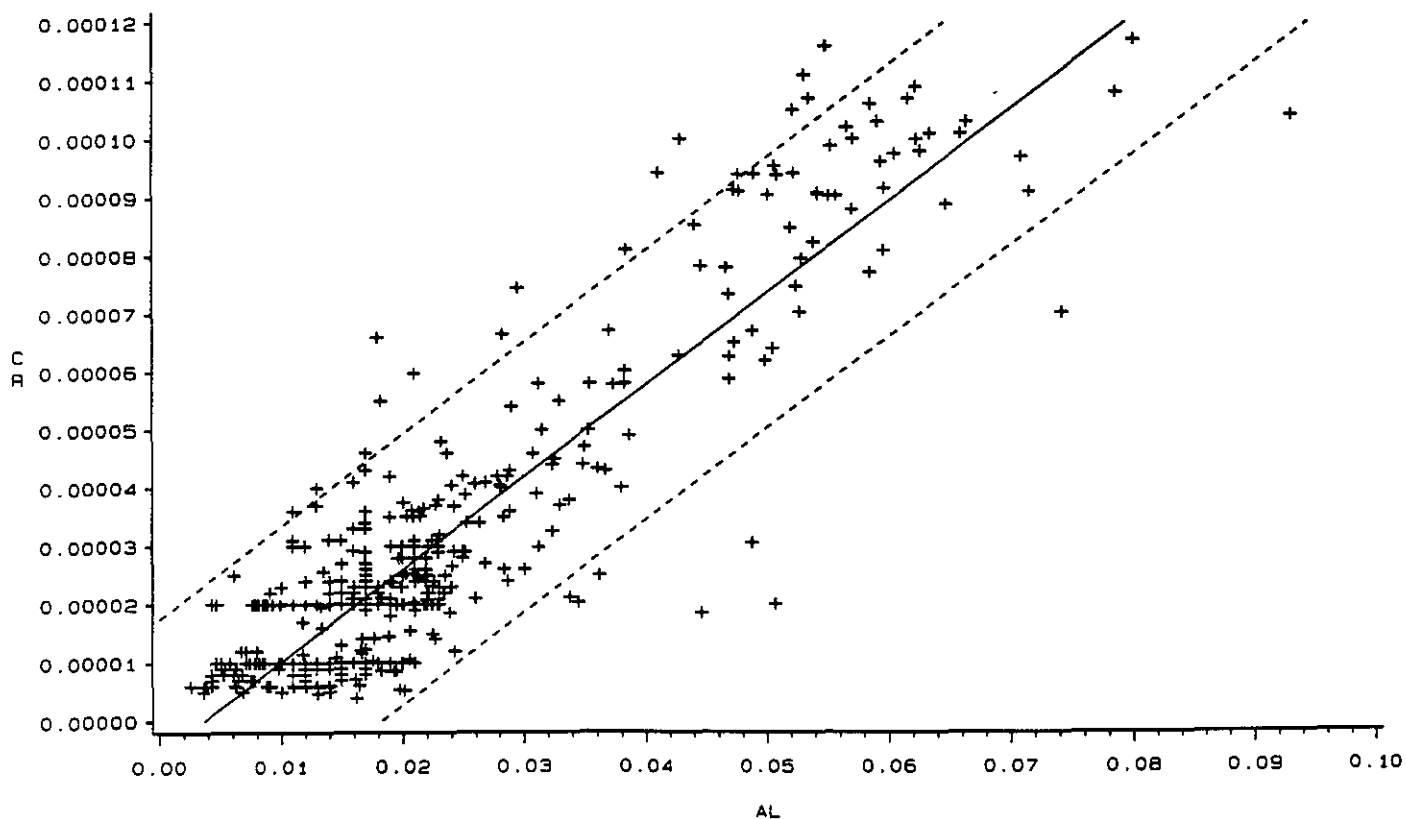


Figure 5.5.2.2 Regression of Cr vs. Al (both in g g⁻¹).

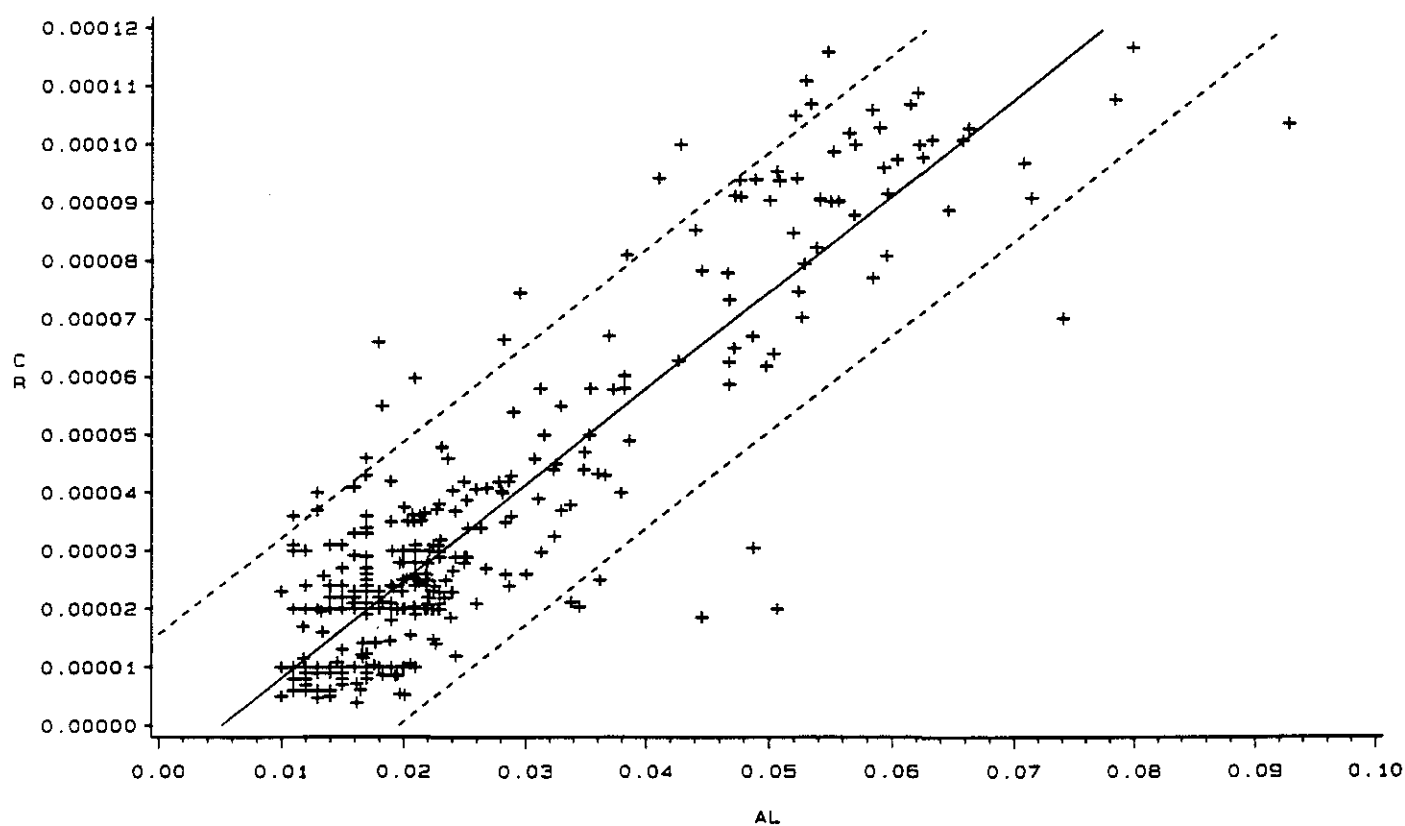


Figure 5.5.2.3 Regression of Cr vs. Al (both in g g^{-1}), for $\text{Al} \geq 1\%$.

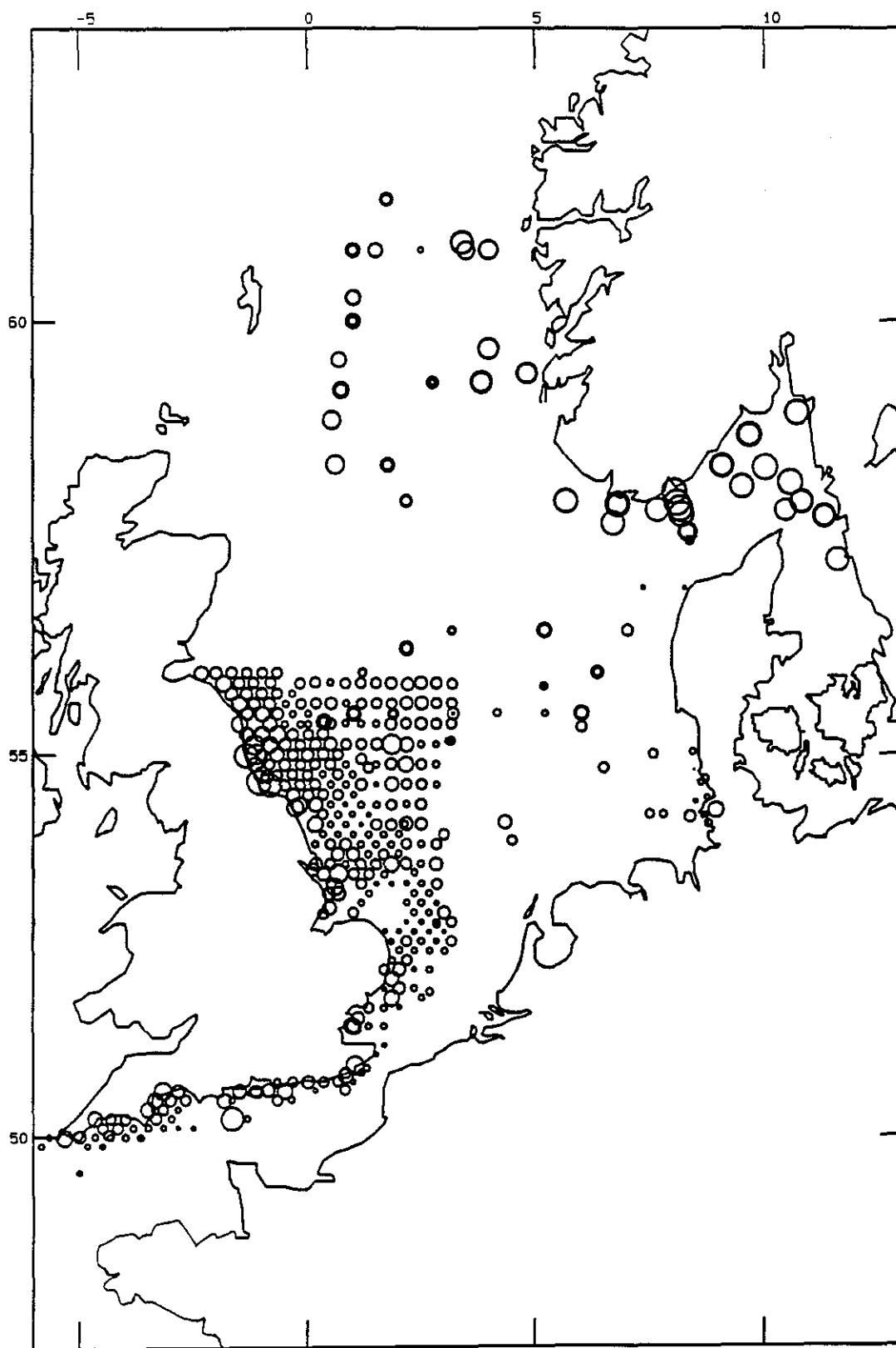


Figure 5.5.2.4 The distribution of chromium concentrations in North Sea sediments $< 2000 \mu\text{m}$ (circle area is proportional to value). The maximum concentration is 117 mg kg^{-1} .

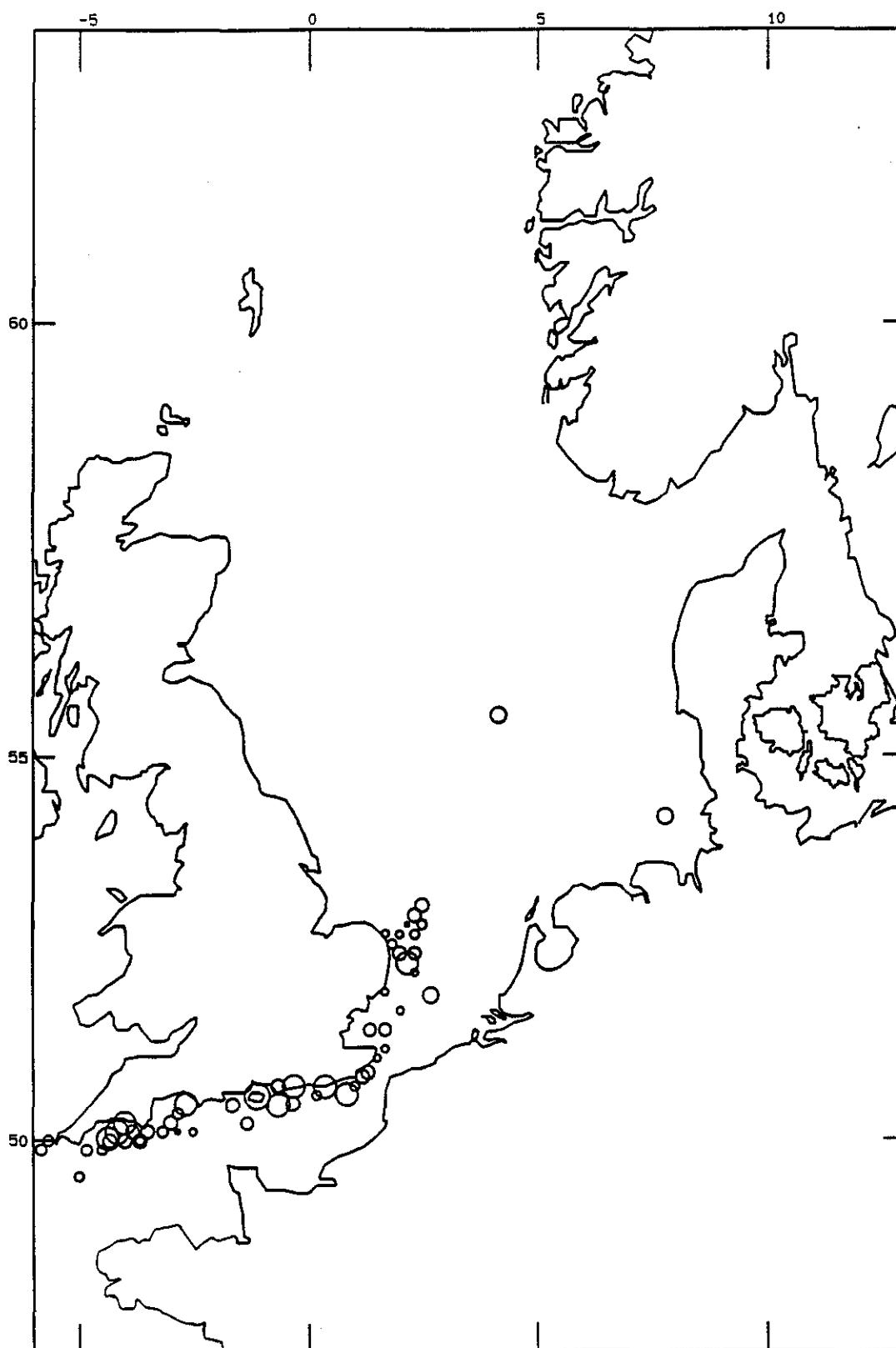


Figure 5.5.2.5 The distribution of chromium concentrations in North Sea sediments $< 2000 \mu\text{m}$, with aluminium $< 1\%$ (circle area is proportional to value). The maximum concentration is 41 mg kg^{-1} .

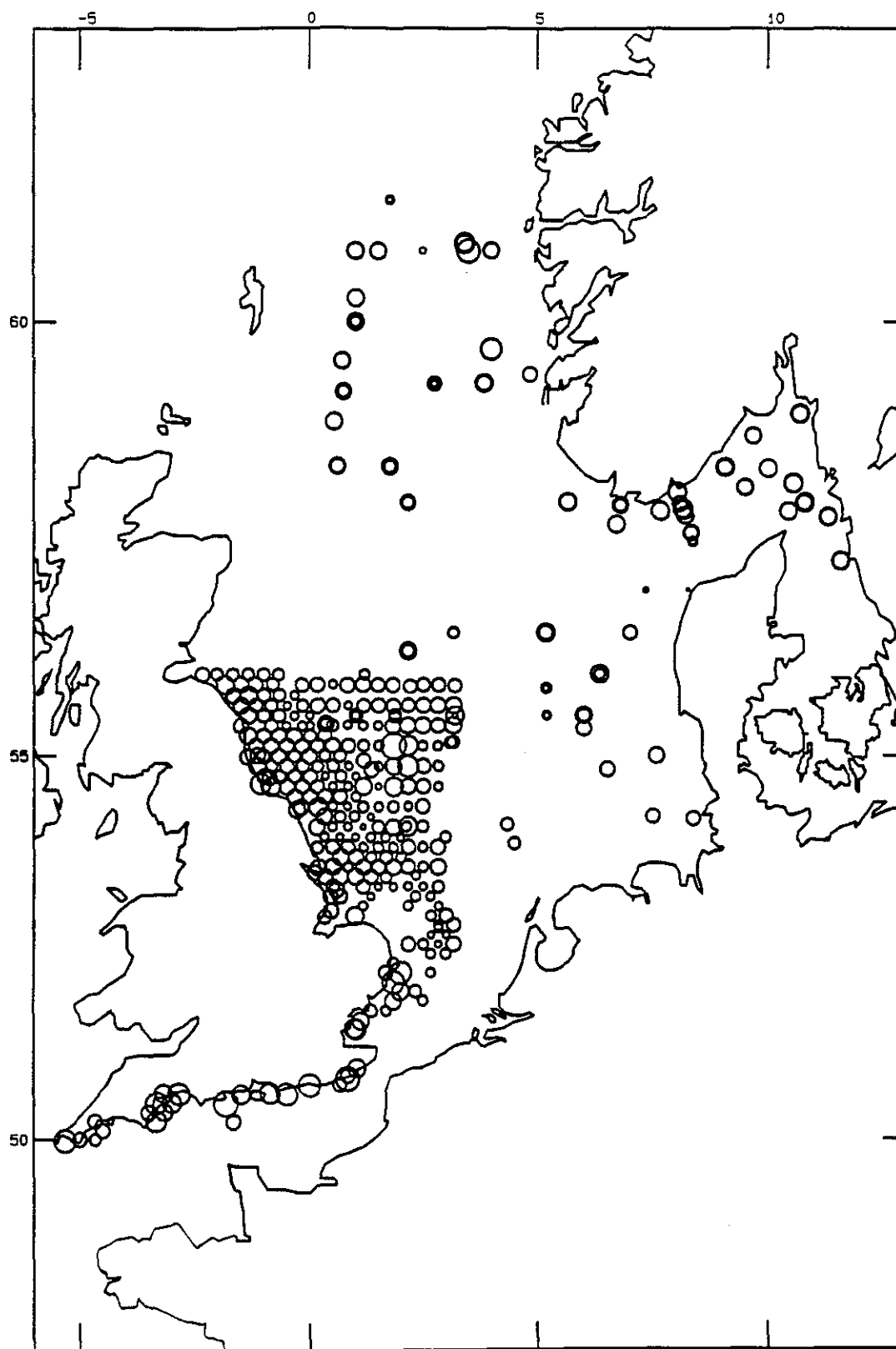


Figure 5.5.2.6 The distribution of chromium/aluminium ratios in North Sea sediments $< 2000 \mu\text{m}$, with aluminium $\geq 1\%$ (circle area is proportional to value).

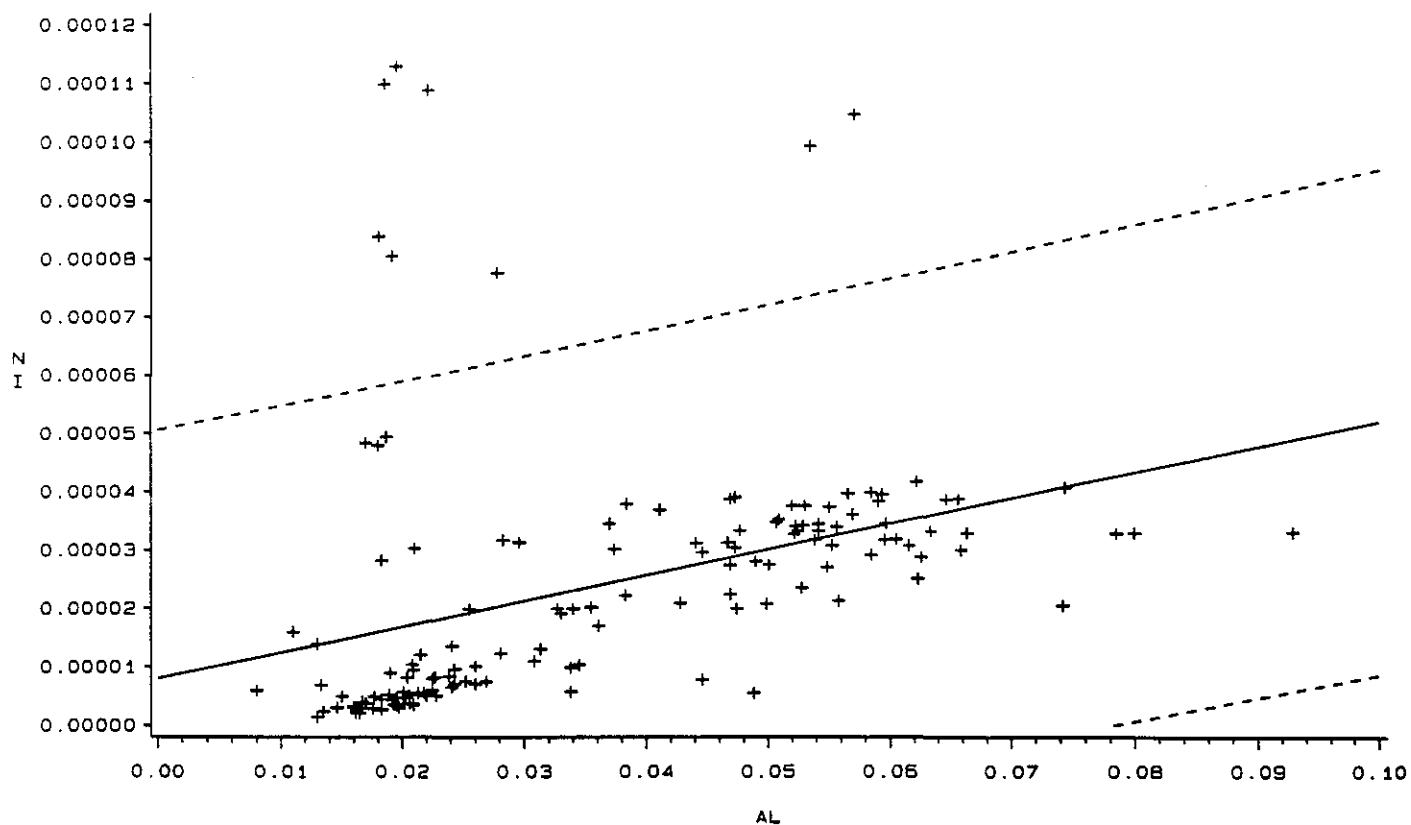


Figure 5.5.3.1 Regression of Ni vs. Al (both in g g^{-1}).

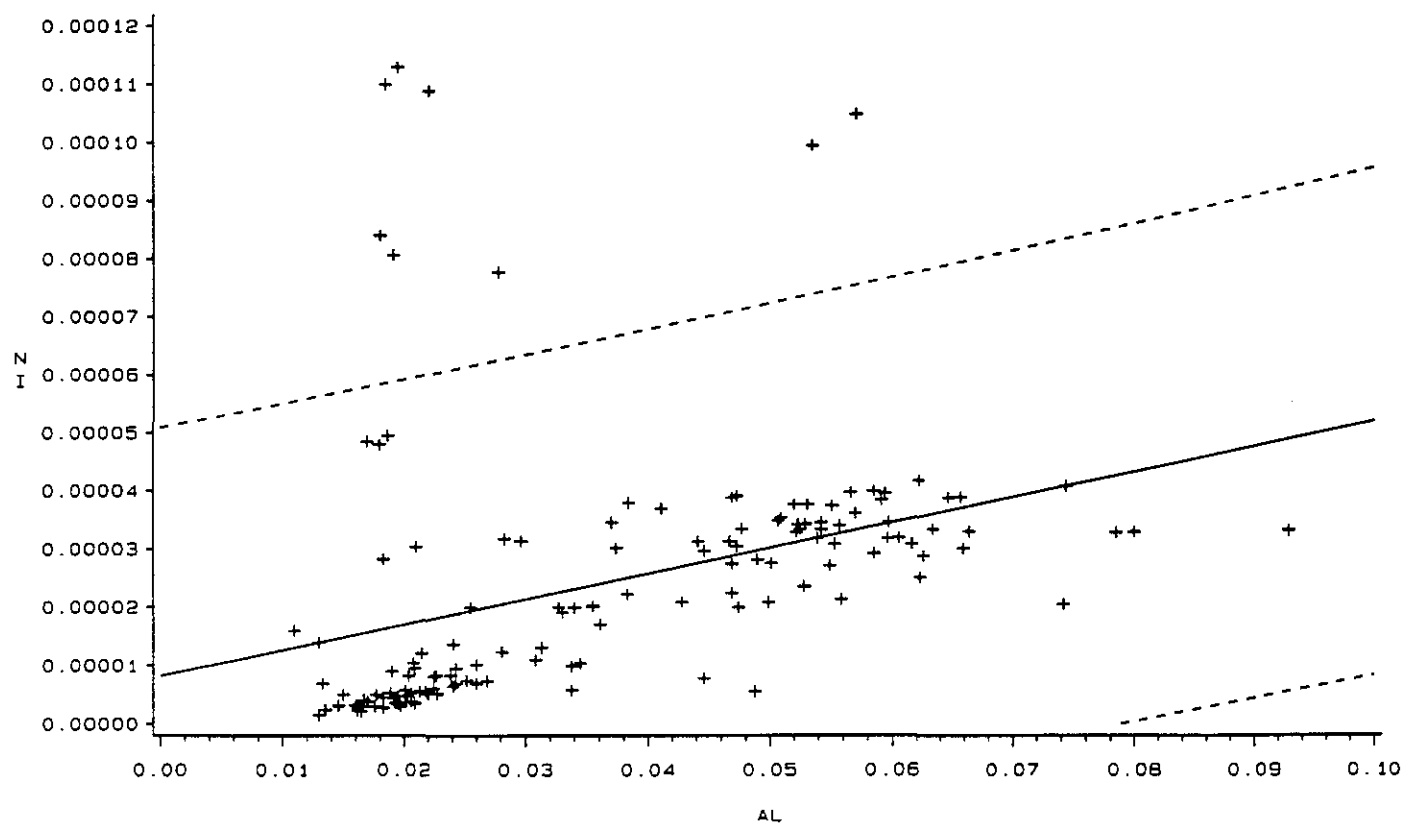


Figure 5.5.3.2 Regression of Ni vs. Al (both in g g^{-1}), for Al $\geq 1\%$.

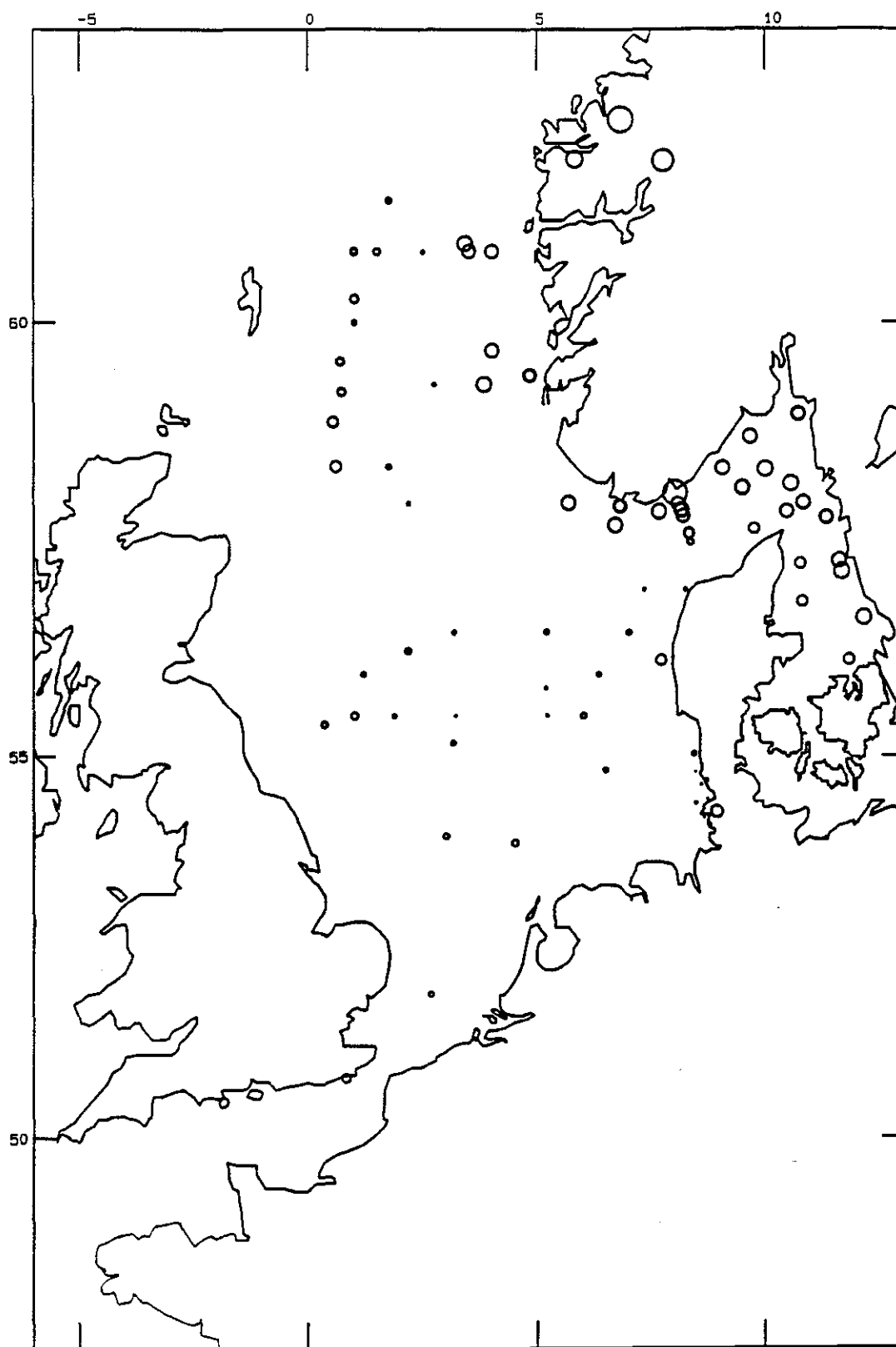


Figure 5.5.3.3 The distribution of nickel concentrations in North Sea sediments $< 2000 \mu\text{m}$ (circle area is proportional to value). The maximum concentration is 113 mg kg^{-1} .

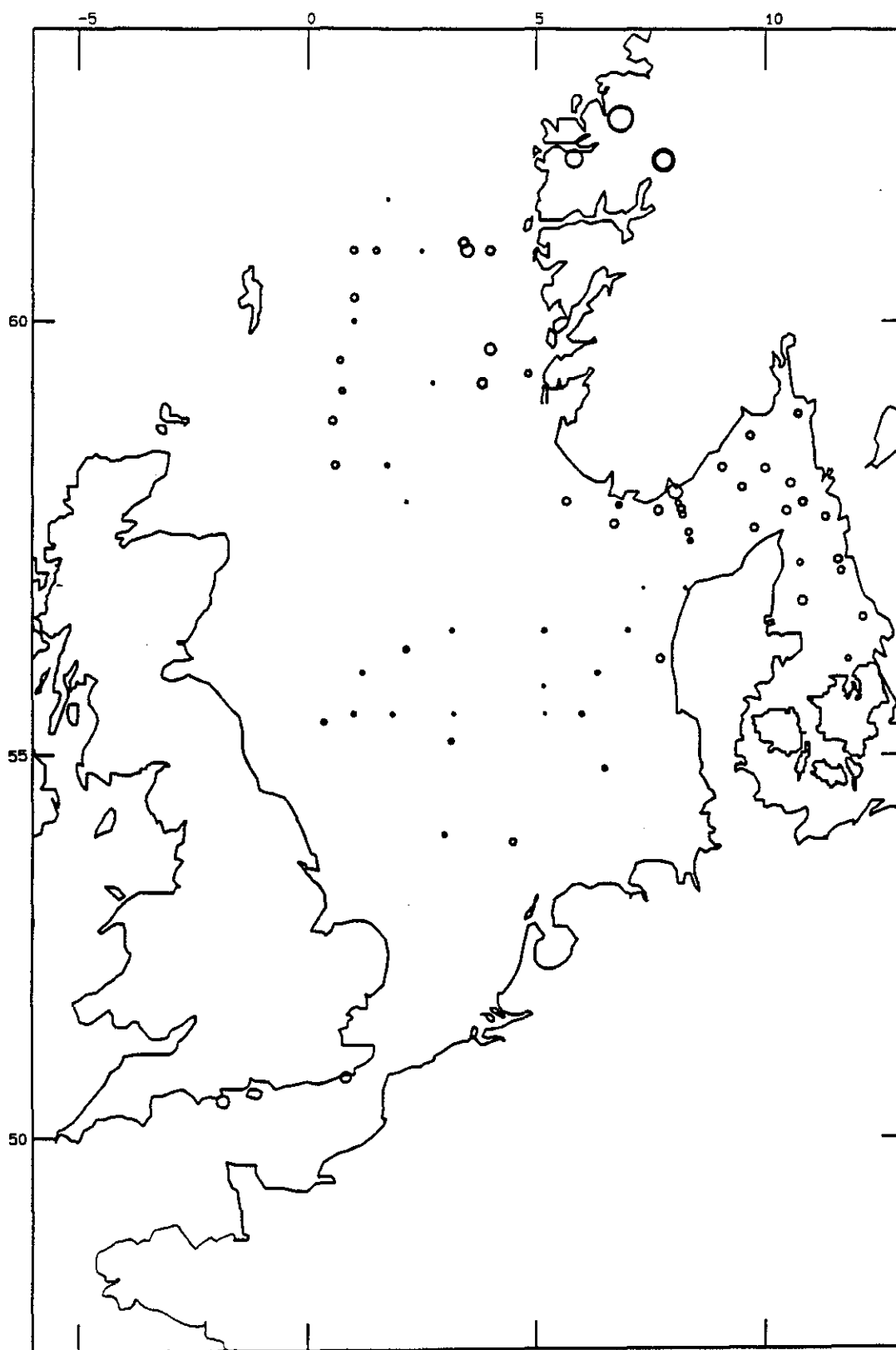


Figure 5.5.3.4 The distribution of nickel/aluminium ratios in North Sea sediments $< 2000 \mu\text{m}$, with aluminium $\geq 1\%$ (circle area is proportional to value).

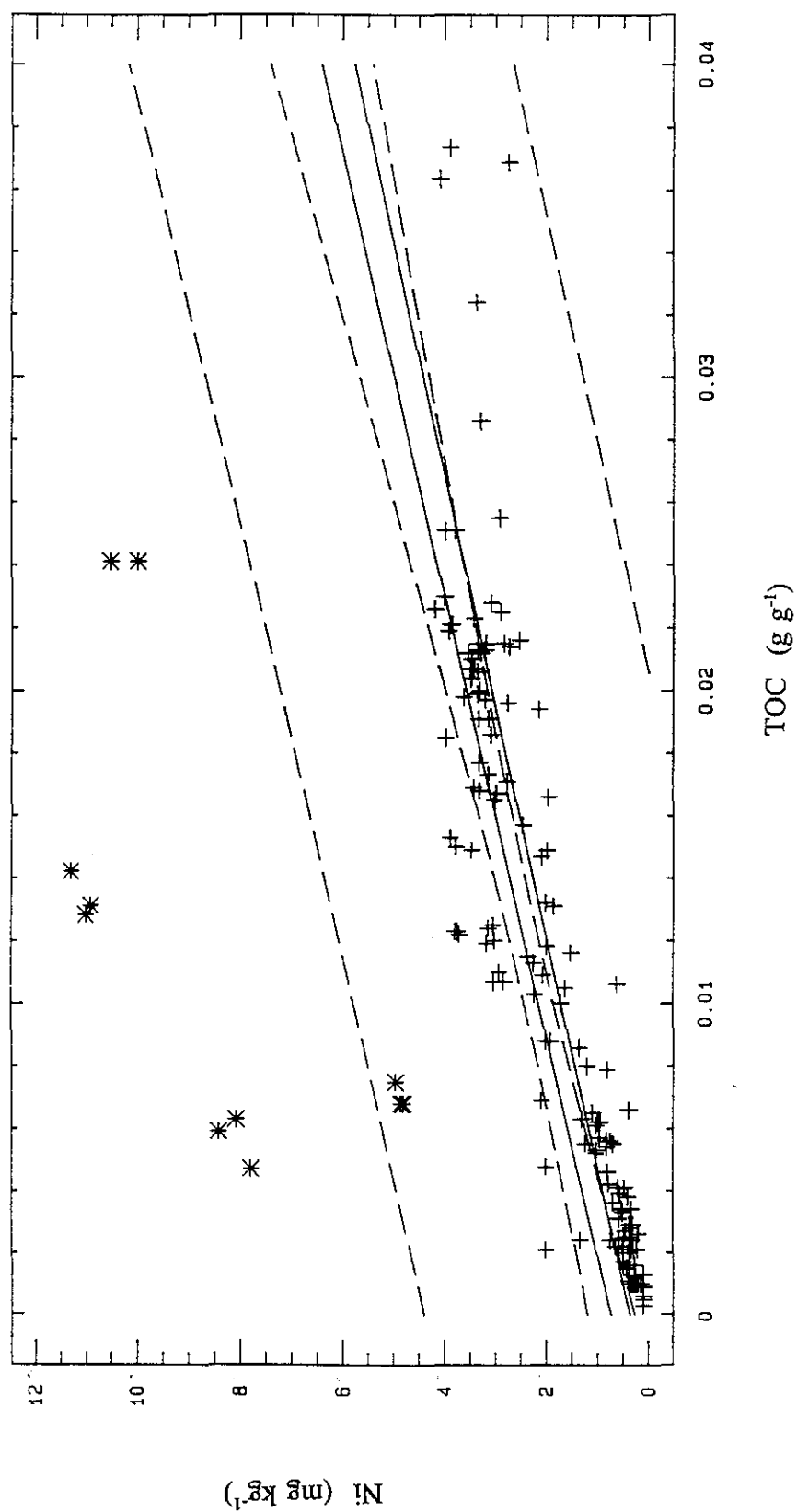


Figure 5.5.3.5 Regression of Ni vs. TOC.

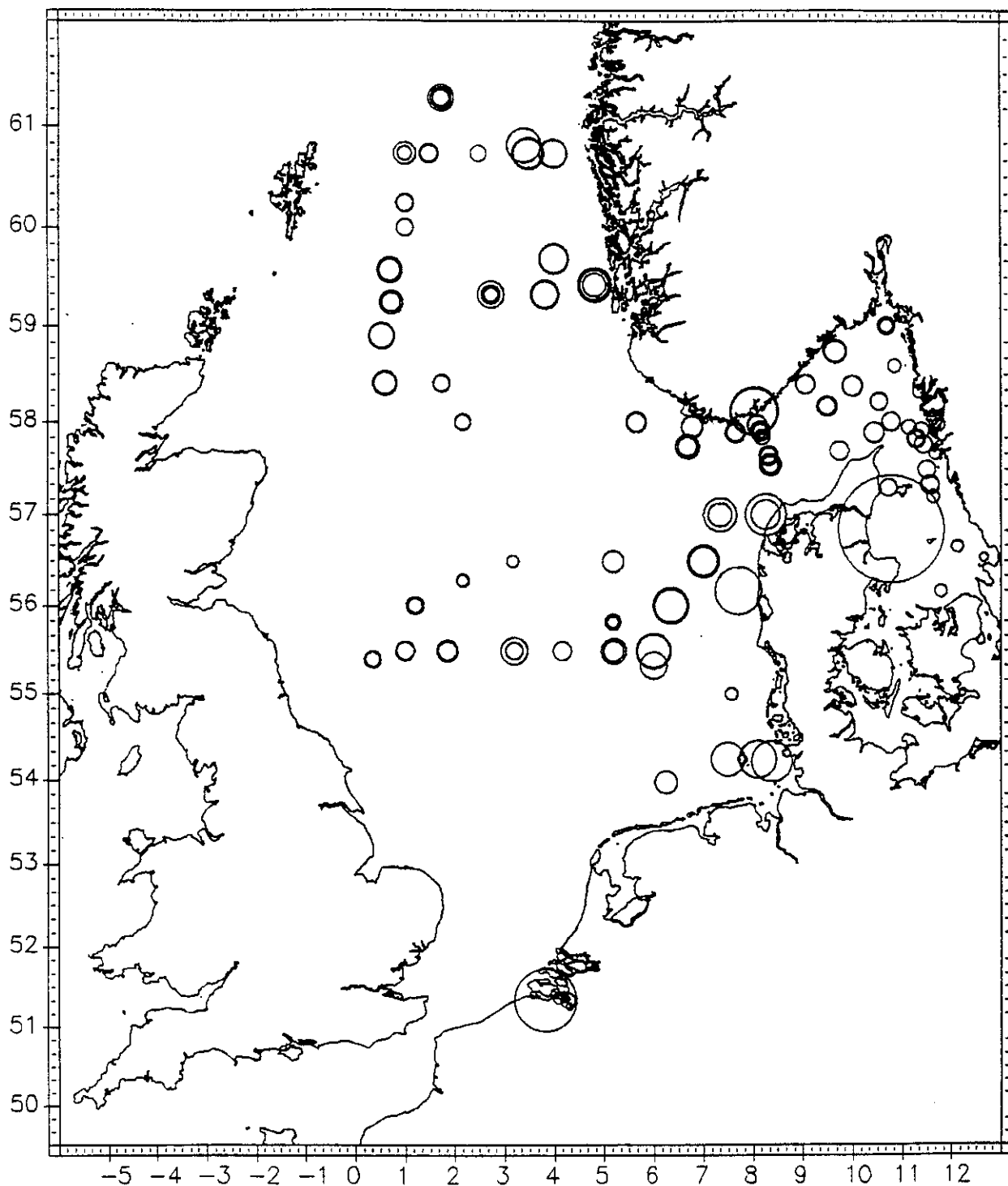


Figure 5.5.3.6 The distribution of nickel/total organic carbon ratios in North Sea sediments $<2000 \mu\text{m}$ (circle diameter is proportional to value).

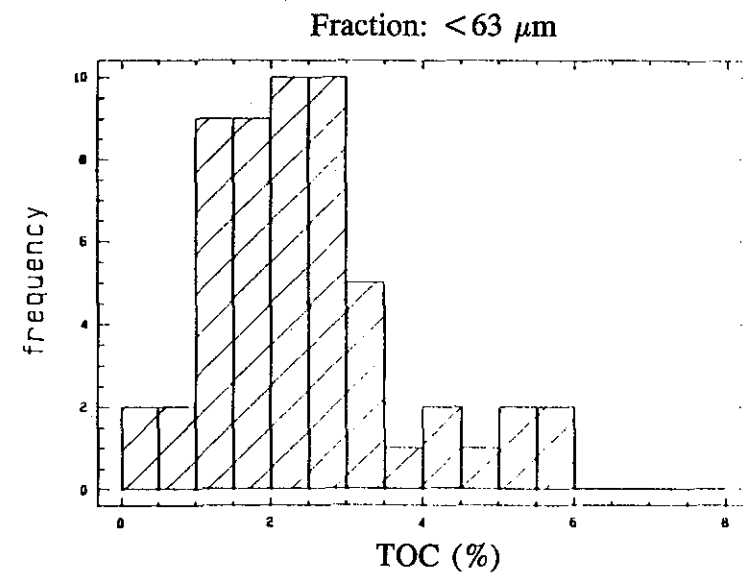
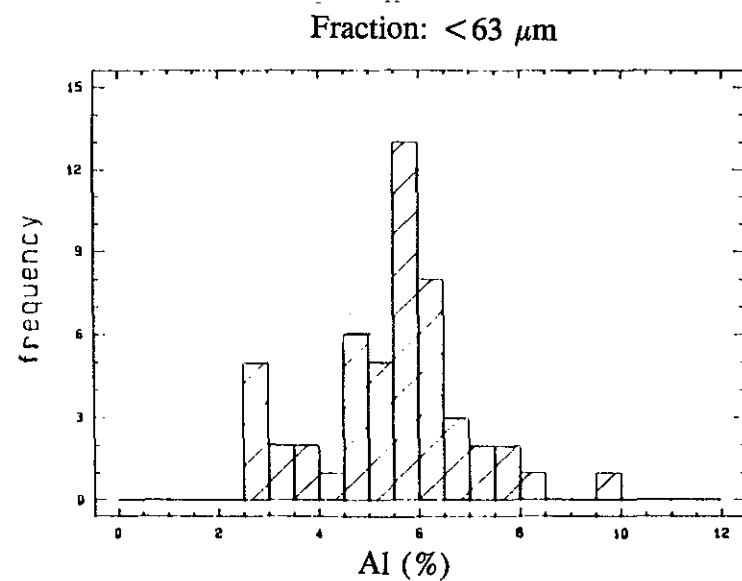
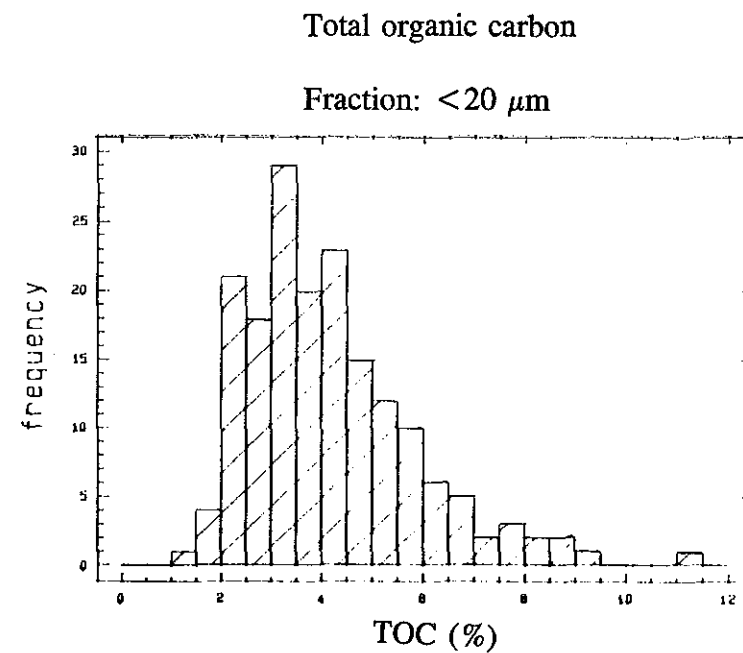
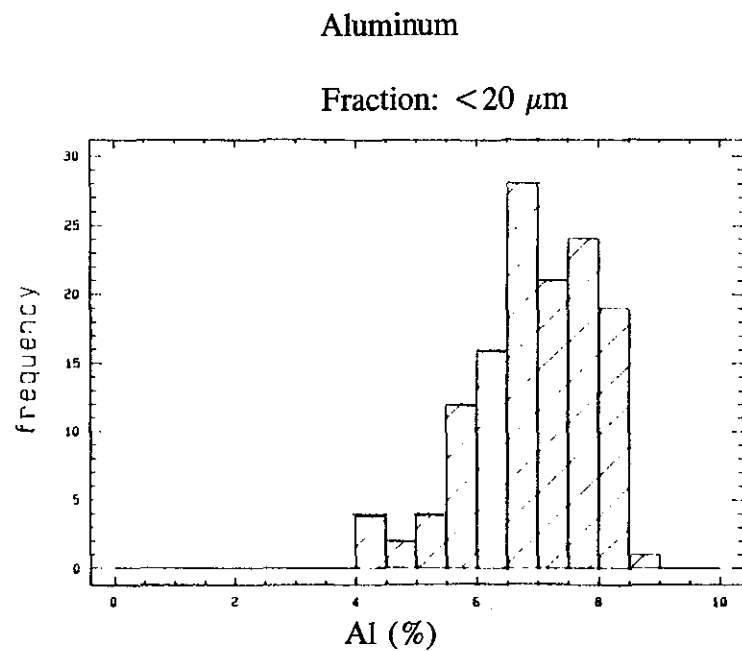
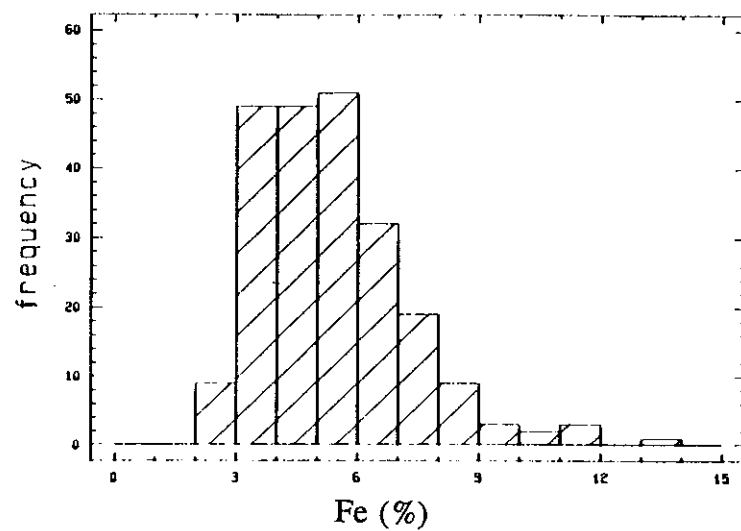


Figure 6.2.1 Frequency distributions of metals and total organic carbon (TOC) in the <20 μm and <63 μm sediment size fractions.

Iron

Fraction: $<20\ \mu\text{m}$ 

Manganese

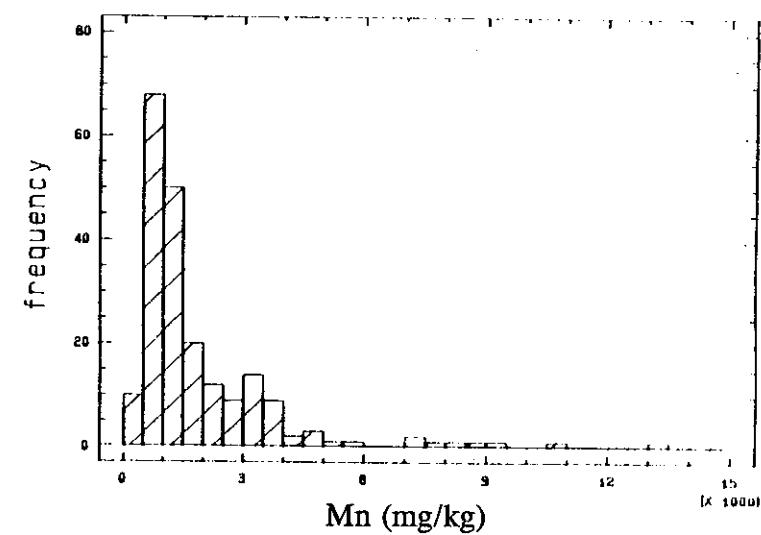
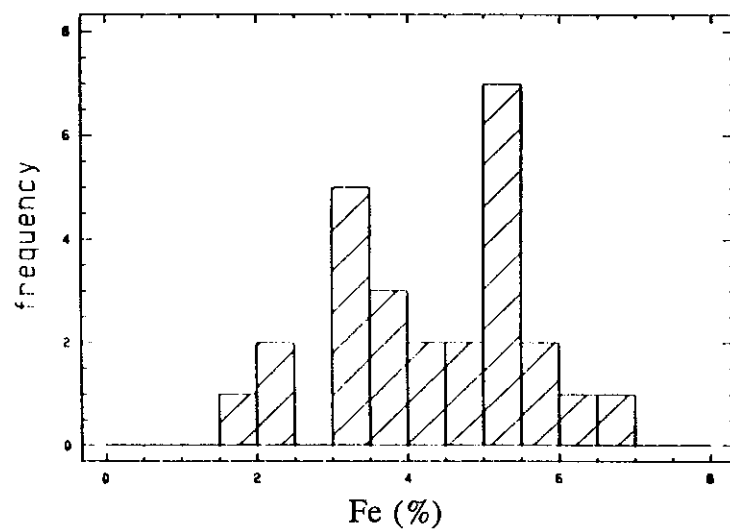
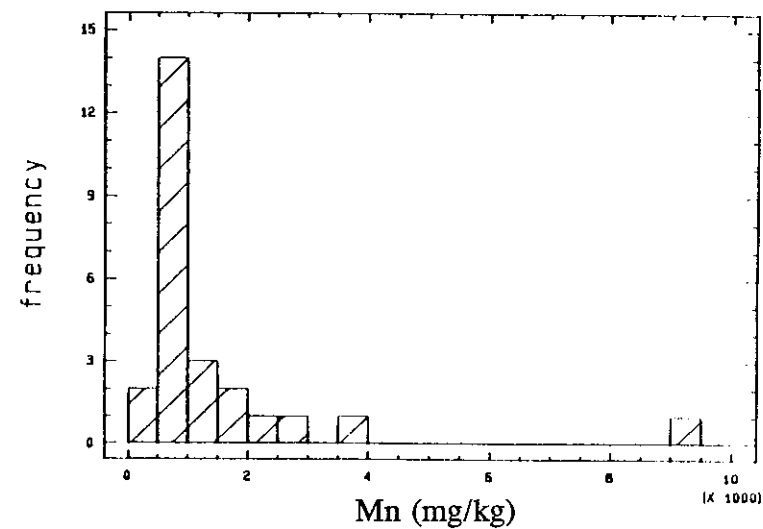
Fraction: $<20\ \mu\text{m}$ Fraction: $<63\ \mu\text{m}$ Fraction: $<63\ \mu\text{m}$ 

Figure 6.2.1 (cont'd) Frequency distributions of metals and total organic carbon (TOC) in the $<20\ \mu\text{m}$ and $<63\ \mu\text{m}$ sediment size fractions.

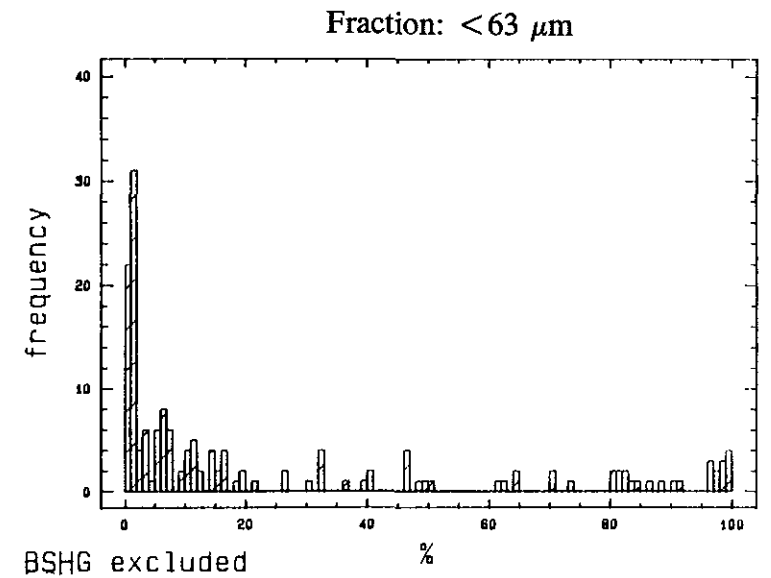
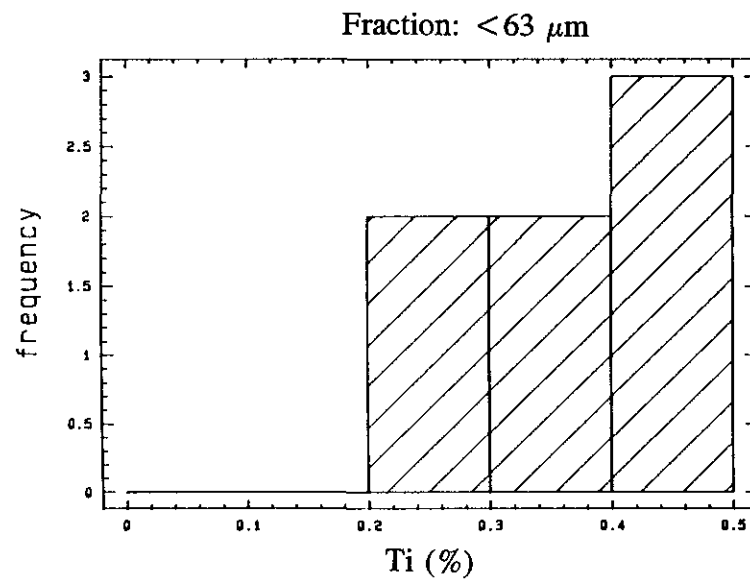
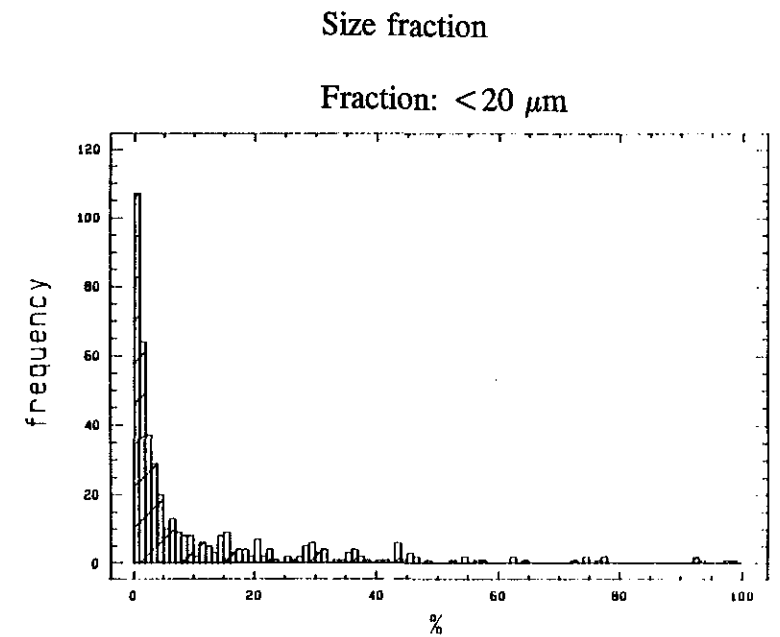
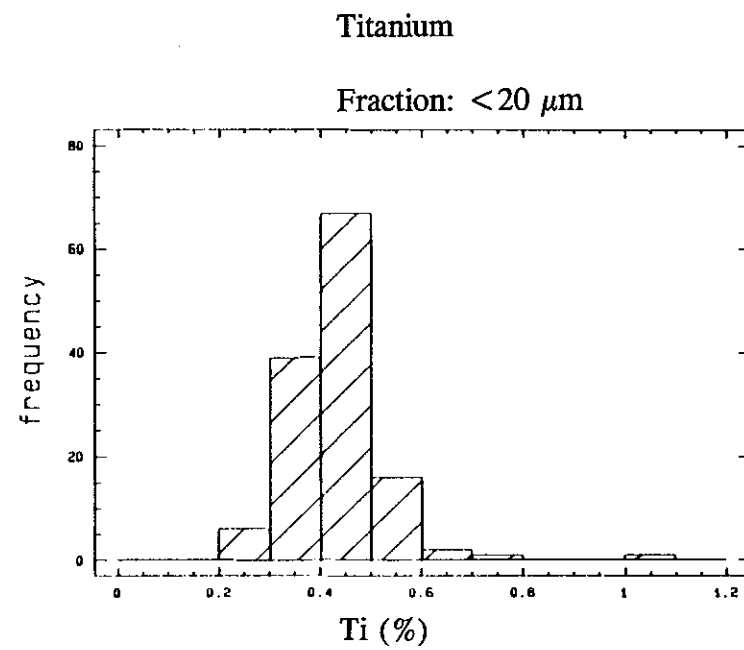


Figure 6.2.1 (Cont'd) Frequency distributions of metals and total organic carbon (TOC) in the <20 μm and <63 μm sediment size fractions.

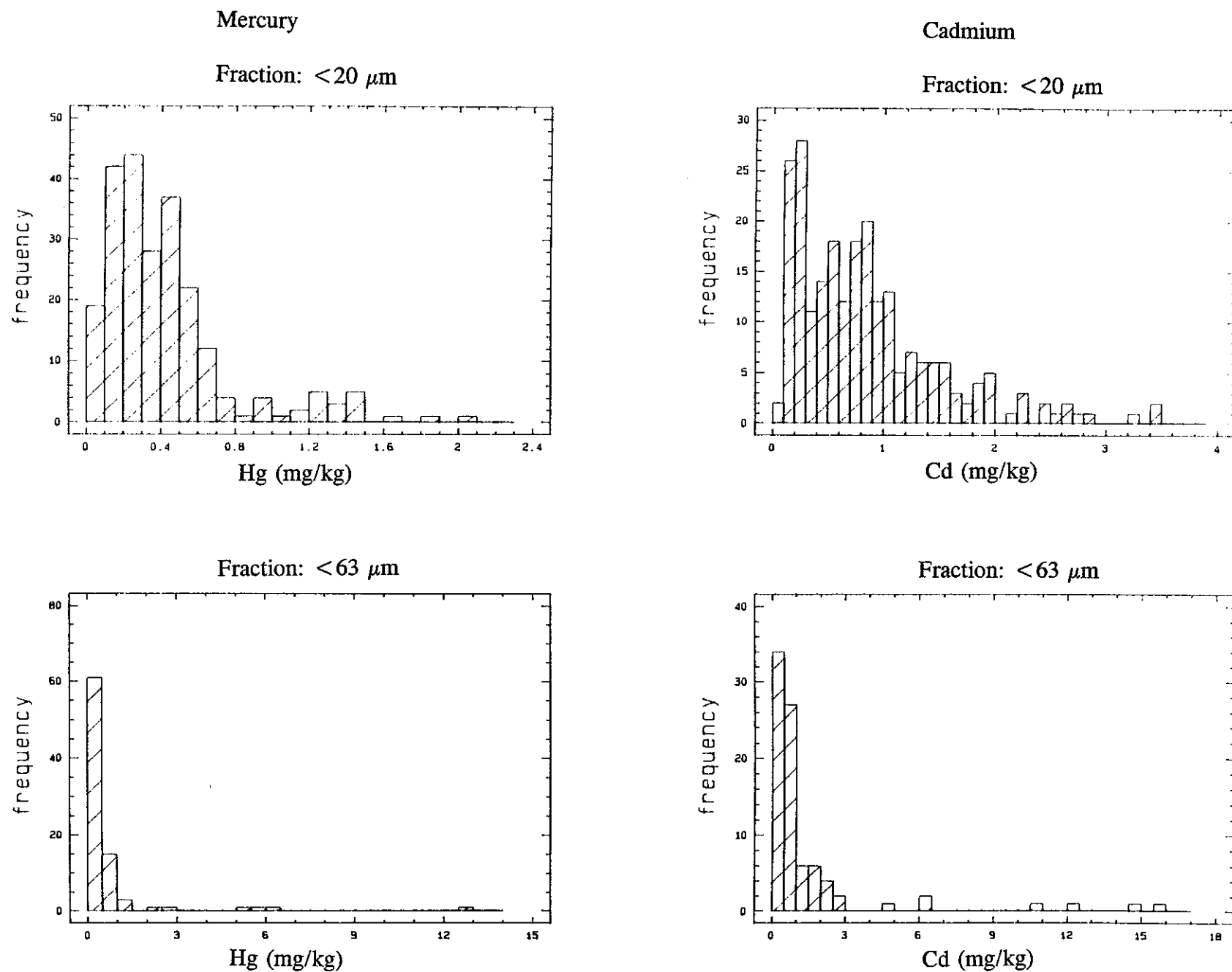


Figure 6.2.1 (Cont'd) Frequency distributions of metals and total organic carbon (TOC) in the $<20\ \mu\text{m}$ and $<63\ \mu\text{m}$ sediment size fractions.

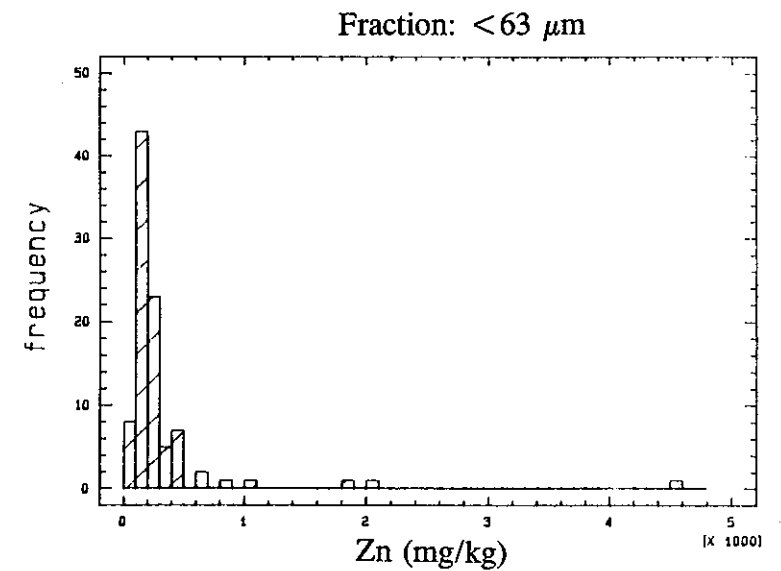
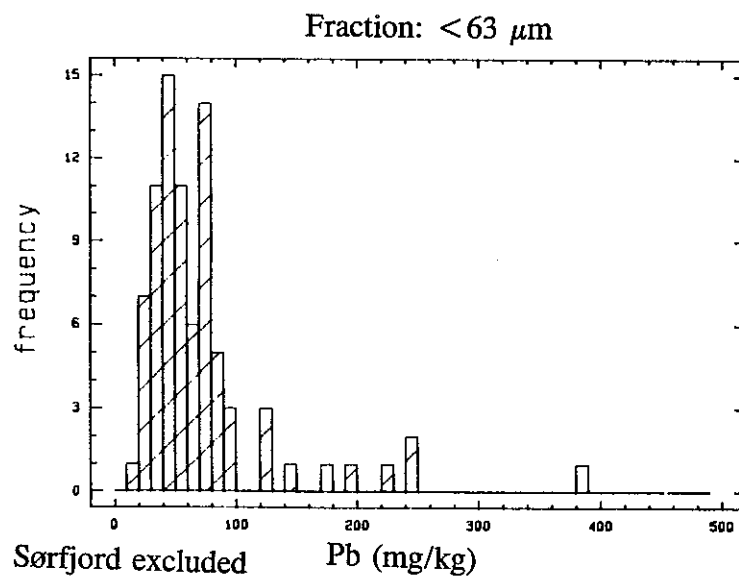
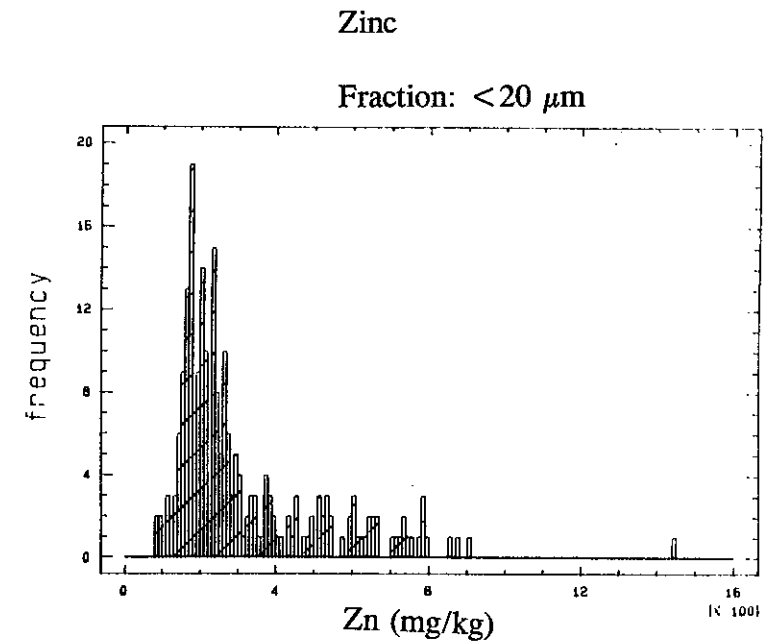
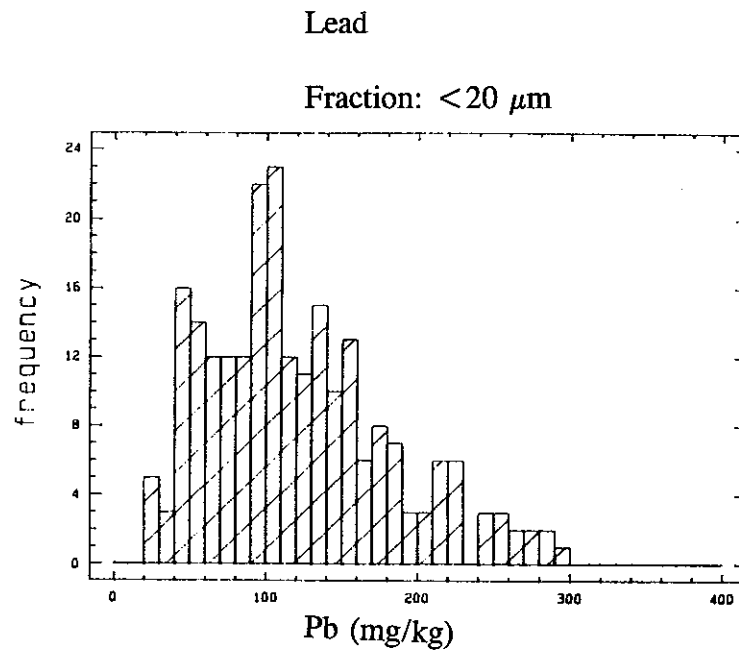


Figure 6.2.1 (Cont'd) Frequency distributions of metals and total organic carbon (TOC) in the <20 μm and <63 μm sediment size fractions.

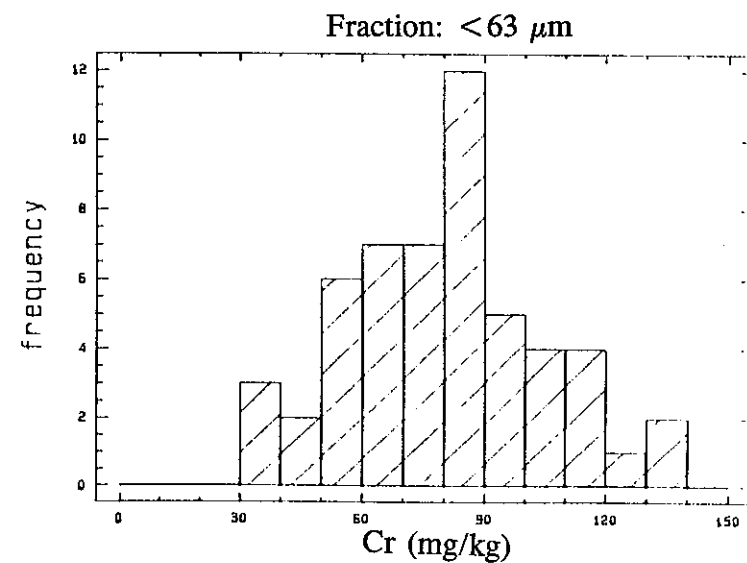
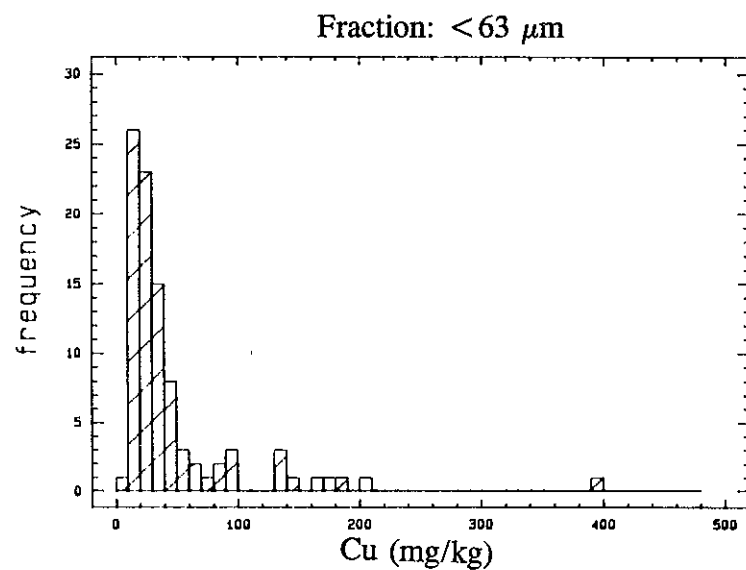
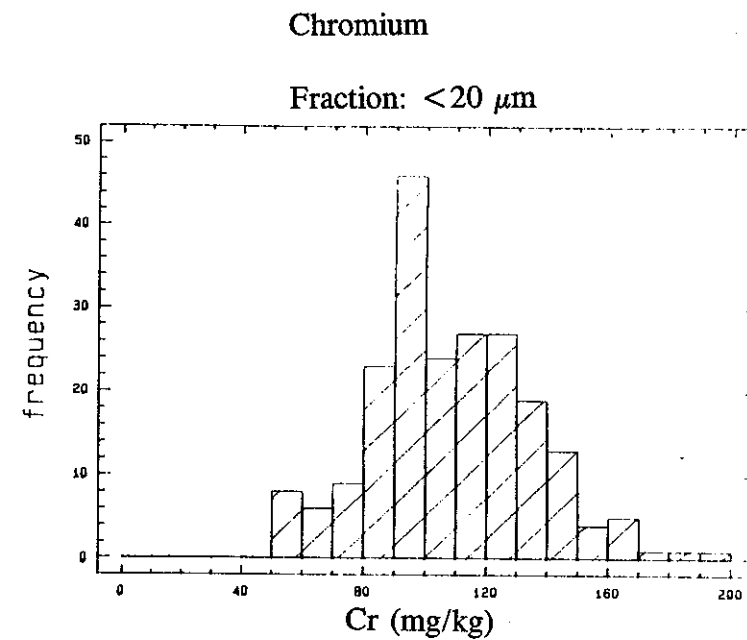
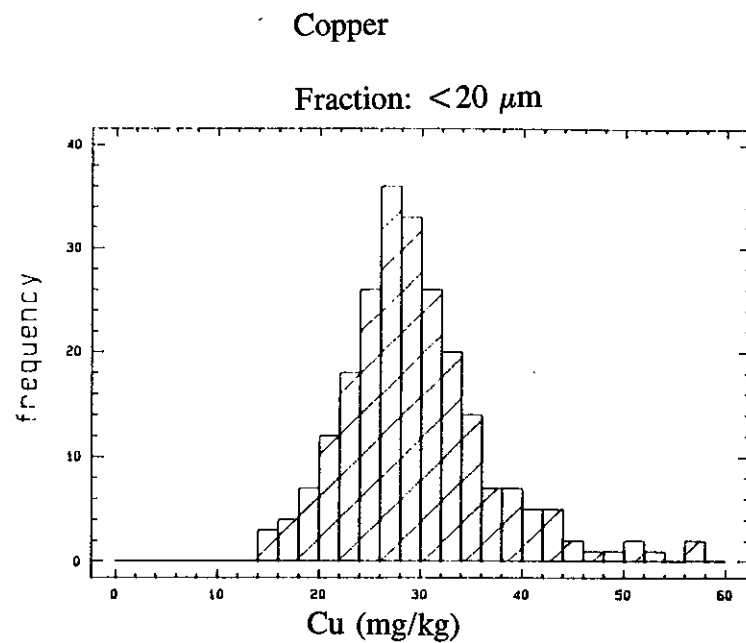
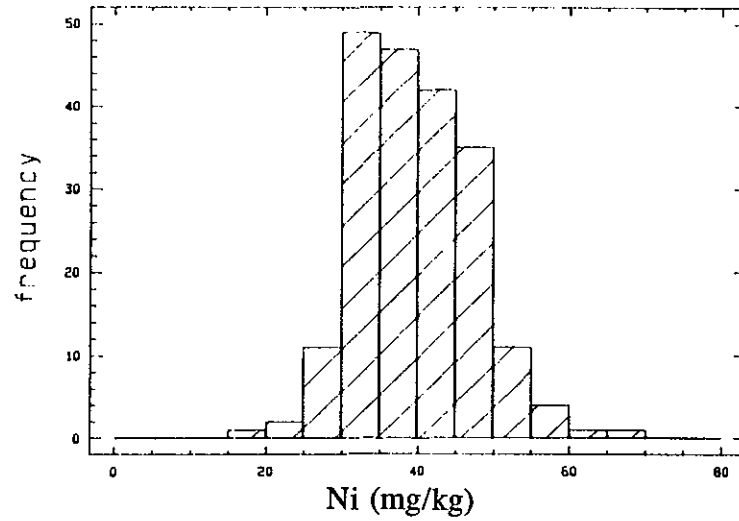


Figure 6.2.1 (Cont'd) Frequency distributions of metals and total organic carbon (TOC) in the $<20\ \mu\text{m}$ and $<63\ \mu\text{m}$ sediment size fractions.

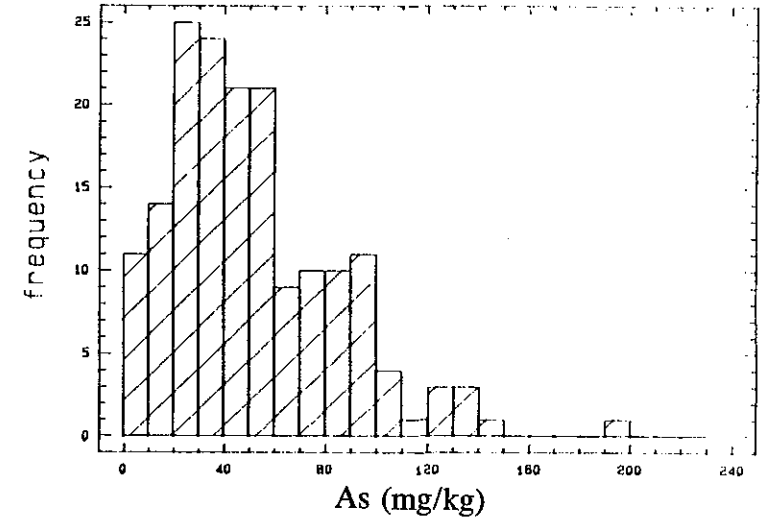
Nickel

Fraction: <20 μm

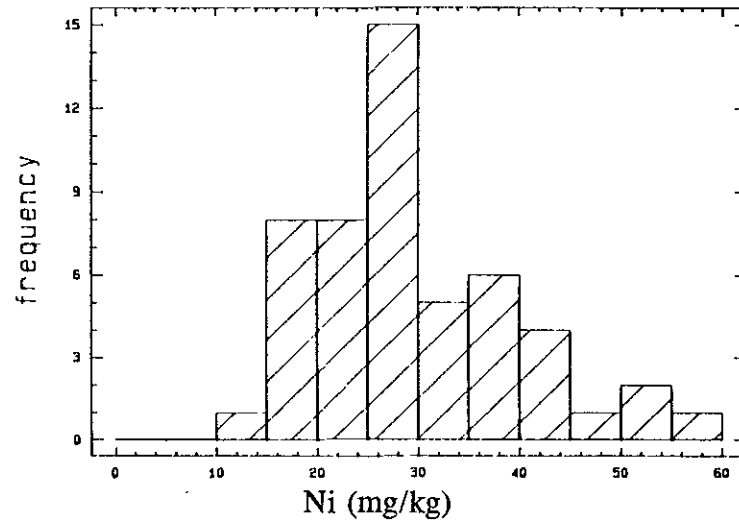


Arsenic

Fraction: <20 μm



Fraction: <63 μm



Fraction: <63 μm

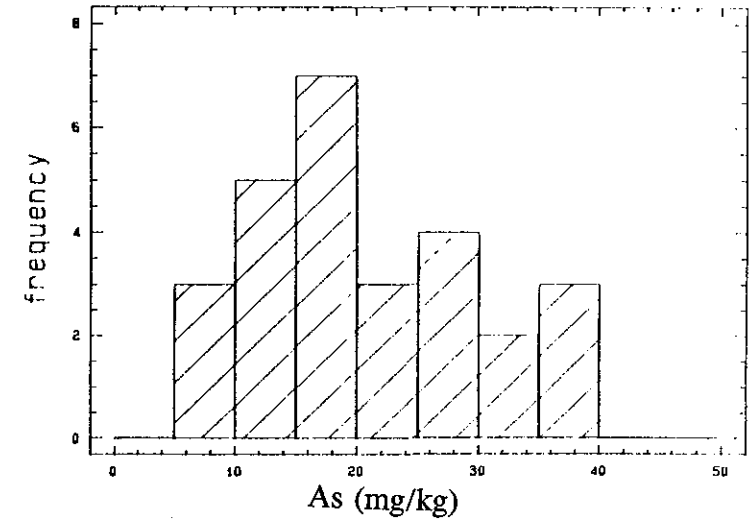


Figure 6.2.1 (Cont'd) Frequency distributions of metals and total organic carbon (TOC) in the <20 μm and <63 μm sediment size fractions.

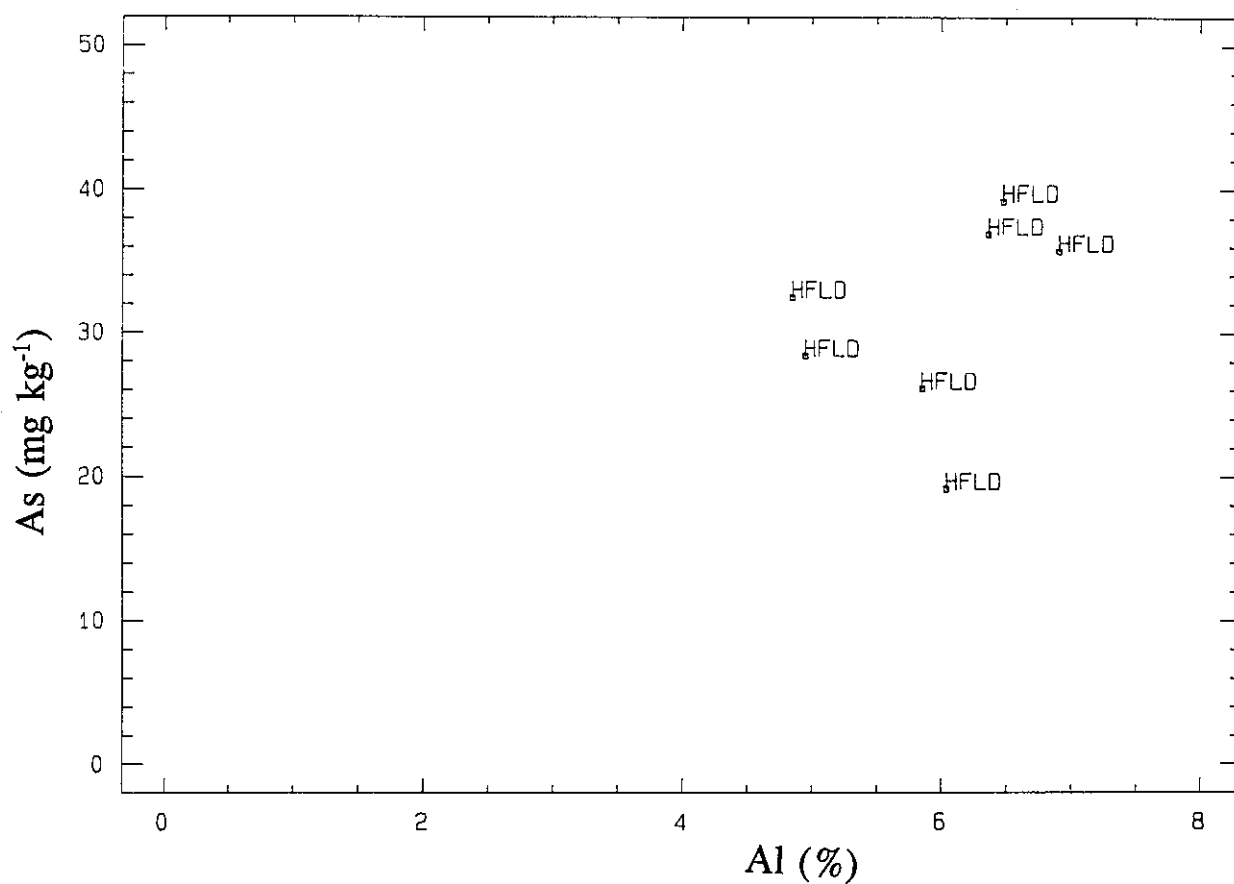


Figure 6.2.2(a) Plot of As vs. Al in fines <63 μm.

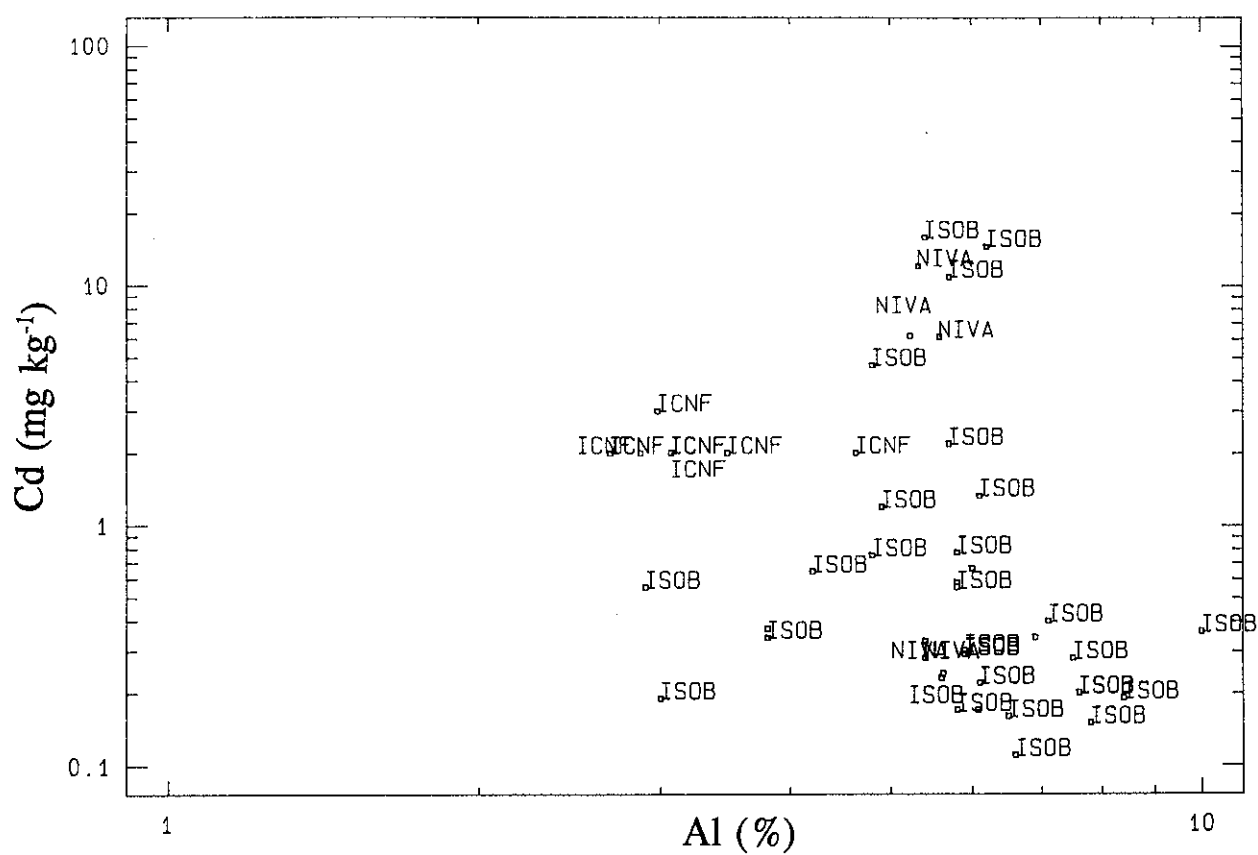


Figure 6.2.2(b) Plot of Cd vs. Al in fines <63 μm.

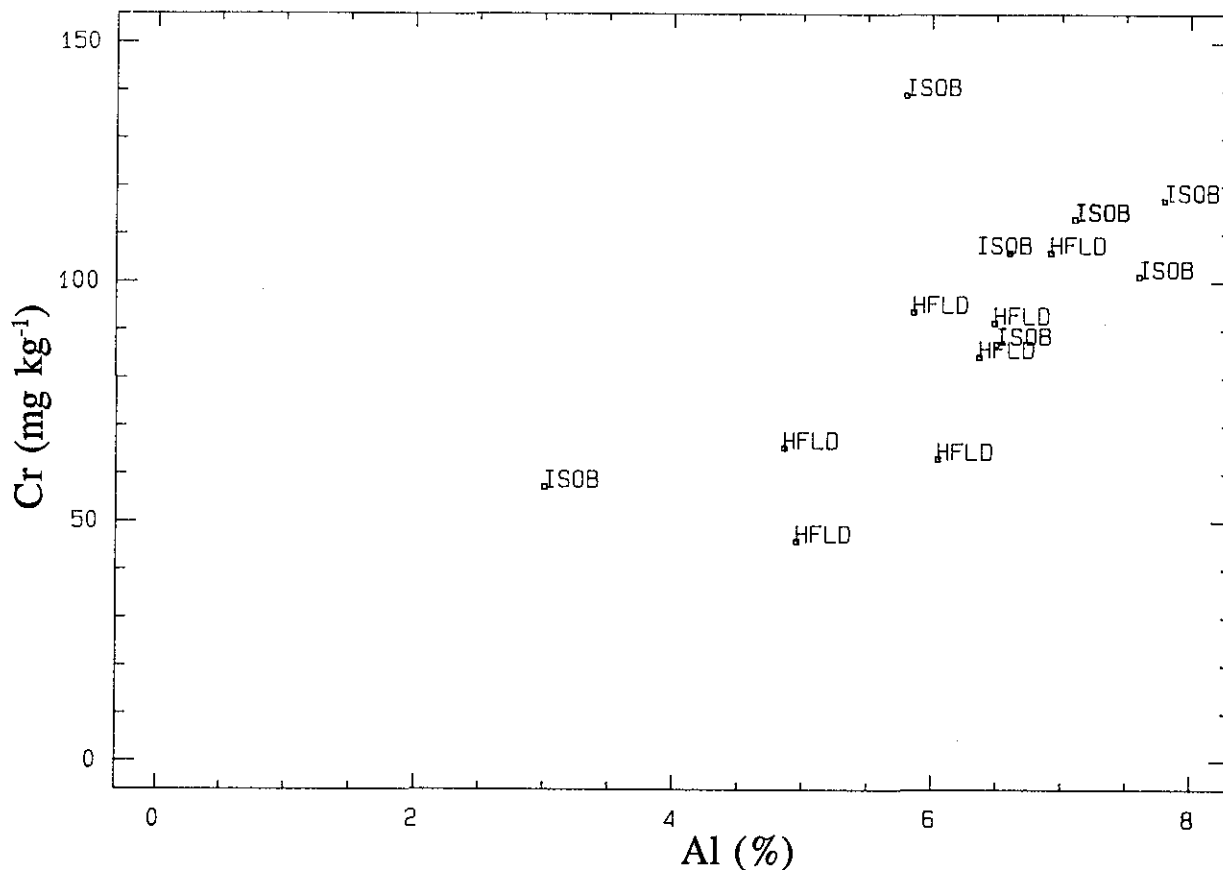


Figure 6.2.2(c) Plot of Cr vs. Al in fines <63 μm .

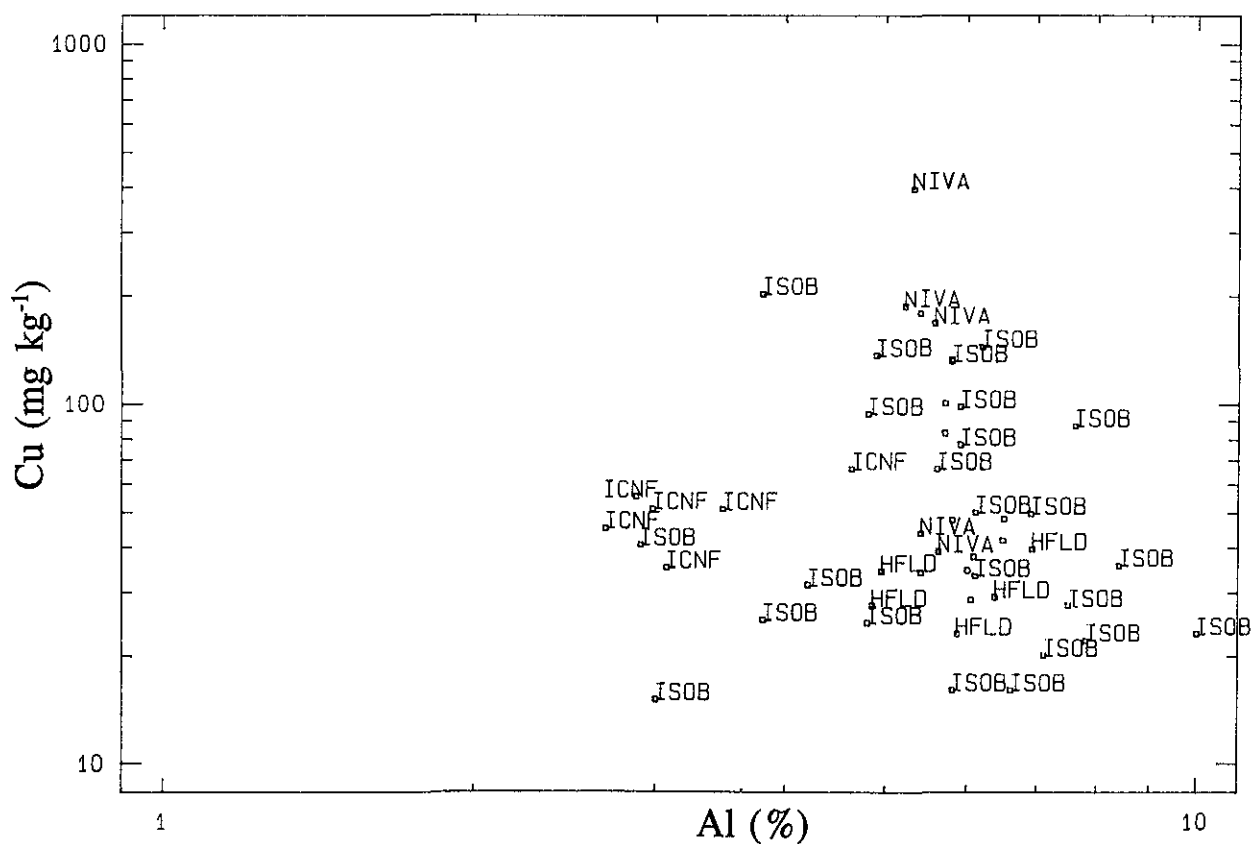


Figure 6.2.2(d) Plot of Cu vs. Al in fines <63 μm .

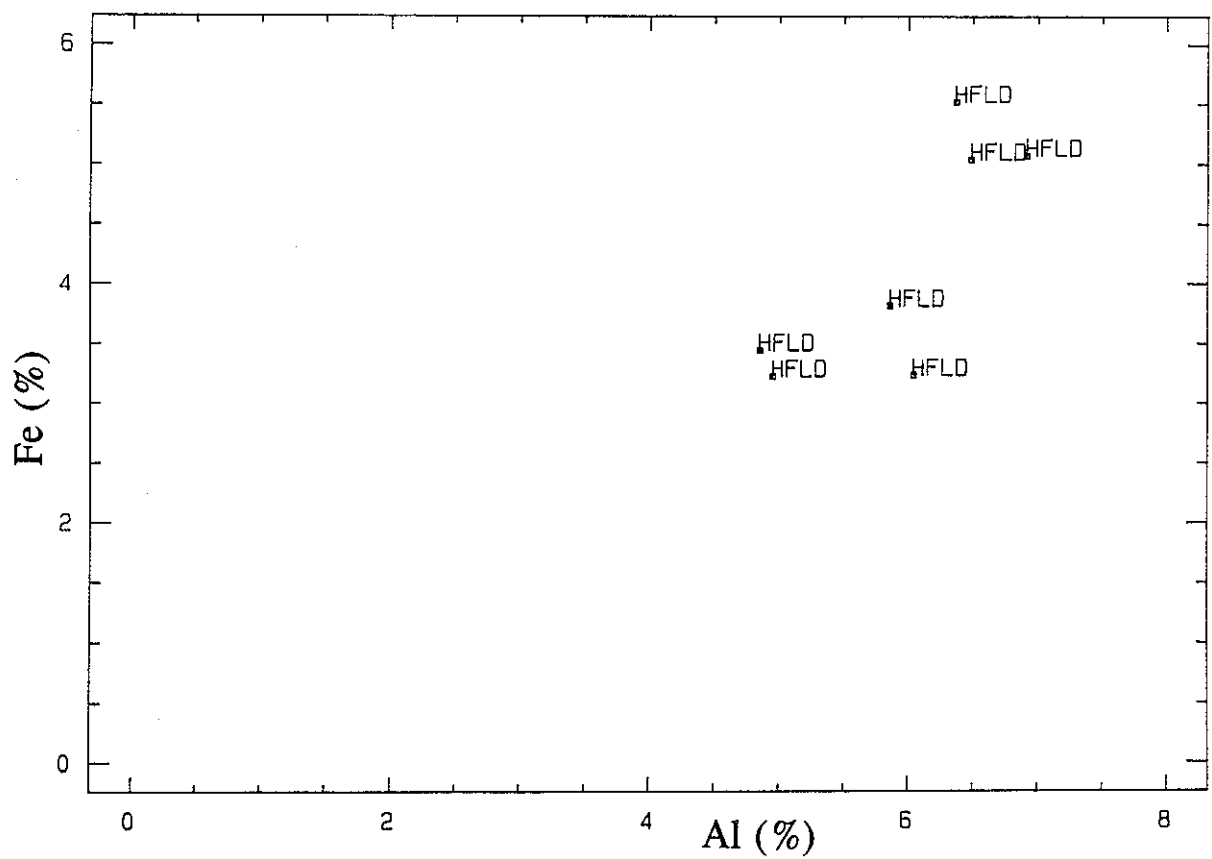


Figure 6.2.2(e) Plot of Fe vs. Al in fines <63 μm .

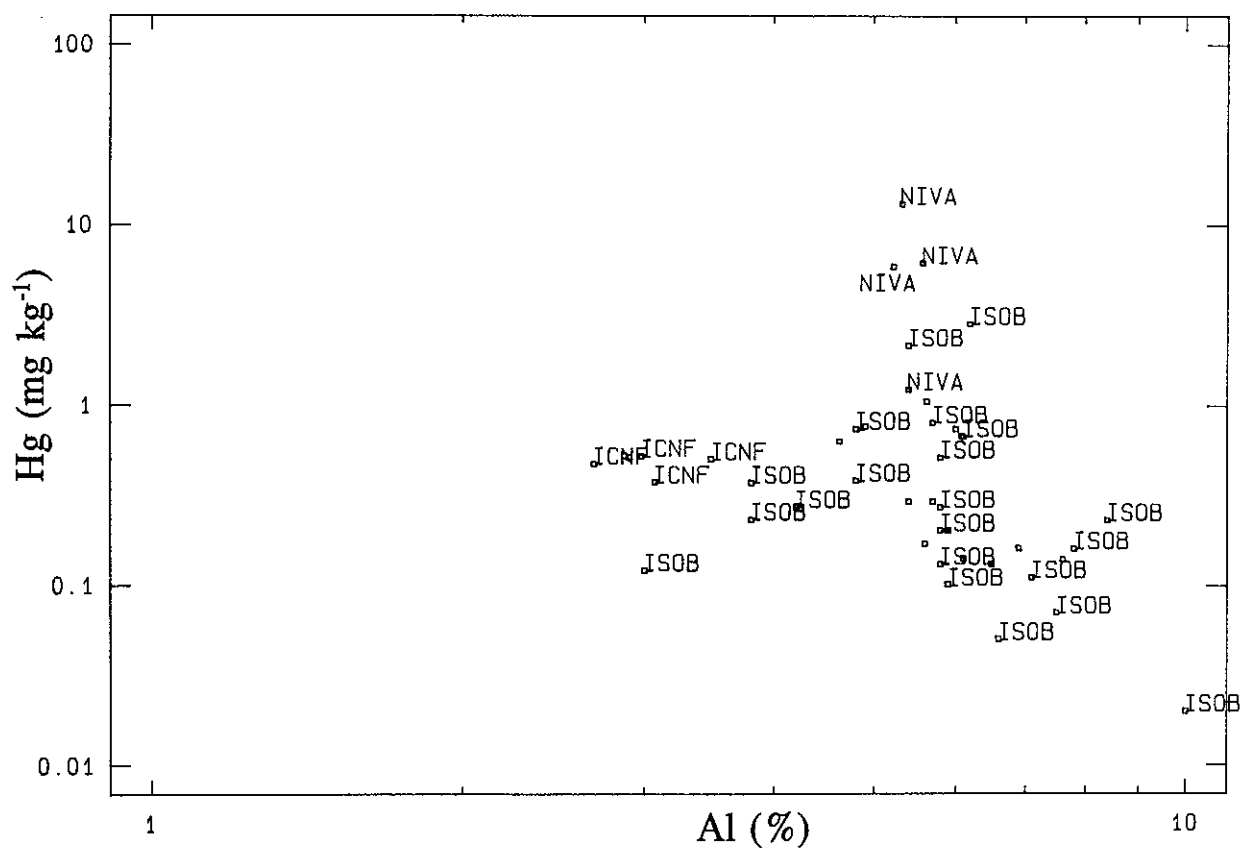


Figure 6.2.2(f) Plot of Hg vs. Al in fines <63 μm .

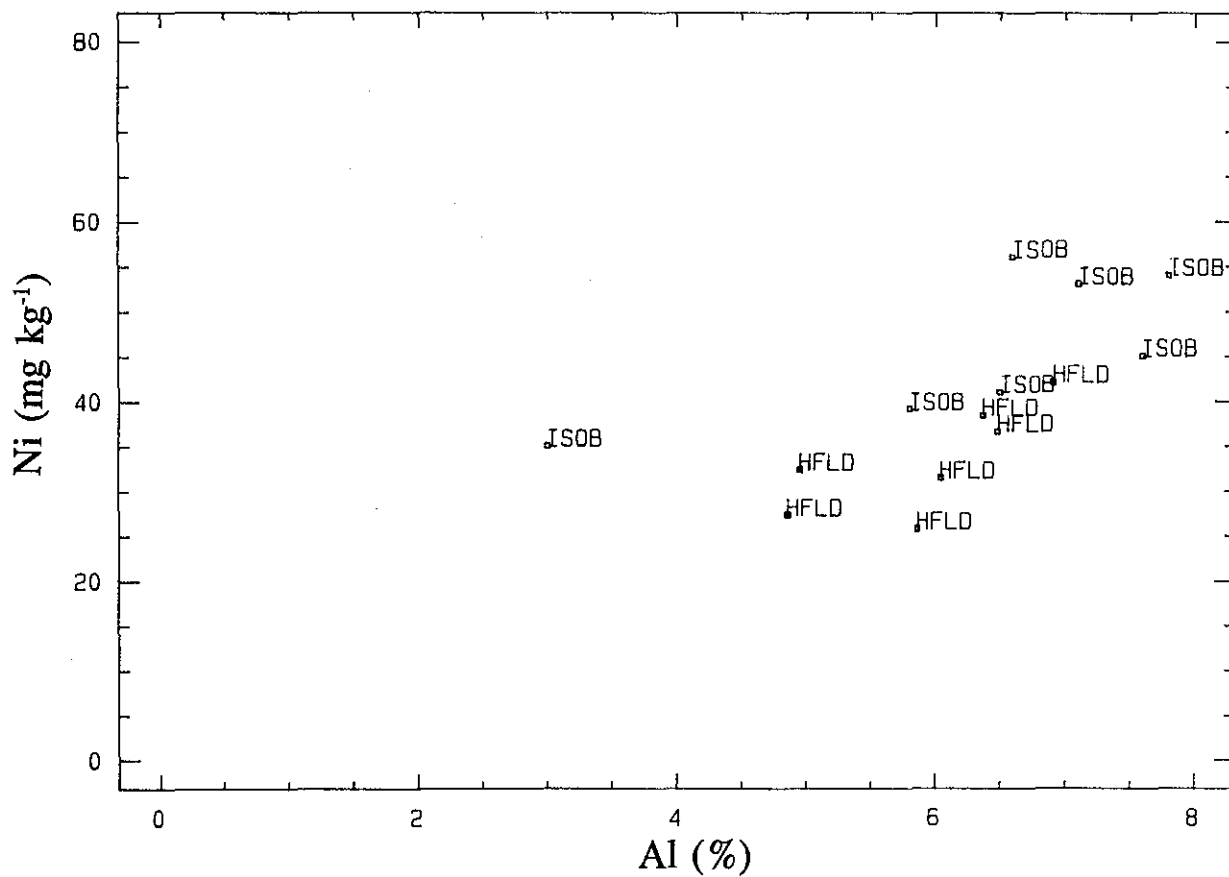


Figure 6.2.2(g) Plot of Ni vs. Al in fines <63 μm.

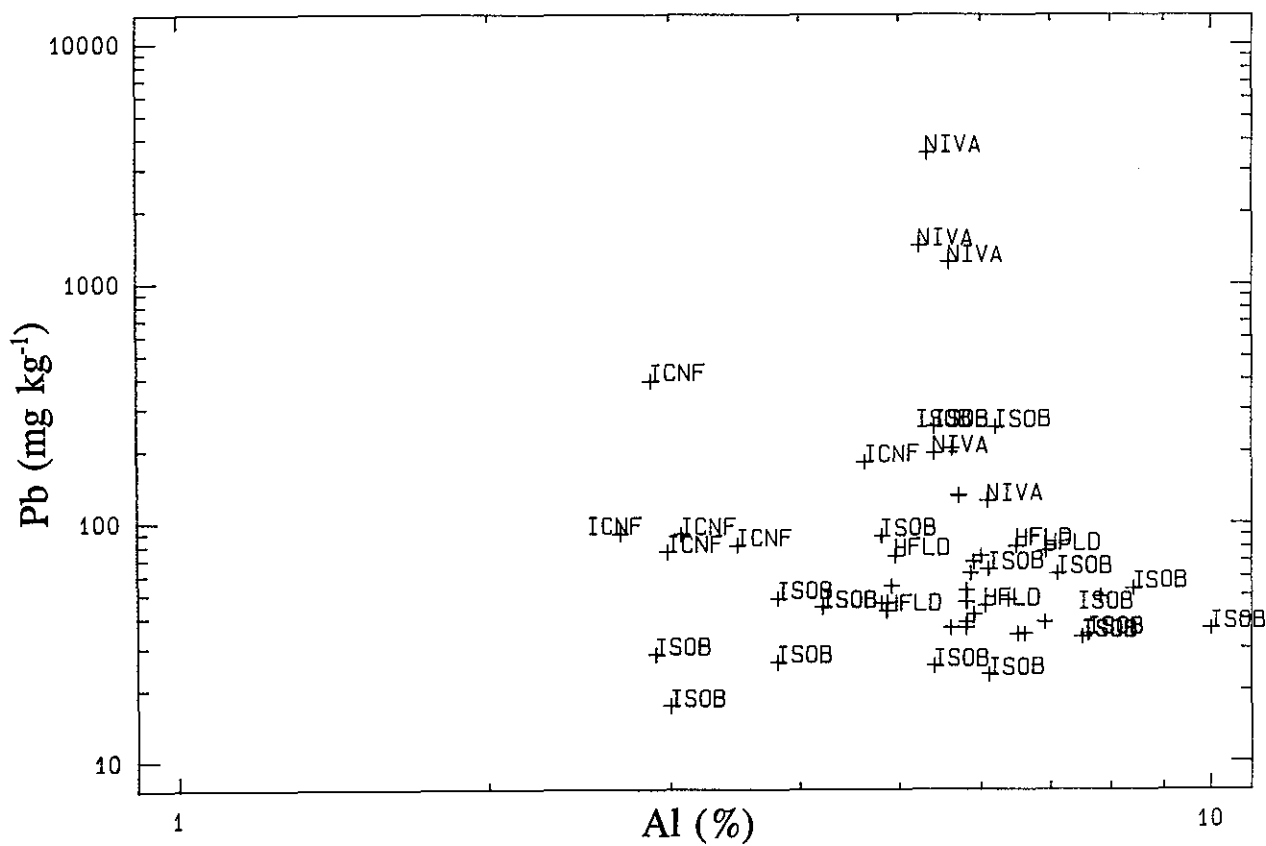


Figure 6.2.2(h) Plot of Pb vs. Al in fines <63 μm.

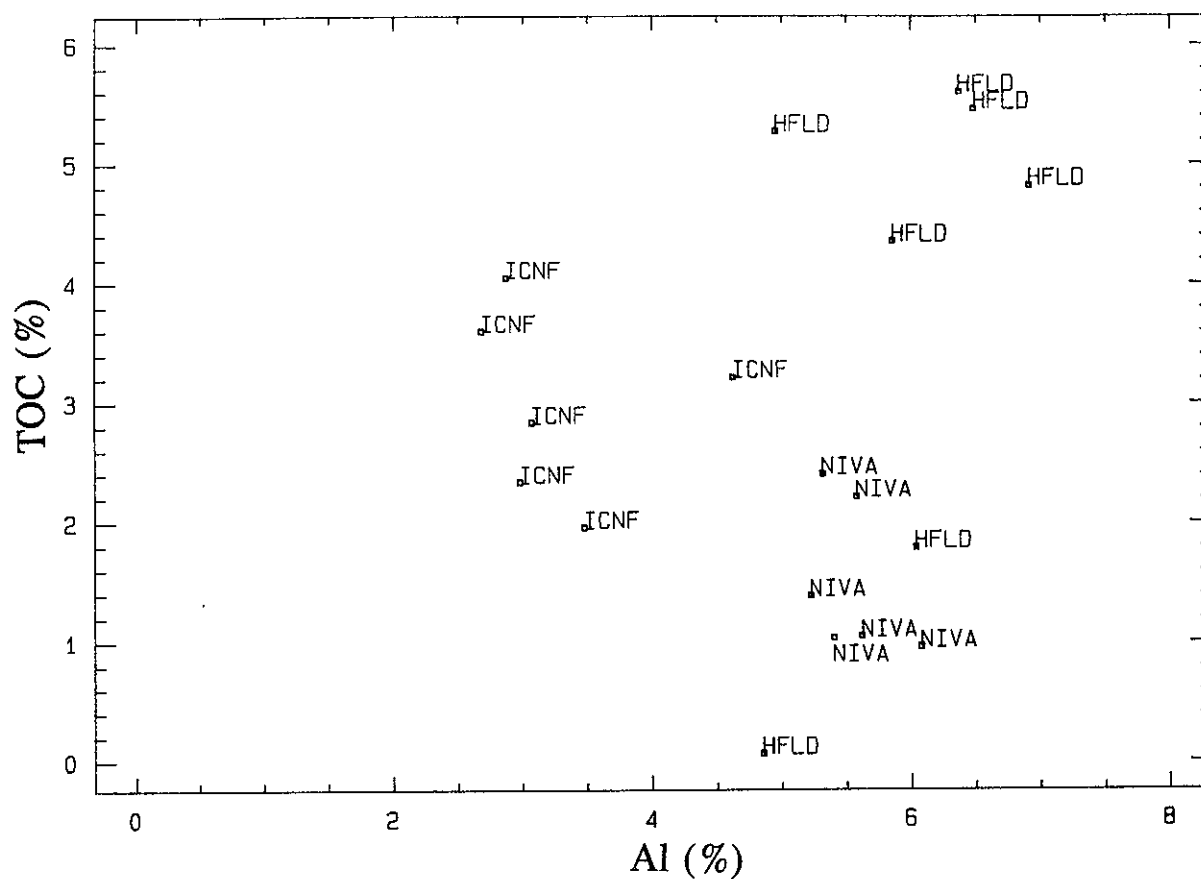


Figure 6.2.2(i) Plot of TOC vs. Al in fines <63 μm.

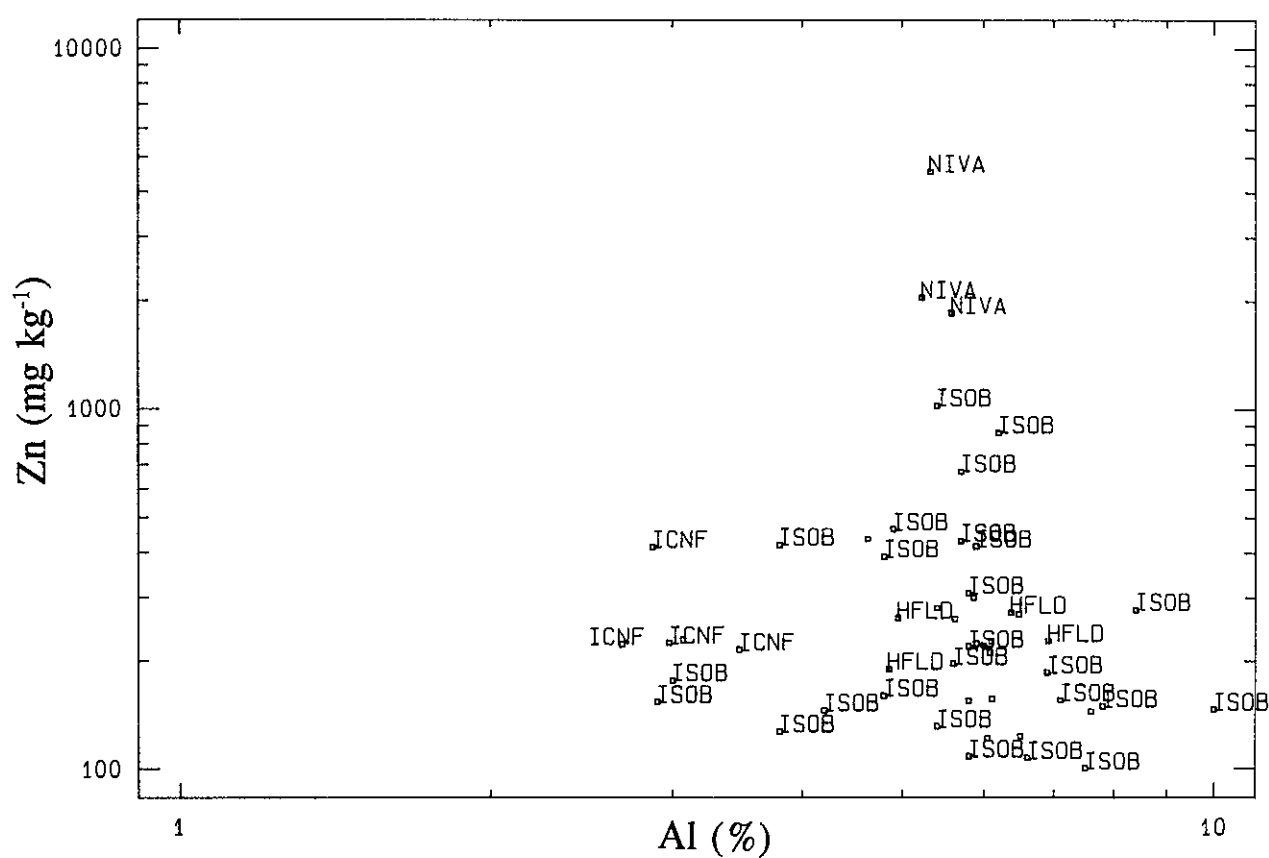


Figure 6.2.2(j) Plot of Zn vs. Al in fines <63 μm.

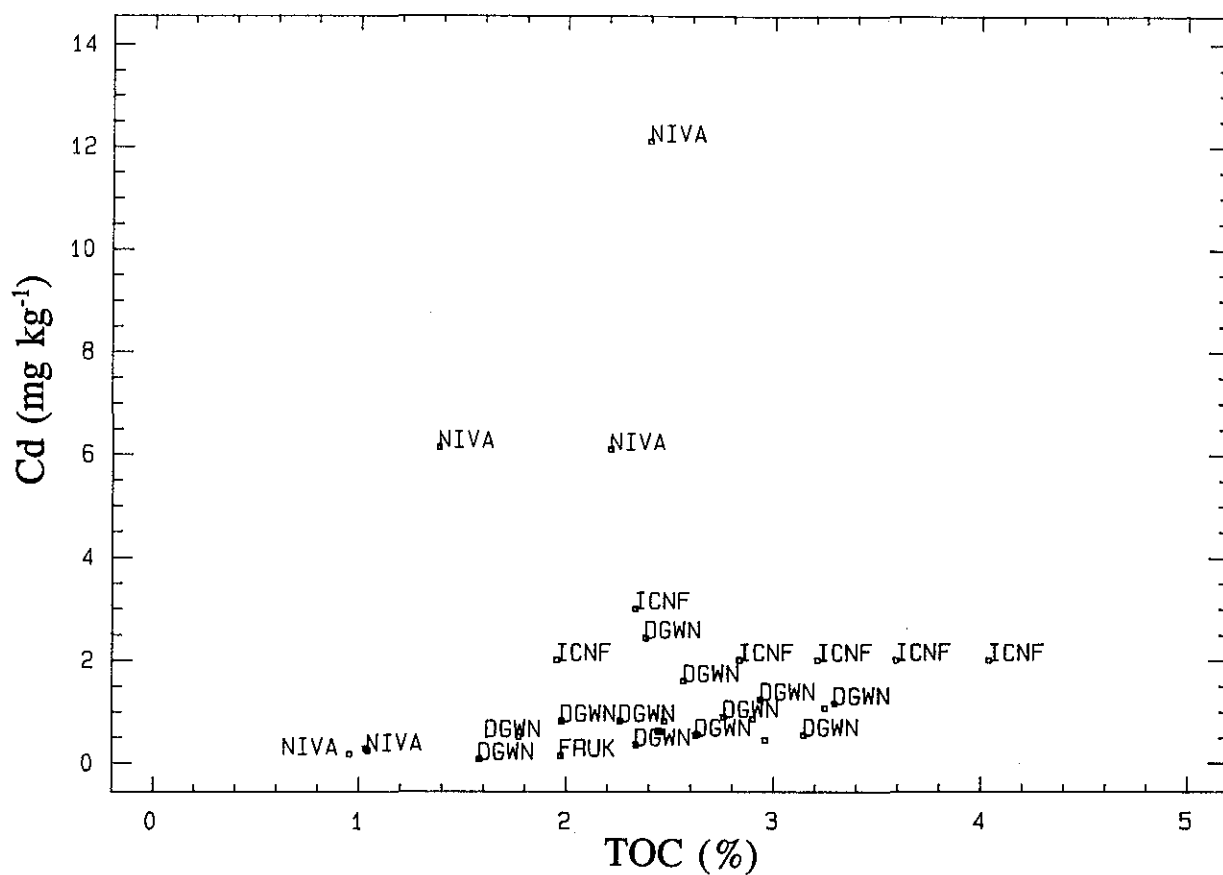


Figure 6.2.3(a) Plot of Cd vs. TOC in fines <63 μm.

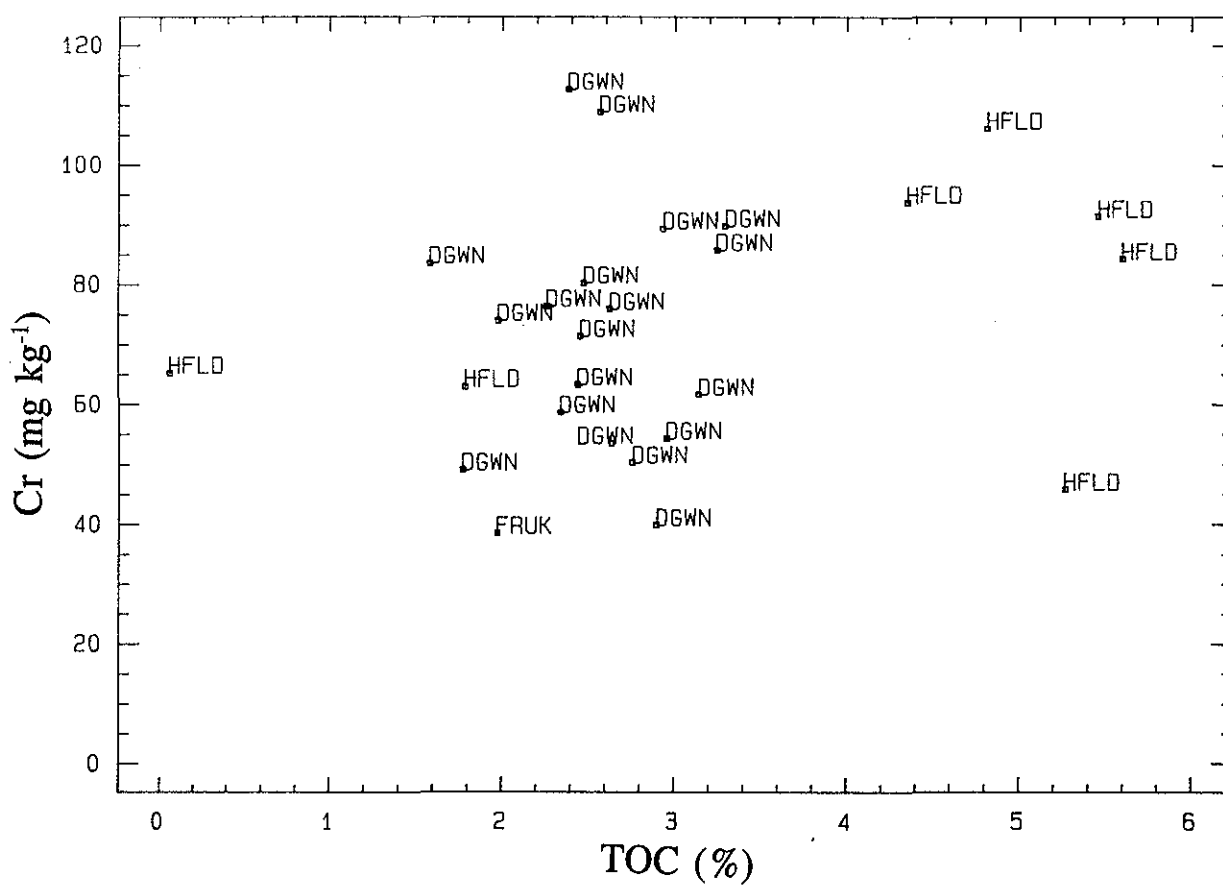


Figure 6.2.3(b) Plot of Cr vs. TOC in fines <63 μm.

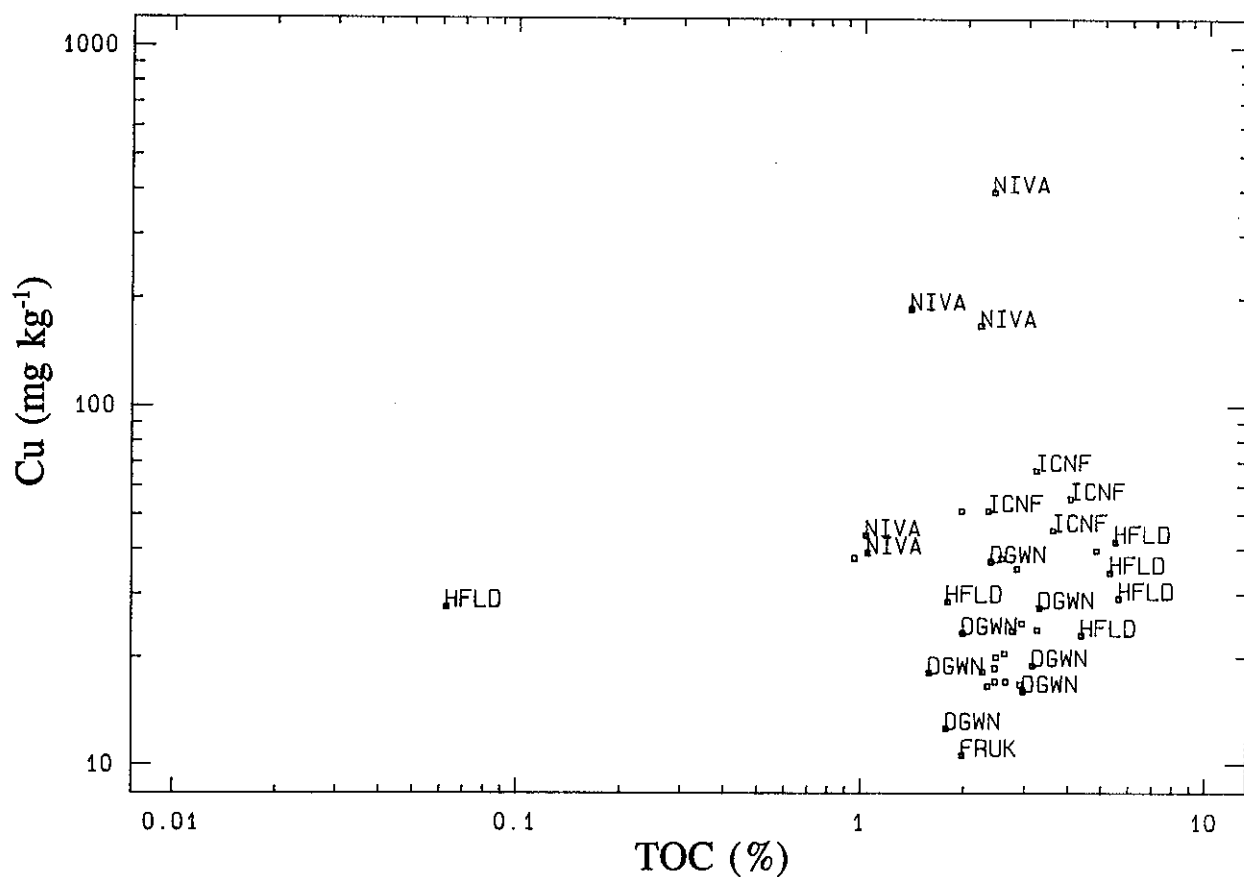


Figure 6.2.3(c) Plot of Cu vs. TOC in fines <63 μm.

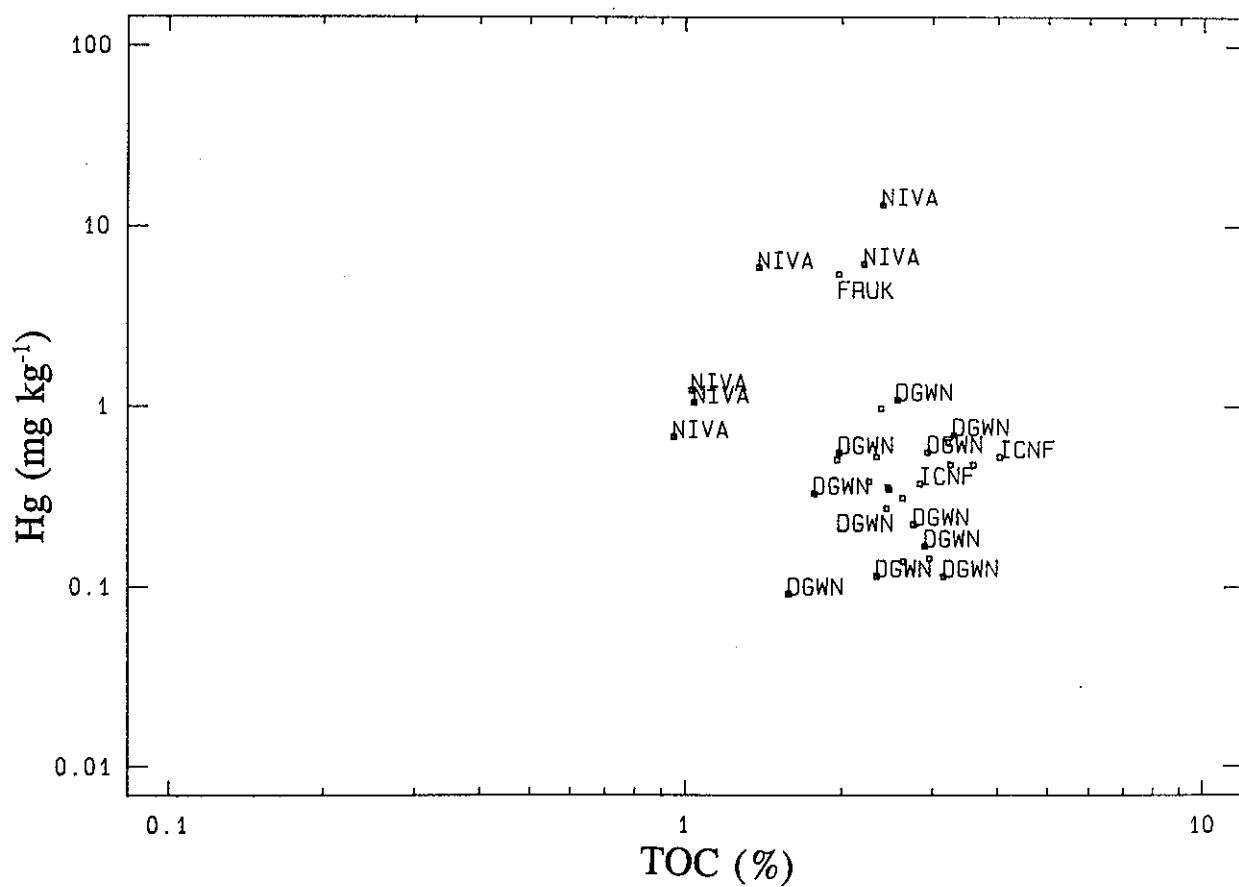


Figure 6.2.3(d) Plot of Hg vs. TOC in fines <63 μm.

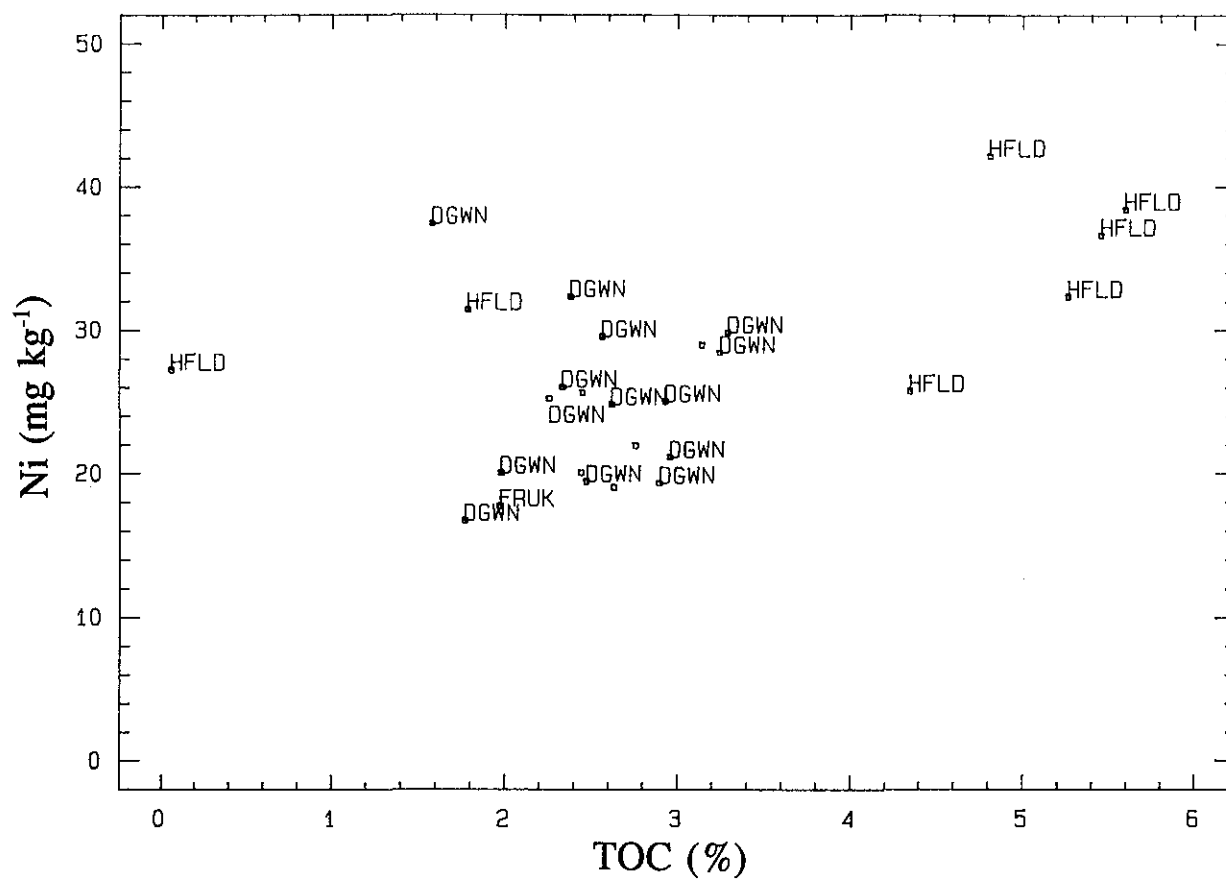


Figure 6.2.3(e) Plot of Ni vs. TOC in fines <63 μm.

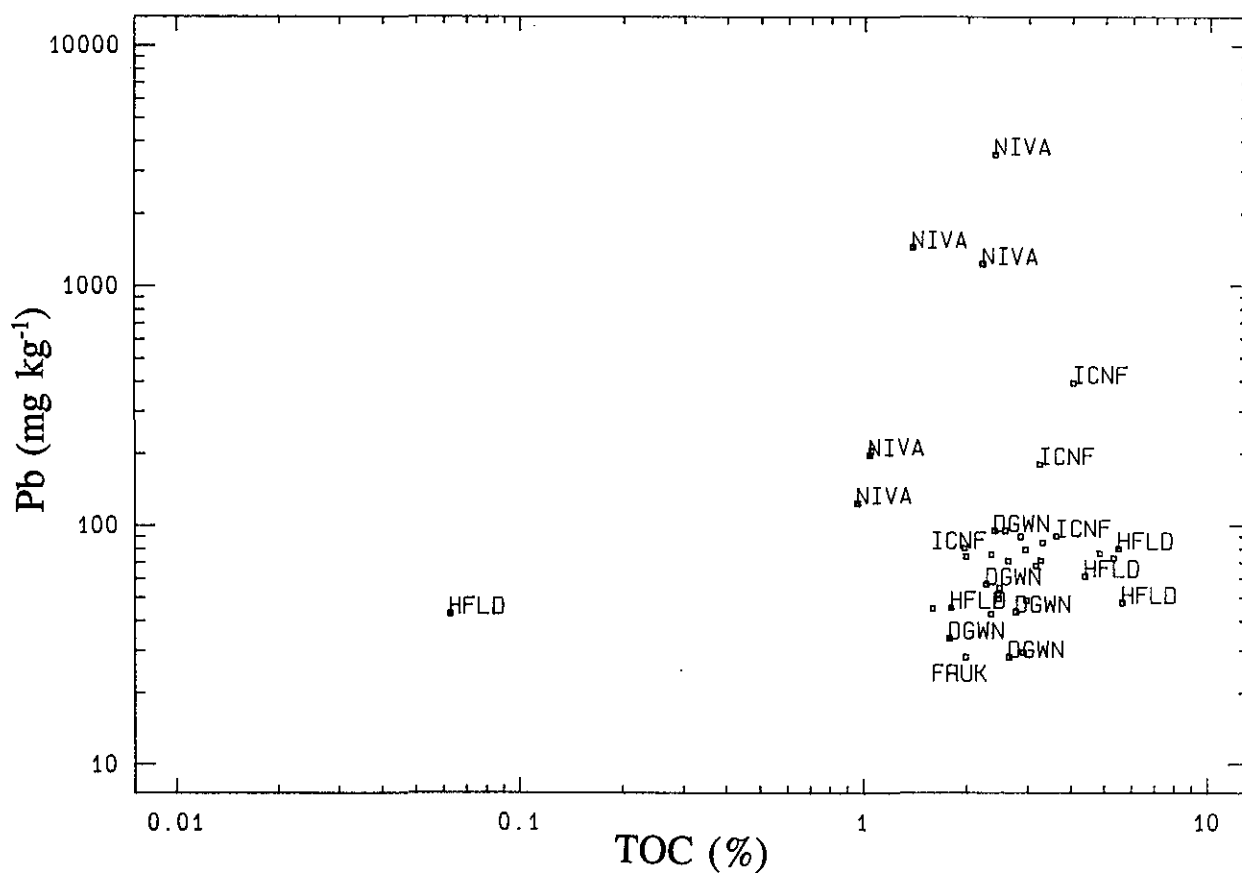


Figure 6.2.3(f) Plot of Pb vs. TOC in fines <63 μm.

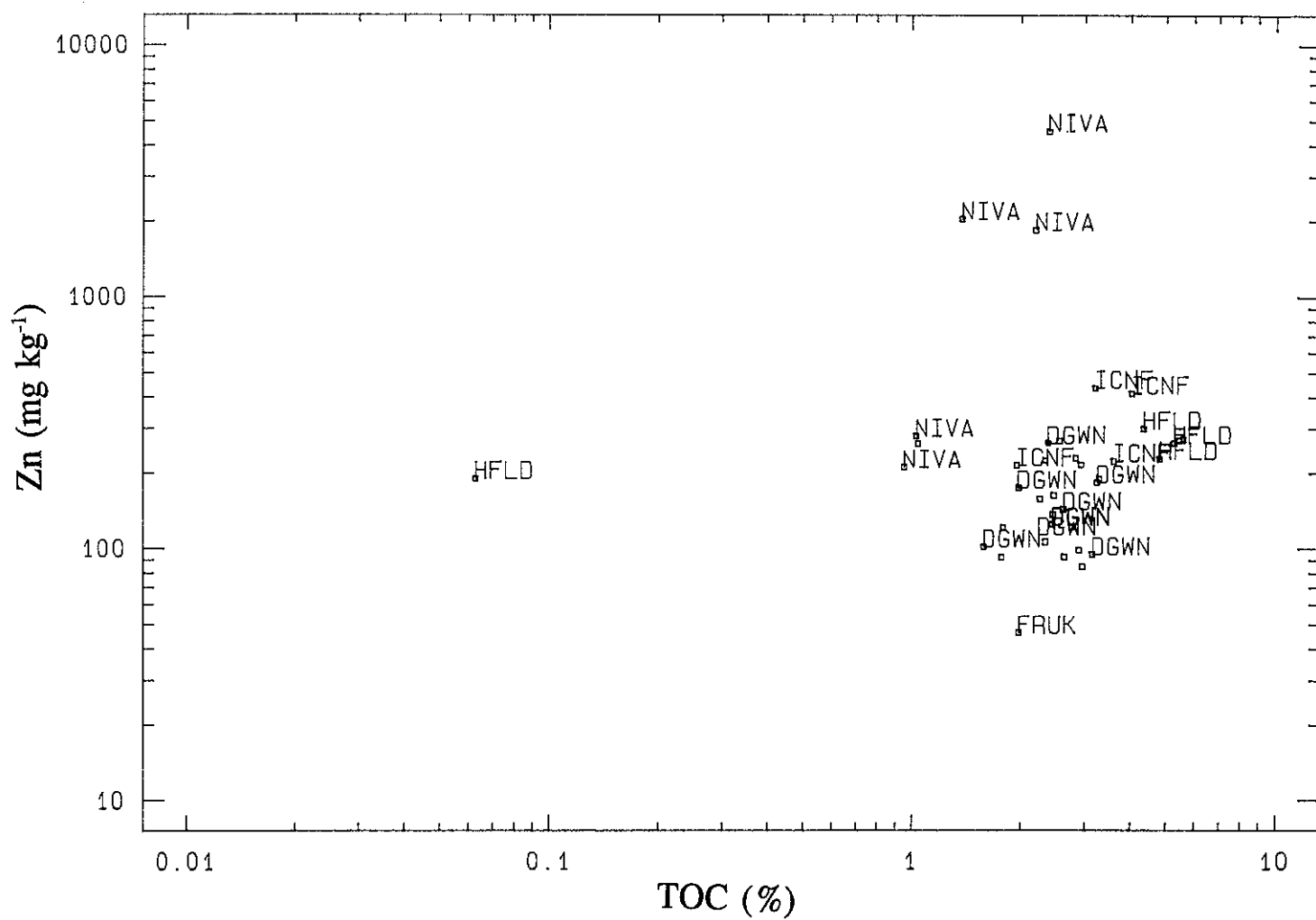


Figure 6.2.3(g) Plot of Zn vs. TOC in fines <63 μm.

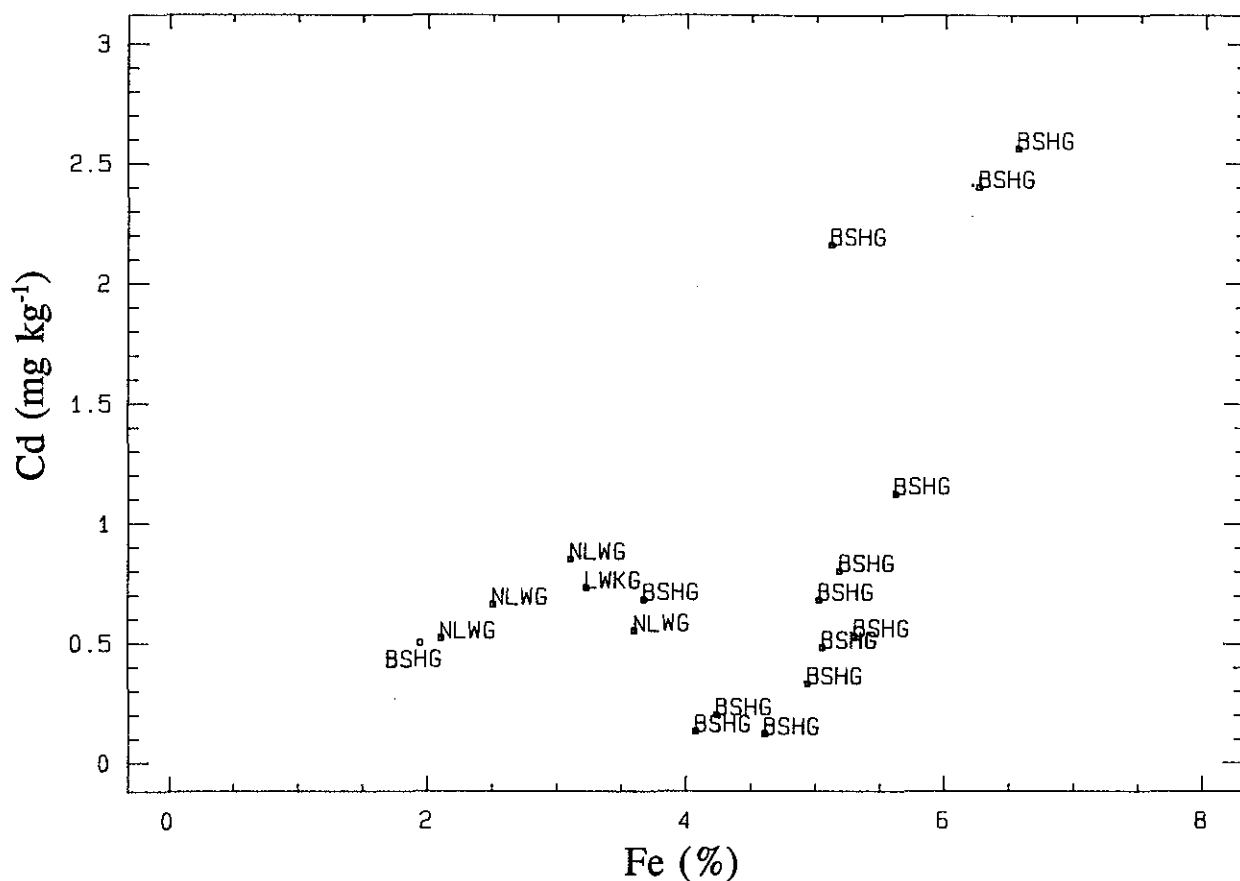


Figure 6.2.4(a) Plot of Cd vs. Fe in fines <63 μm.

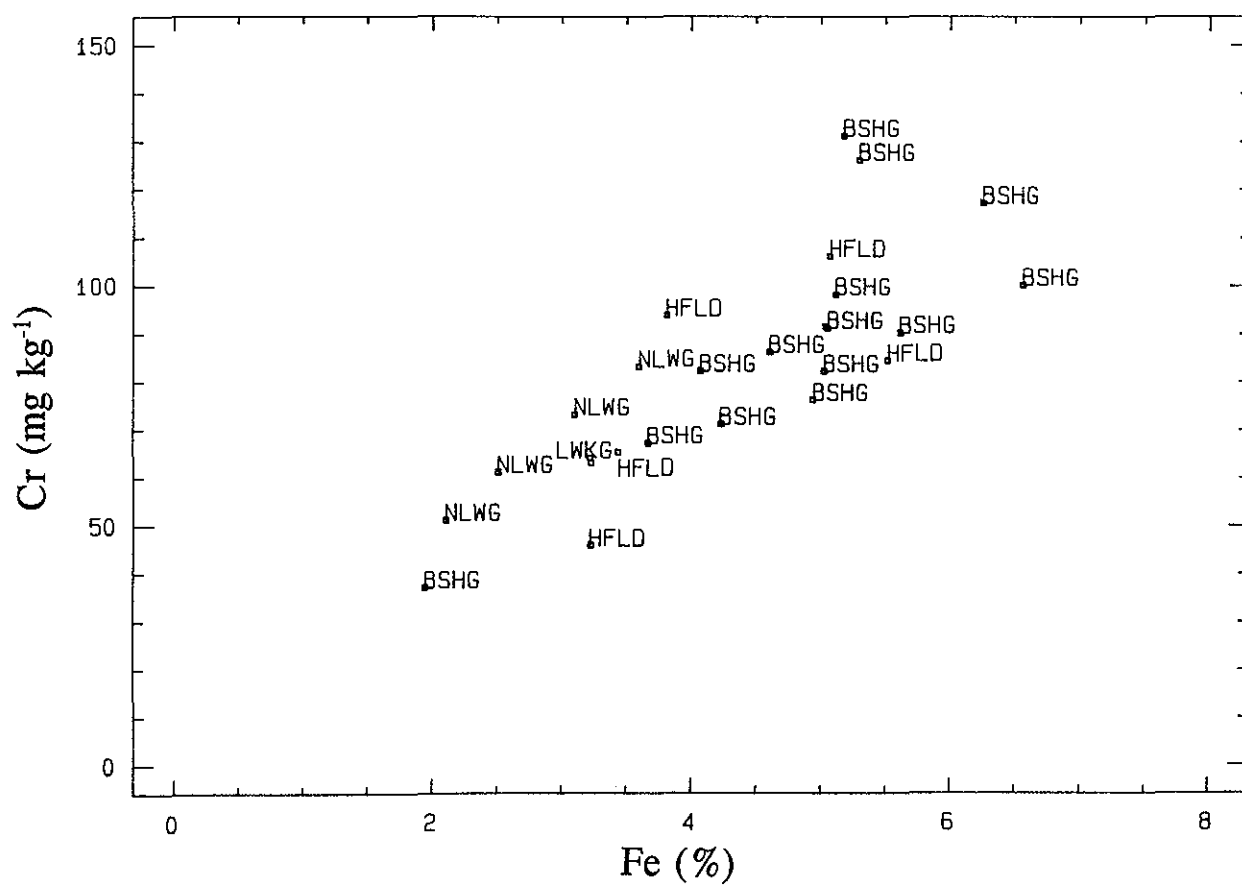


Figure 6.2.4(b) Plot of Cr vs. Fe in fines <63 μm.

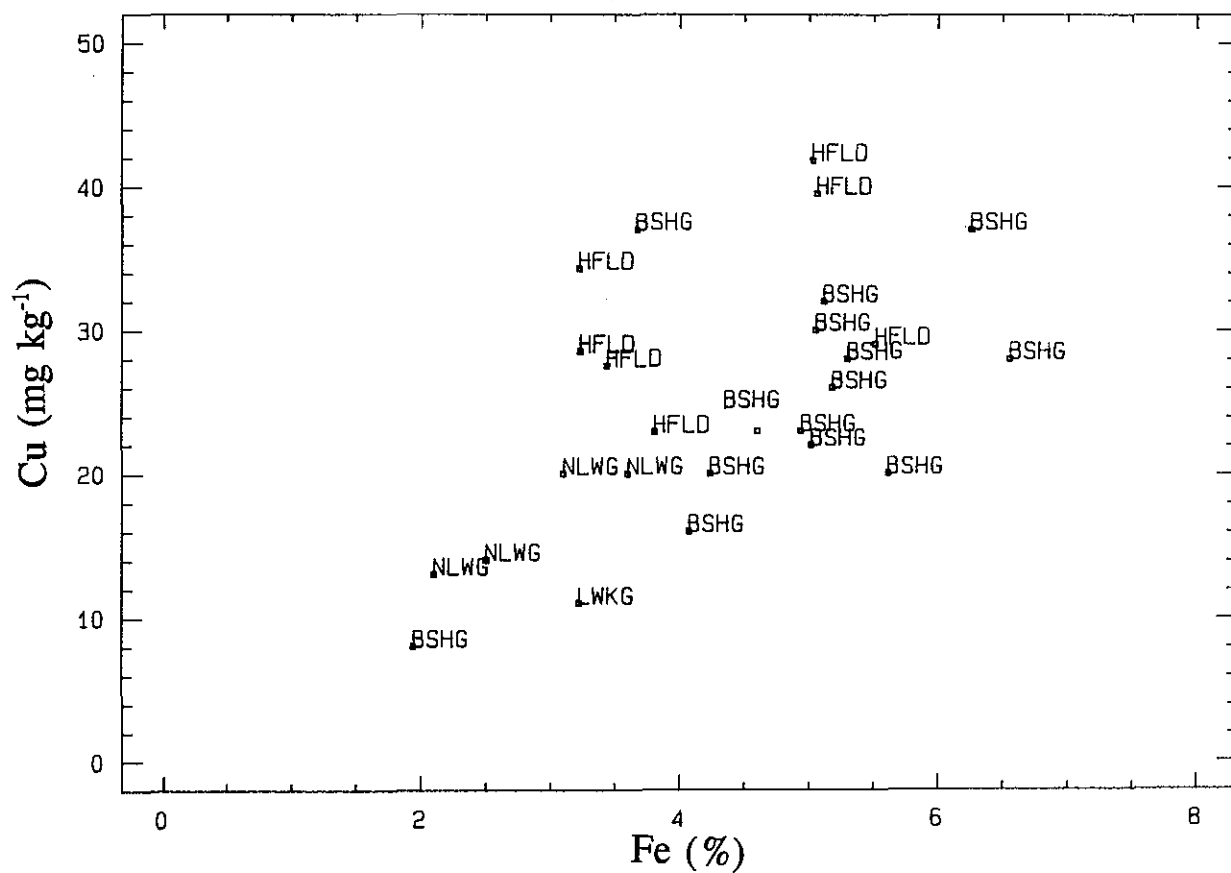


Figure 6.2.4(c) Plot of Cu vs. Fe in fines <63 μm.

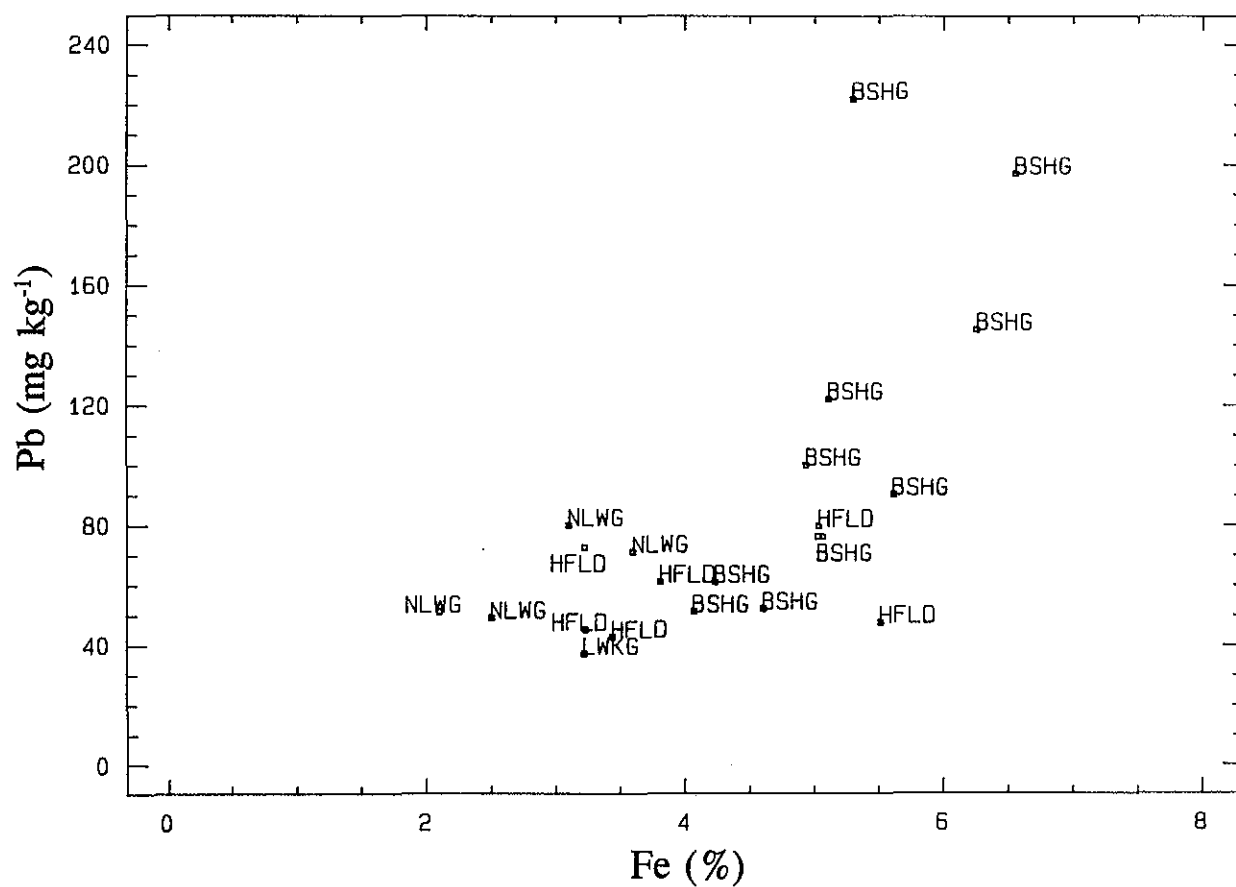


Figure 6.2.4(d) Plot of Pb vs. Fe in fines <63 μm.

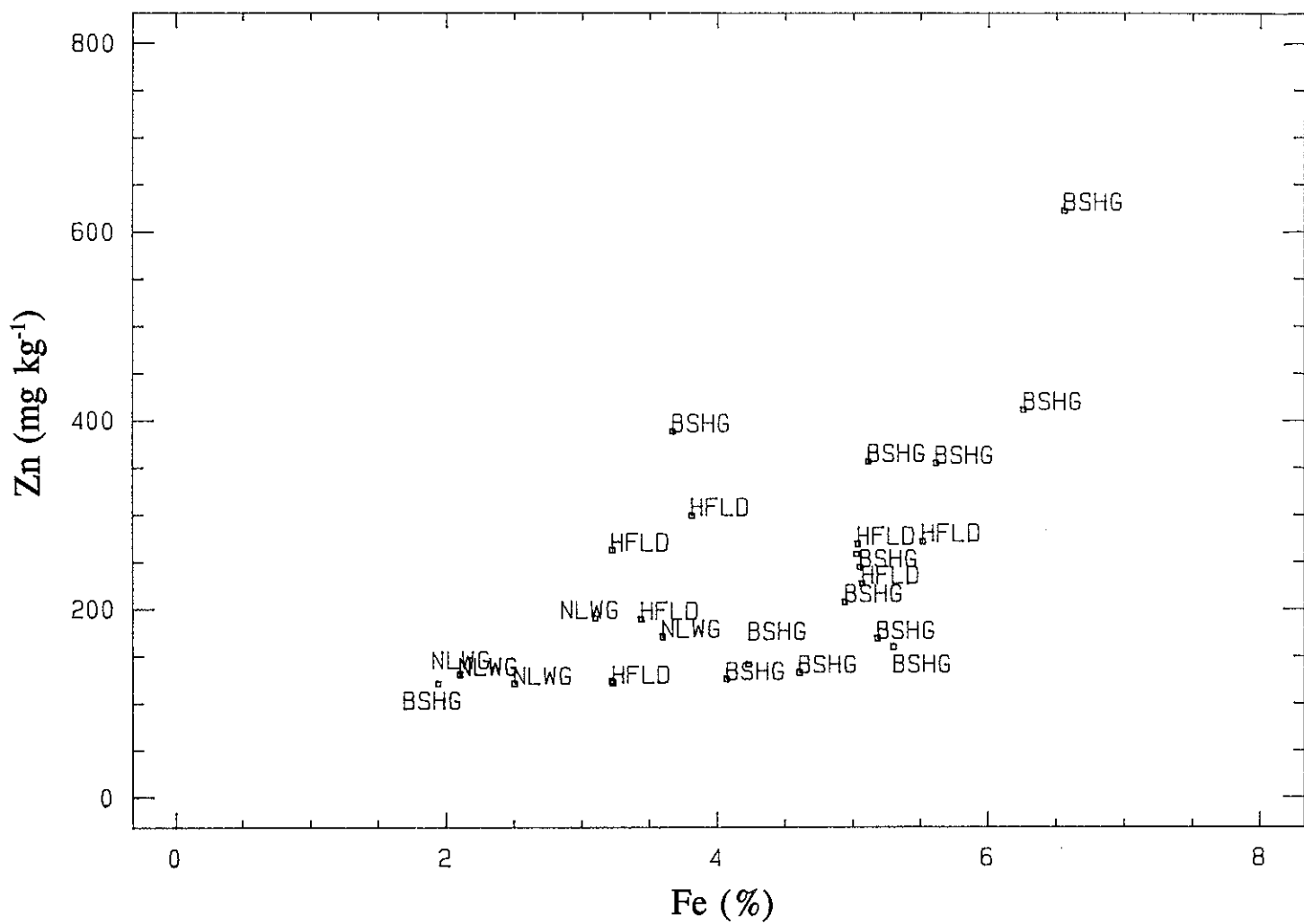


Figure 6.2.4(e) Plot of Zn vs. Fe in fines <63 μm.

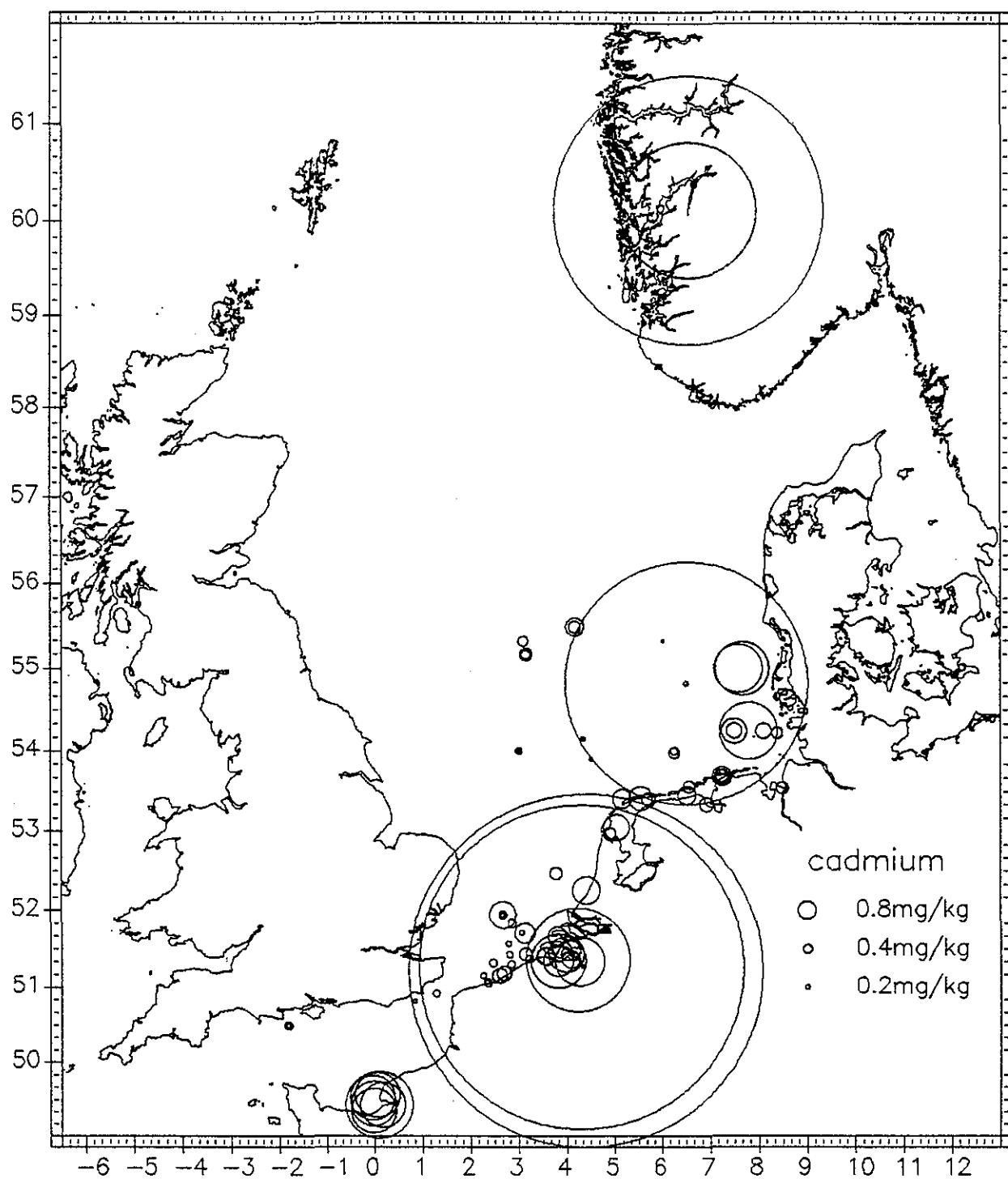


Figure 6.3.1 The distribution of cadmium concentrations in North Sea sediment fines <63 μm (circle diameter proportional to value).

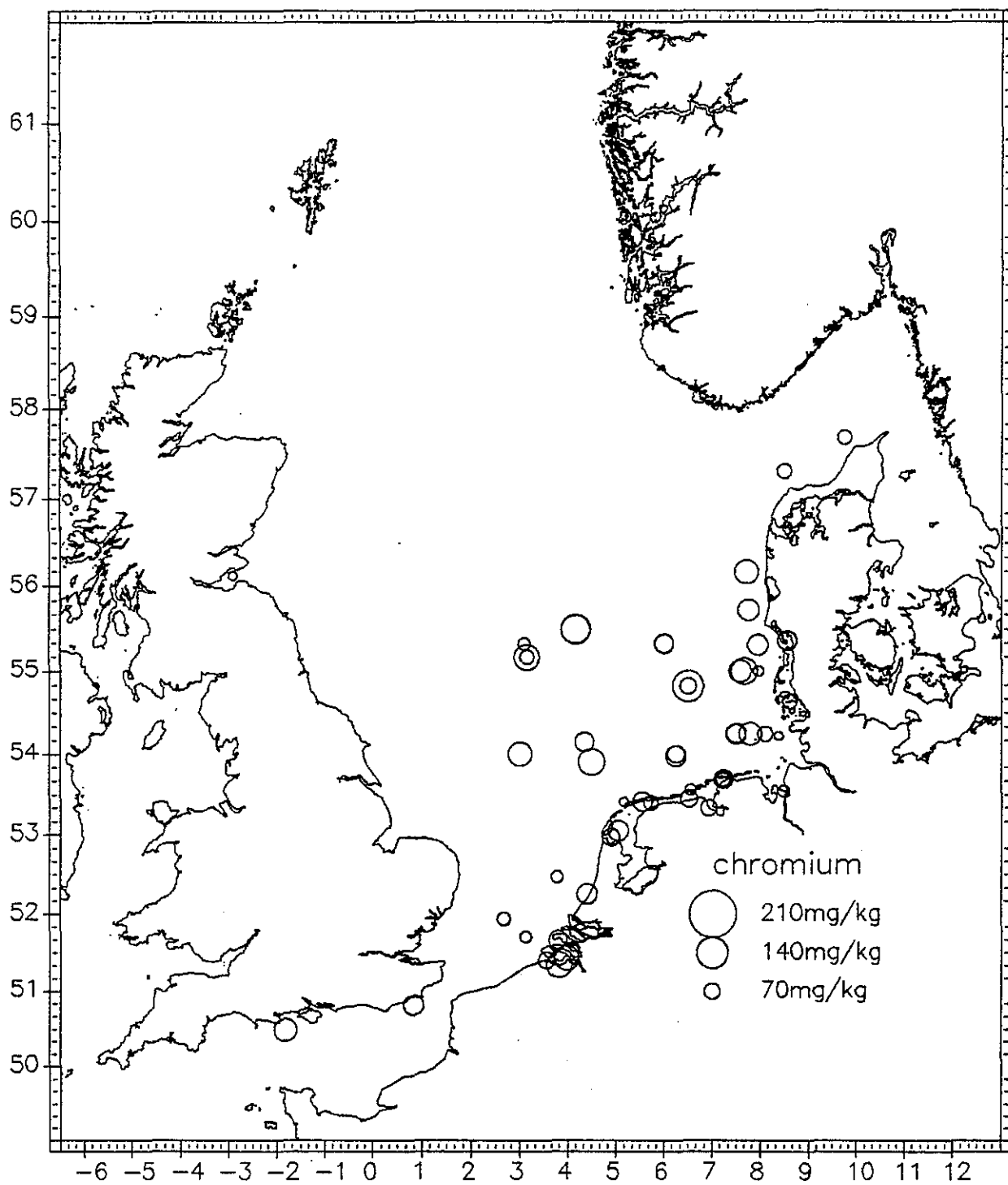


Figure 6.3.2 The distribution of chromium concentrations in North Sea sediment fines < 63 μm (circle diameter proportional to value).

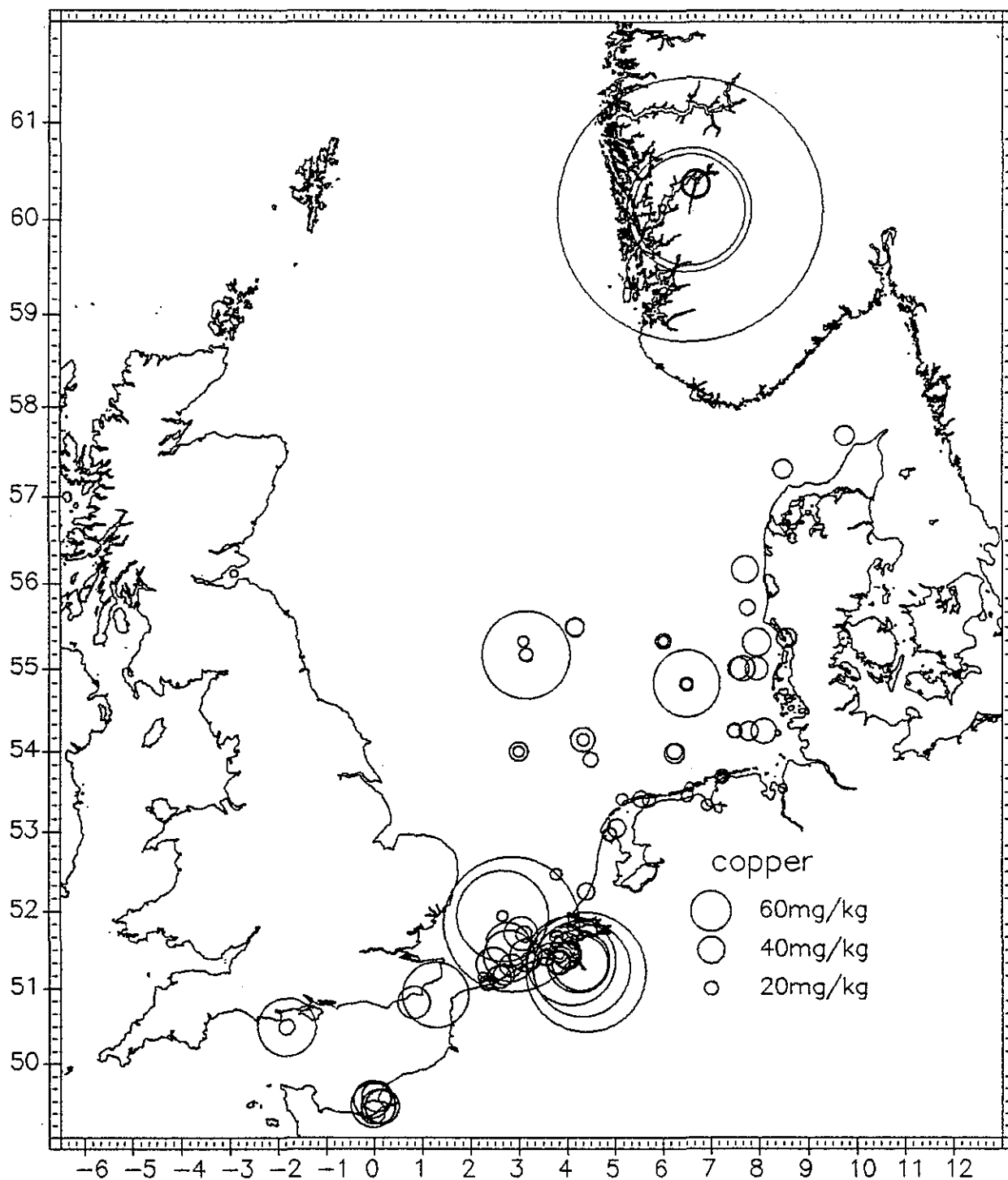


Figure 6.3.3 The distribution of copper concentrations in North Sea sediment fines <63 μm (circle diameter proportional to value).

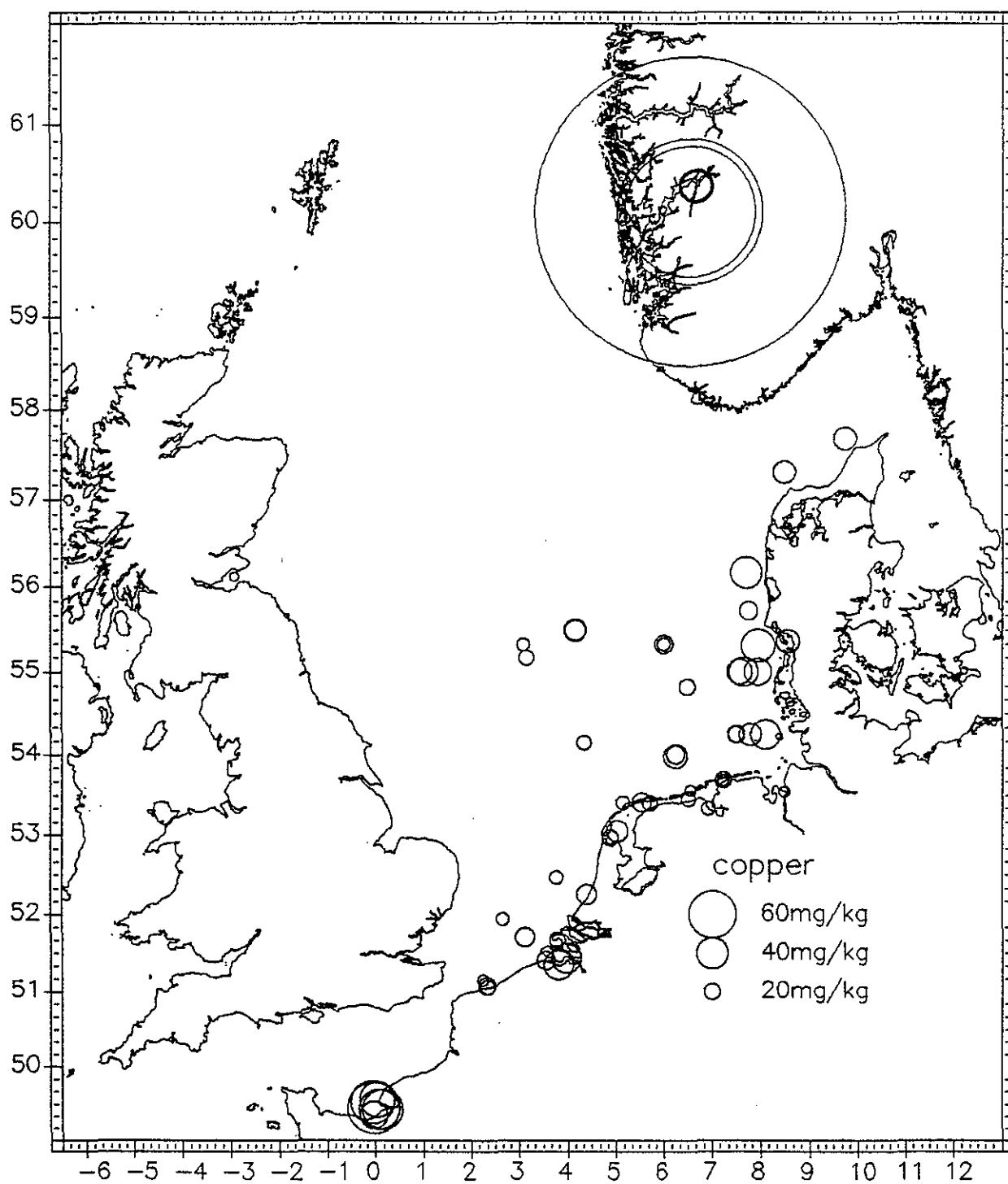


Figure 6.3.4 The distribution of copper concentrations in North Sea sediment fines $<63 \mu\text{m}$, excluding data from laboratory ISOB (circle diameter proportional to value).

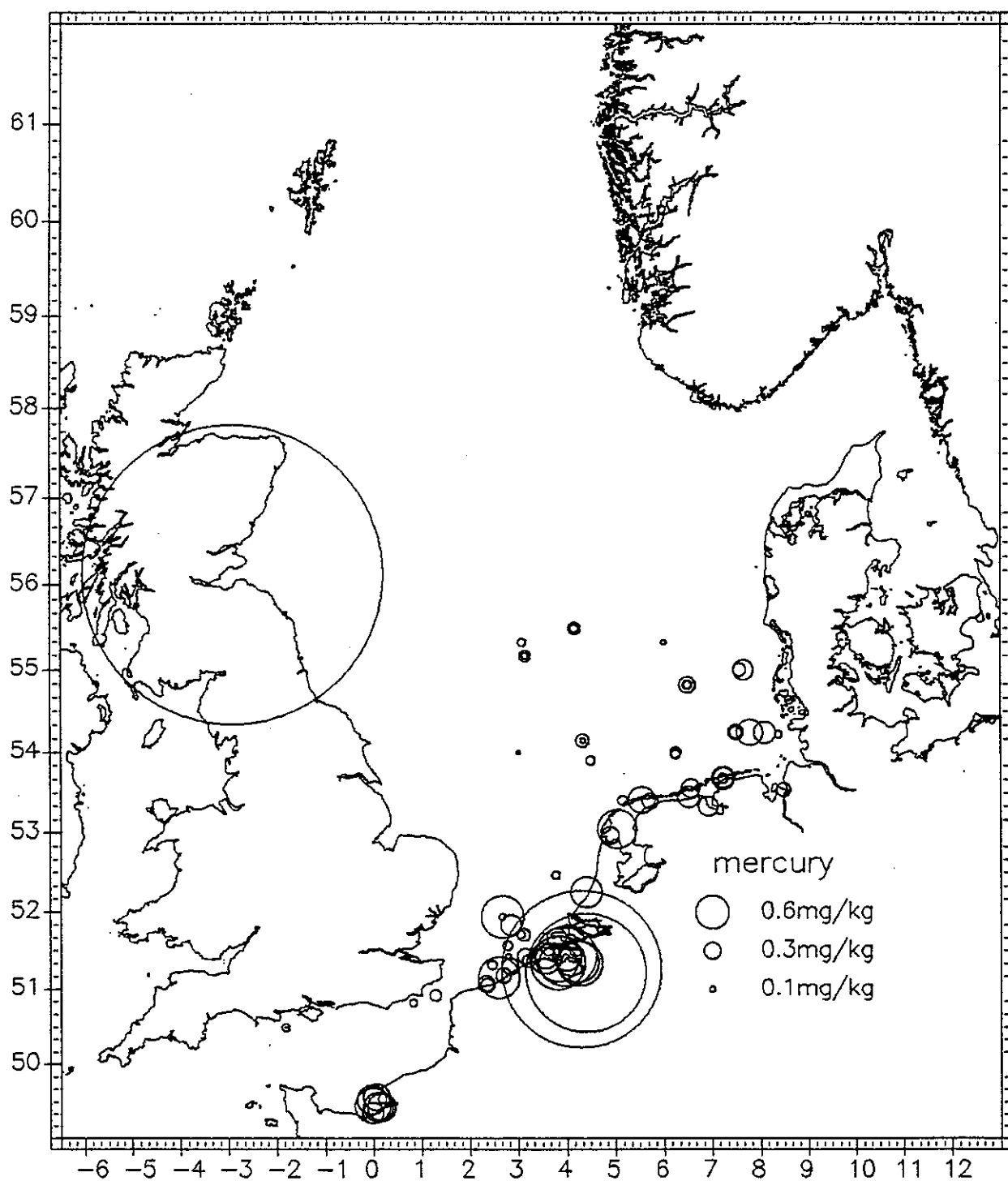


Figure 6.3.5 The distribution of mercury concentrations in North Sea sediment fines <63 μm (circle diameter proportional to value).

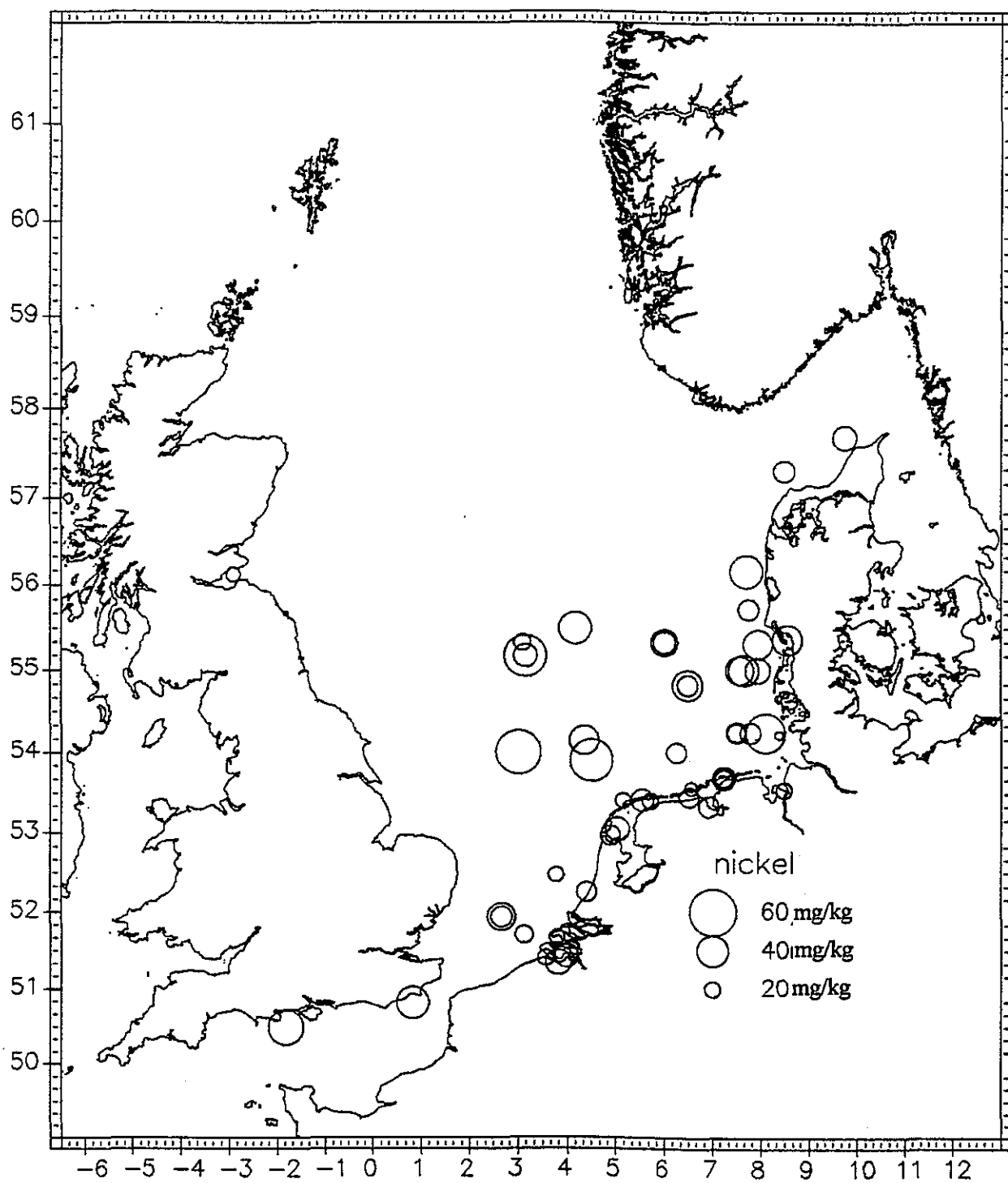


Figure 6.3.6 The distribution of nickel concentrations in North Sea sediment fines <63 μm (circle diameter proportional to value).

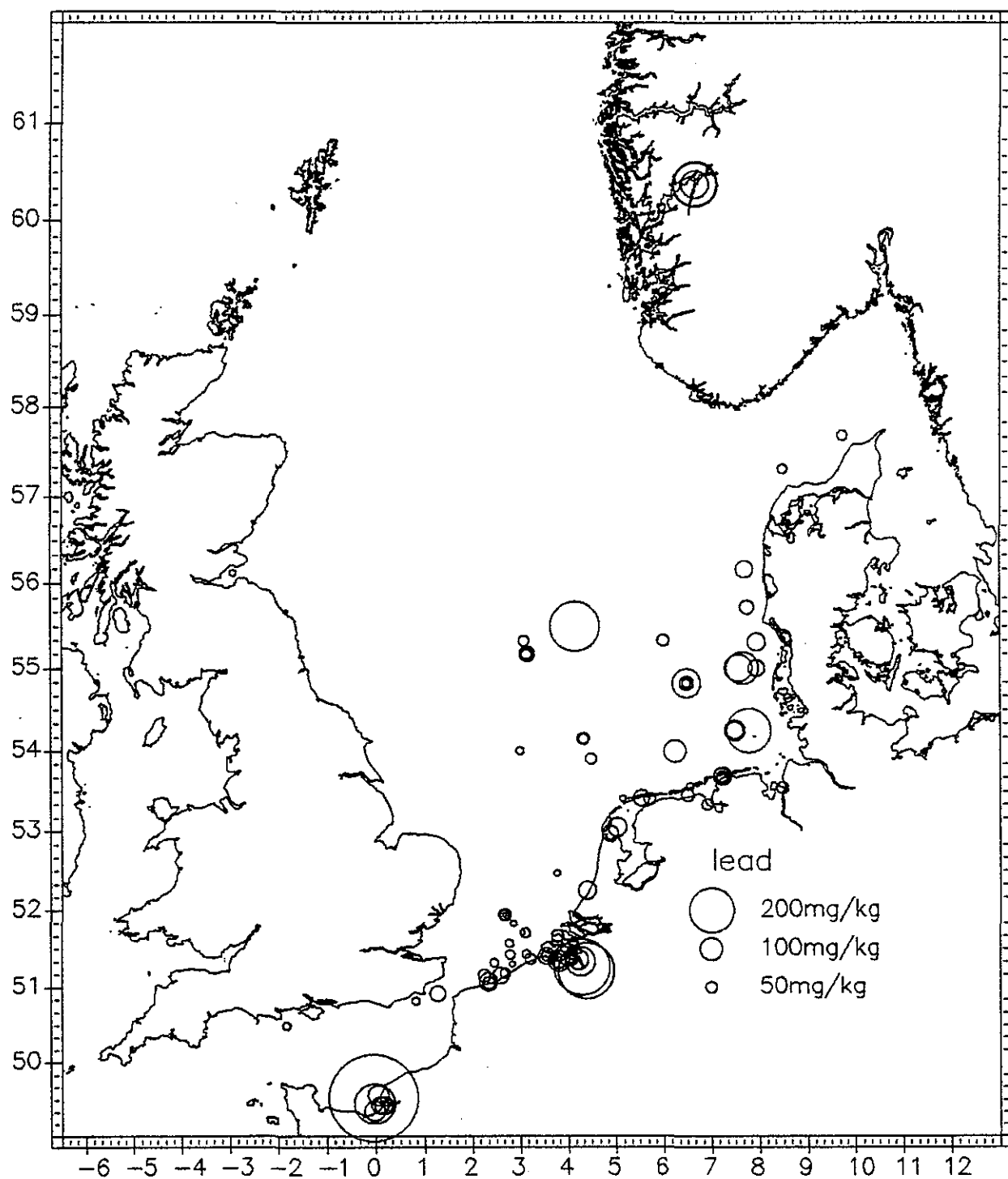


Figure 6.3.7 The distribution of lead concentrations in North Sea sediment fines <63 μm (circle diameter proportional to value).

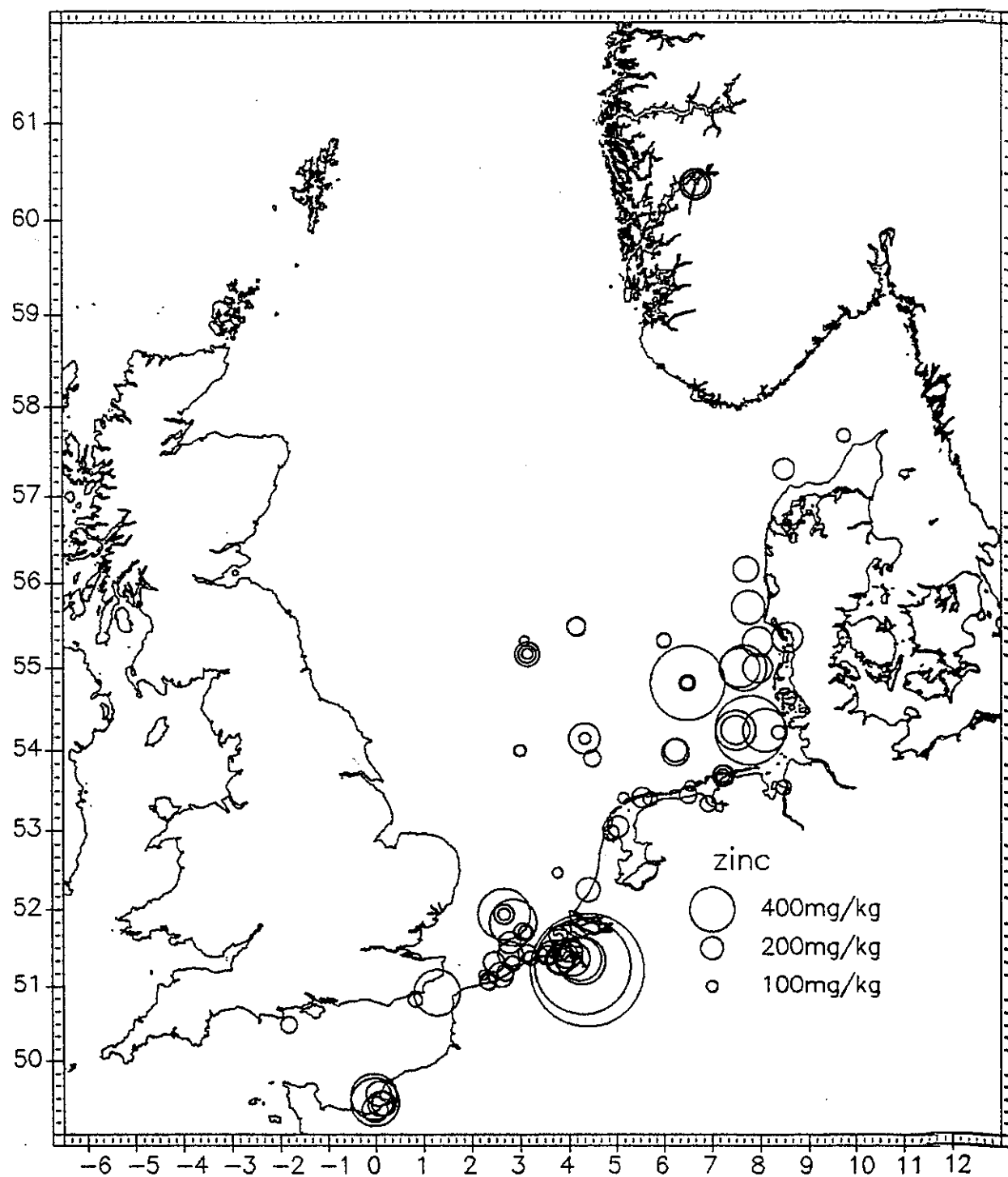


Figure 6.3.8 The distribution of zinc concentrations in North Sea sediment fines <63 μm (circle diameter proportional to value).

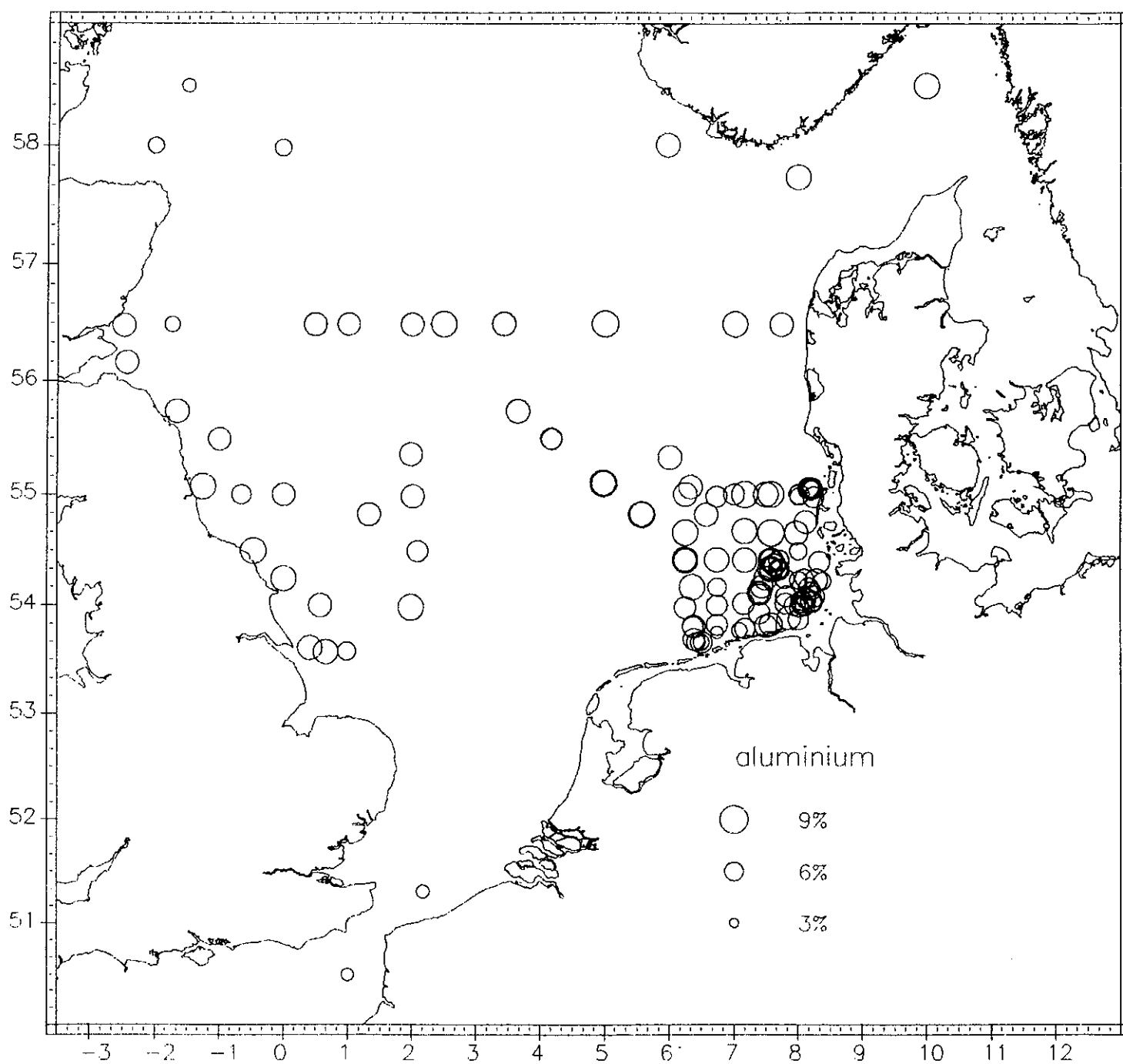


Figure 6.4.1 The distribution of aluminium concentrations in North Sea sediment fines <20 μm (circle diameter proportional to value).

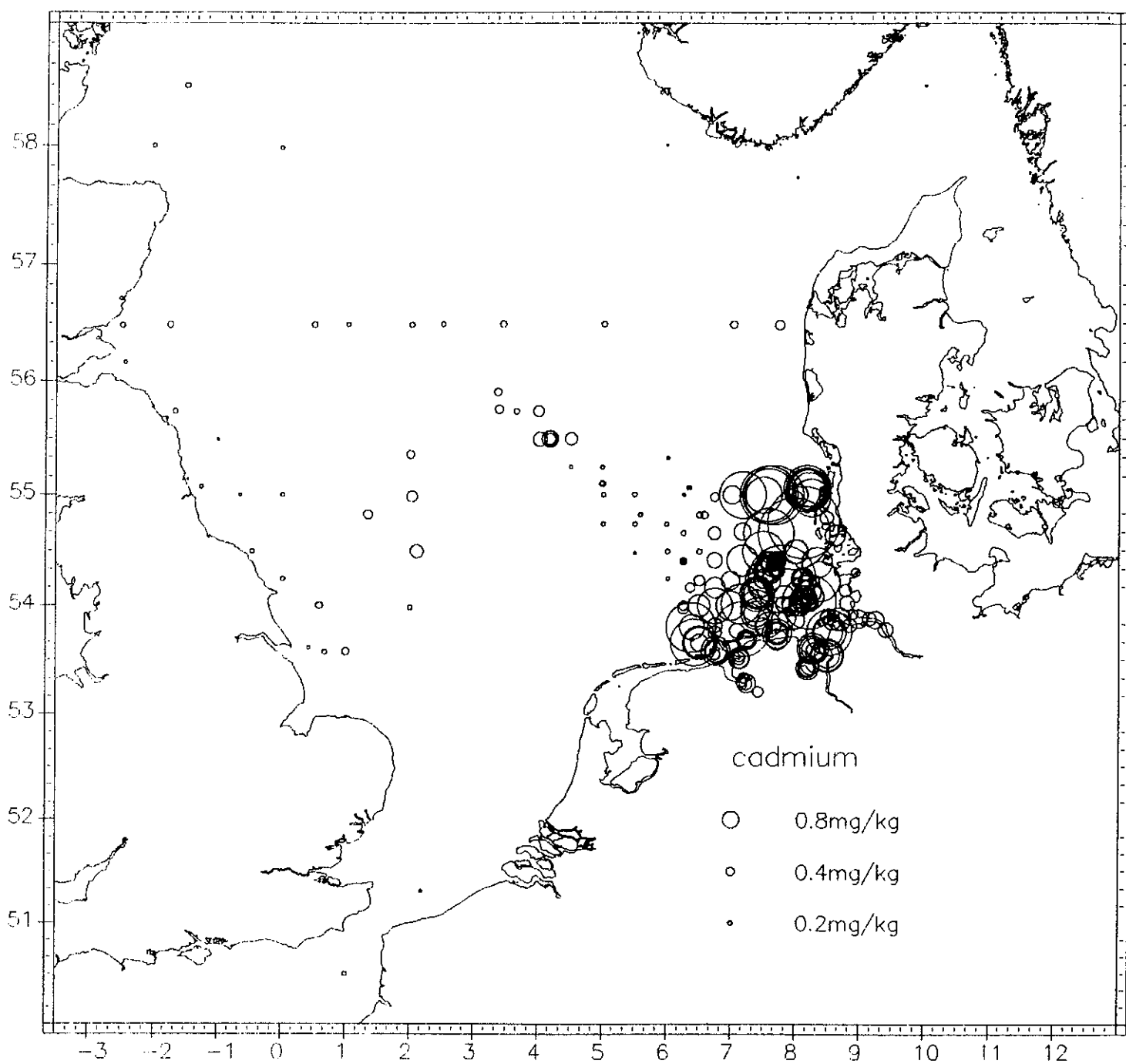


Figure 6.4.2 The distribution of cadmium concentrations in North Sea sediment fines $< 20 \mu\text{m}$ (circle diameter proportional to value).

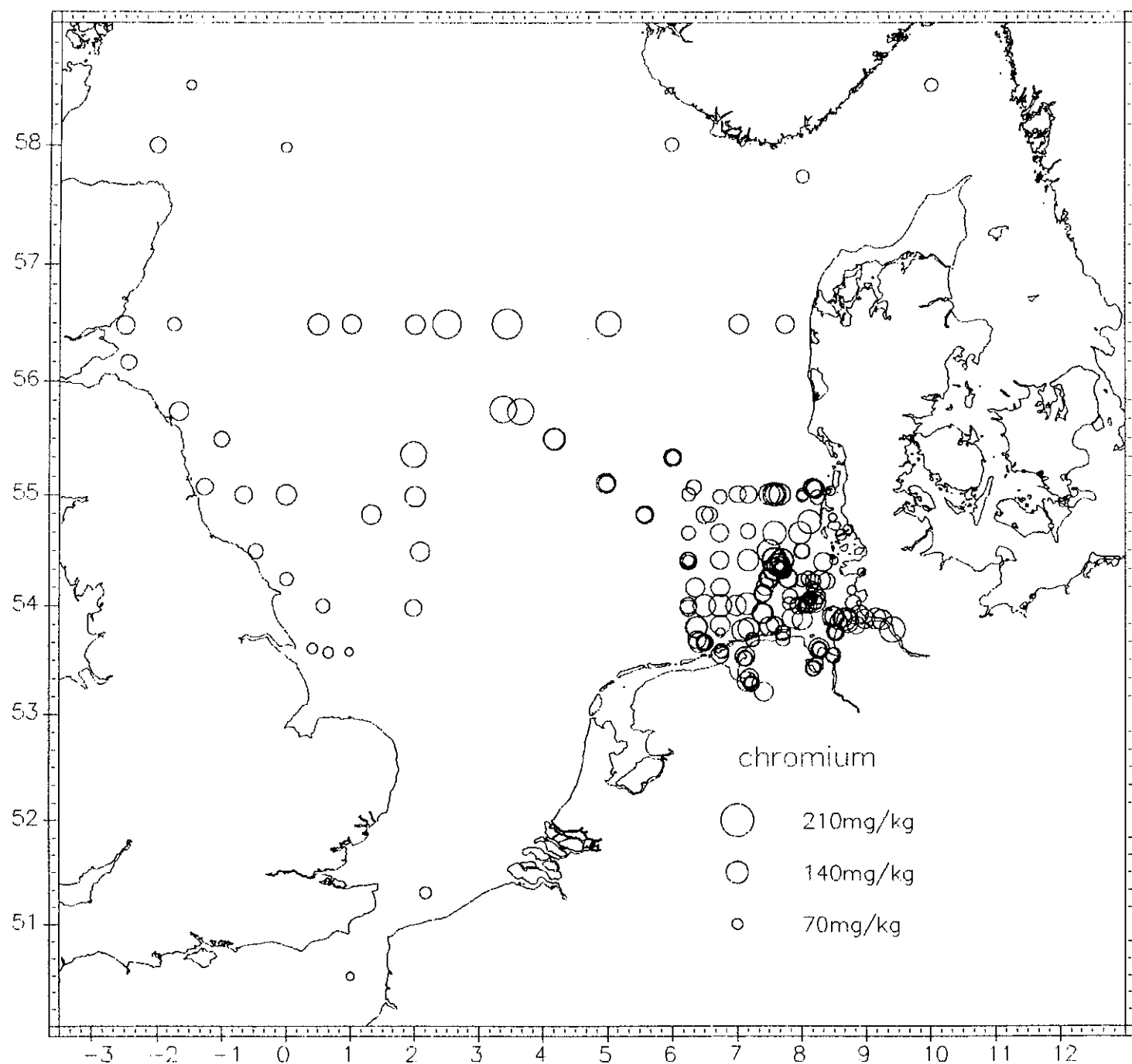


Figure 6.4.3 The distribution of chromium concentrations in North Sea sediment fines <20 μm (circle diameter proportional to value).

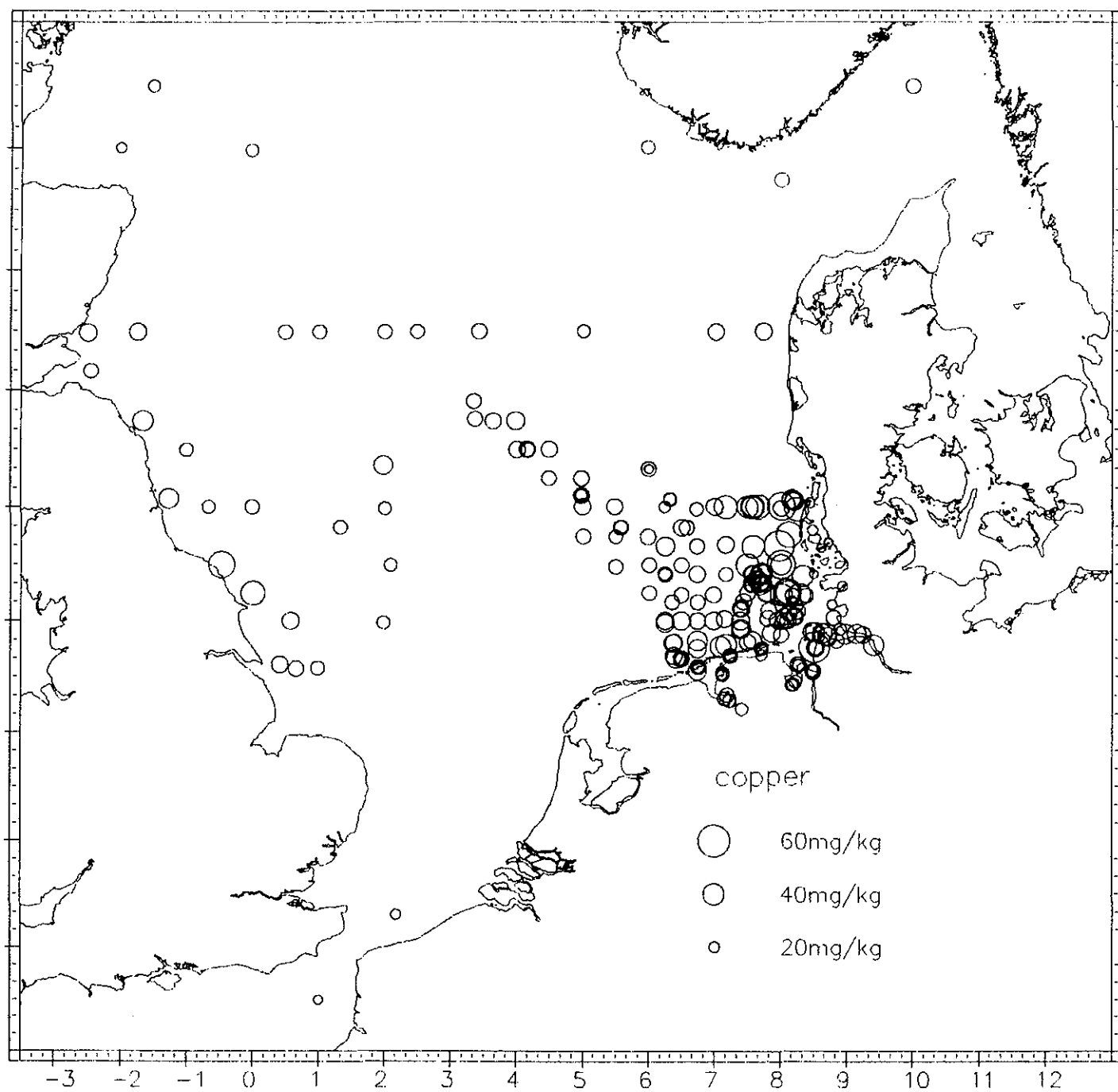


Figure 6.4.4 The distribution of copper concentrations in North Sea sediment fines <20 μm (circle diameter proportional to value).

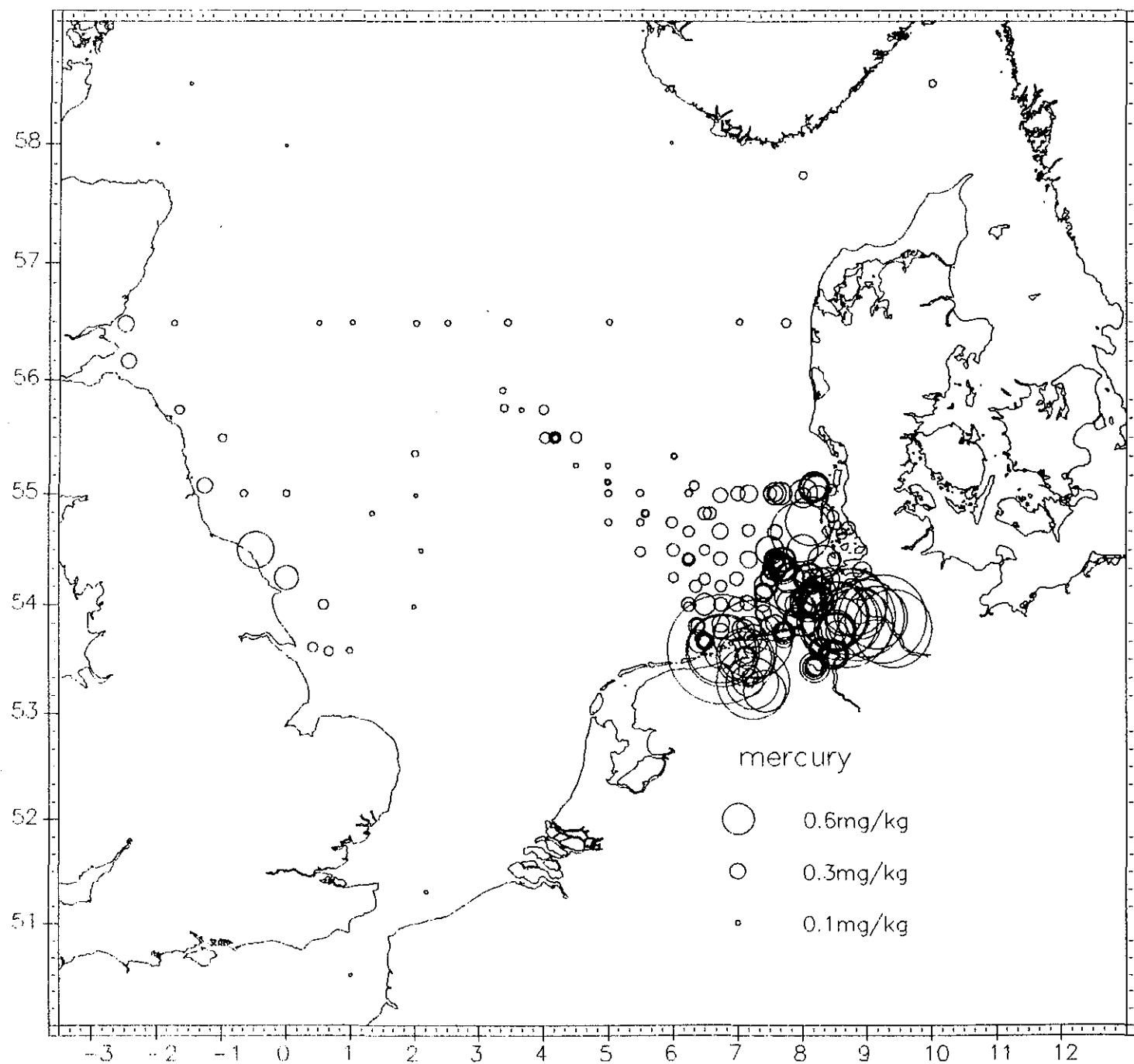


Figure 6.4.5 The distribution of mercury concentrations in North Sea sediment fines $< 20 \mu\text{m}$ (circle diameter proportional to value).

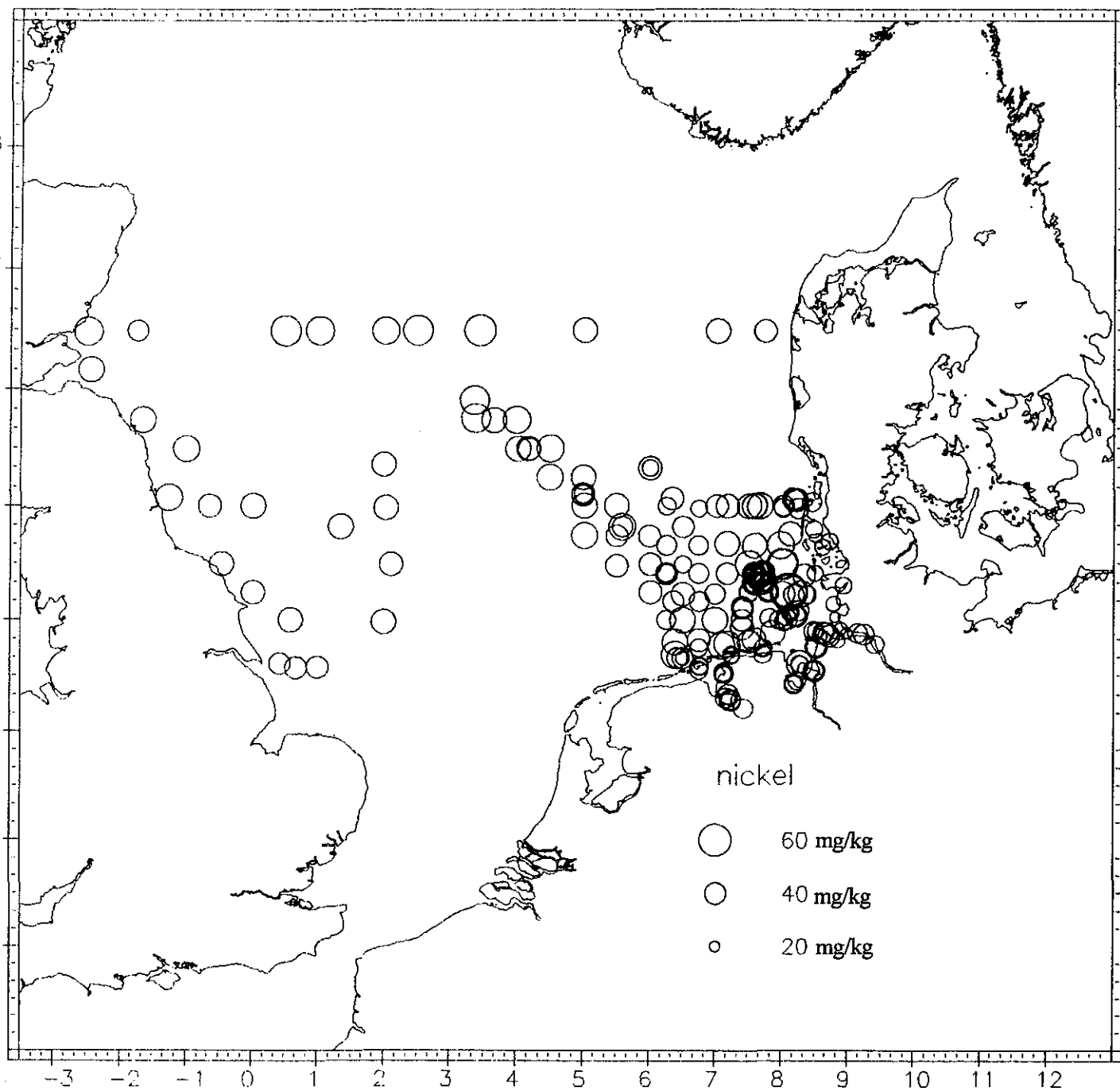


Figure 6.4.6 The distribution of nickel concentrations in North Sea sediment fines $<20\ \mu\text{m}$ (circle diameter proportional to value).

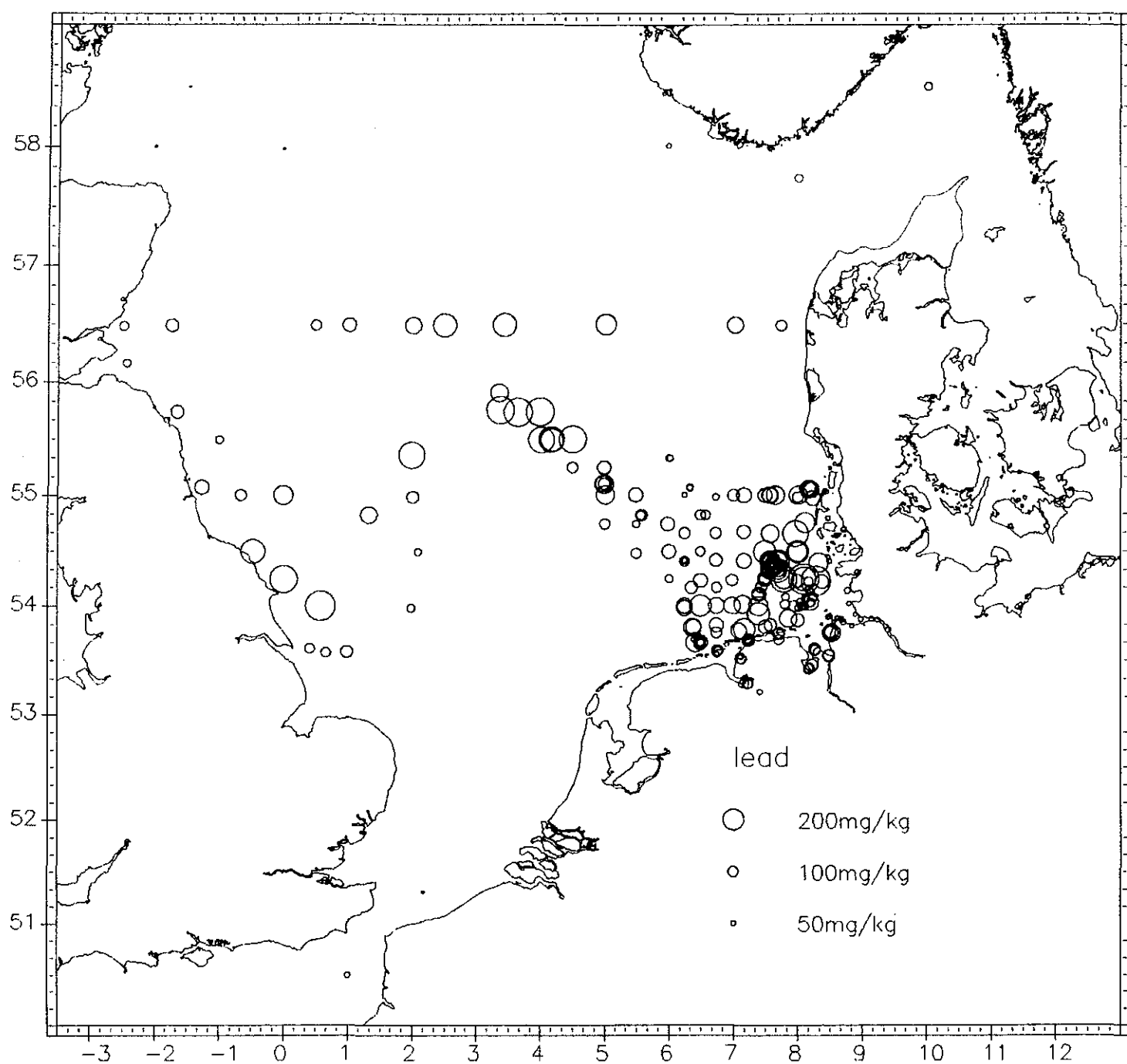


Figure 6.4.7 The distribution of lead concentrations in North Sea sediment fines $<20 \mu\text{m}$ (circle diameter proportional to value).

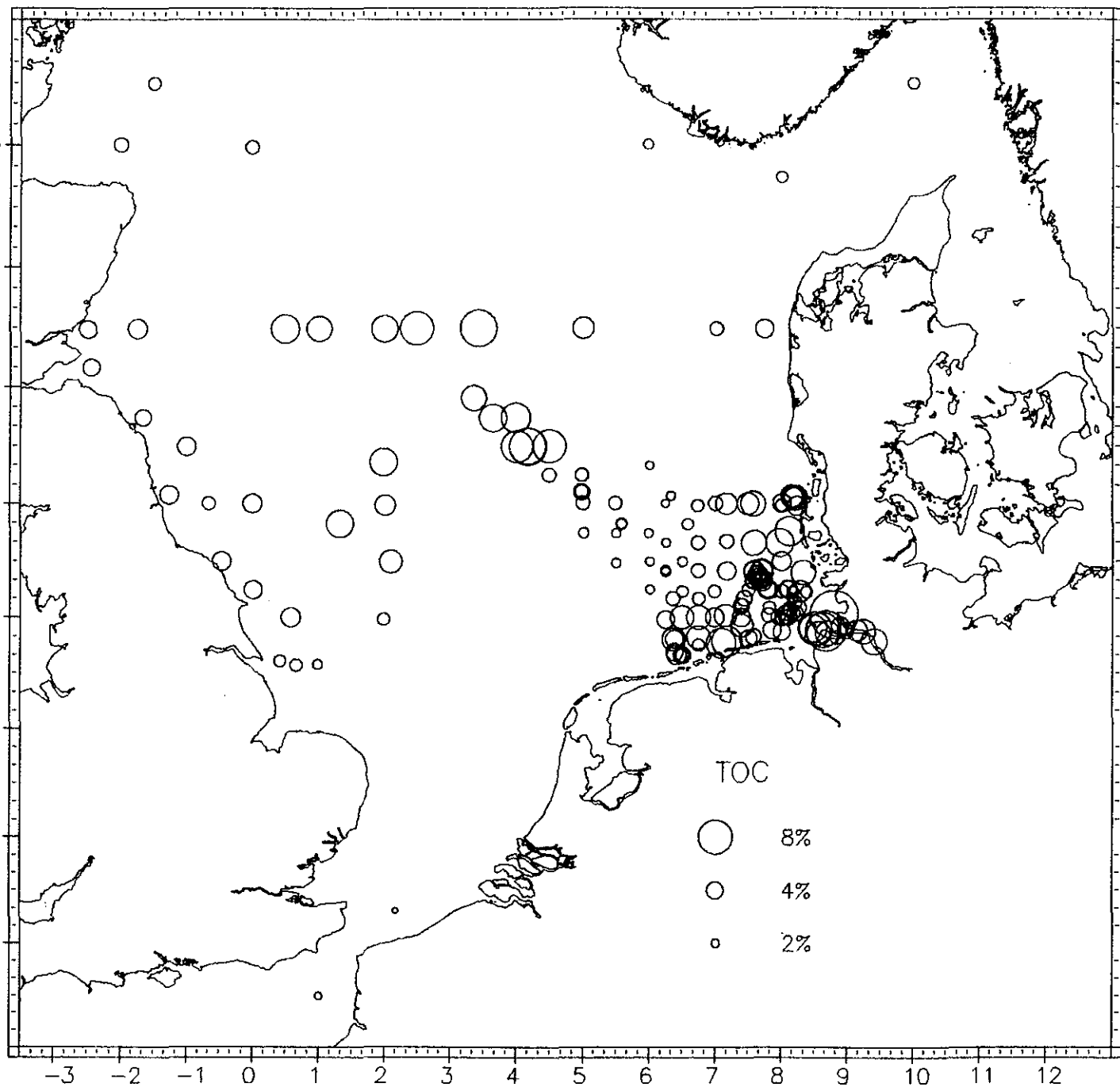


Figure 6.4.8 The distribution of total organic carbon concentrations in North Sea sediment fines $<20\ \mu\text{m}$ (circle diameter proportional to value).

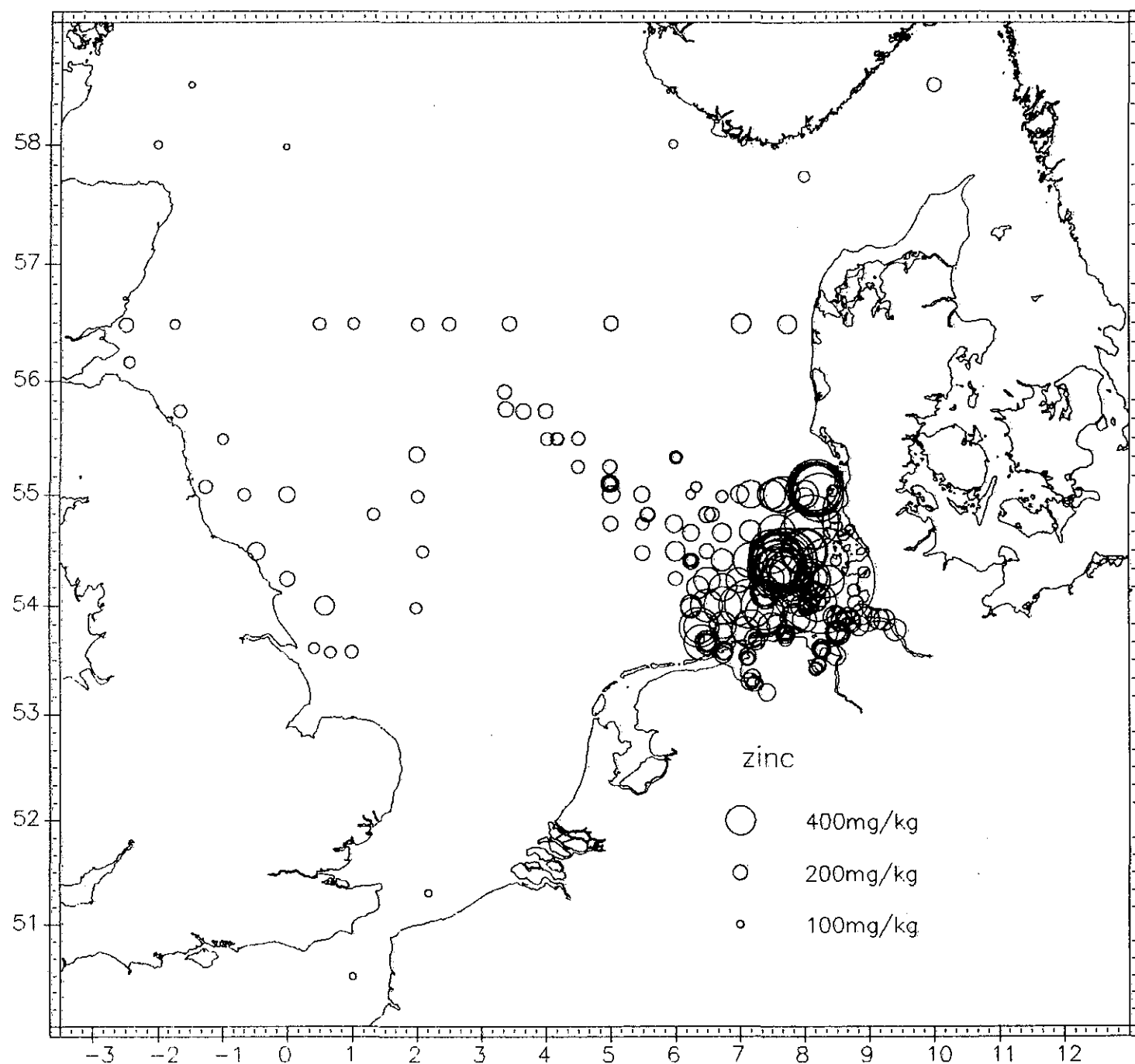


Figure 6.4.9 The distribution of zinc concentrations in North Sea sediment fines $<20\ \mu\text{m}$ (circle diameter proportional to value).

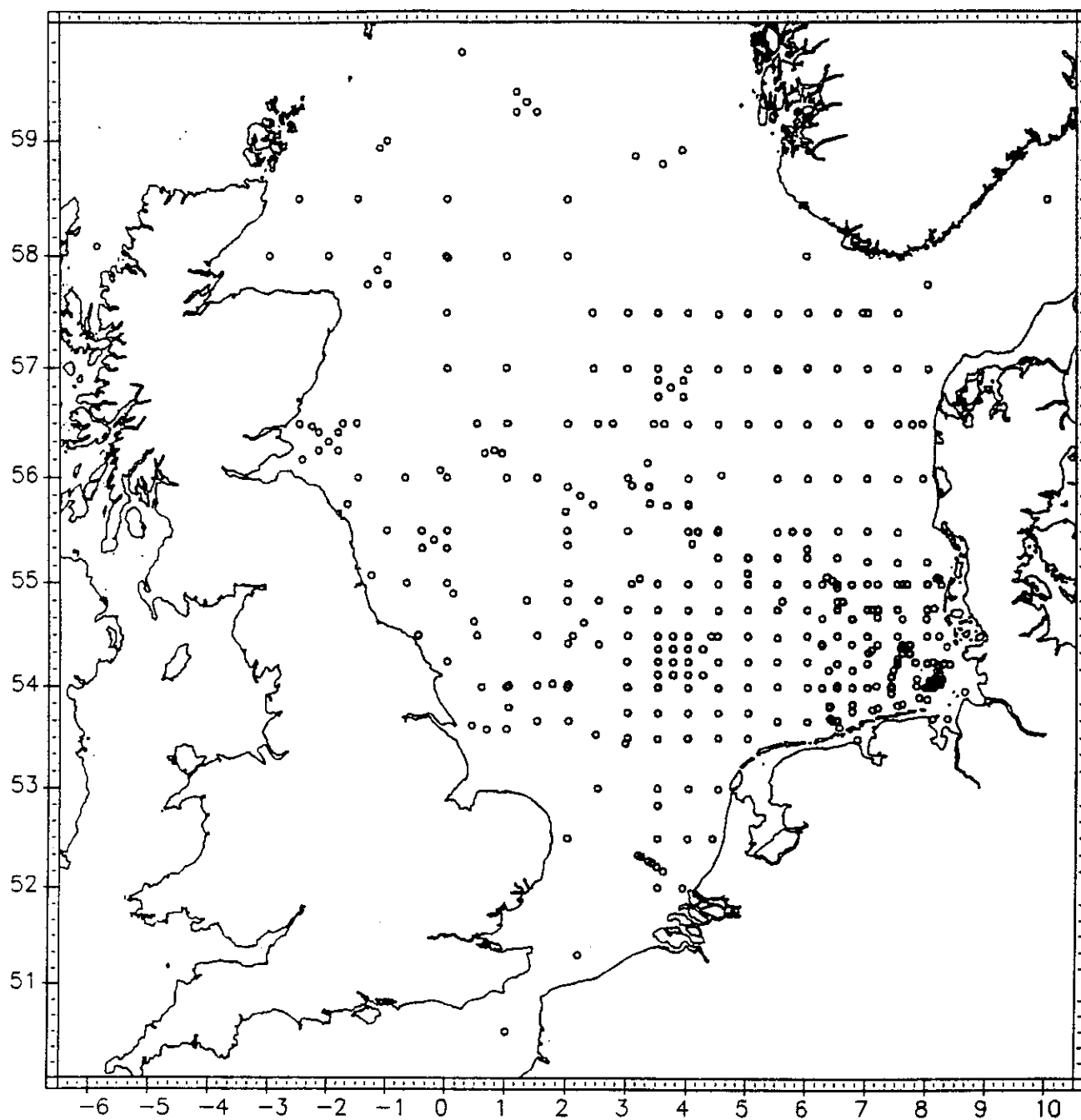


Figure 6.5.1 Locations sampled by laboratory BSHG for sediments $<20\ \mu\text{m}$ (data prior to 1990).

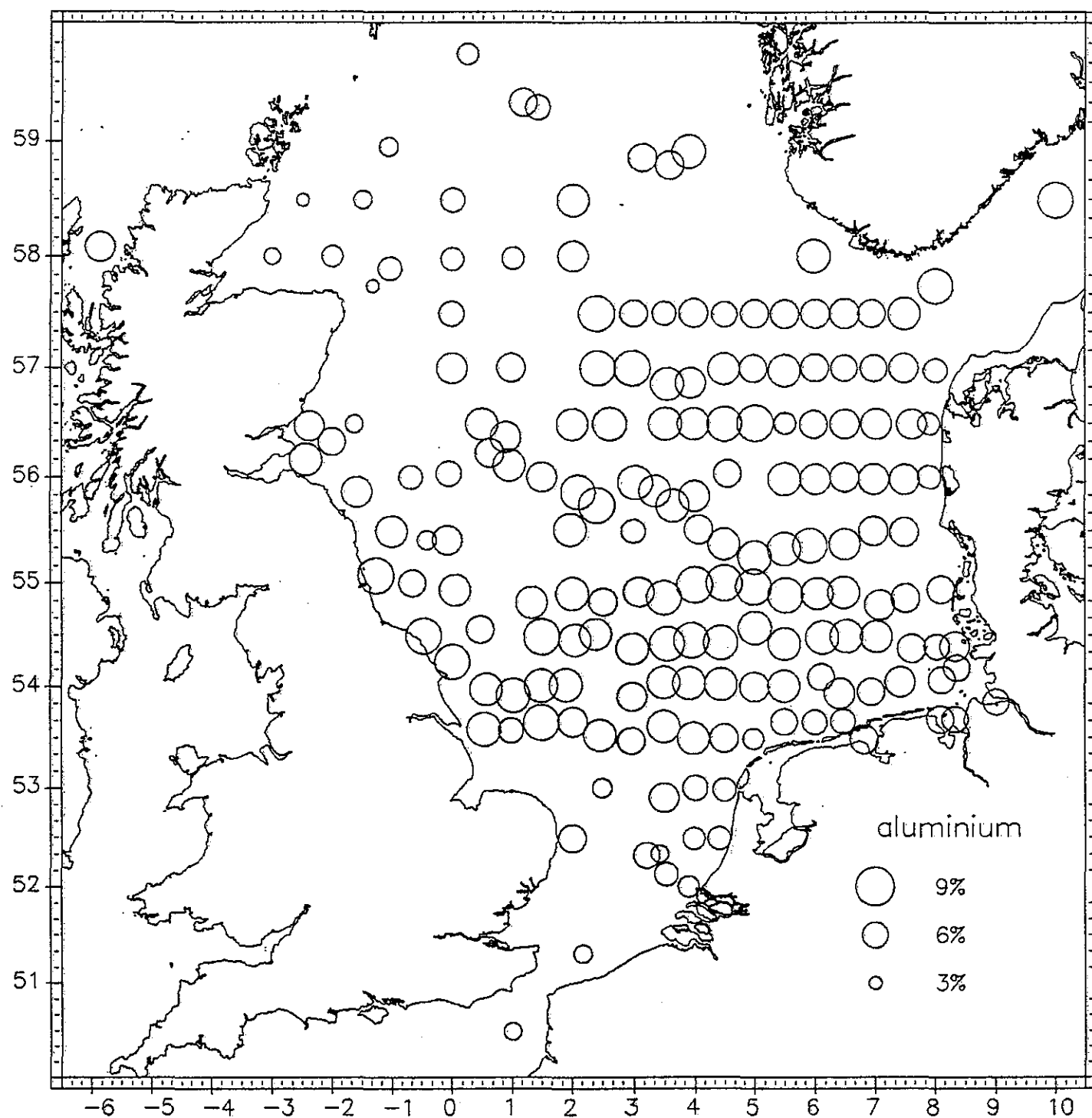


Figure 6.5.2 The distribution of aluminium concentrations in North Sea sediment fines <20 μm (BSHG data) (circle diameter proportional to value).

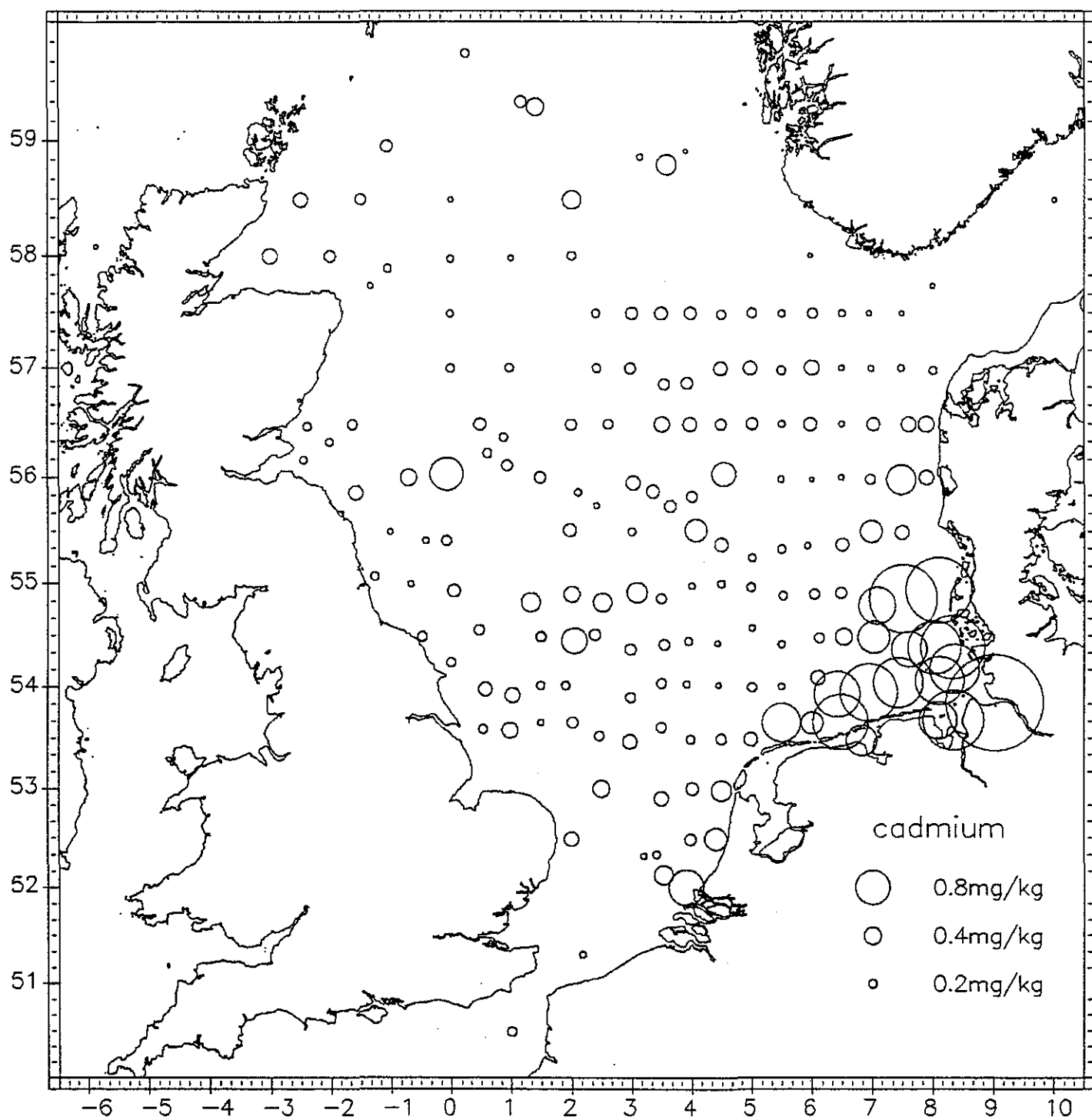


Figure 6.5.3 The distribution of cadmium concentrations in North Sea sediment fines <20 μm (BSHG data) (circle diameter proportional to value).

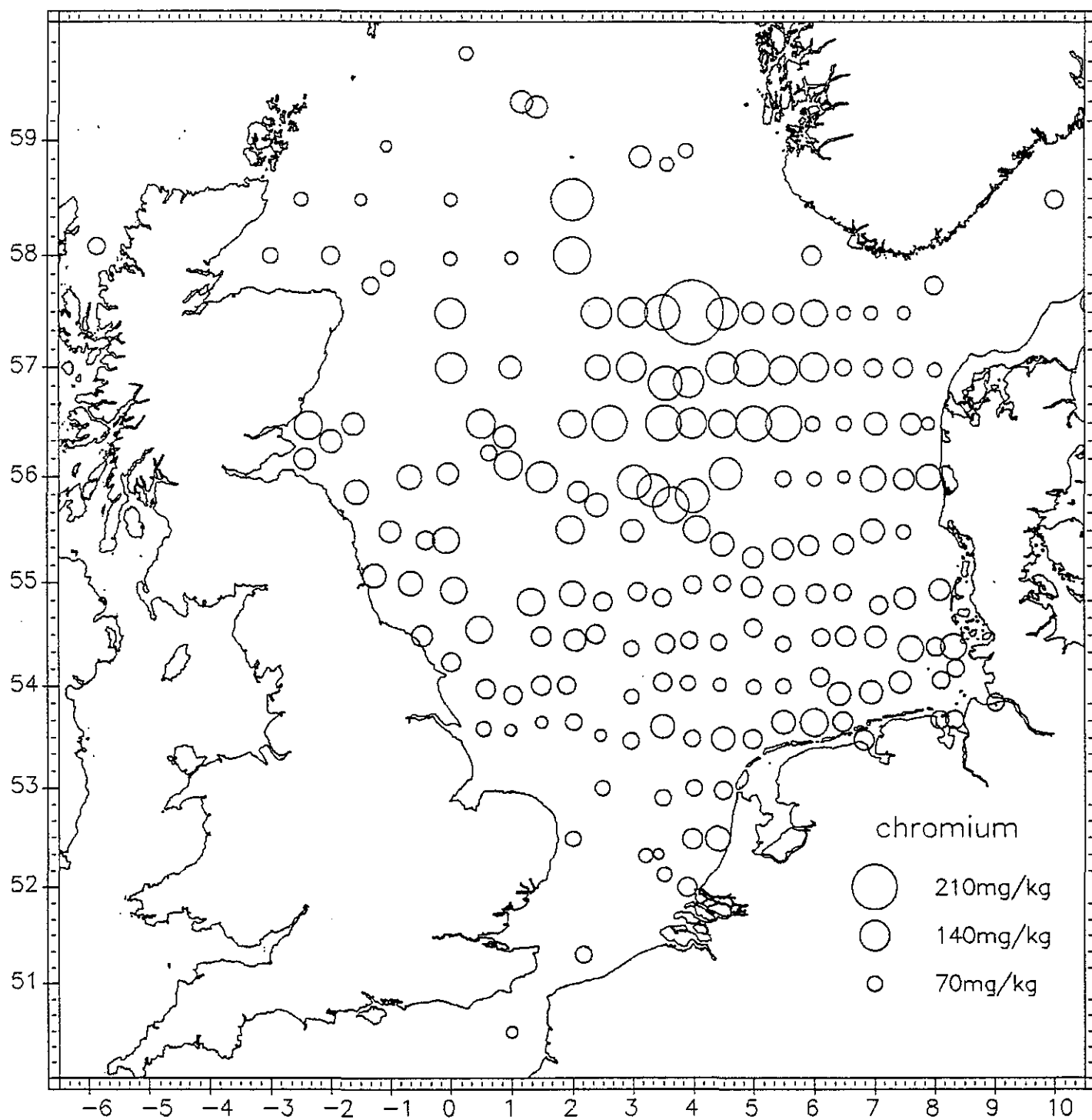


Figure 6.5.4 The distribution of chromium concentrations in North Sea sediment fines $<20\ \mu\text{m}$ (BSHG data) (circle diameter proportional to value).

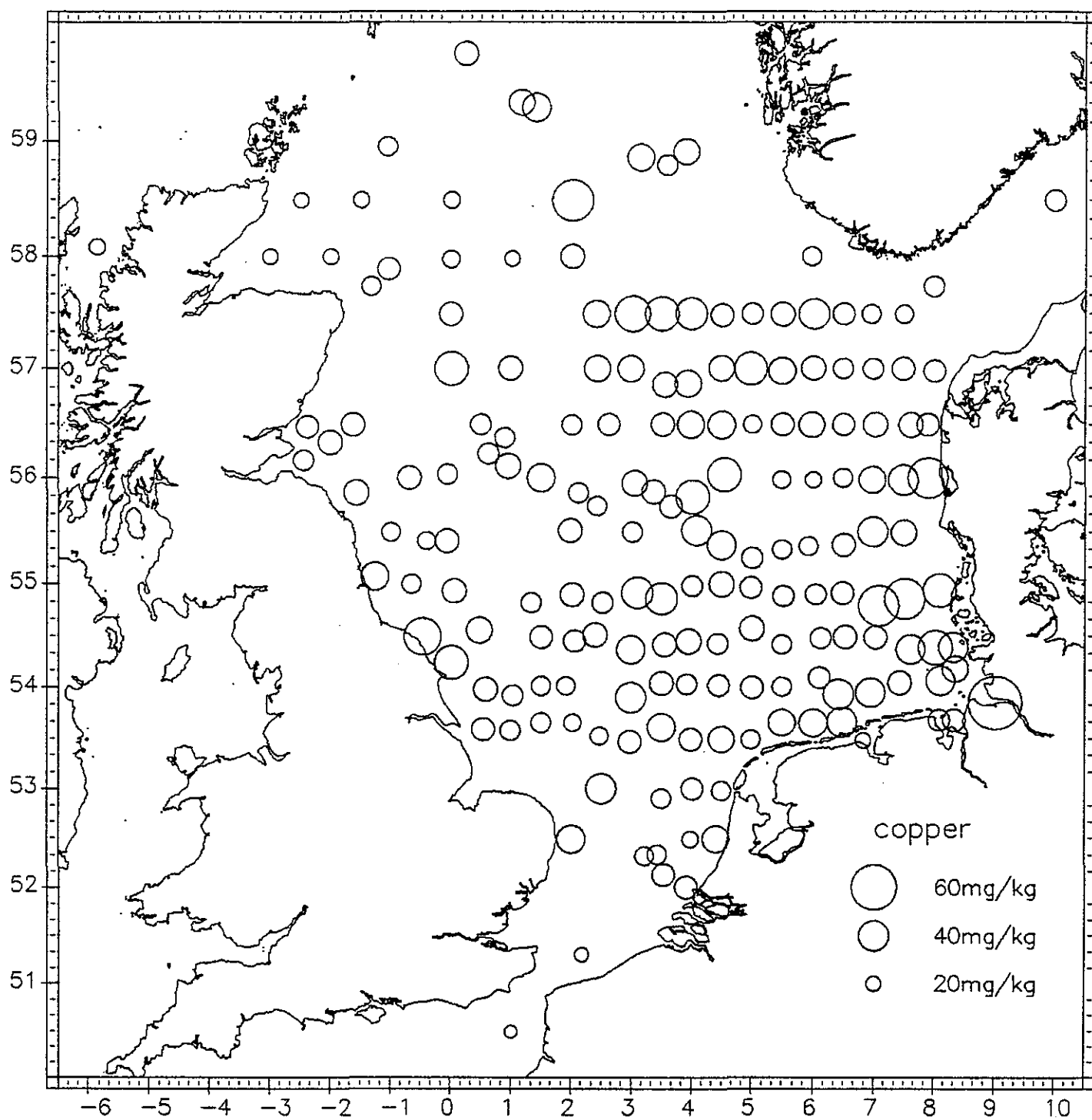


Figure 6.5.5 The distribution of copper concentrations in North Sea sediment fines <20 μm (BSHG data) (circle diameter proportional to value).

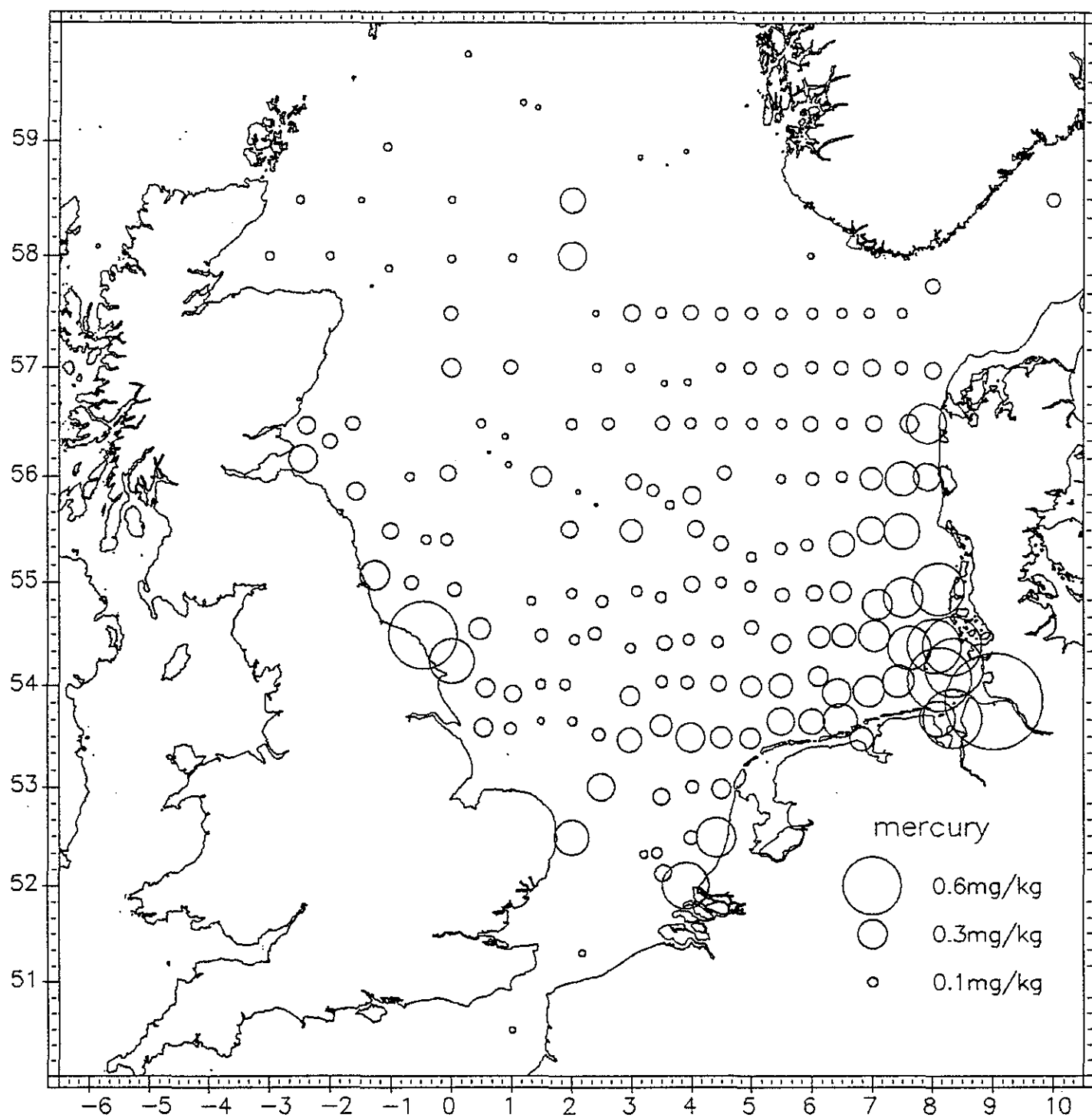


Figure 6.5.6 The distribution of mercury concentrations in North Sea sediment fines <20 μm (BSHG data including samples taken in 1976) (circle diameter proportional to value).

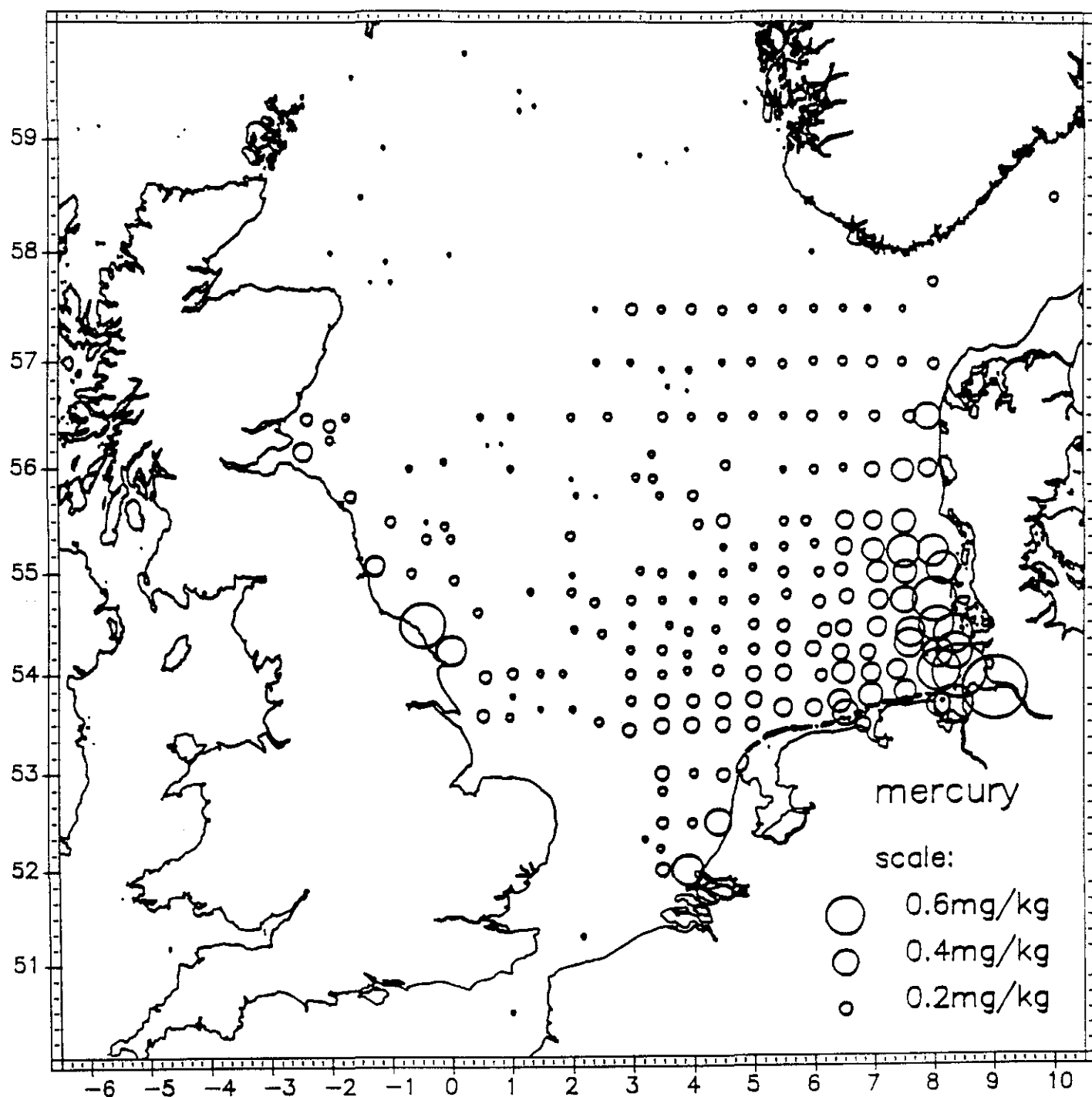


Figure 6.5.7 The distribution of mercury concentrations in North Sea sediment fines <20 μm (BSHG data from 1985 and thereafter) (circle diameter proportional to value).

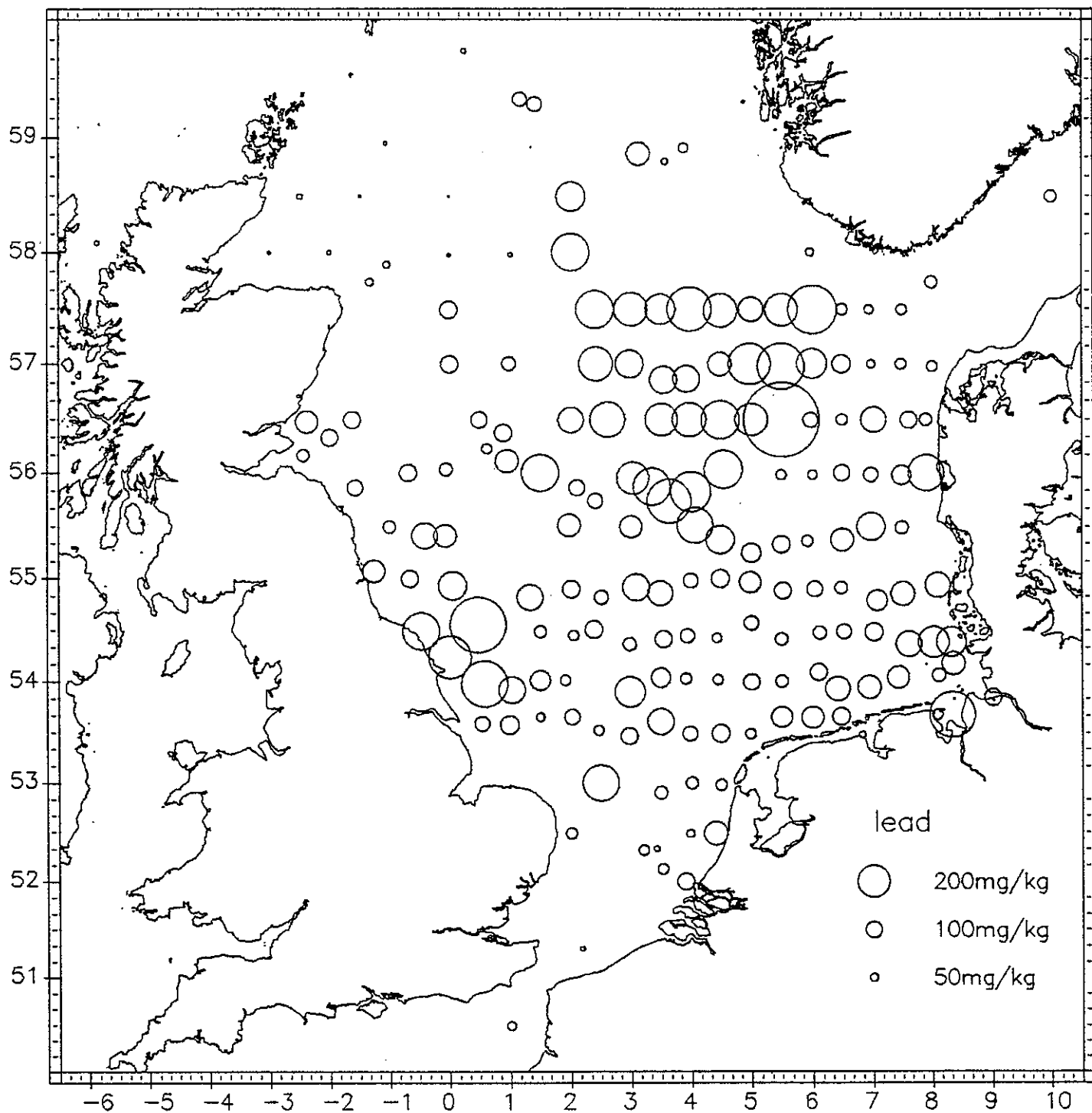


Figure 6.5.8 The distribution of lead concentrations in North Sea sediment fines $<20\ \mu\text{m}$ (BSHG data) (circle diameter proportional to value).

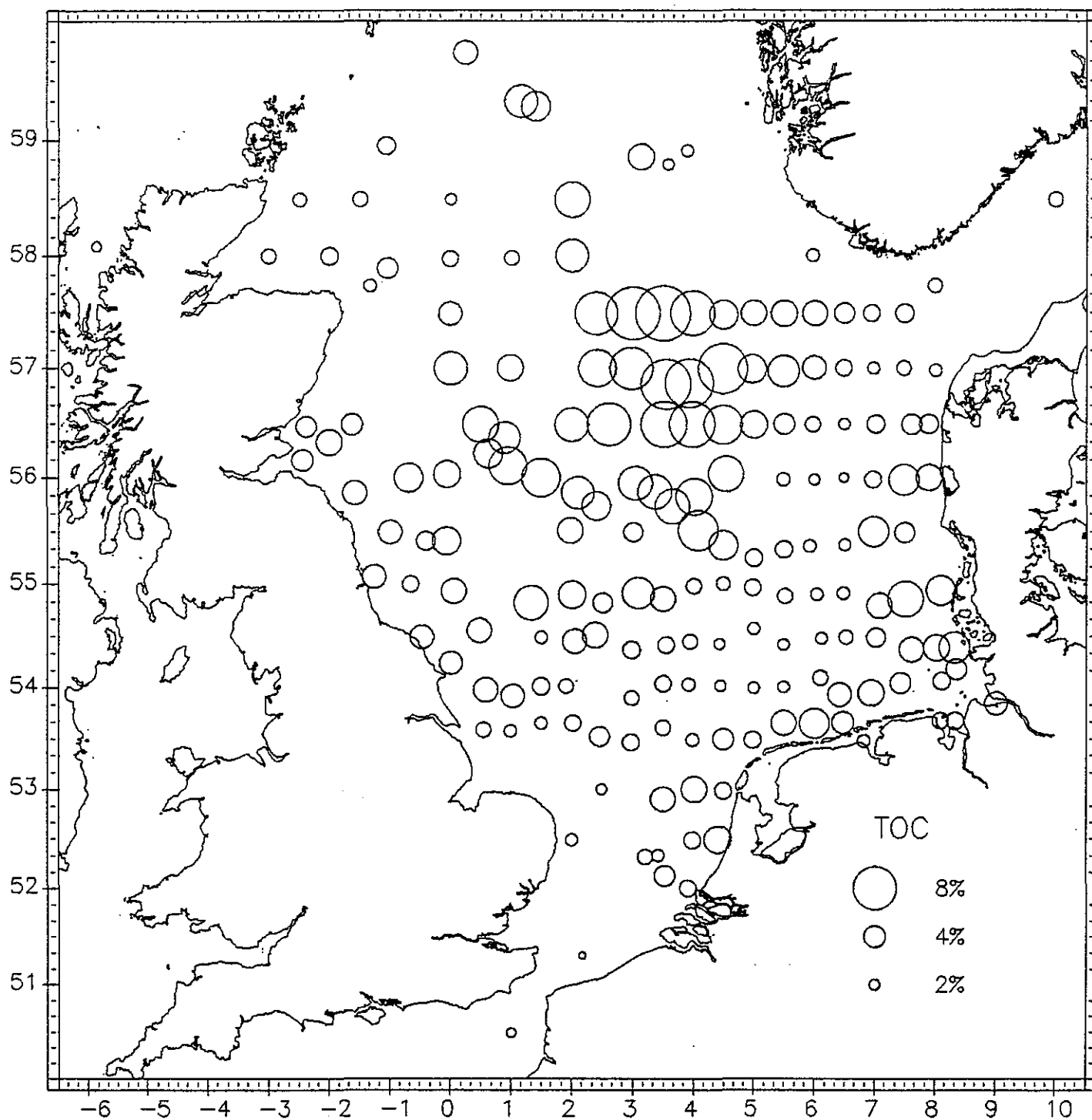


Figure 6.5.9 The distribution of total organic carbon (TOC) concentrations in North Sea sediment fines <20 μm (BSHG data) (circle diameter proportional to value).

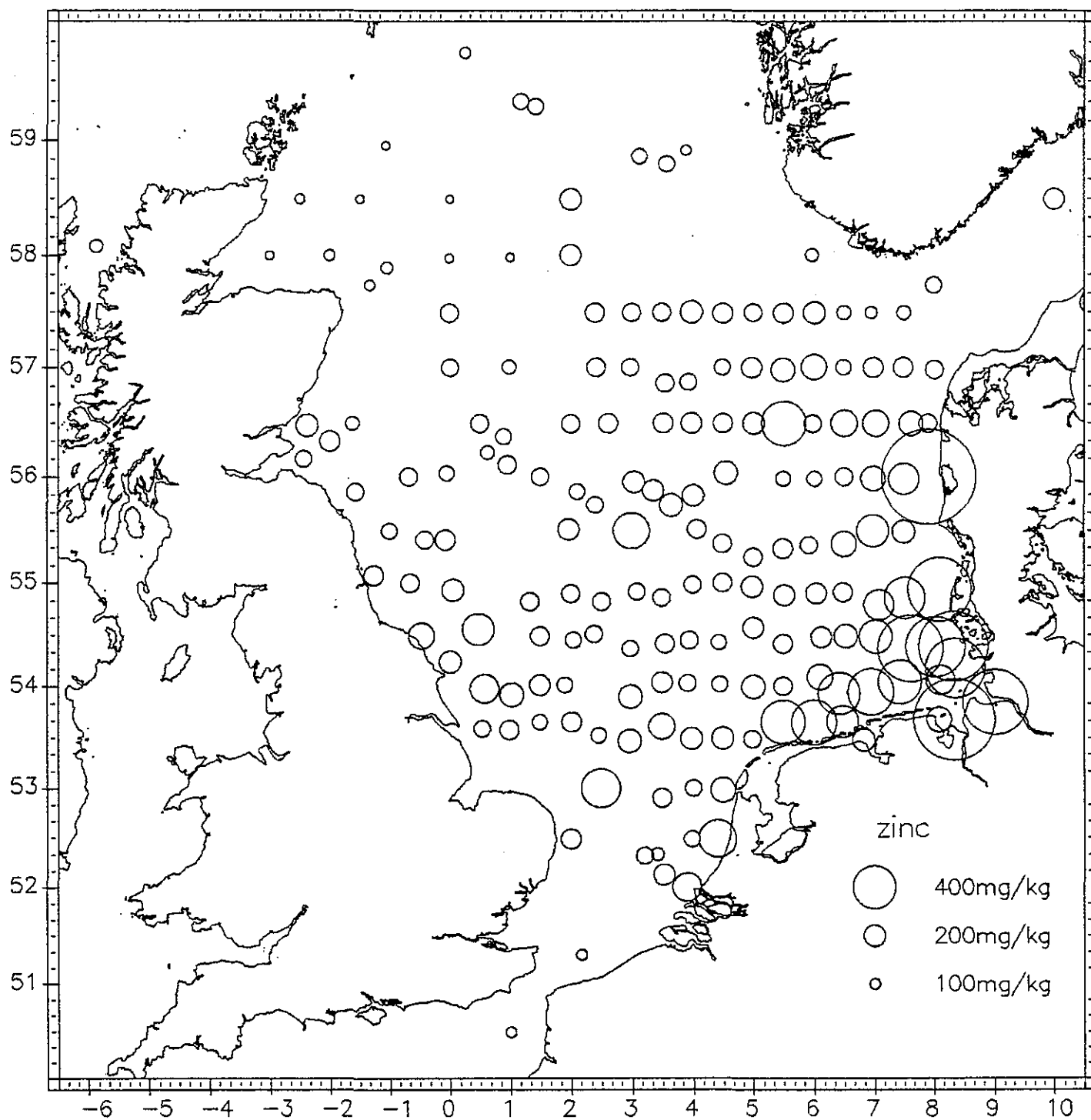


Figure 6.5.10 The distribution of zinc concentrations in North Sea sediment fines <20 μm (BSHG data) (circle diameter proportional to value).

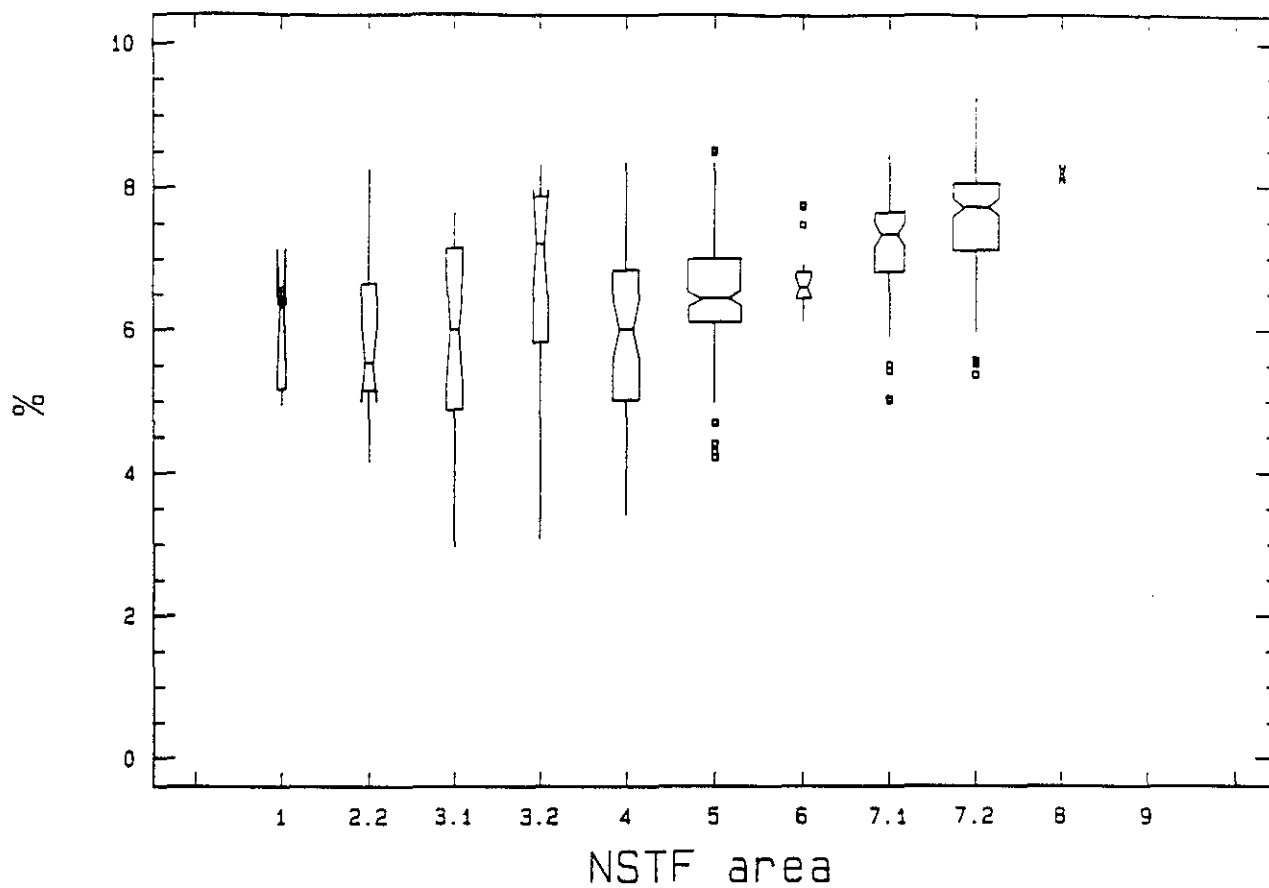


Figure 6.5.11 Distributions of aluminium concentrations in sediment fines $<20\ \mu\text{m}$ for different areas of the North Sea (BSHG data).

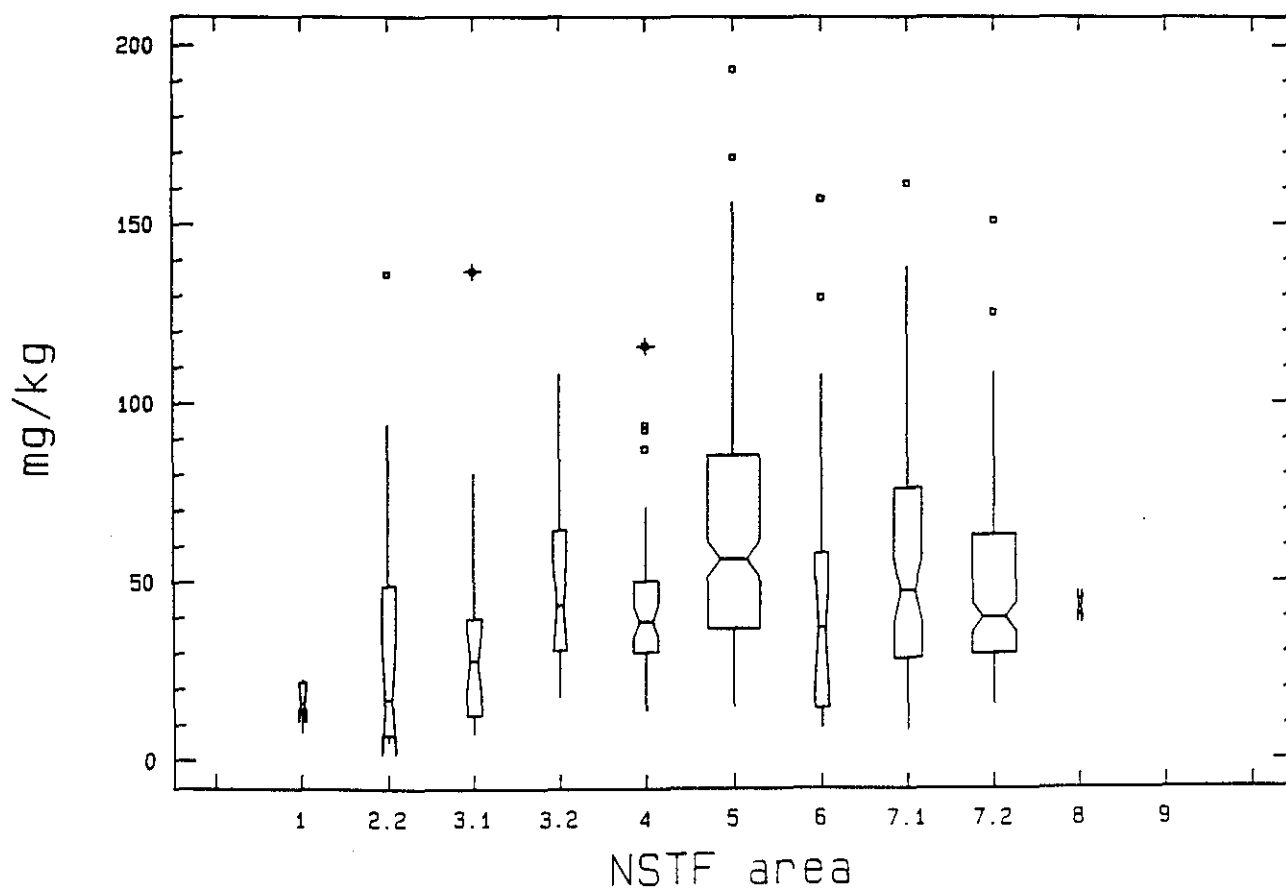


Figure 6.5.12 Distributions of arsenic concentrations in sediment fines $<20\ \mu\text{m}$ for different areas of the North Sea (BSHG data).

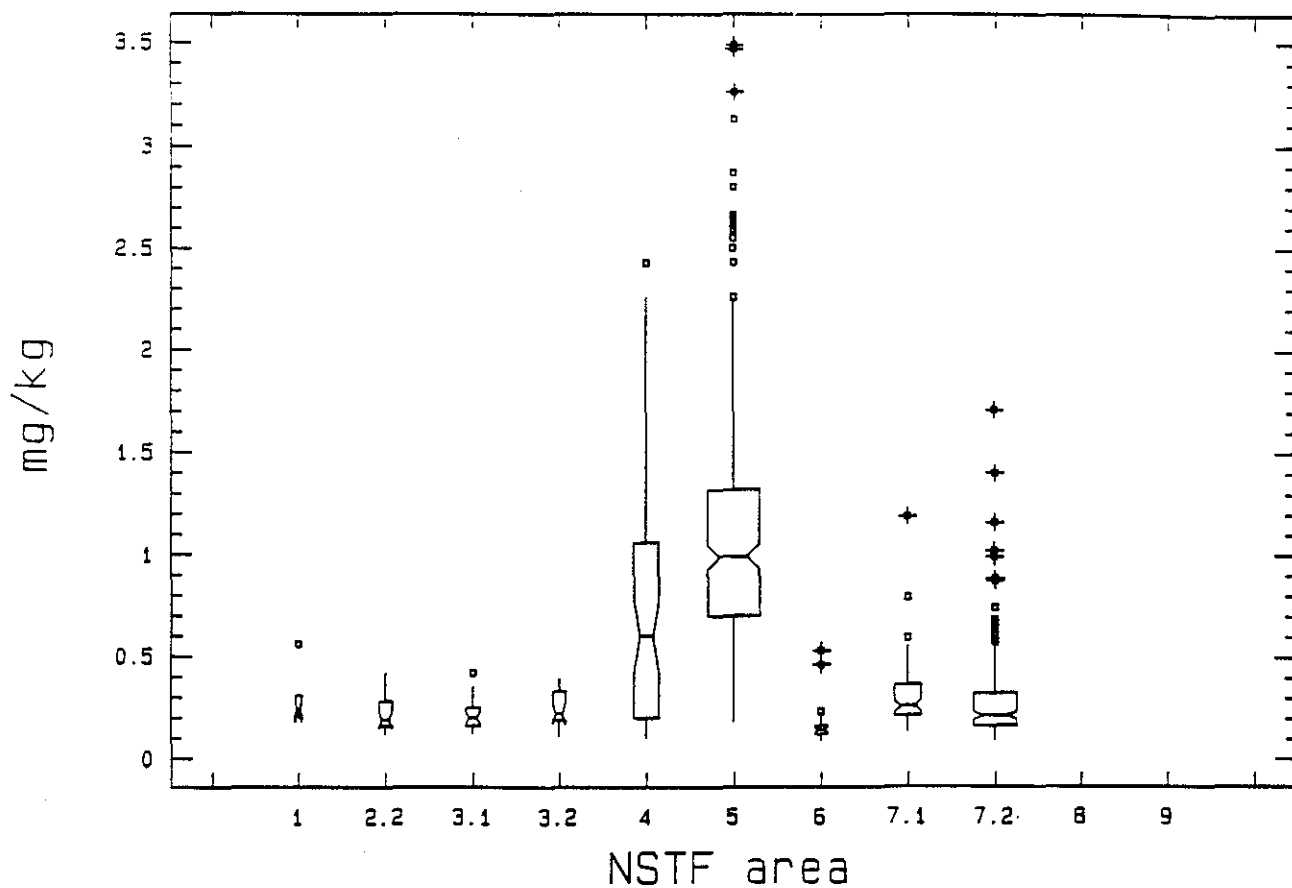


Figure 6.5.13 Distributions of cadmium concentrations in sediment fines $<20 \mu\text{m}$ for different areas of the North Sea (BSHG data).

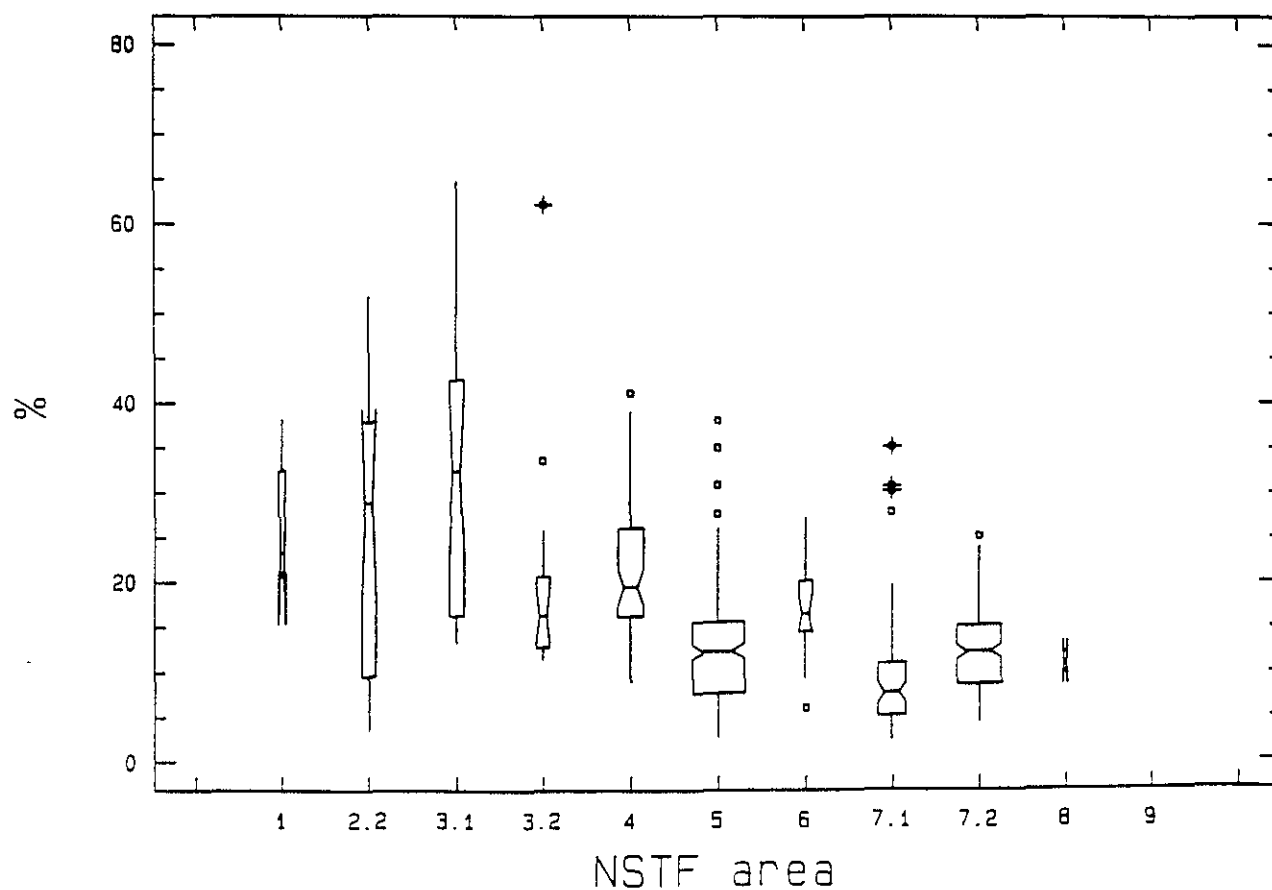


Figure 6.5.14 Distributions of calcium carbonate concentrations in sediment fines $<20 \mu\text{m}$ for different areas of the North Sea (BSHG data).

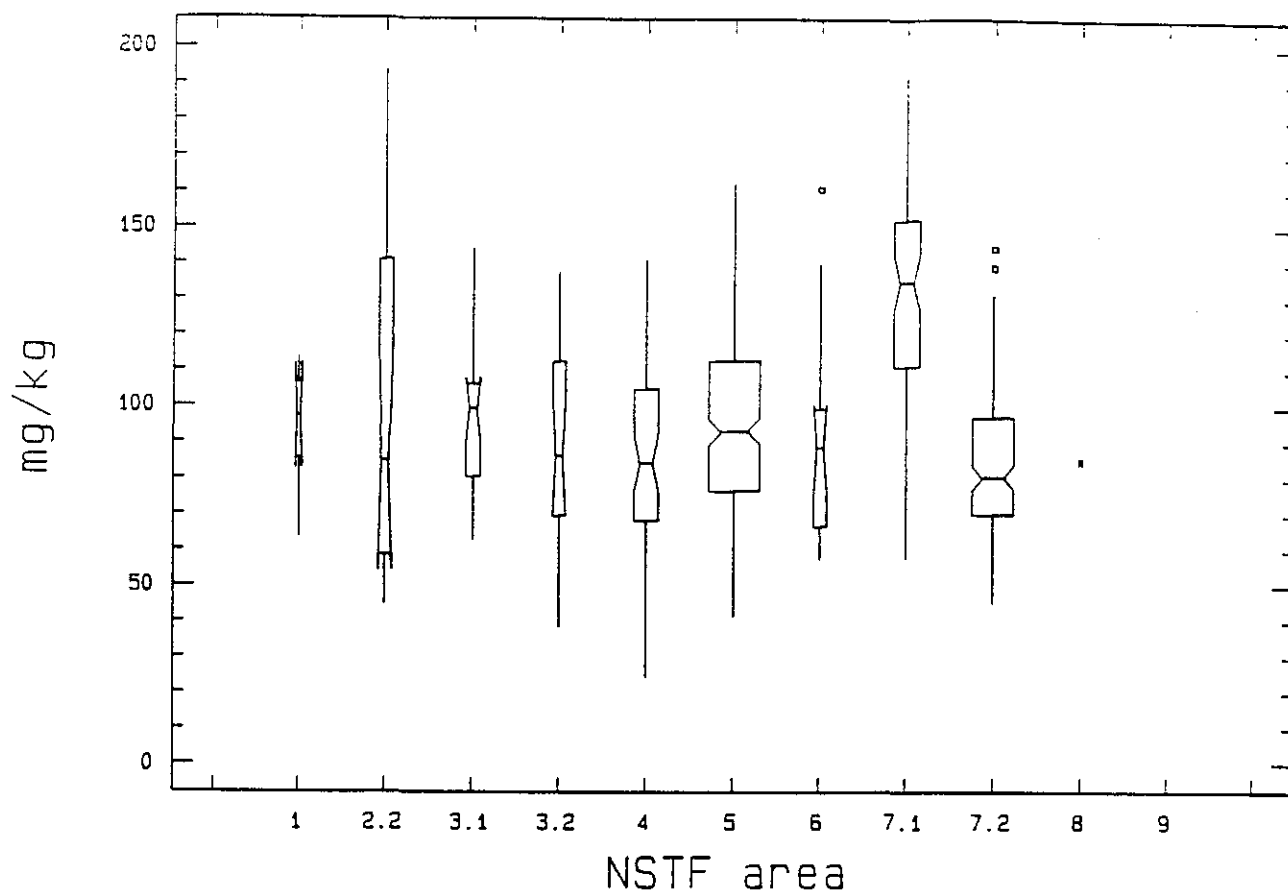


Figure 6.5.15 Distributions of chromium concentrations in sediment fines <20 μm for different areas of the North Sea (BSHG data).

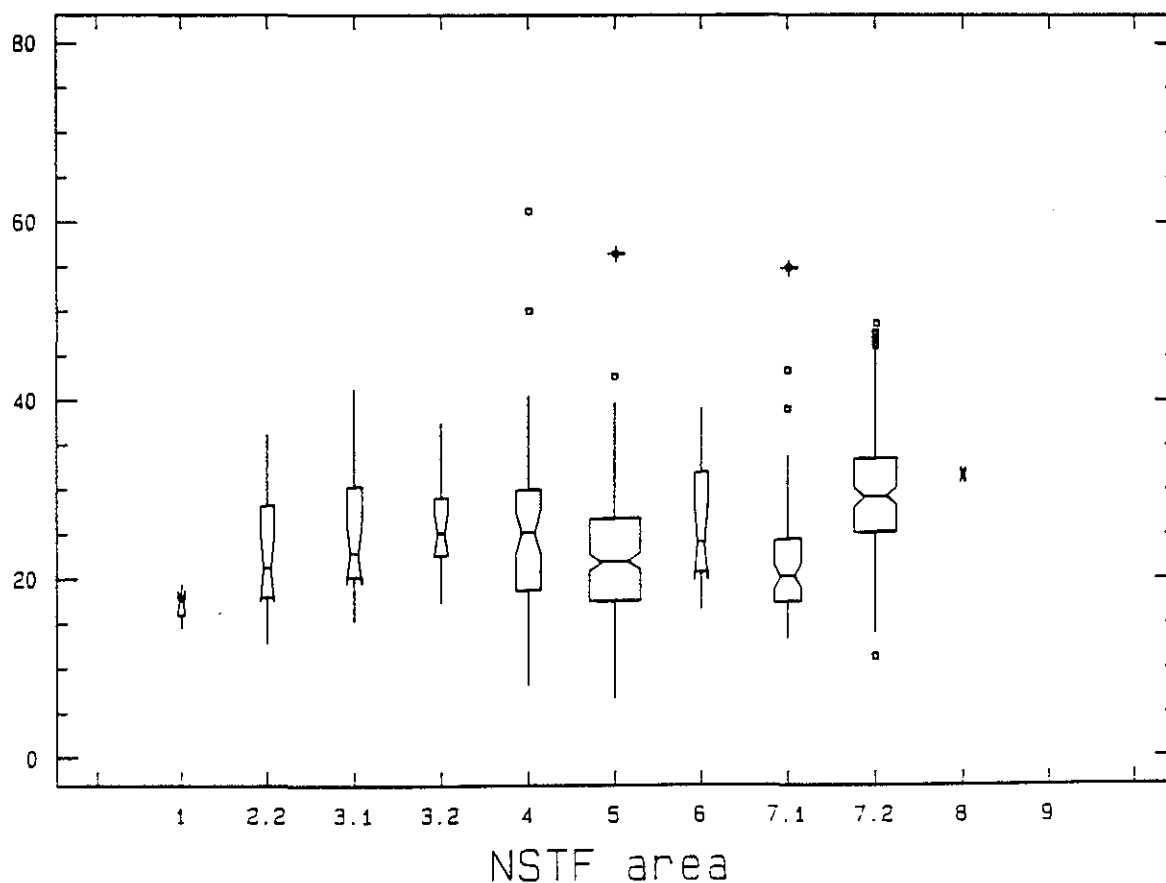


Figure 6.5.16 Distributions of chromium/total organic carbon ratios in sediment fines <20 μm for different areas of the North Sea (BSHG data).

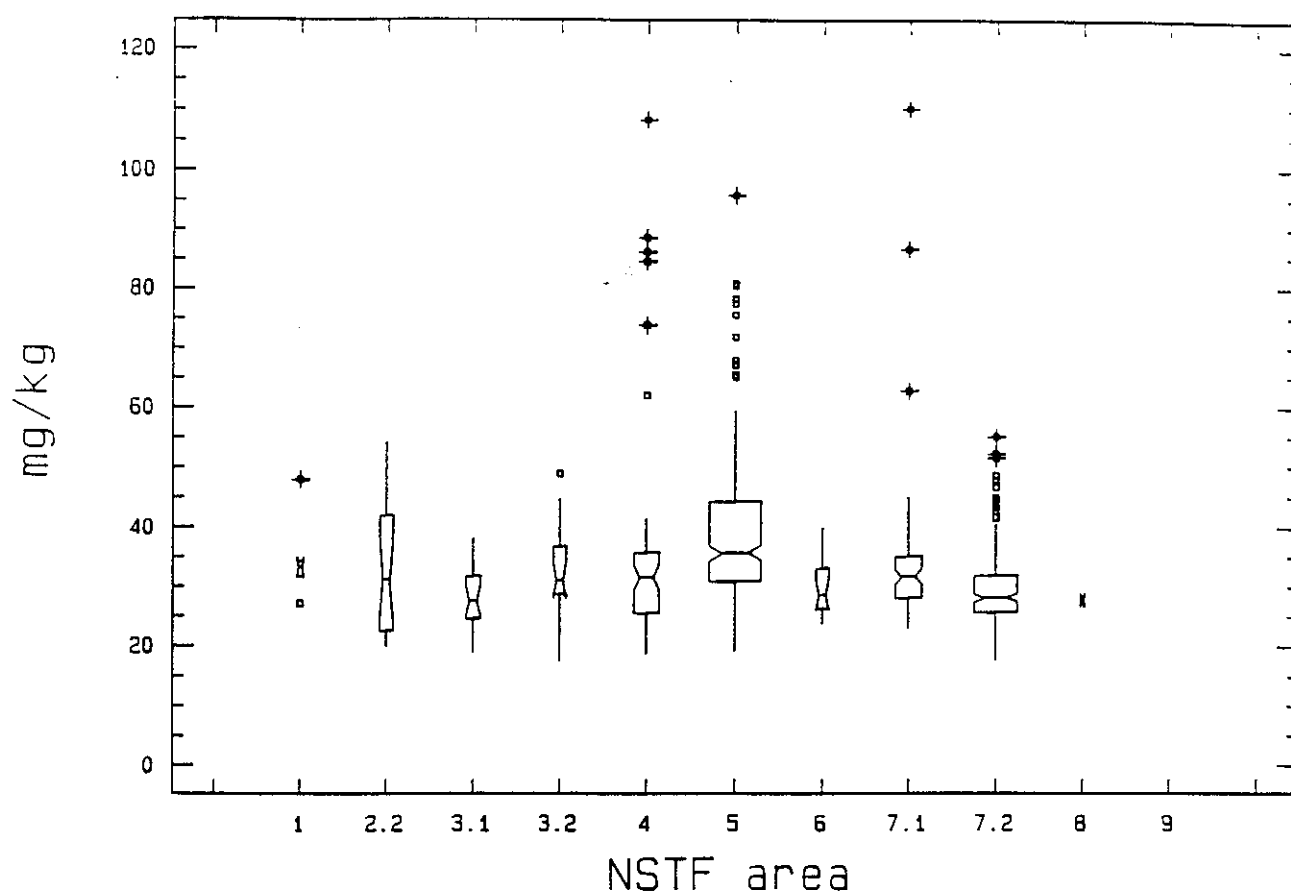


Figure 6.5.17 Distributions of copper concentrations in sediment fines <20 μm for different areas of the North Sea (BSHG data).

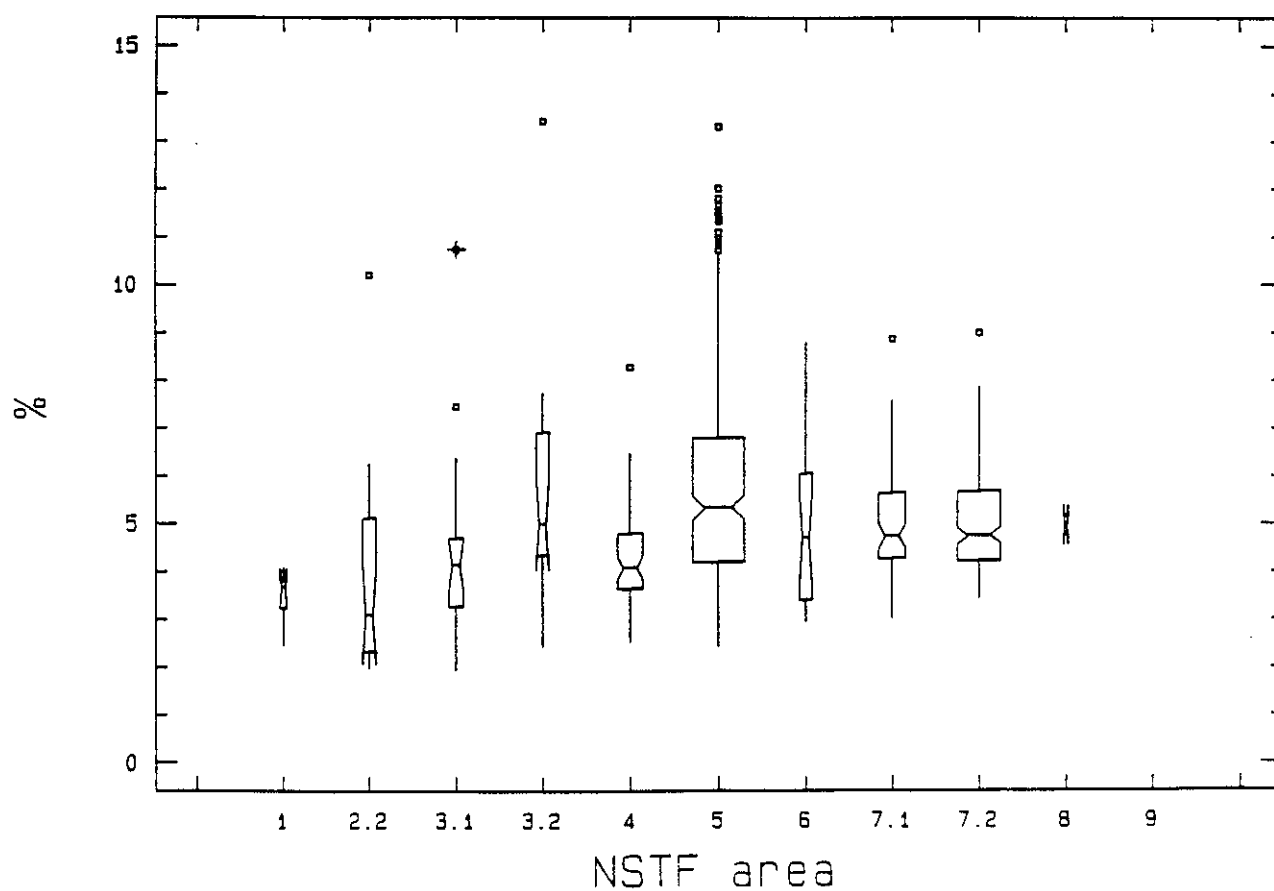


Figure 6.5.18 Distributions of iron concentrations in sediment fines <20 μm for different areas of the North Sea (BSHG data).

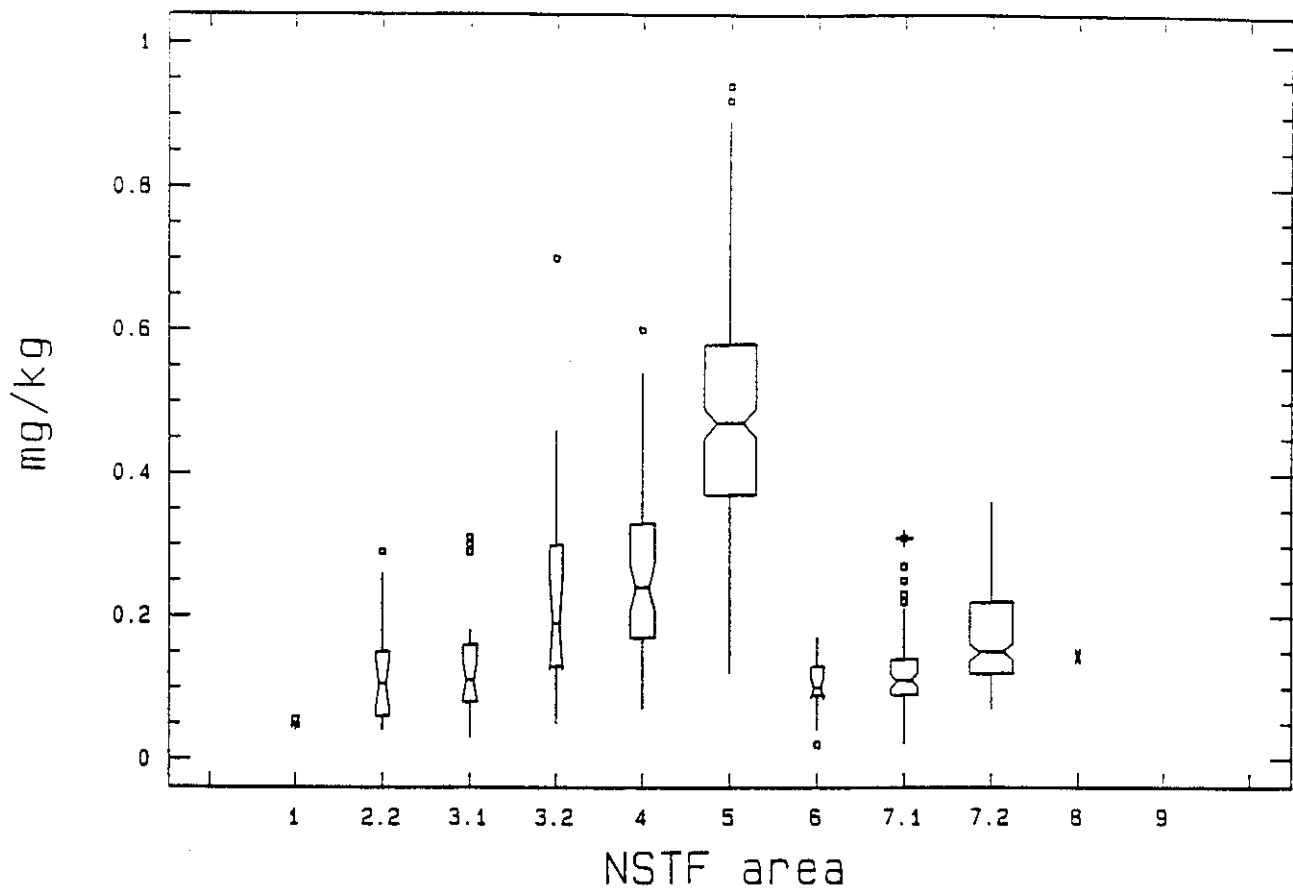


Figure 6.5.19 Distributions of mercury concentrations in sediment fines $<20\ \mu\text{m}$ for different areas of the North Sea (BSHG data).

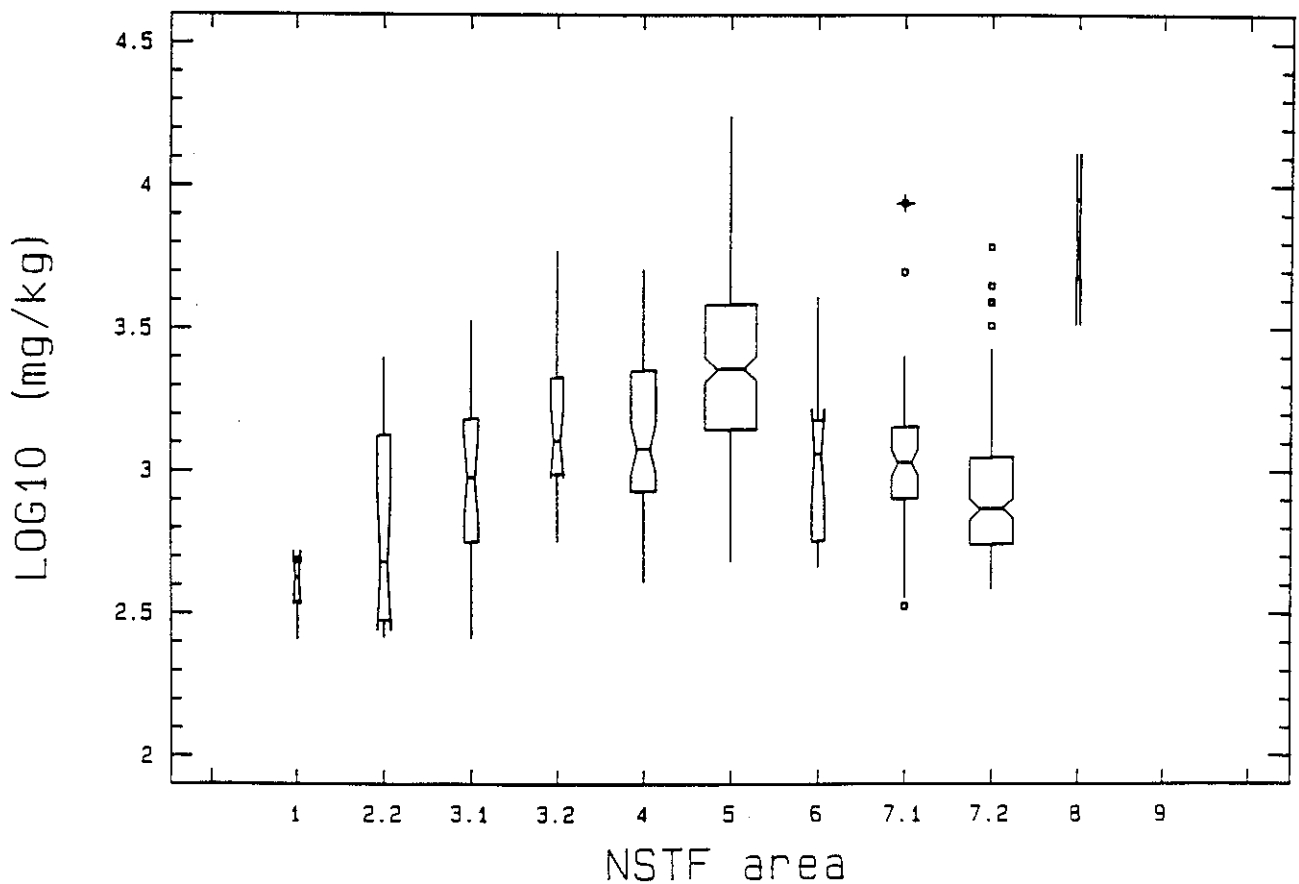


Figure 6.5.20 Distributions of manganese concentrations in sediment fines $<20\ \mu\text{m}$ for different areas of the North Sea (BSHG data).

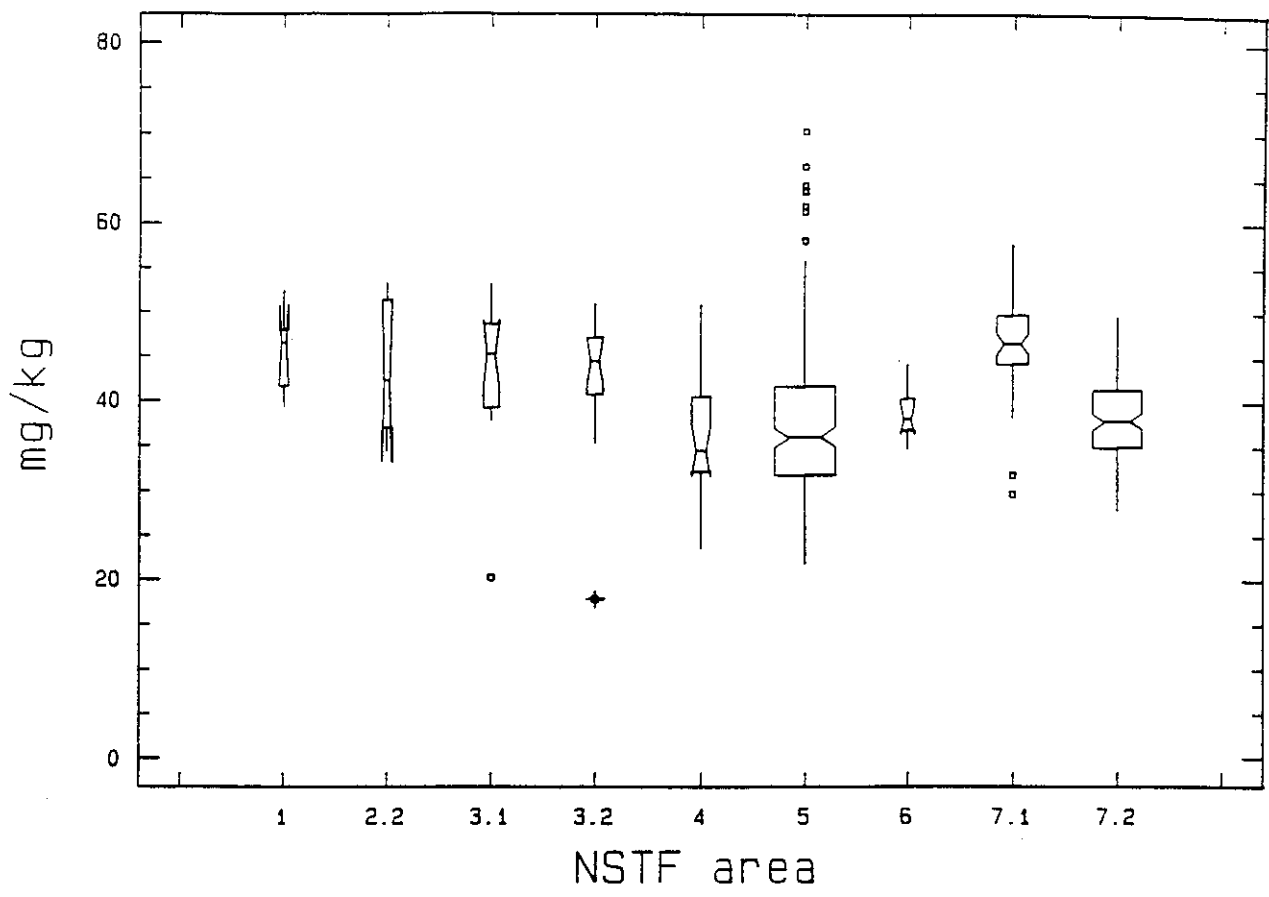


Figure 6.5.21 Distributions of nickel concentrations in sediment fines <20 μm for different areas of the North Sea (BSHG data).

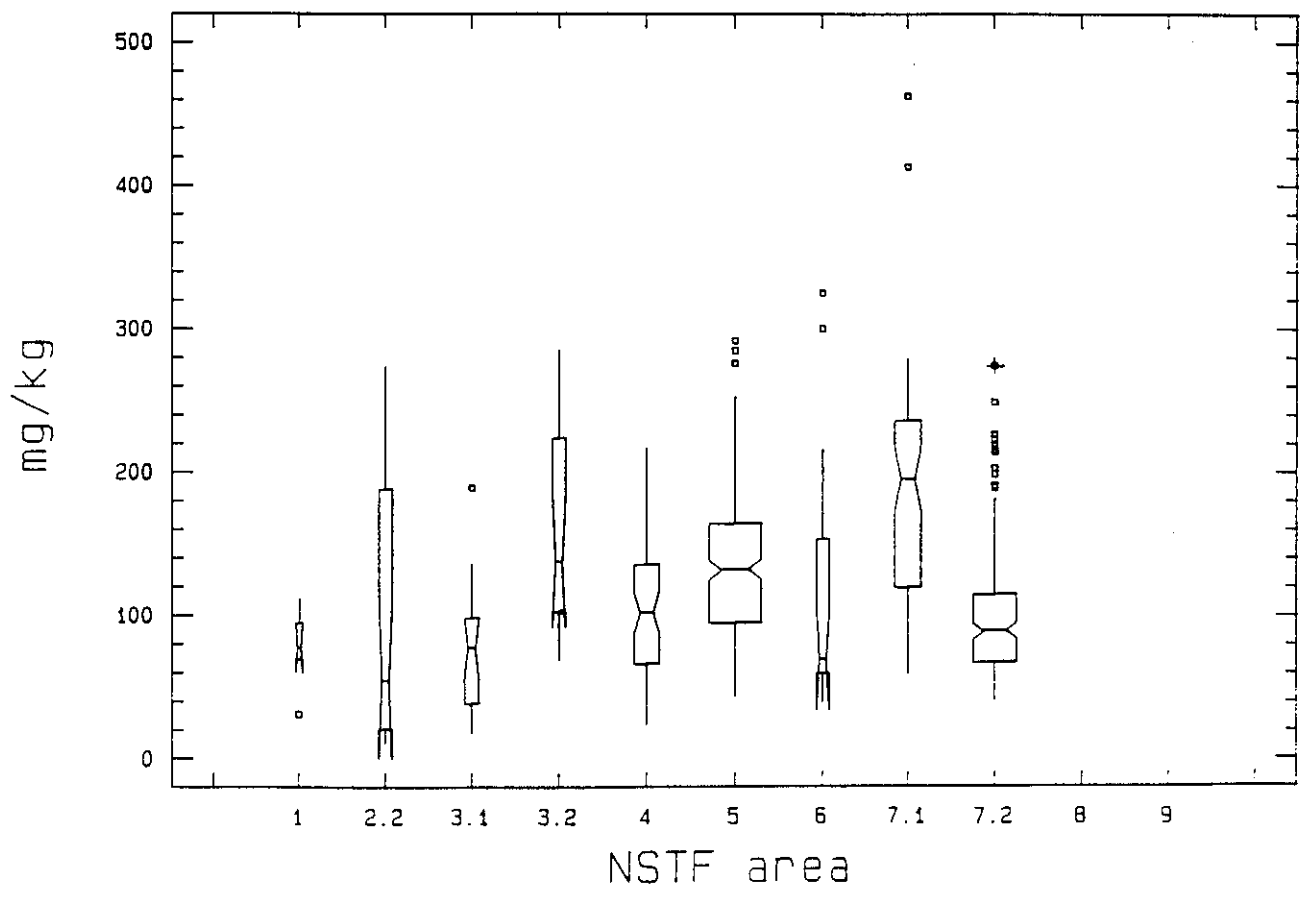


Figure 6.5.22 Distributions of lead concentrations in sediment fines <20 μm for different areas of the North Sea (BSHG data).

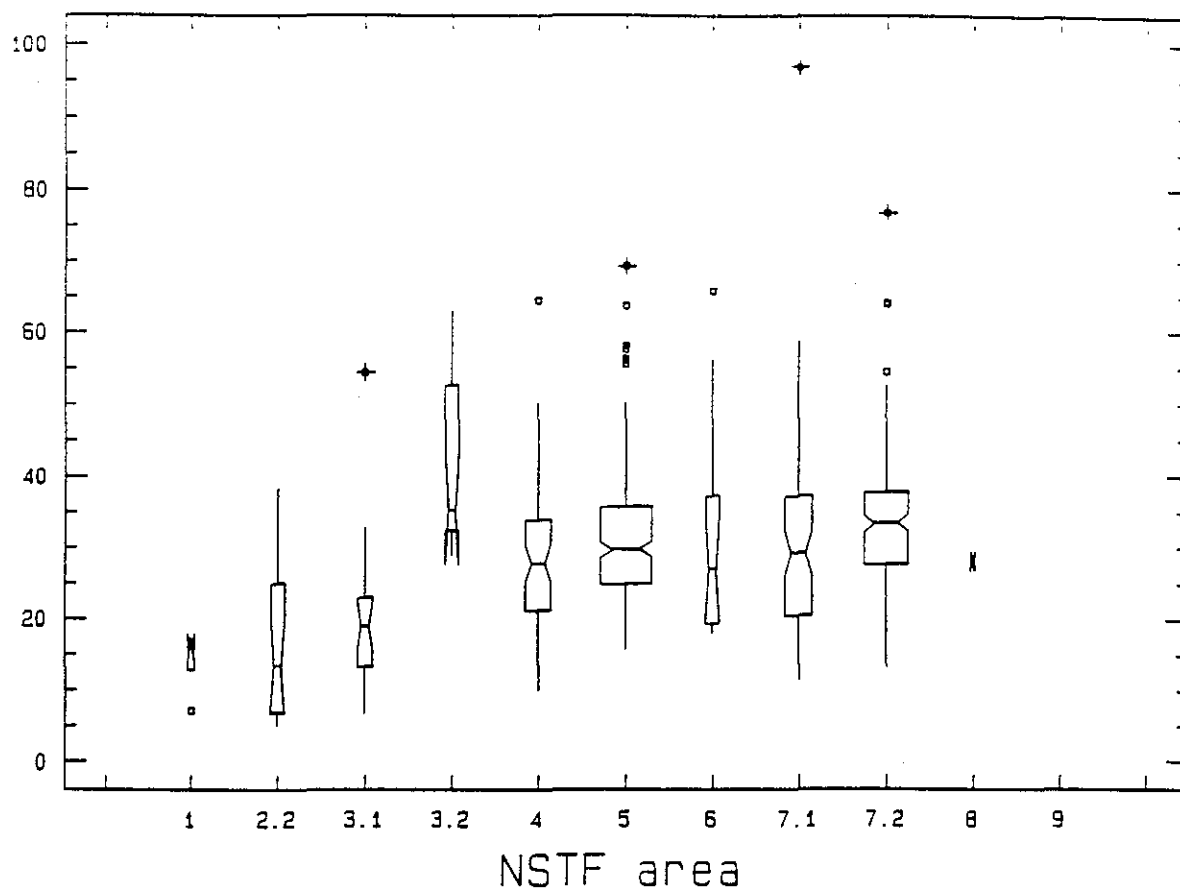


Figure 6.5.23 Distributions of lead/total organic carbon ratios in sediment fines $<20\ \mu\text{m}$ for different areas of the North Sea (BSHG data).

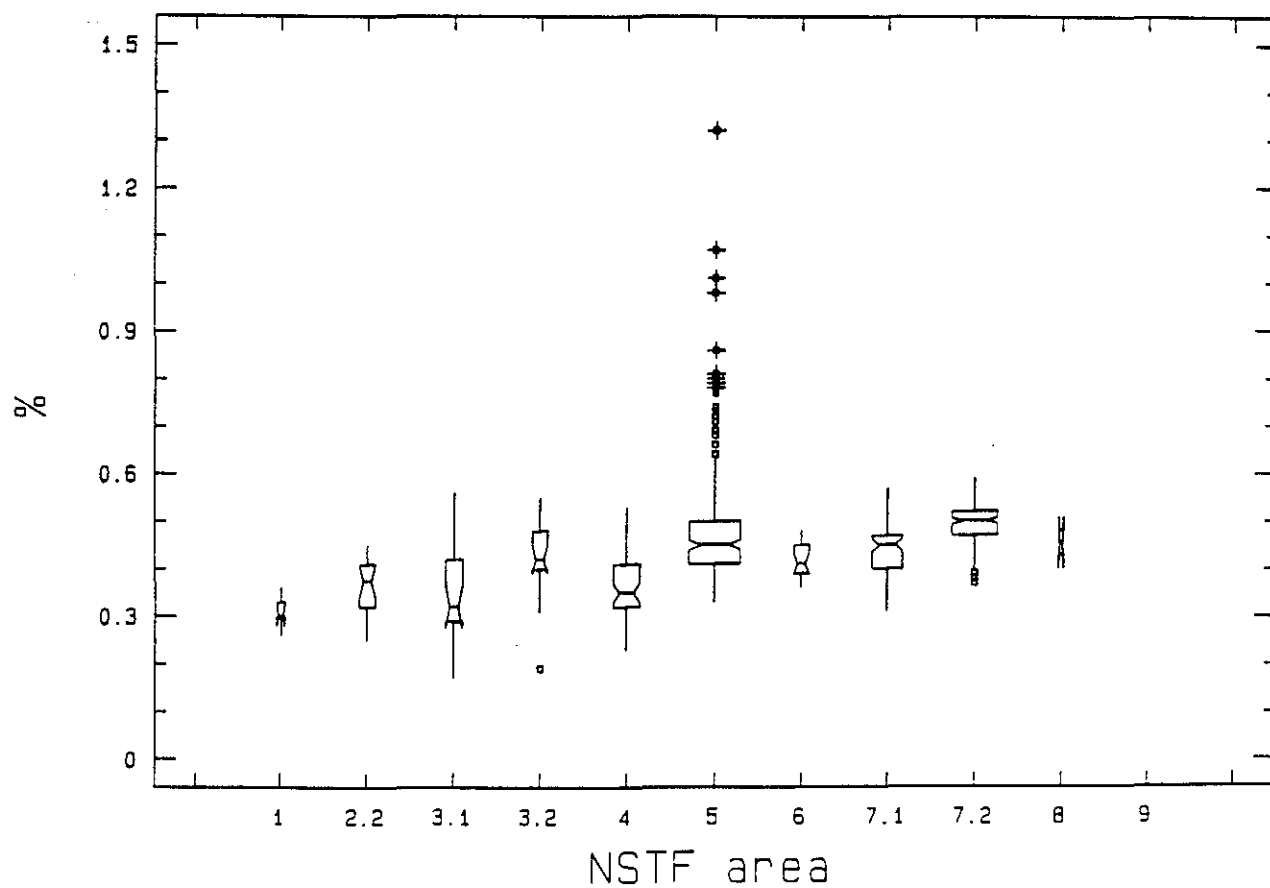


Figure 6.5.24 Distributions of titanium concentrations in sediment fines $<20\ \mu\text{m}$ for different areas of the North Sea (BSHG data).

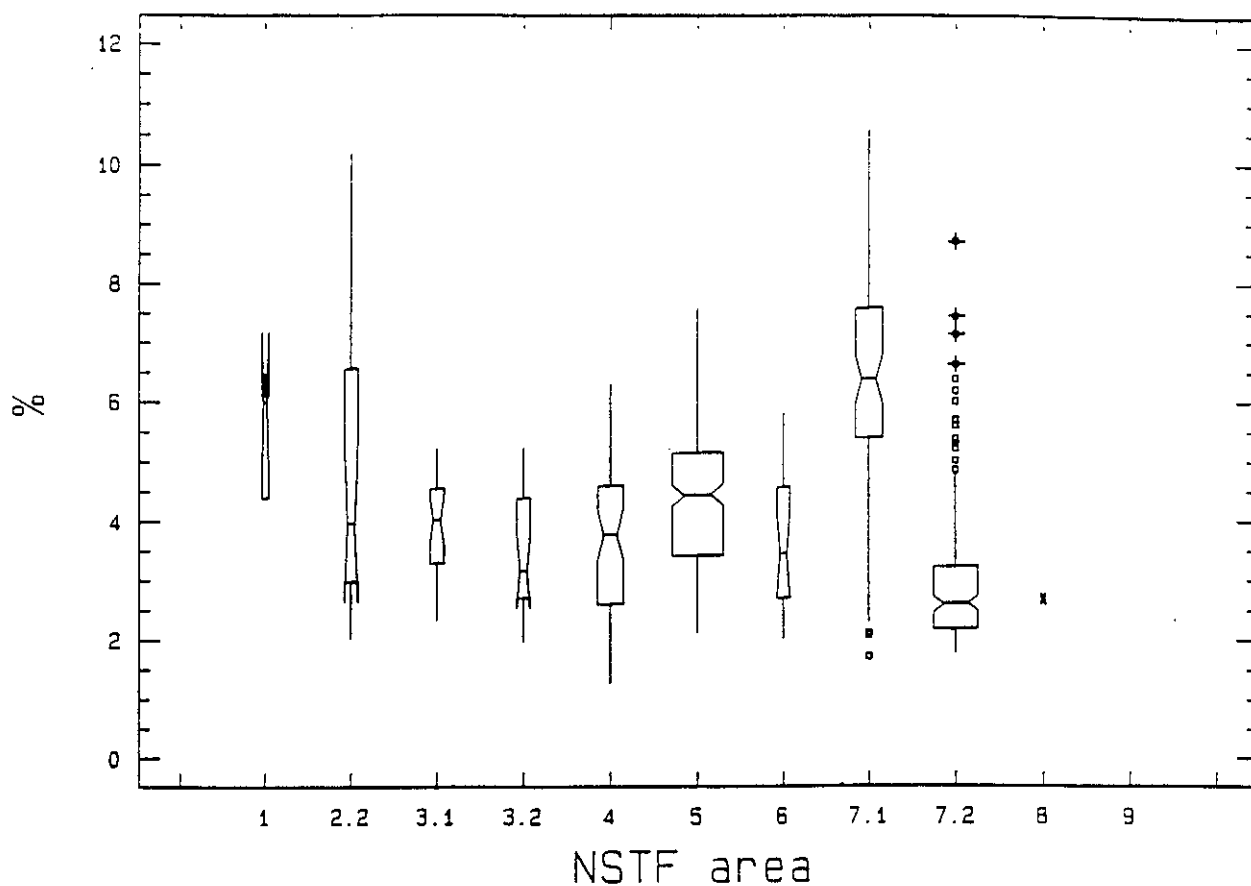


Figure 6.5.25 Distributions of total organic carbon concentrations in sediment fines <20 μm for different areas of the North Sea (BSHG data).

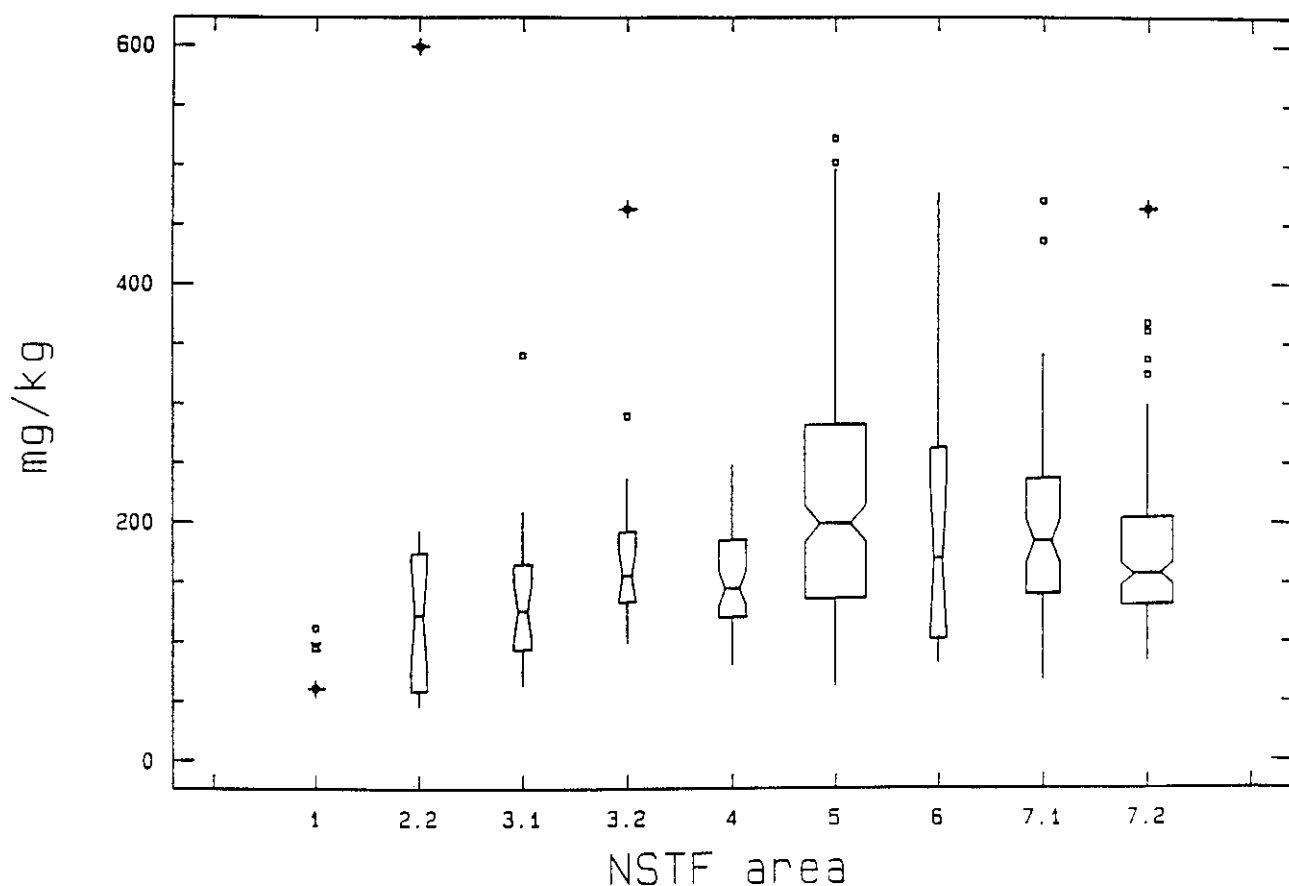


Figure 6.5.26 Distributions of vanadium concentrations in sediment fines <20 μm for different areas of the North Sea (BSHG data).

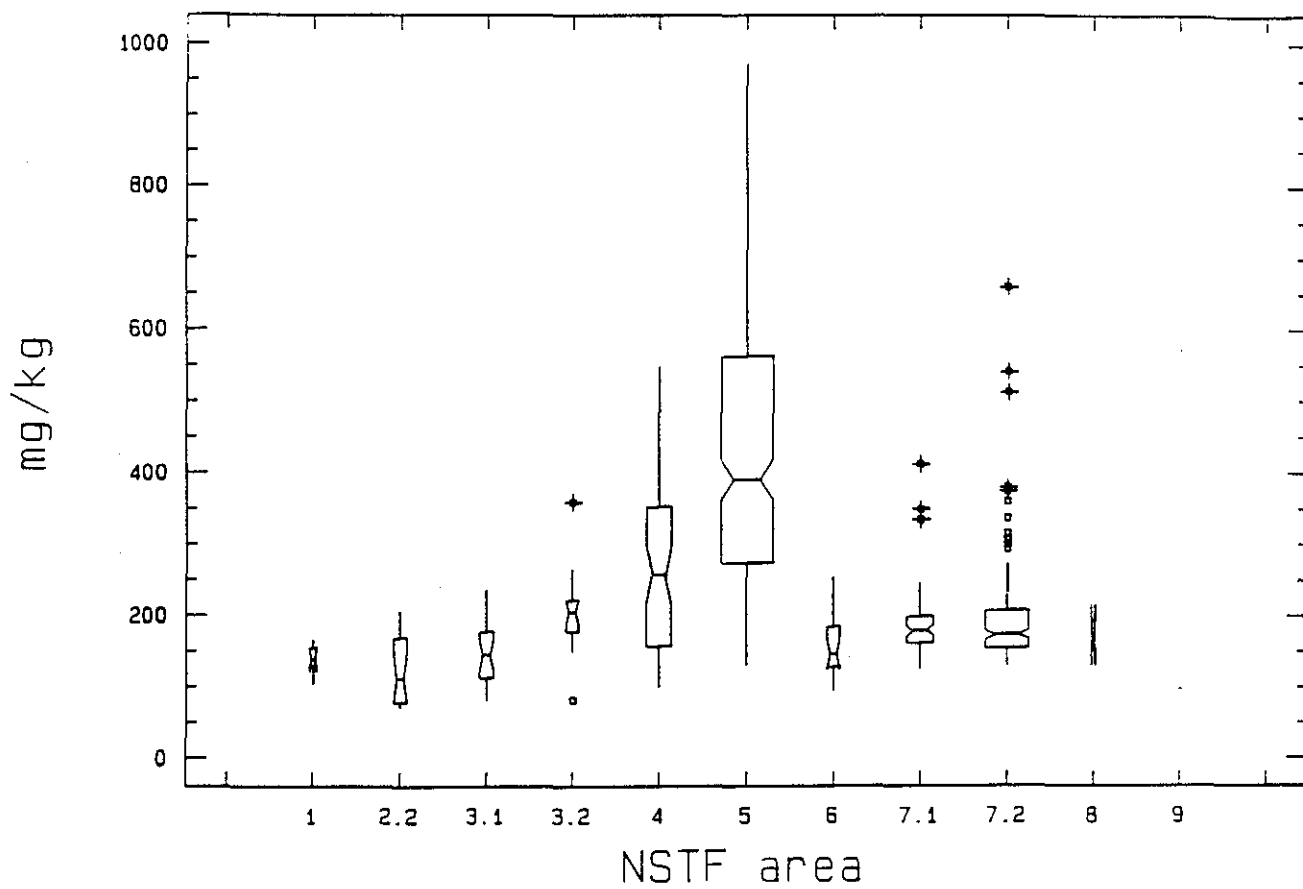


Figure 6.5.27 Distributions of zinc concentrations in sediment fines <20 μm for different areas of the North Sea (BSHG data).

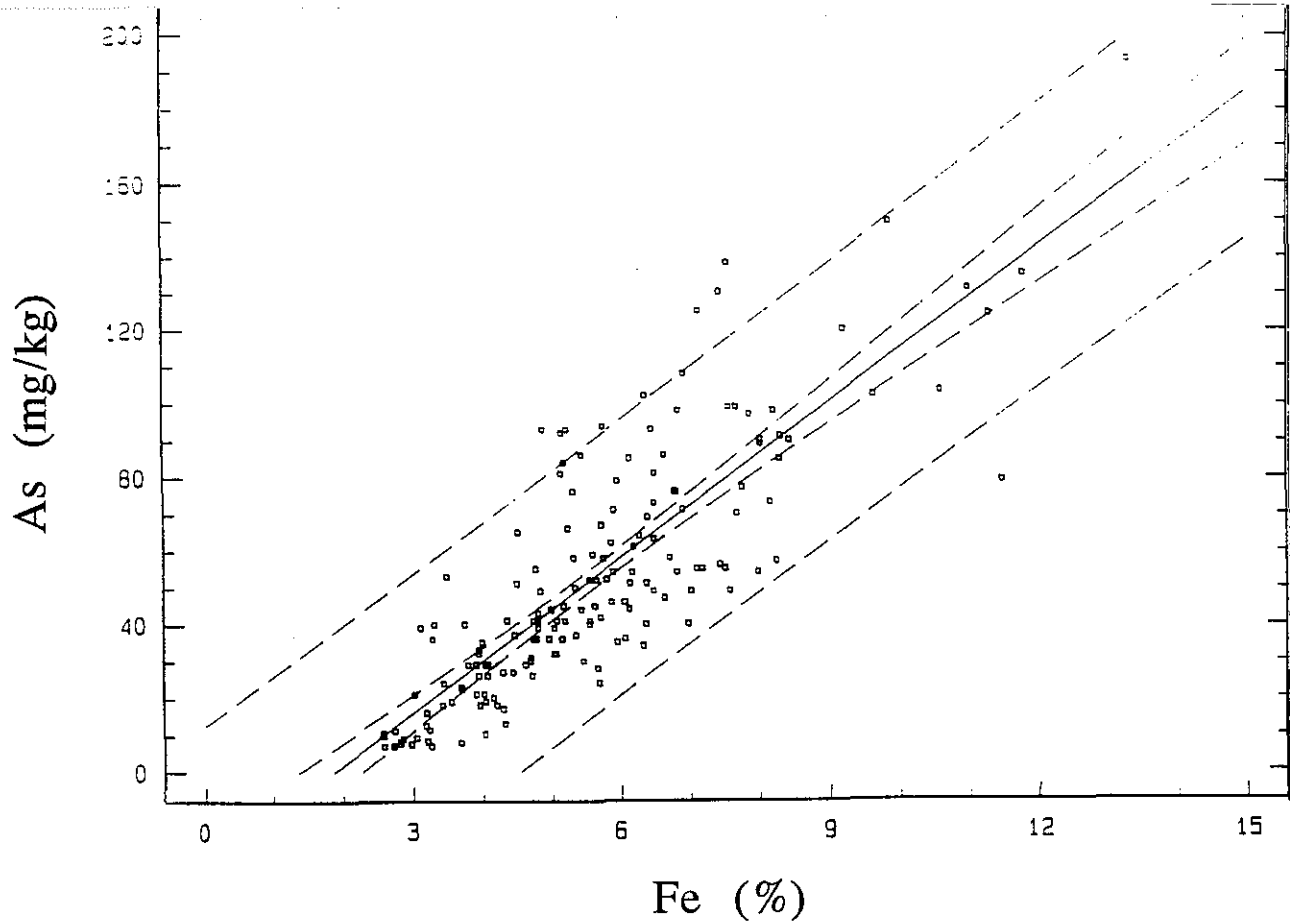


Figure 6.6.1 Regression of arsenic vs. iron in sediment fines <20 μm.

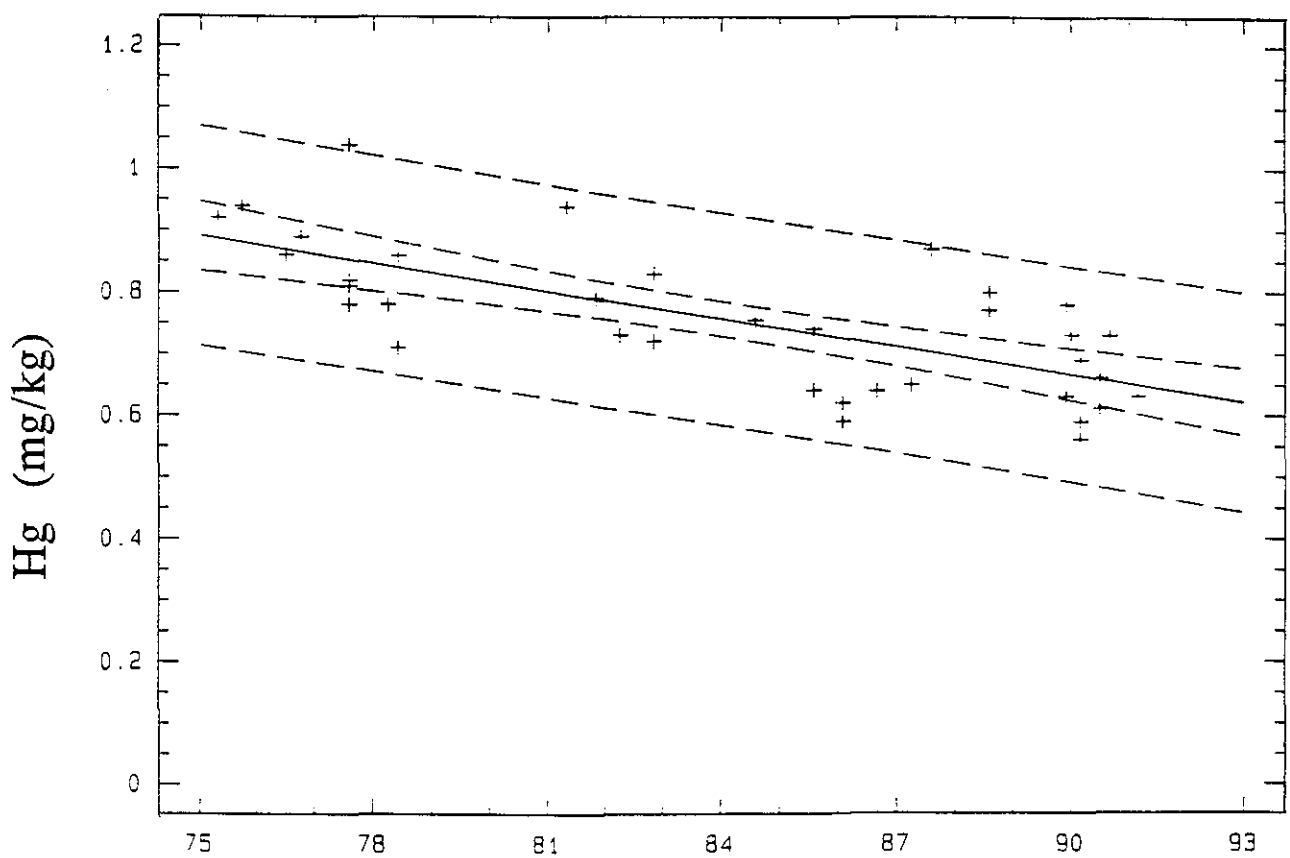


Figure 6.7.1 Temporal trends of mercury concentrations in sediment fines in the inner German Bight from 1975 to 1992.

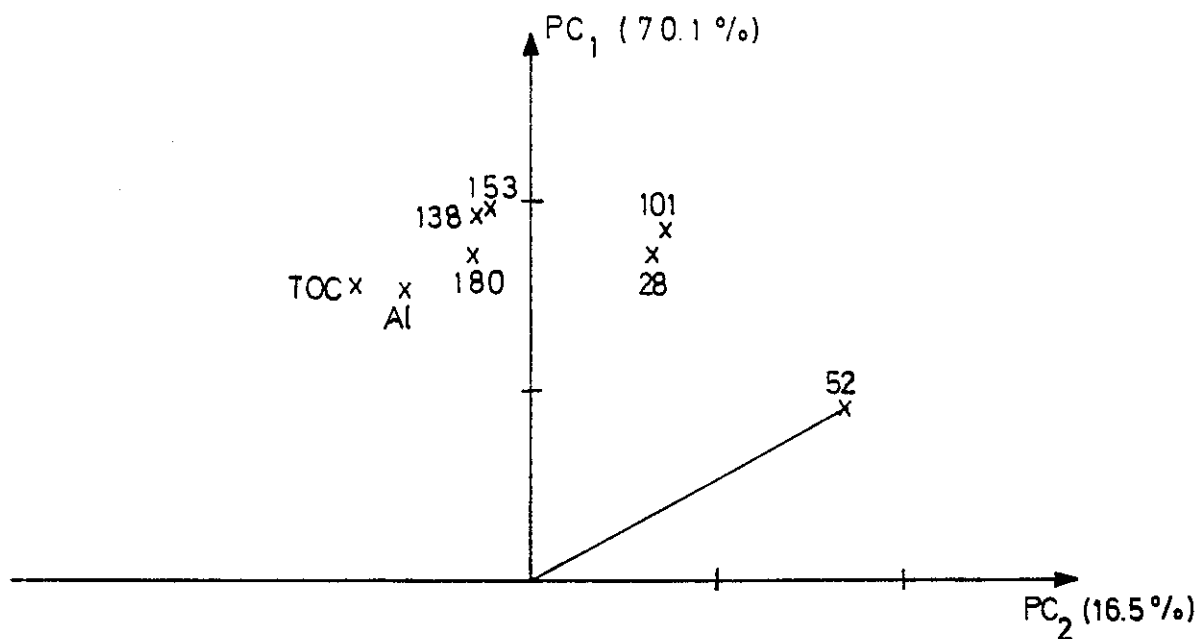


Figure 7.1.1.1 (a) Factor analysis of selected chlorobiphenyl congeners, total organic carbon and aluminium data in whole sediments ($<2000 \mu\text{m}$). Variance explained by PC1 and PC2 = 86.6% (21 observations).

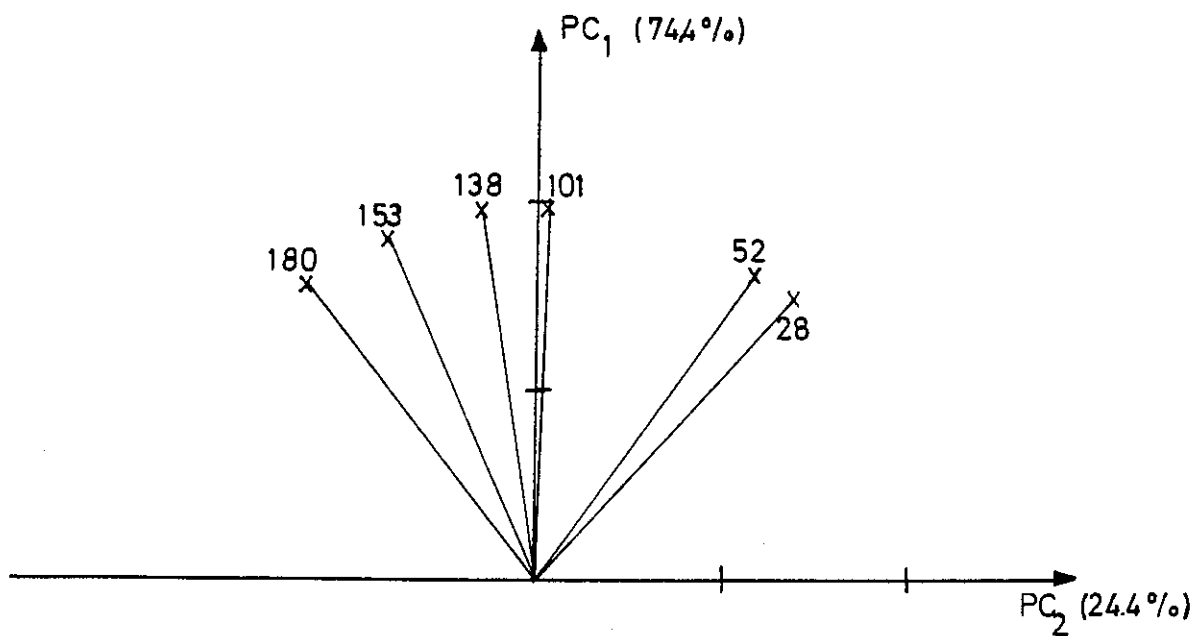


Figure 7.1.1.1 (b) Factor analysis of selected chlorobiphenyl congeners for "contaminated" samples only (i.e., CBs 28, 52 and 101 with concentrations $>0.5 \mu\text{g kg}^{-1}$ and CBs 138, 153 and 180 with concentrations $>1 \mu\text{g kg}^{-1}$). Variance explained by PC1 and PC2 = 98.8% (8 observations).

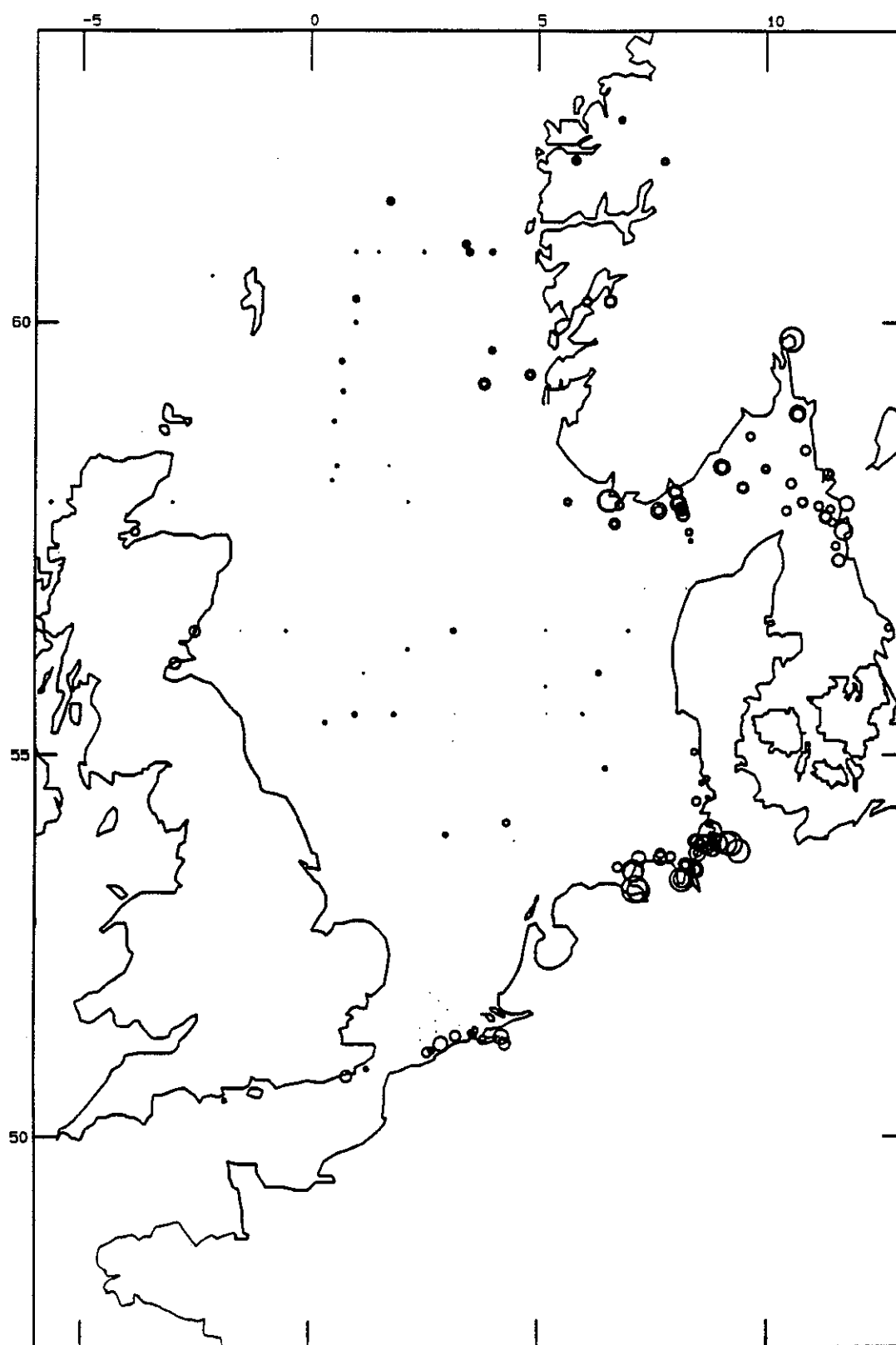


Figure 7.1.1.2 The distribution of CB153 concentrations in North Sea sediments $<2000 \mu\text{m}$ (circle area is proportional to value). The maximum concentration shown is $3 \mu\text{g kg}^{-1}$; higher values have been excluded.

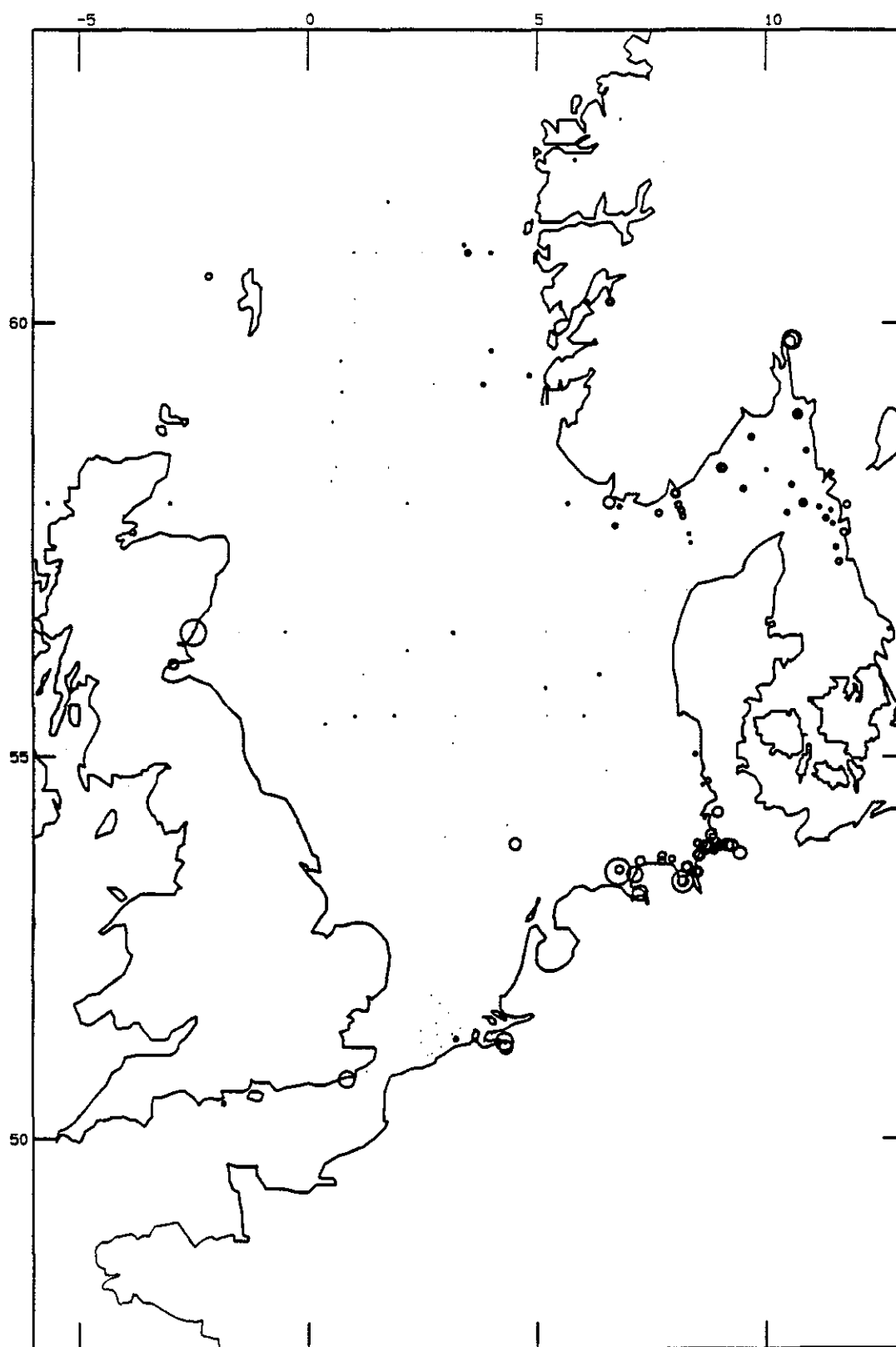


Figure 7.1.1.3 The distribution of CB52 concentrations in North Sea sediments $<2000 \mu\text{m}$ (circle area is proportional to value). The maximum concentration shown is $3 \mu\text{g kg}^{-1}$; higher values have been excluded.

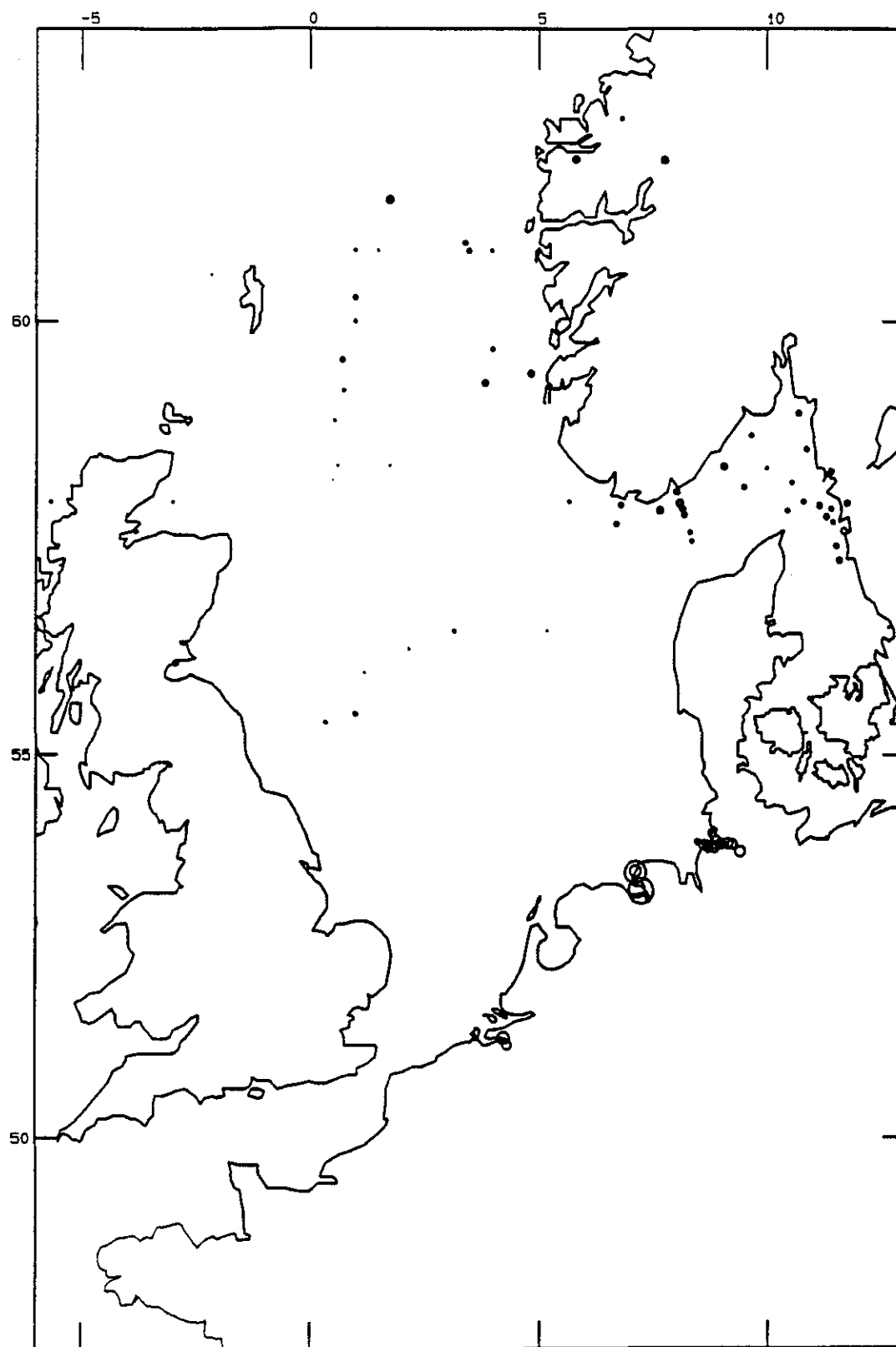


Figure 7.1.1.4 The distribution of CB153/total organic carbon ratios in North Sea sediments $<2000\ \mu\text{m}$, with $\text{TOC} \geq 0.3\%$ (circle area is proportional to value).

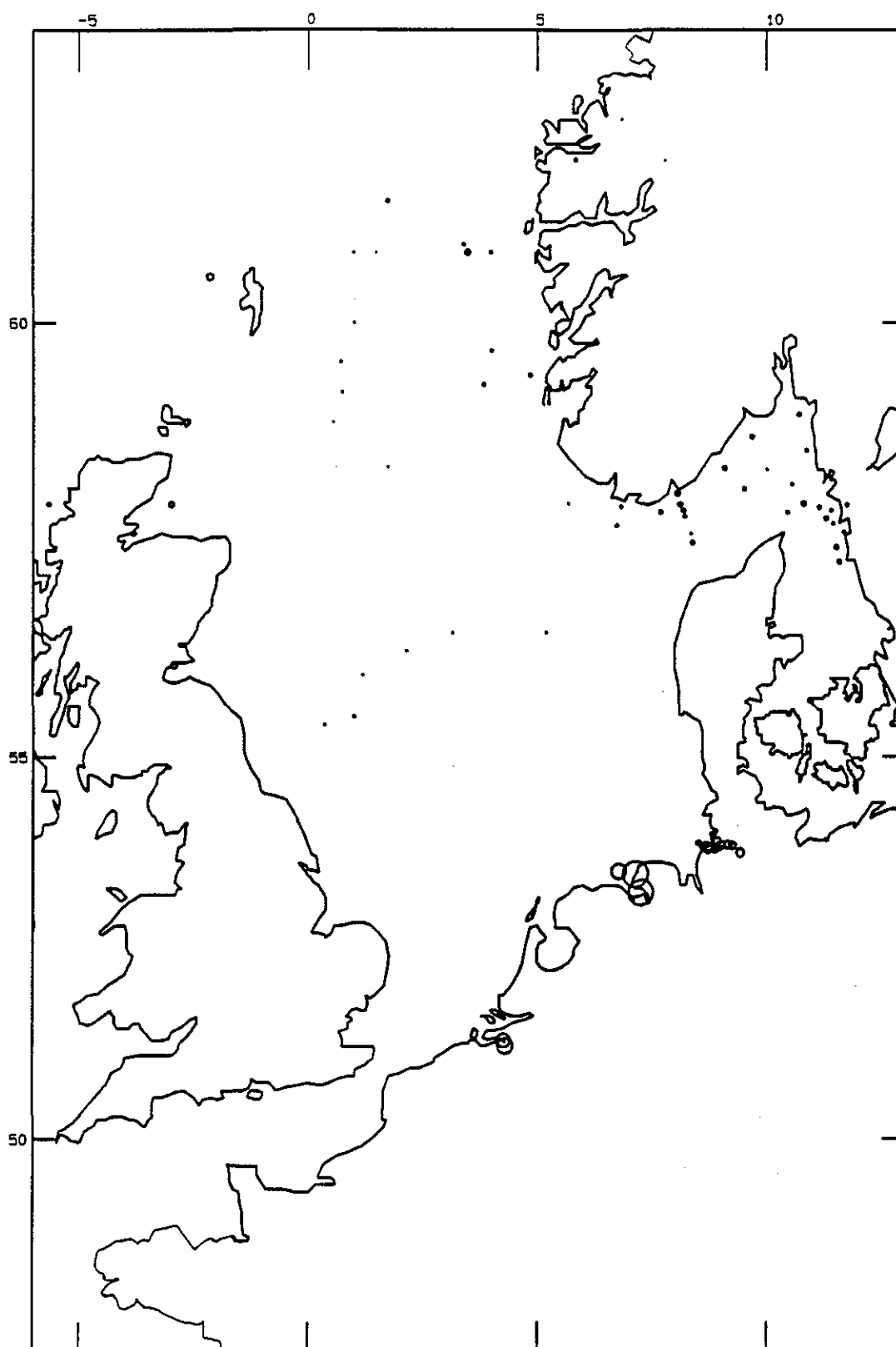


Figure 7.1.1.5 The distribution of CB52/total organic carbon ratios in North Sea sediments $<2000\ \mu\text{m}$, with $\text{TOC} \geq 0.3\%$ (circle area is proportional to value).

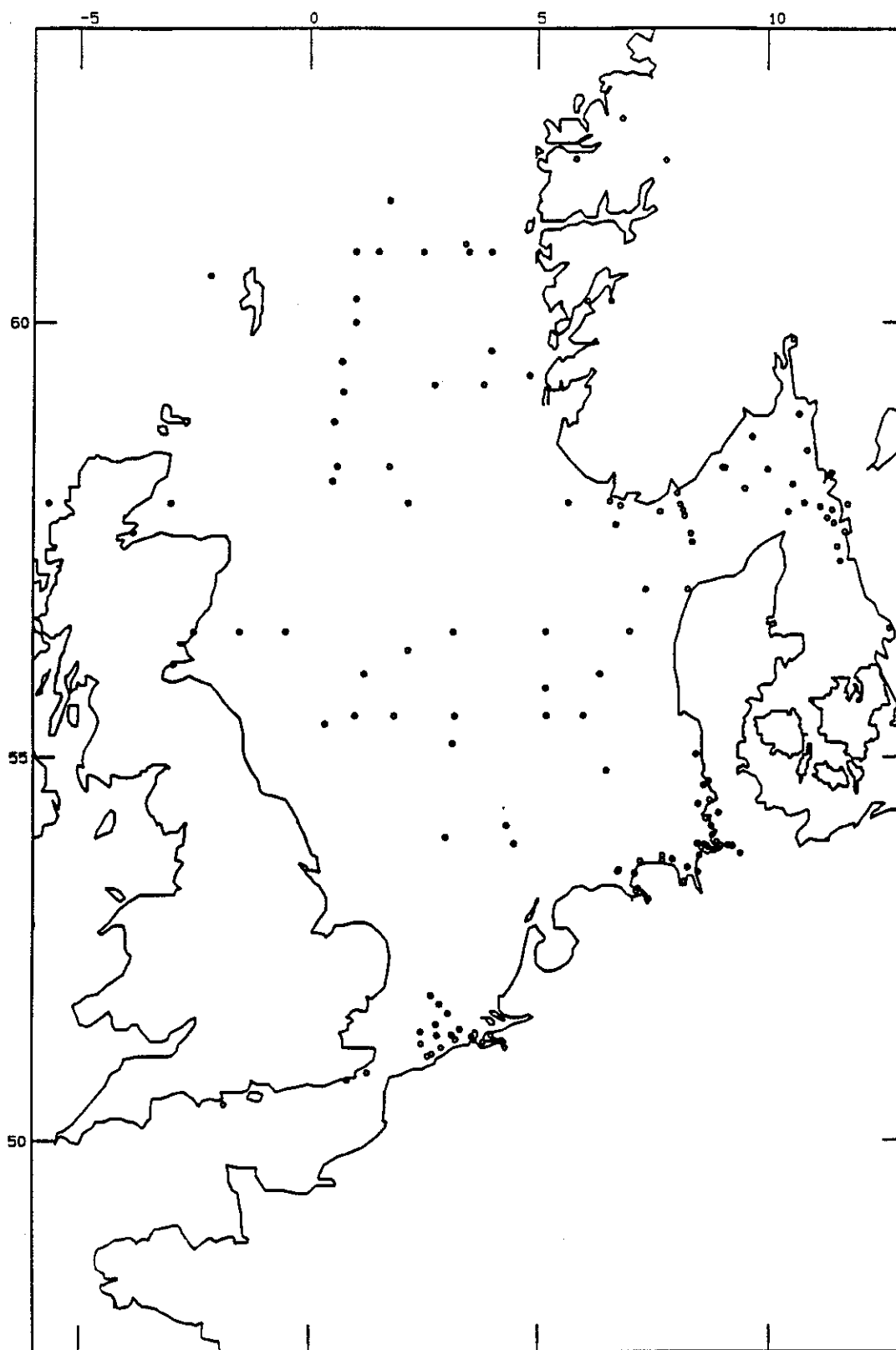


Figure 7.1.1.6 Locations sampled for CBs in sediments <2000 μm.

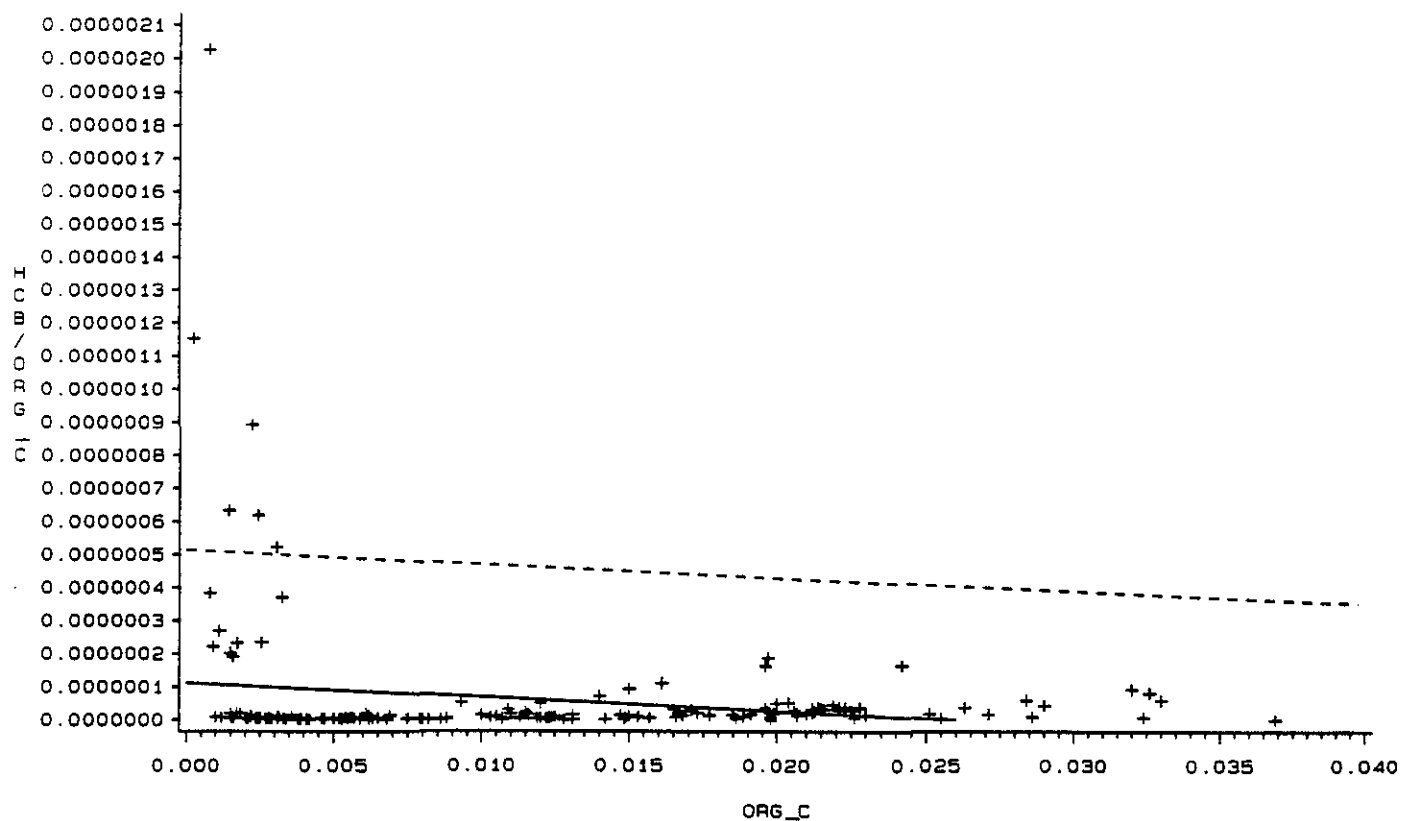


Figure 7.1.2.1 Regression of HCB/TOC vs. TOC.

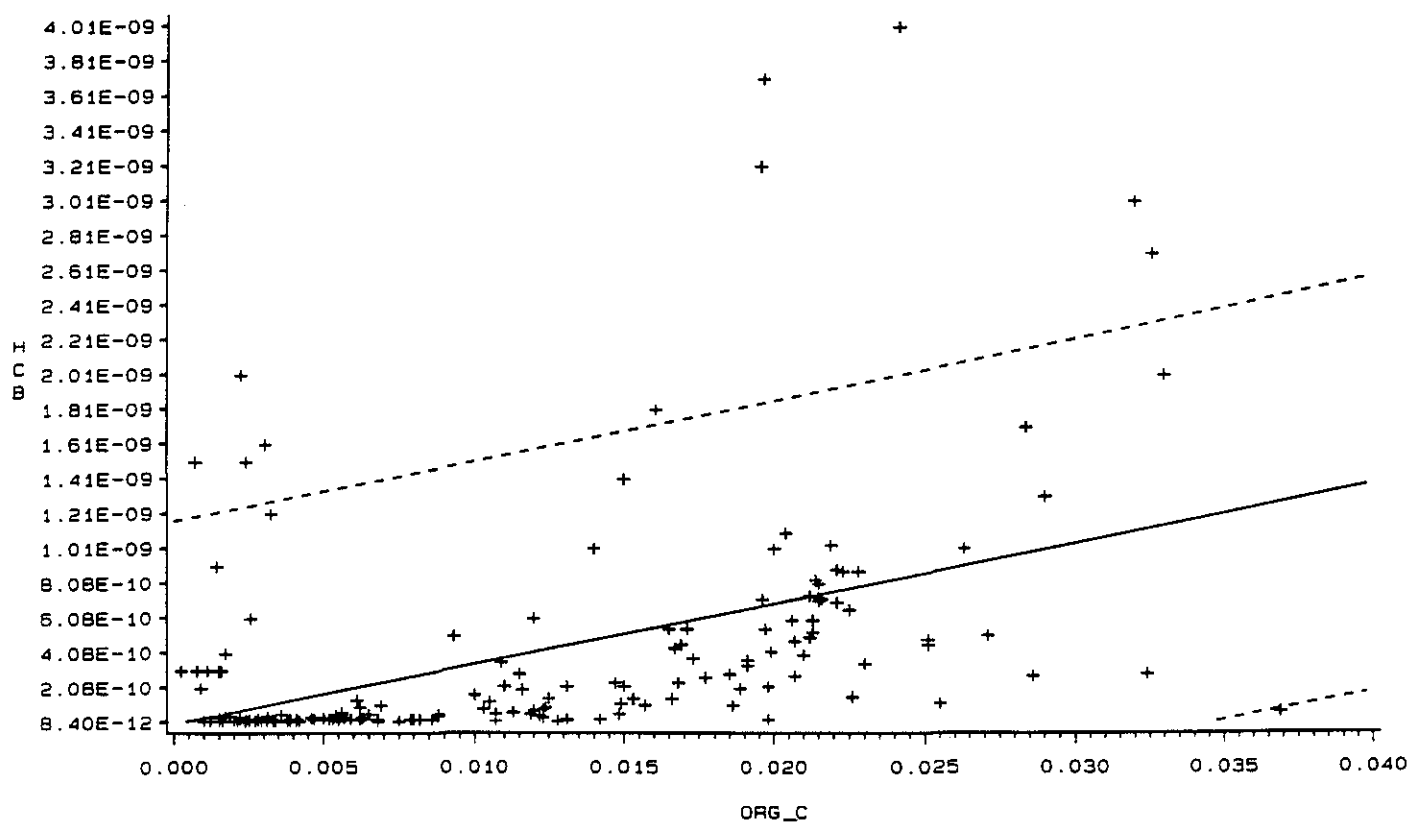


Figure 7.1.2.2 Regression of HCB vs. TOC.

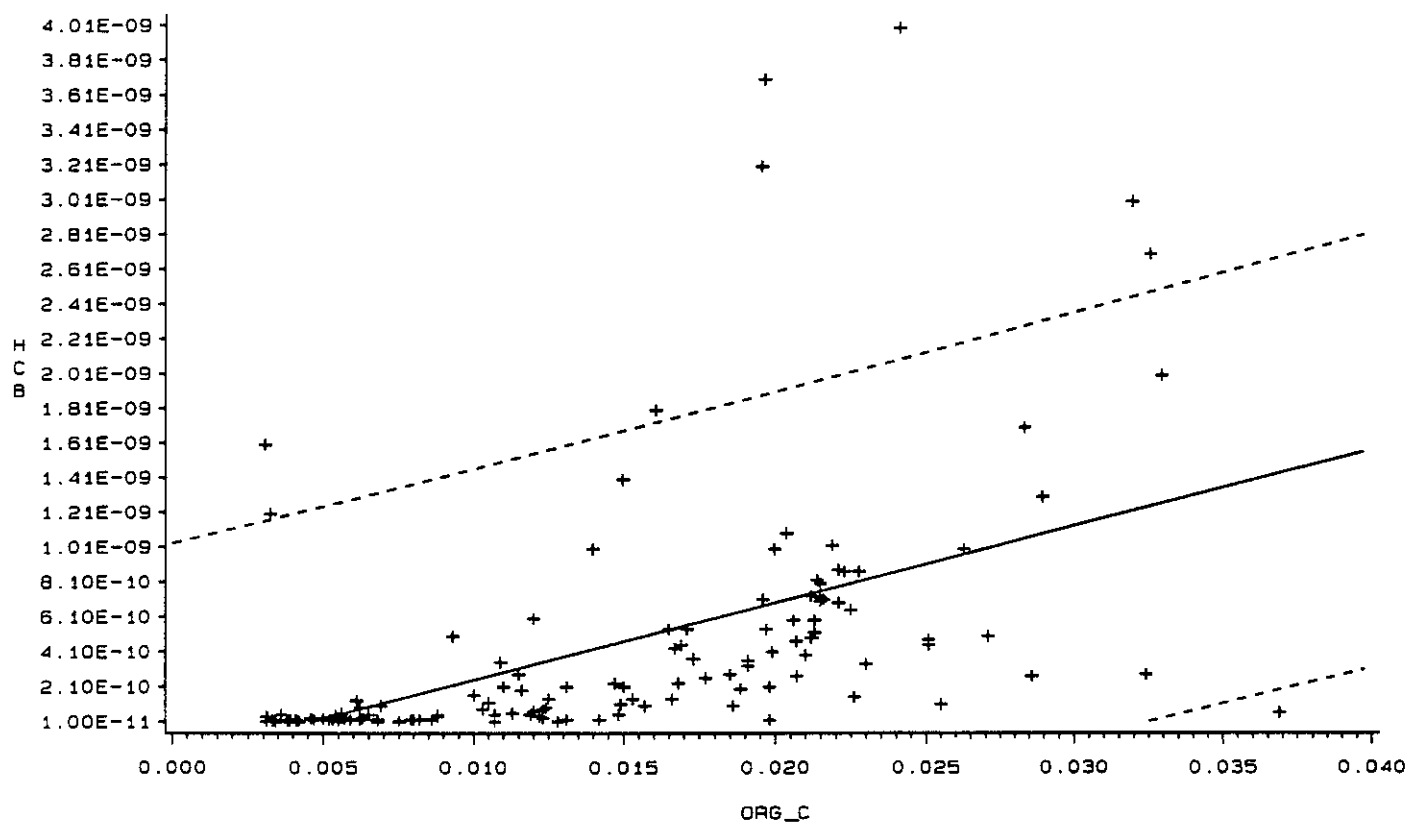


Figure 7.1.2.3 Regression of HCB vs. TOC, for TOC $\geq 0.3\%$.

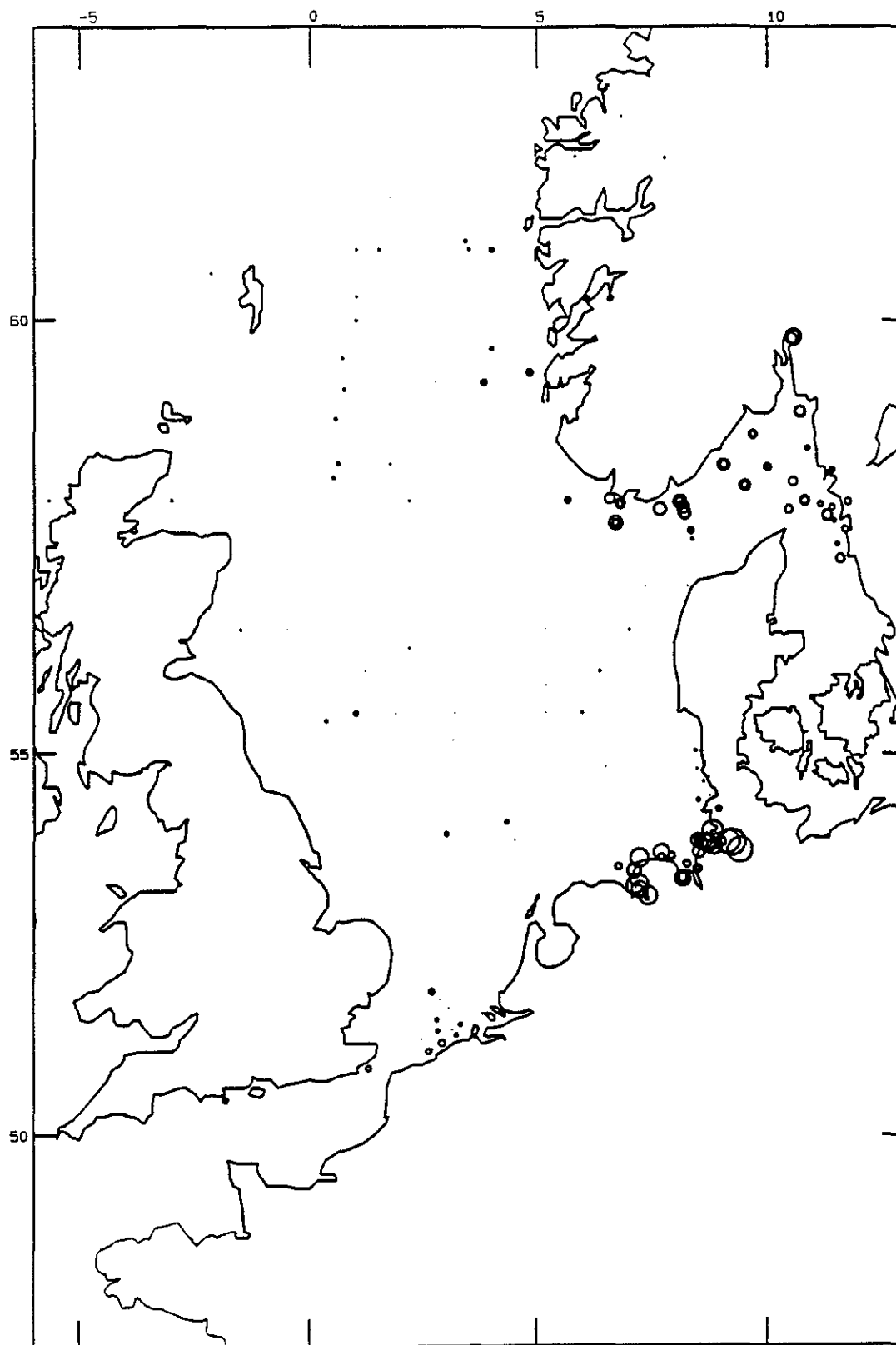


Figure 7.1.2.4 The distribution of HCB concentrations in North Sea sediments $<2000 \mu\text{m}$ (circle area is proportional to value). The maximum concentration shown is 4 mg kg^{-1} ; higher values have been excluded.

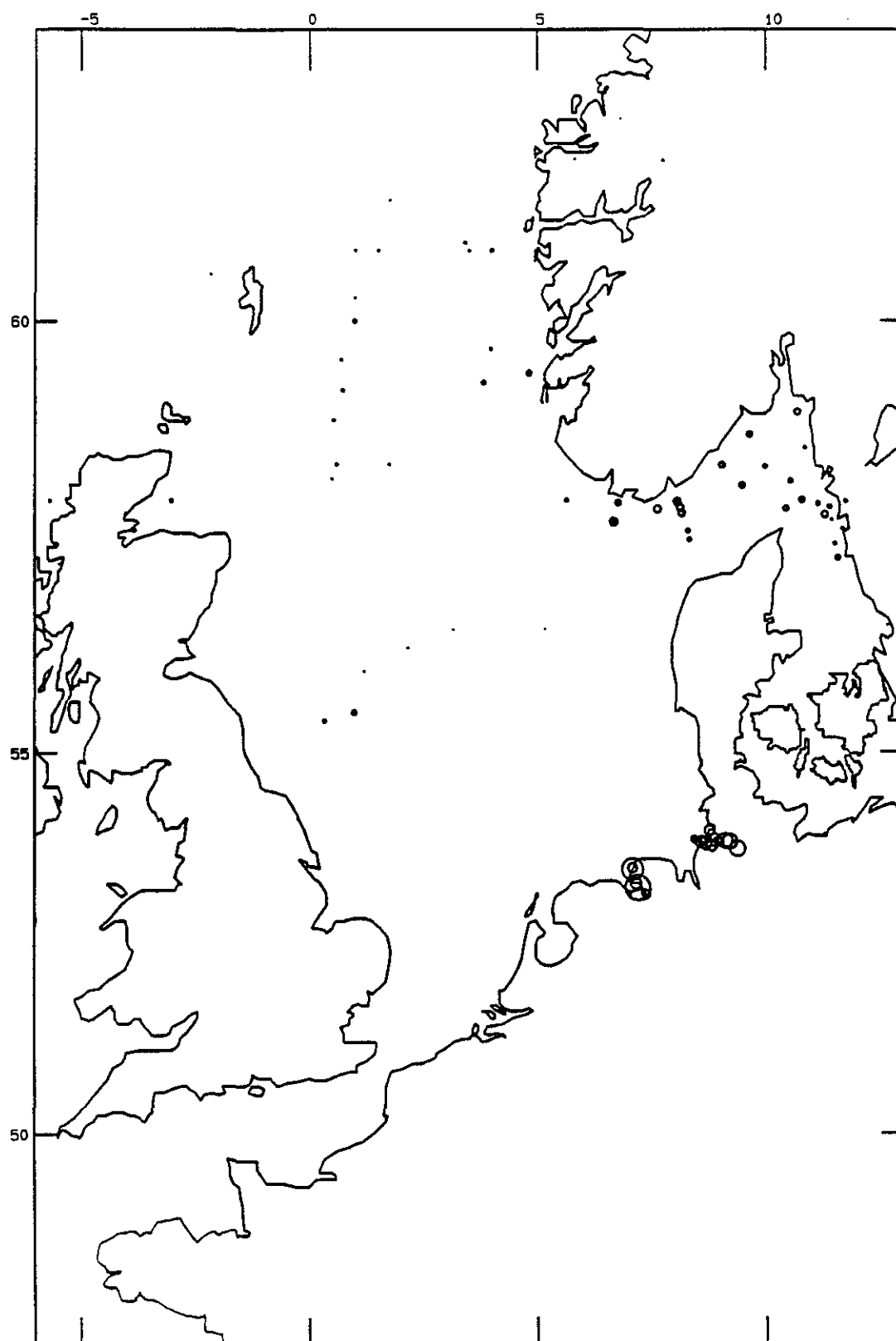


Figure 7.1.2.5 The distribution of HCB/TOC ratios in North Sea sediments $<2000\ \mu\text{m}$, with $\text{TOC} \geq 0.3\%$ (circle area is proportional to value).

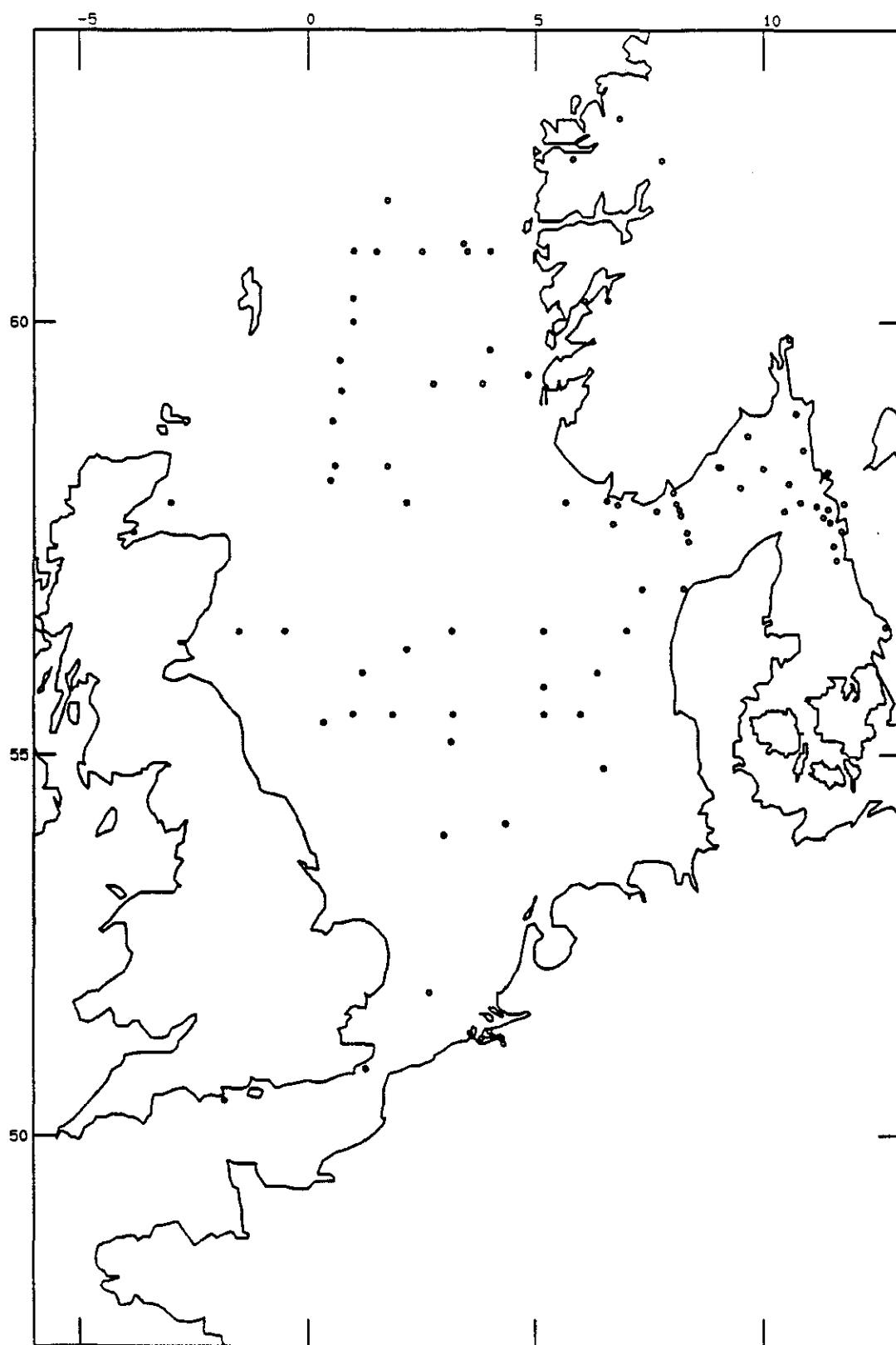


Figure 7.2.1.1 Locations sampled for PAHs in sediments <2000 μm .

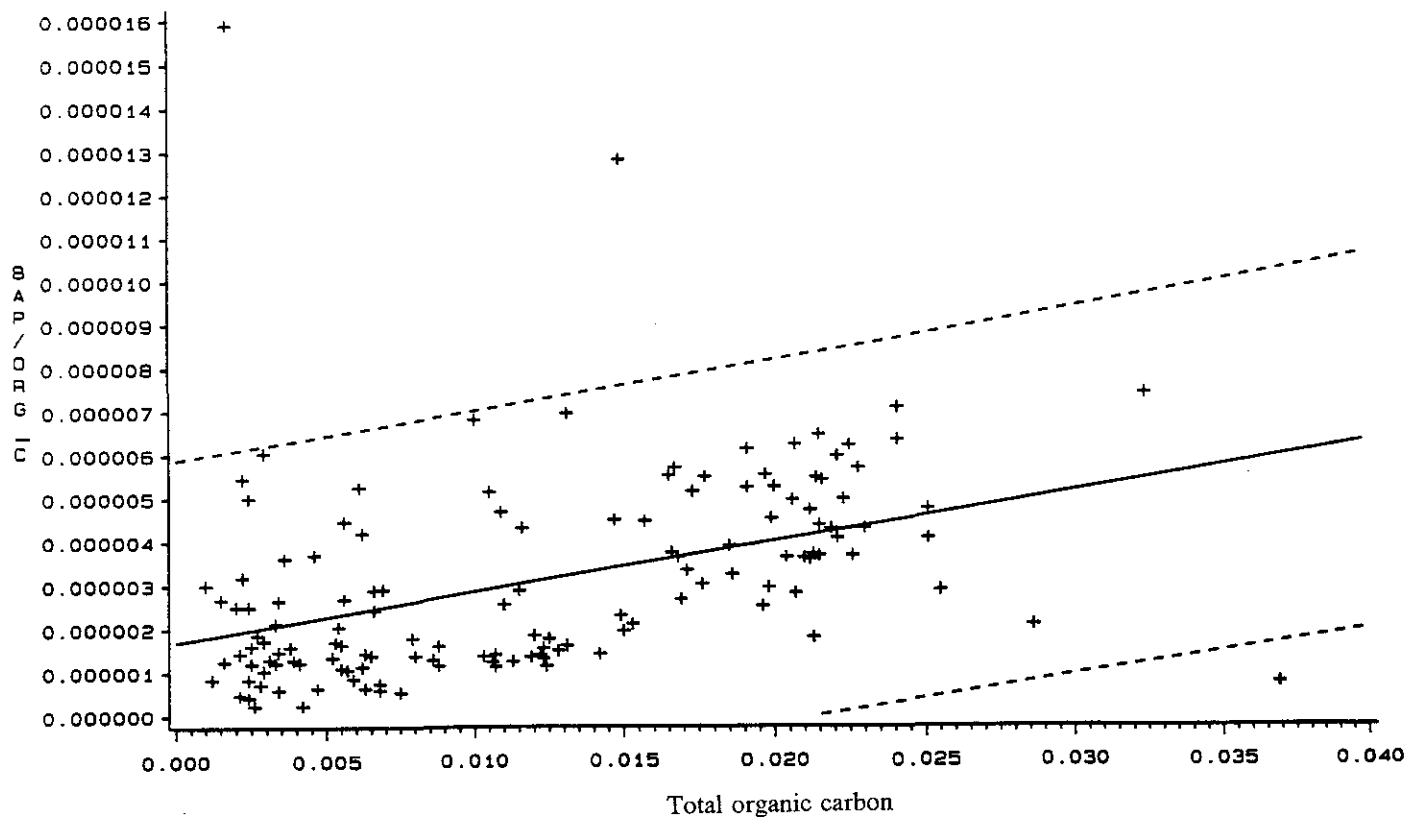


Figure 7.2.1.2 Regression of BAP/TOC vs. TOC.

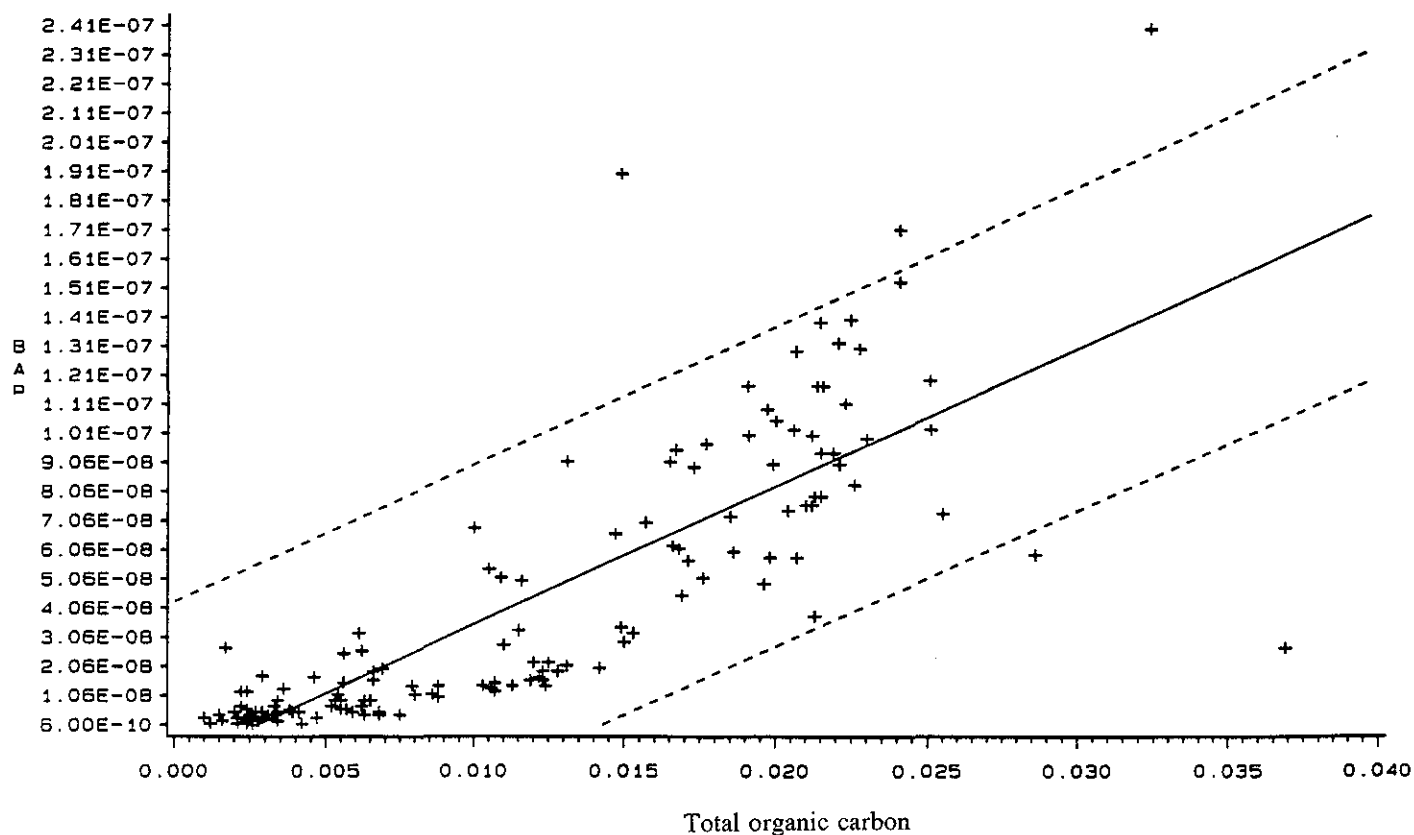


Figure 7.2.1.3 Regression of BAP vs. TOC.

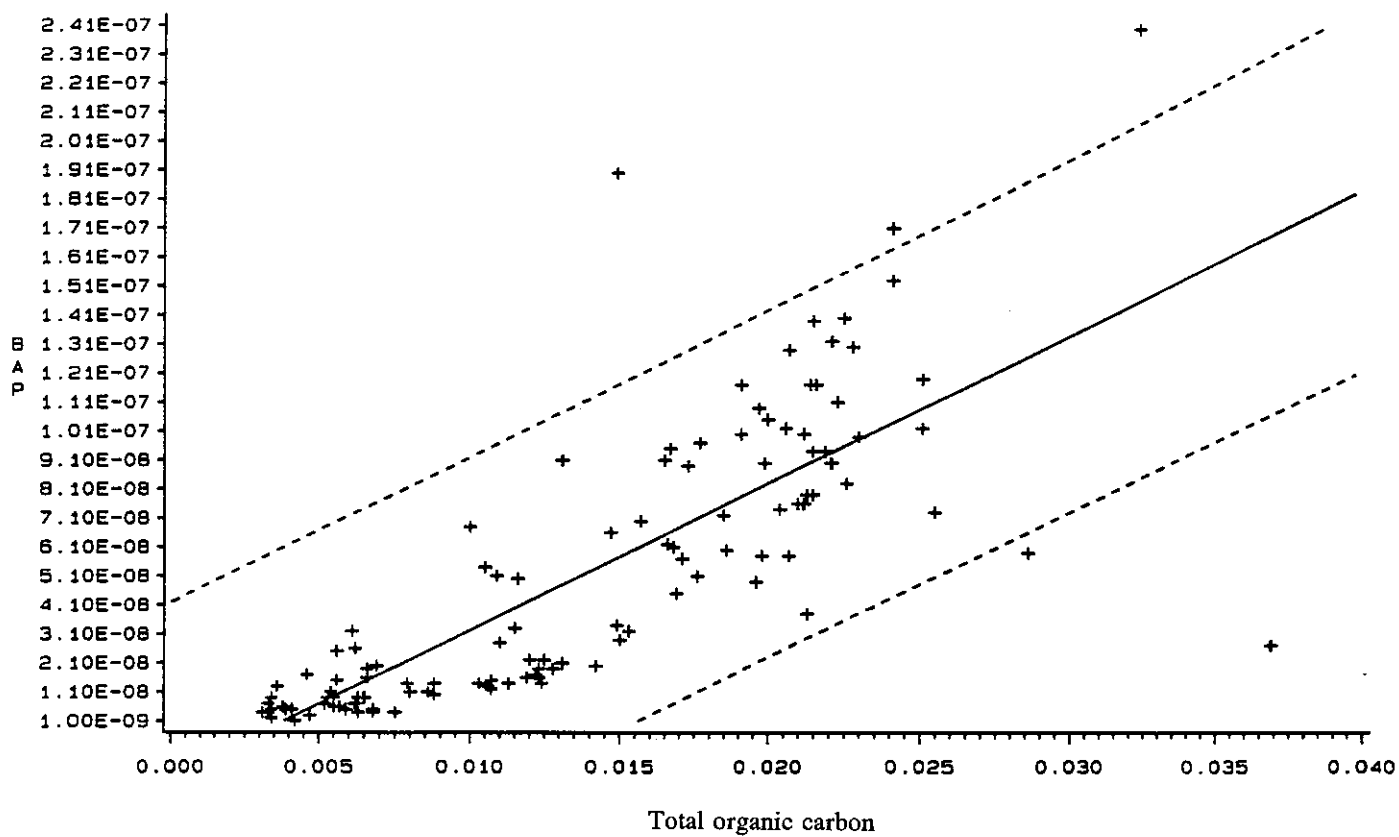


Figure 7.2.1.4 Regression of BAP vs. TOC, for TOC $\geq 0.3\%$.

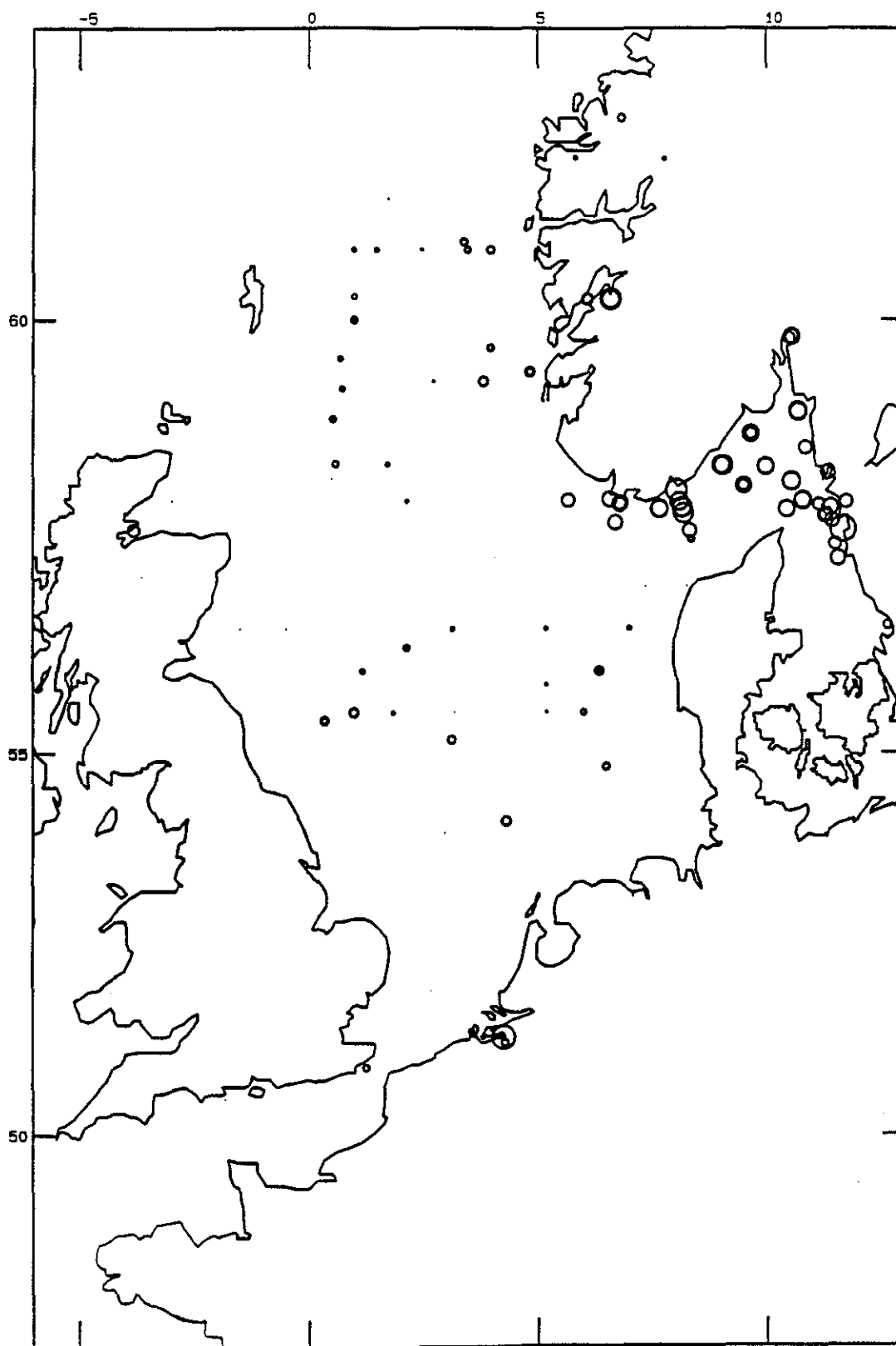


Figure 7.2.1.5 The distribution of benzo[a]pyrene (BAP) concentrations in North Sea sediments $<2000 \mu\text{m}$ (circle area is proportional to value). The maximum concentration is $240 \mu\text{g kg}^{-1}$.

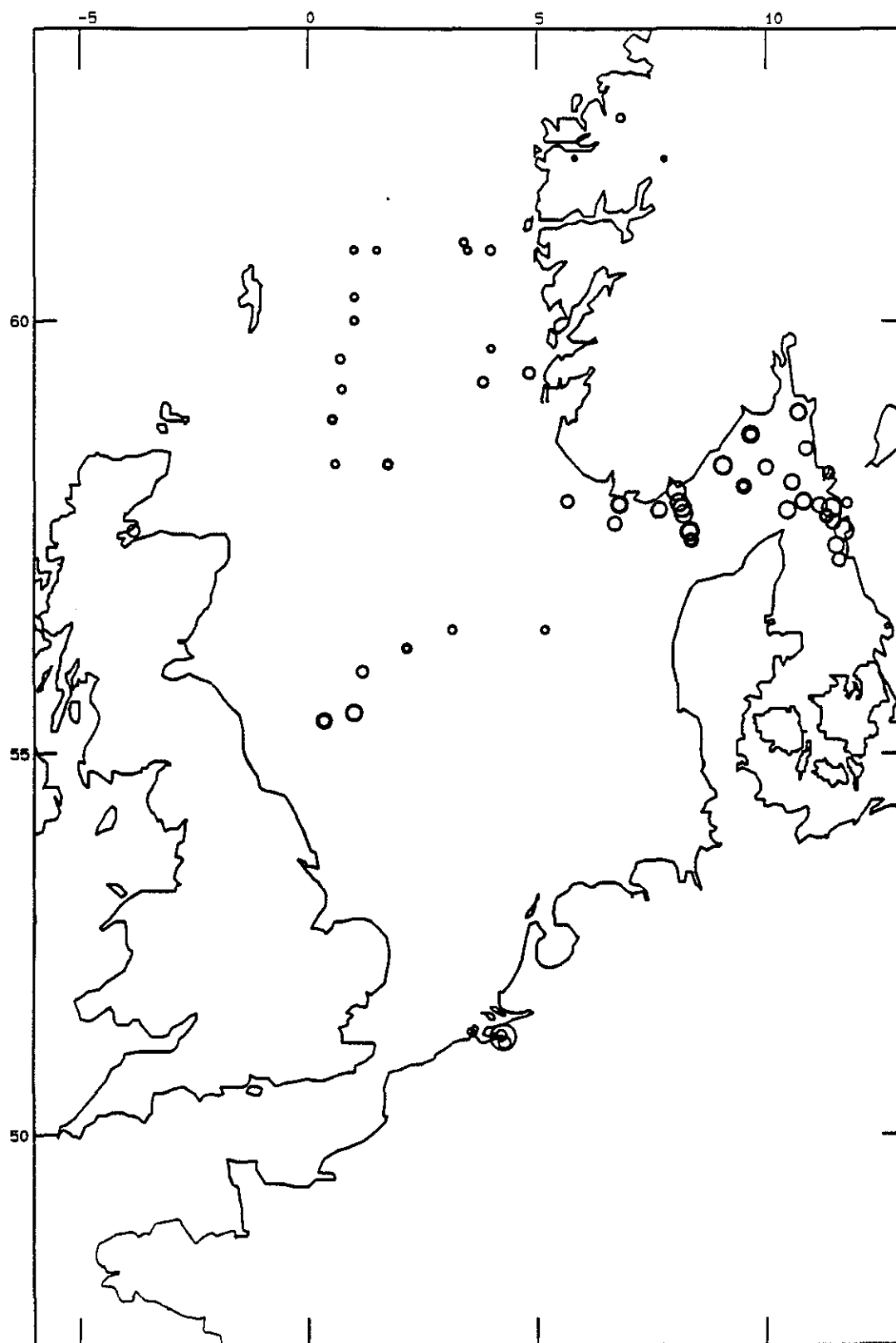


Figure 7.2.1.6 The distribution of BAP/TOC ratios in North Sea sediments $< 2000 \mu\text{m}$, with $\text{TOC} \geq 0.3\%$ (circle area is proportional to value).

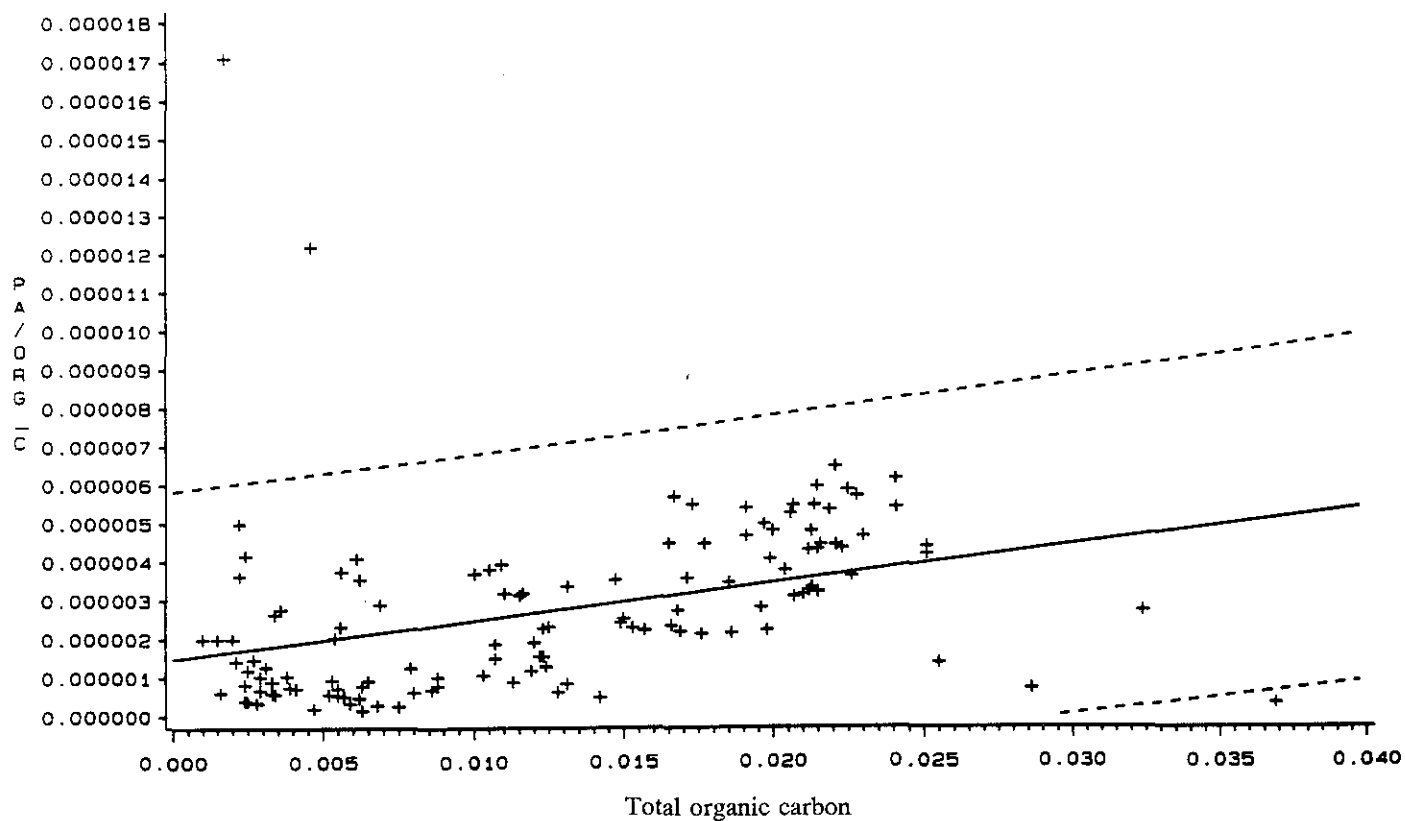


Figure 7.2.1.7 Regression of PA/TOC vs. TOC.

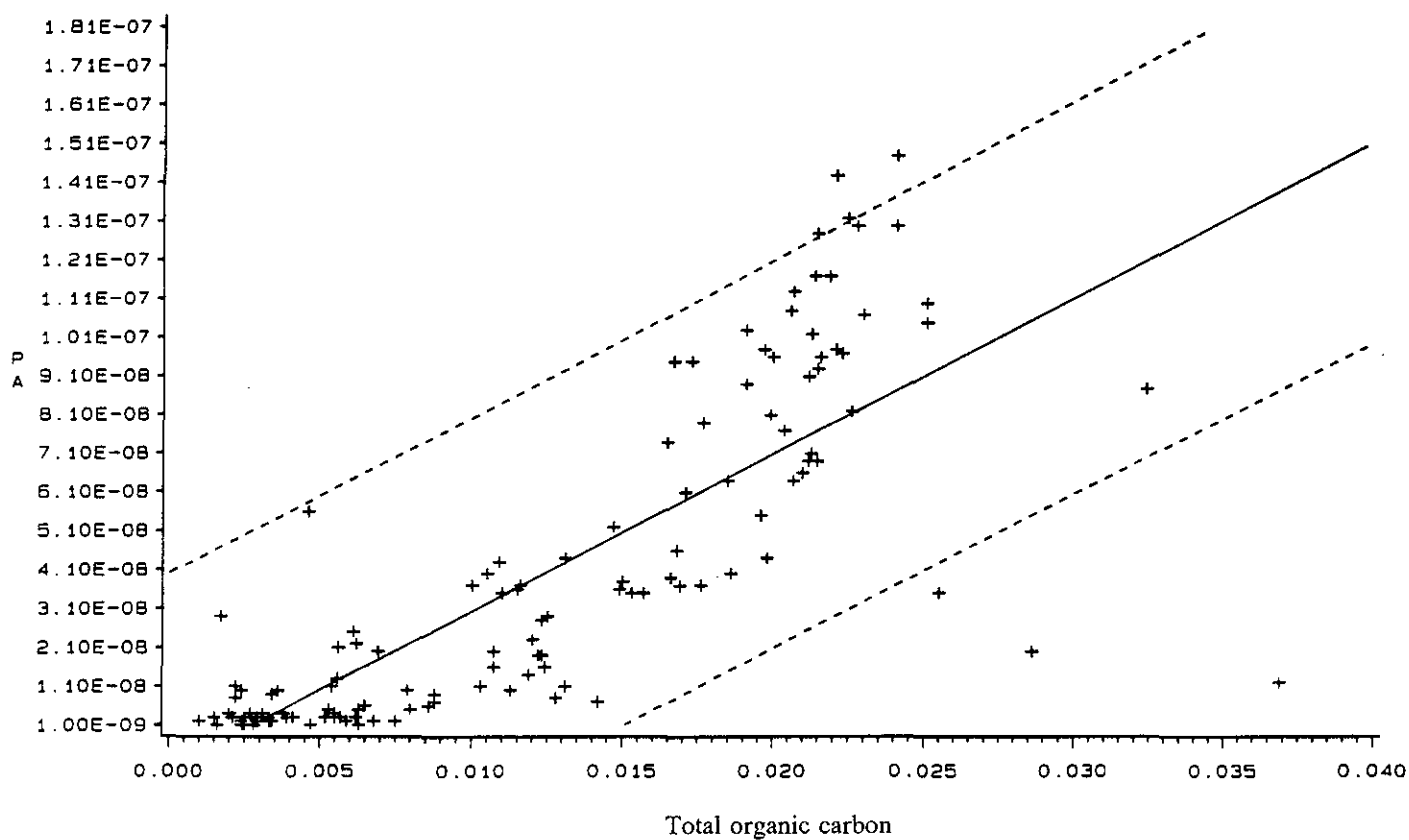


Figure 7.2.1.8 Regression of PA vs. TOC.

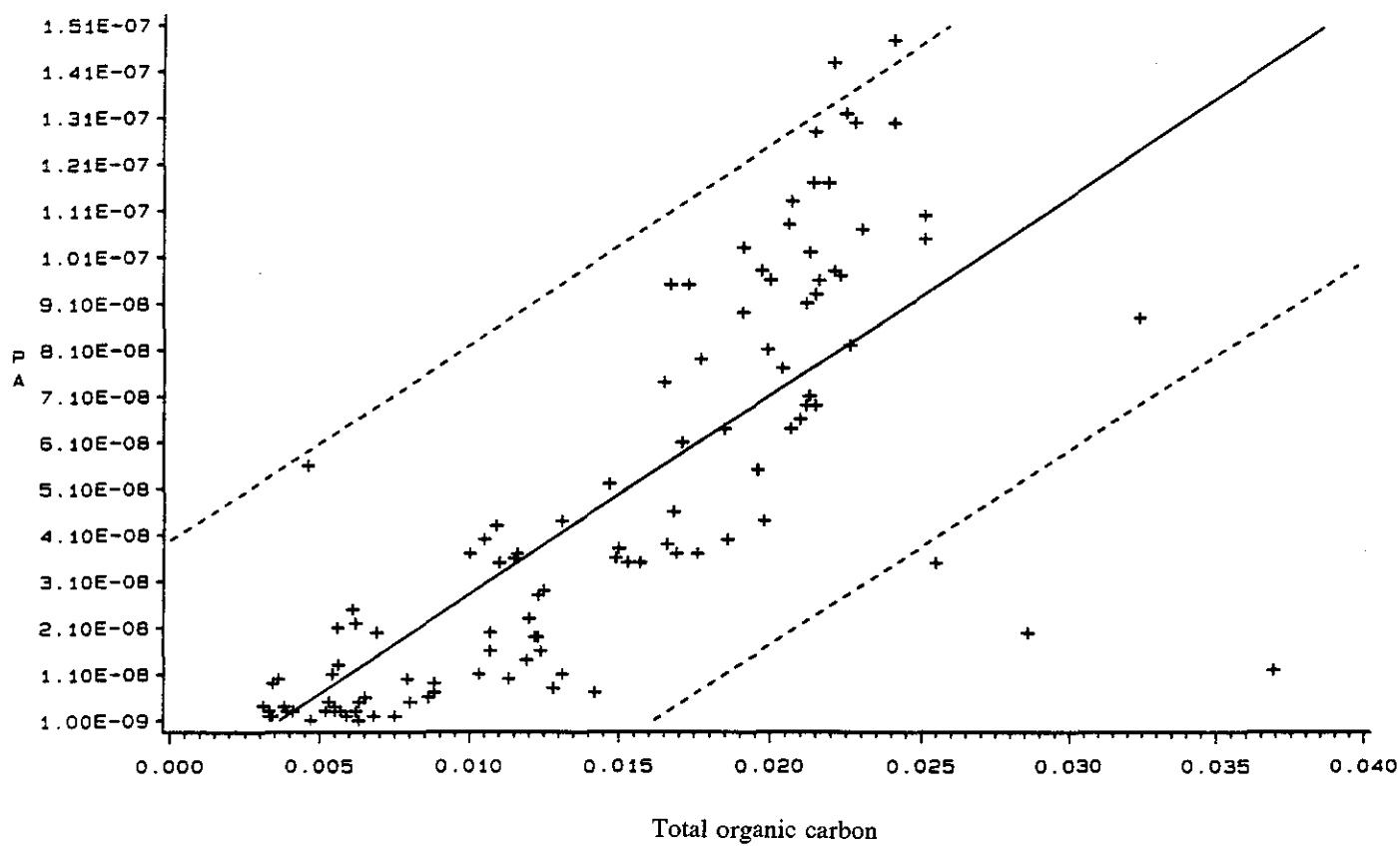


Figure 7.2.1.9 Regression of PA vs. TOC, for TOC $\geq 0.3\%$.

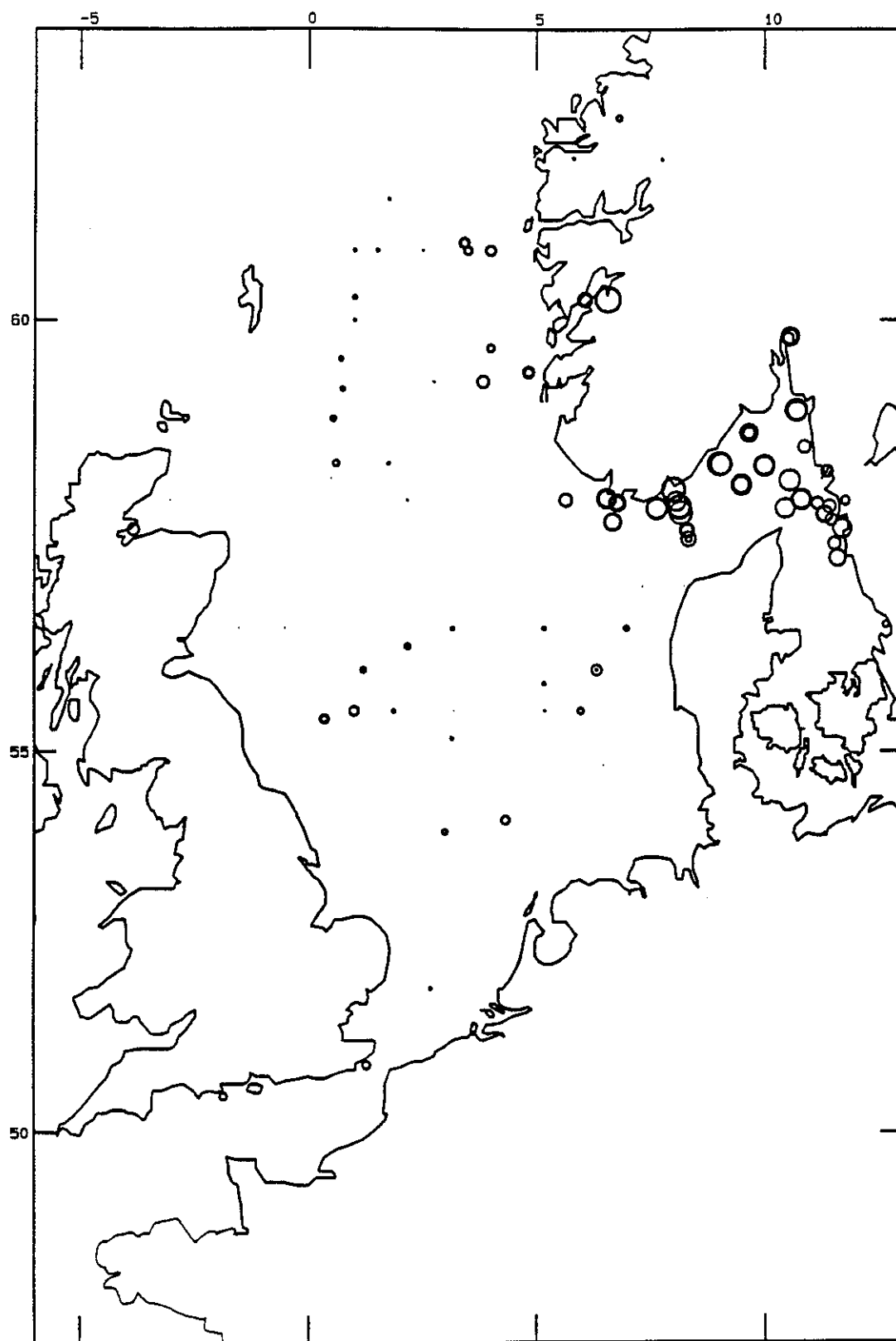


Figure 7.2.1.10 The distribution of phenanthrene (PA) concentrations in North Sea sediments $<2000\ \mu\text{m}$ (circle area is proportional to value). The maximum concentration is $72\ \mu\text{g kg}^{-1}$.

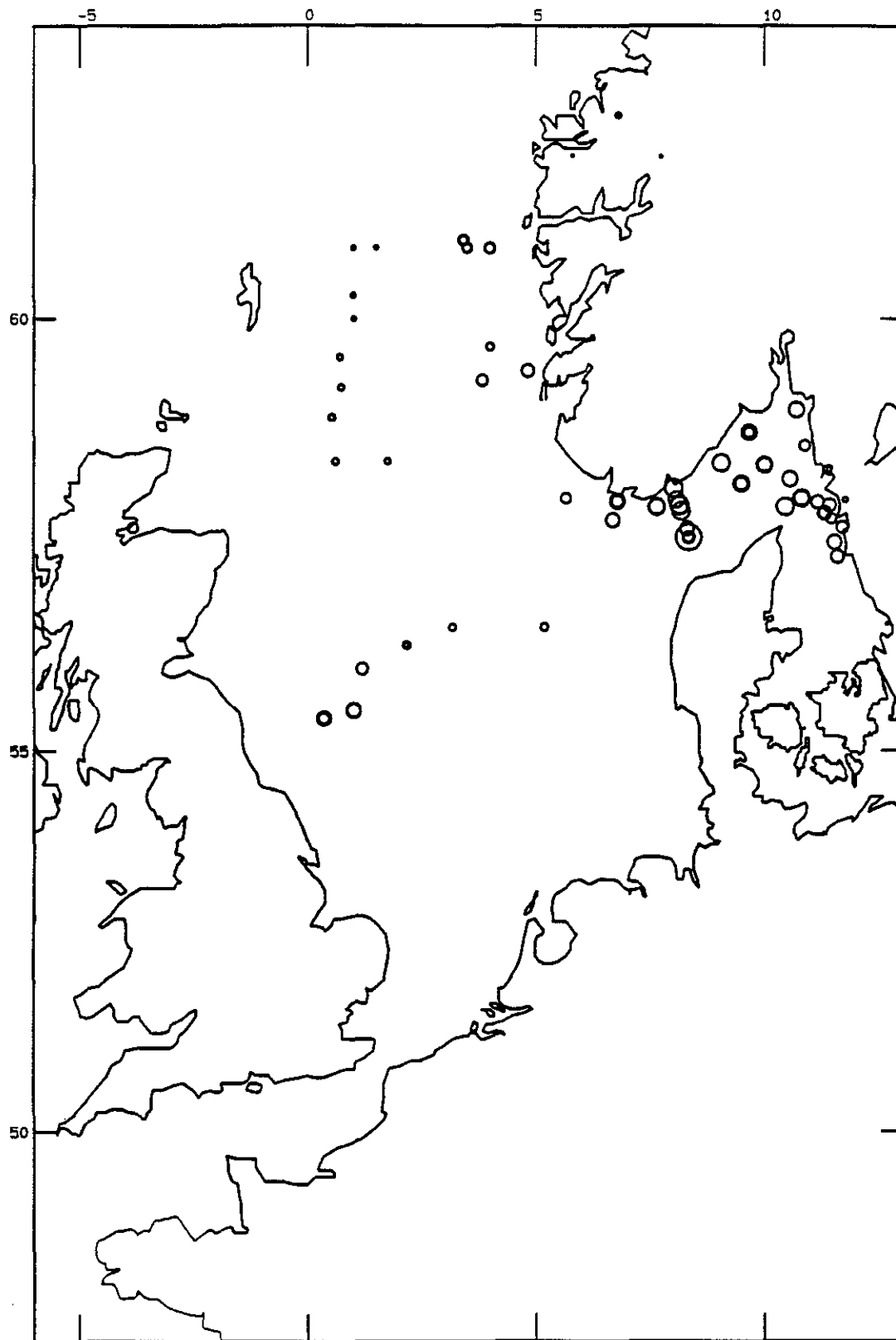


Figure 7.2.1.11 The distribution of PA/TOC ratios in North Sea sediments $<2000\ \mu\text{m}$, with $\text{TOC} \geq 0.3\%$ (circle area is proportional to value).

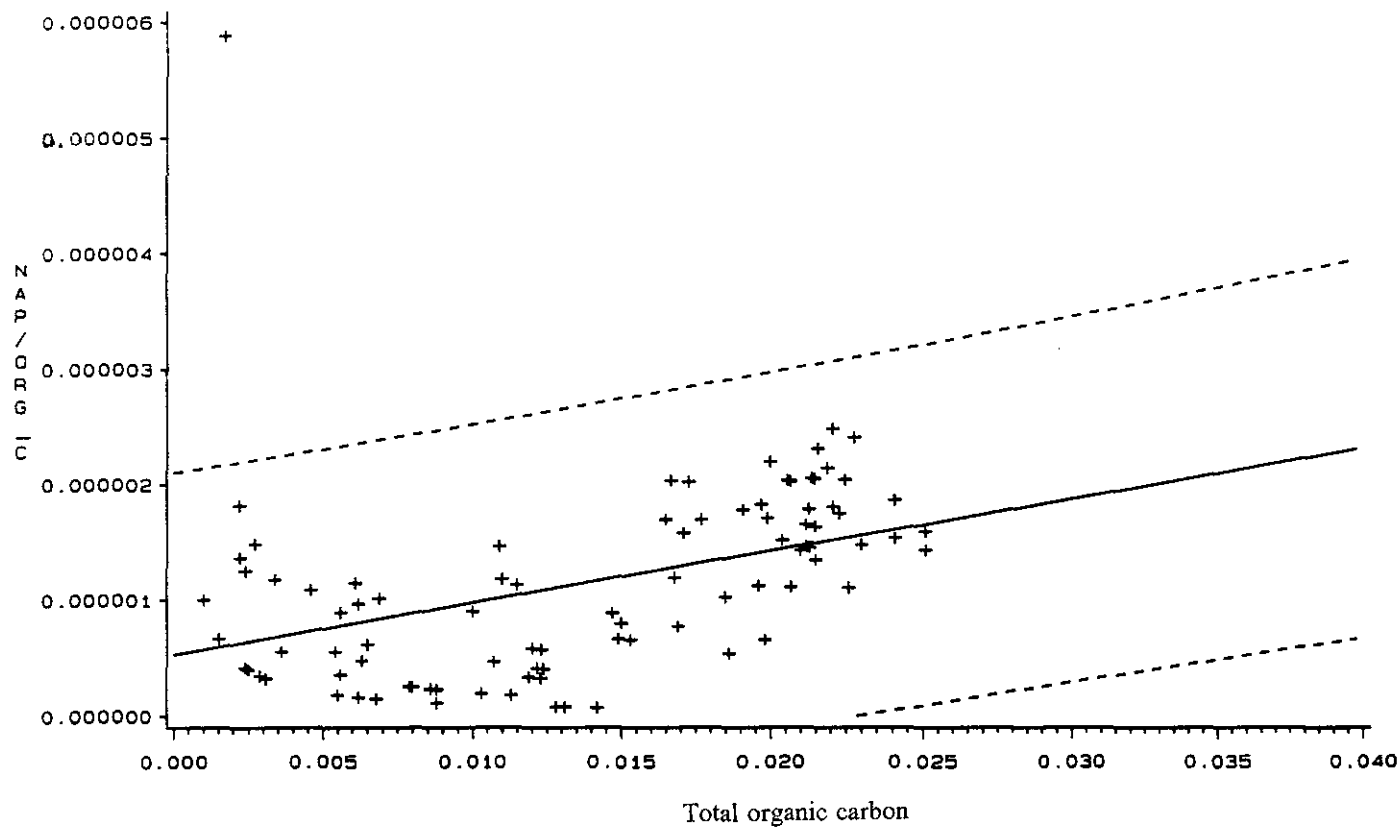


Figure 7.2.1.12 Regression of NAP/TOC vs. TOC.

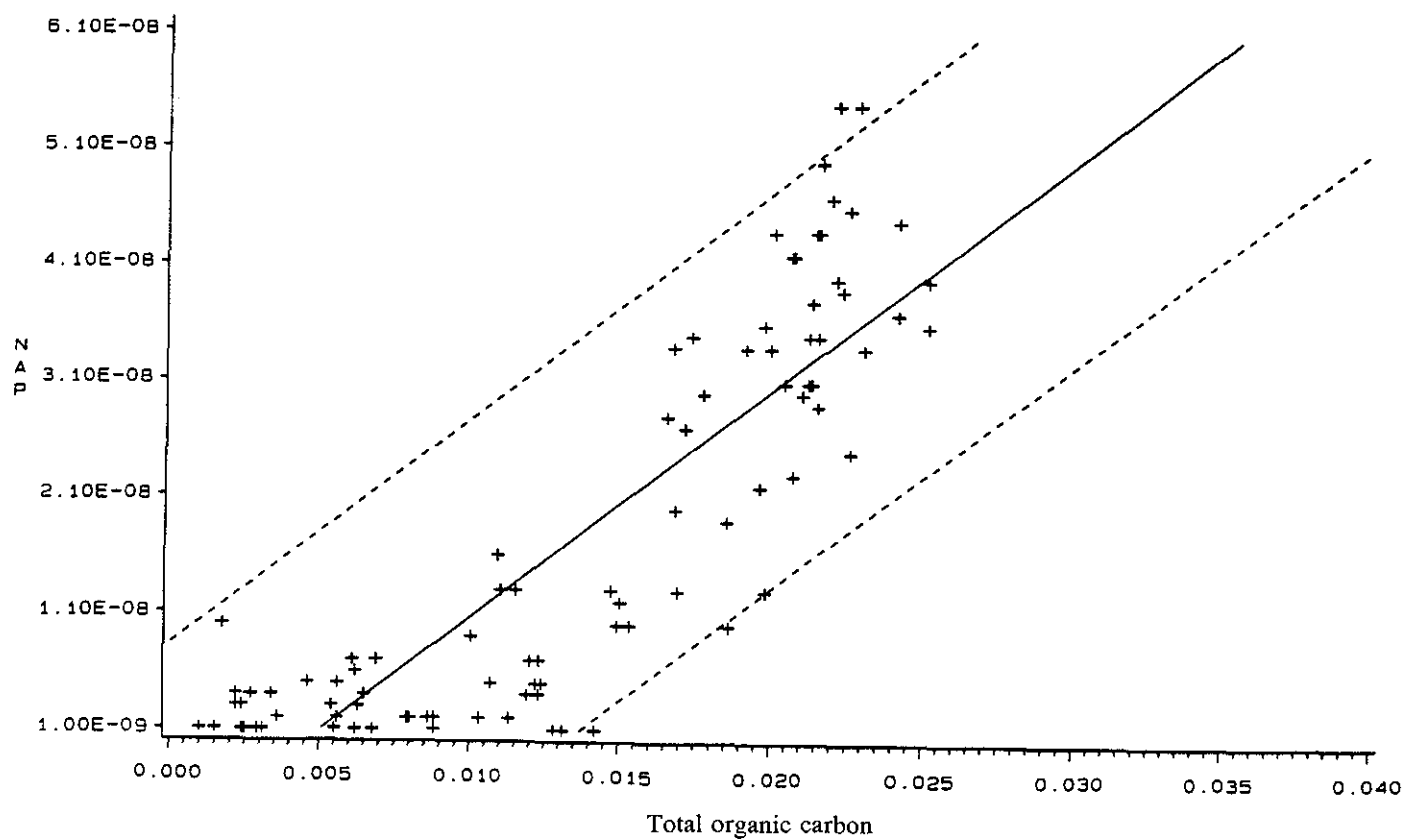


Figure 7.2.1.13 Regression of NAP vs. TOC.

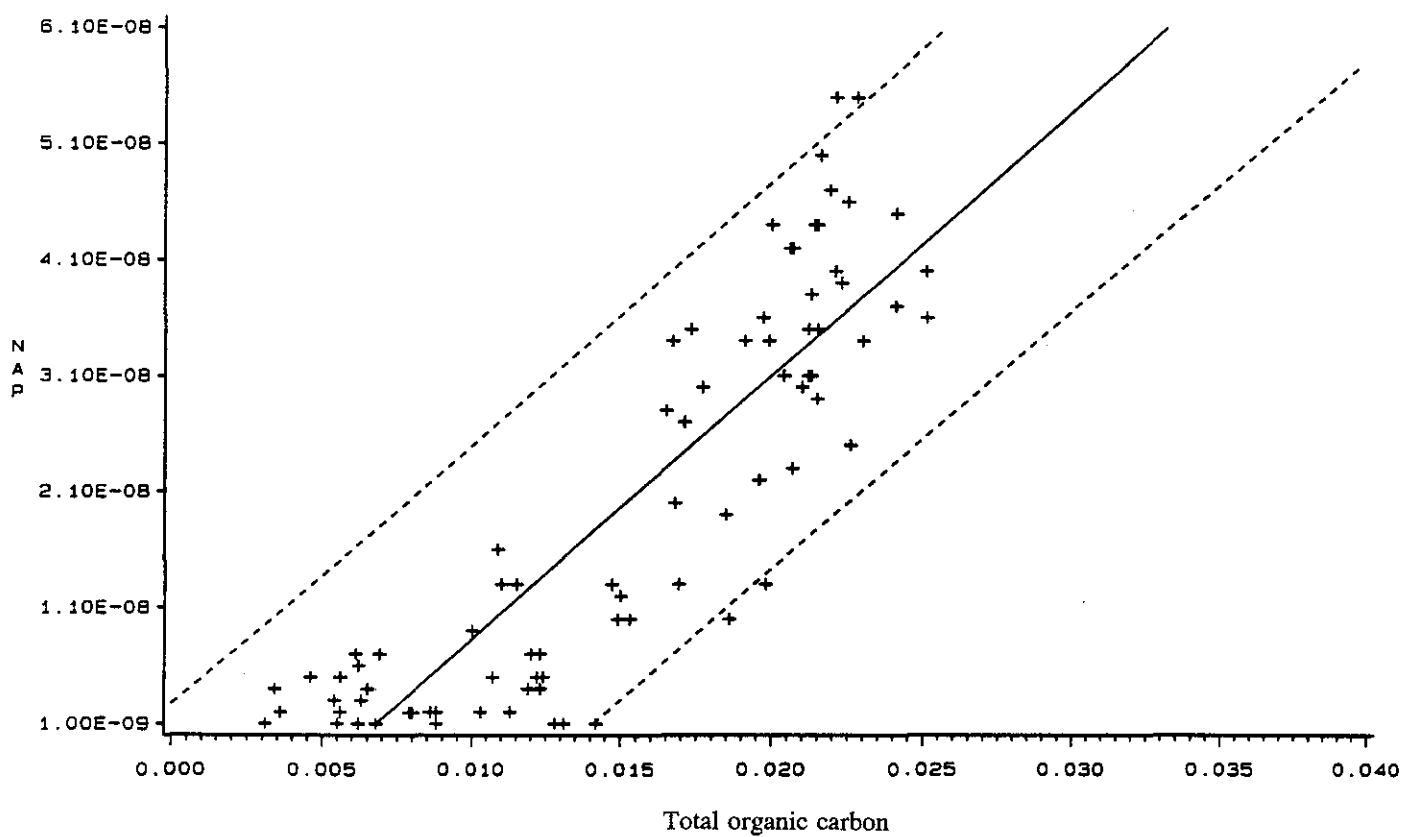


Figure 7.2.1.14 Regression of NAP vs. TOC, for TOC $\geq 0.3\%$.

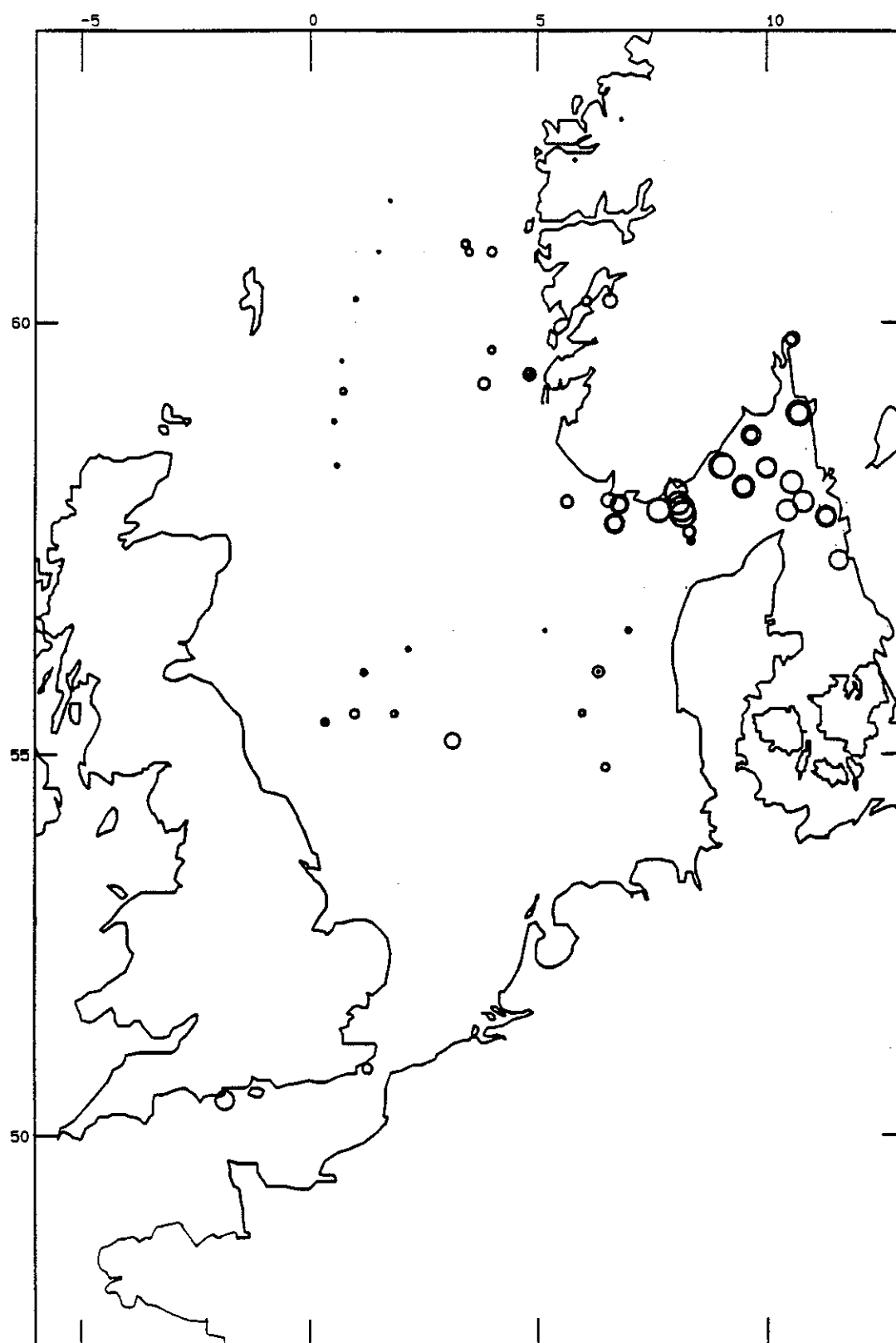


Figure 7.2.1.15 The distribution of naphthalene (NAP) concentrations in North Sea sediments $<2000\ \mu\text{m}$ (circle area is proportional to value). The maximum concentration is $55\ \mu\text{g kg}^{-1}$.

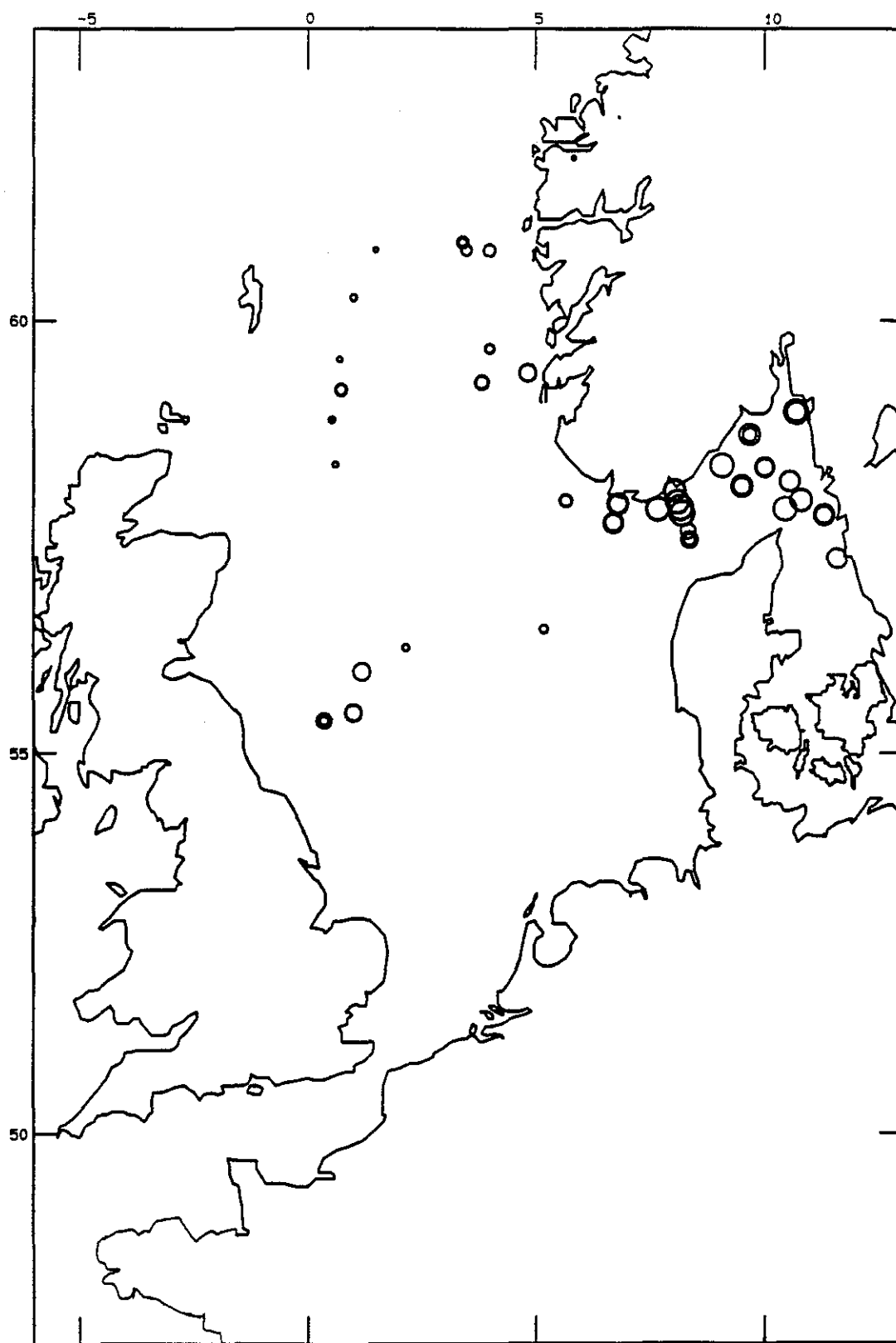


Figure 7.2.1.16 The distribution of NAP/TOC ratios in North Sea sediments $<2000 \mu\text{m}$, with $\text{TOC} \geq 0.3\%$ (circle area is proportional to value).

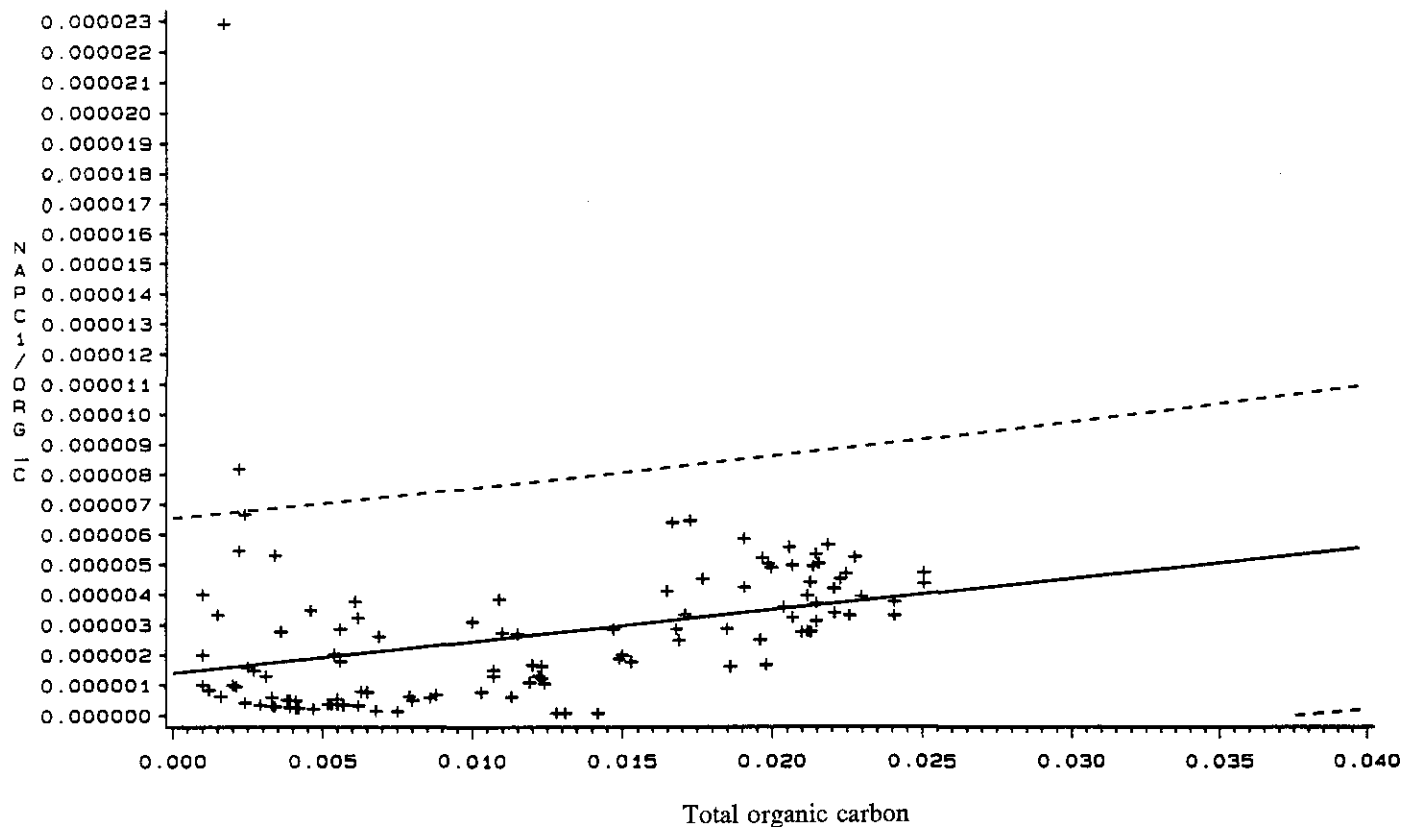


Figure 7.2.1.17 Regression of NAPC1/TOC vs. TOC.

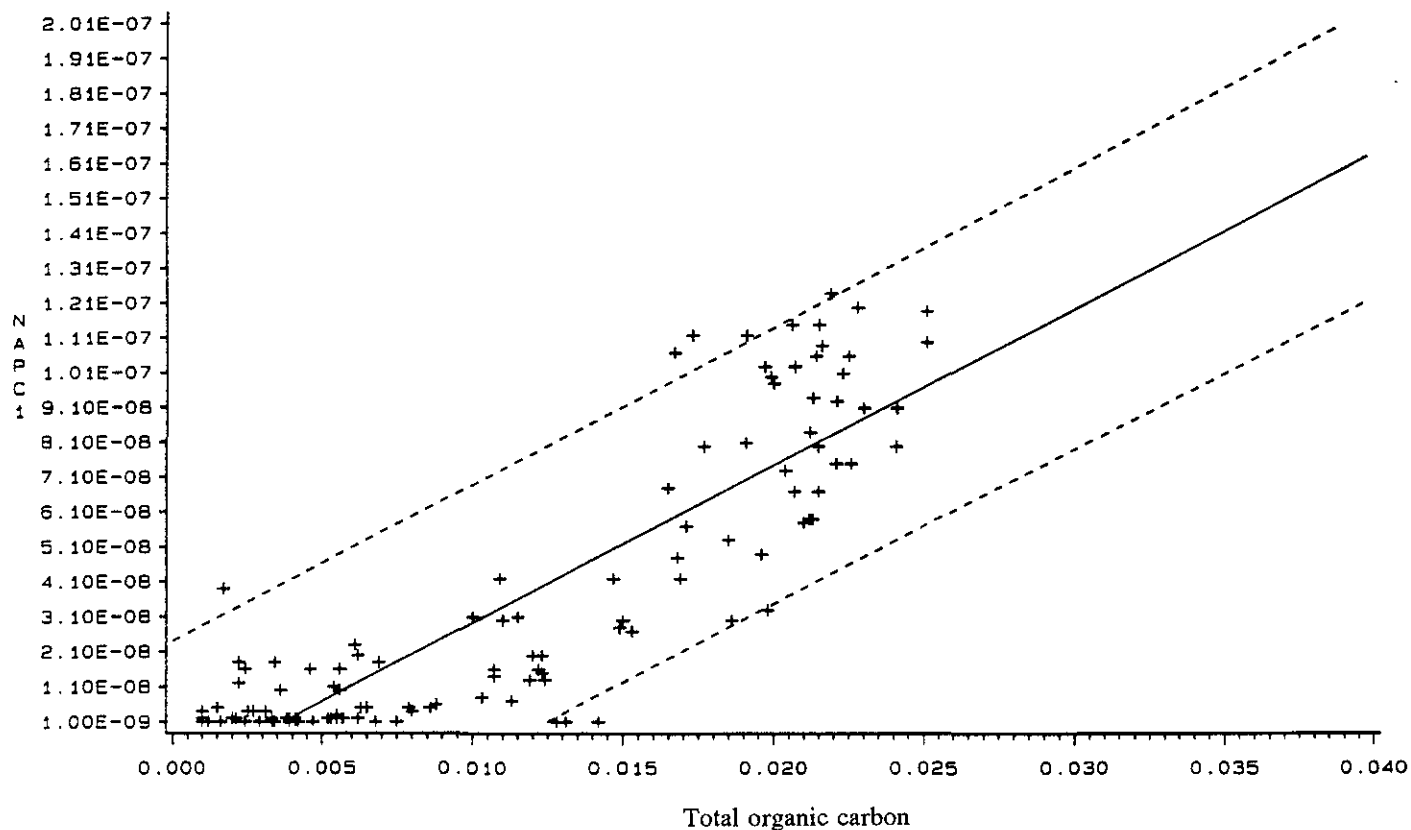


Figure 7.2.1.18 Regression of NAPC1 vs. TOC.

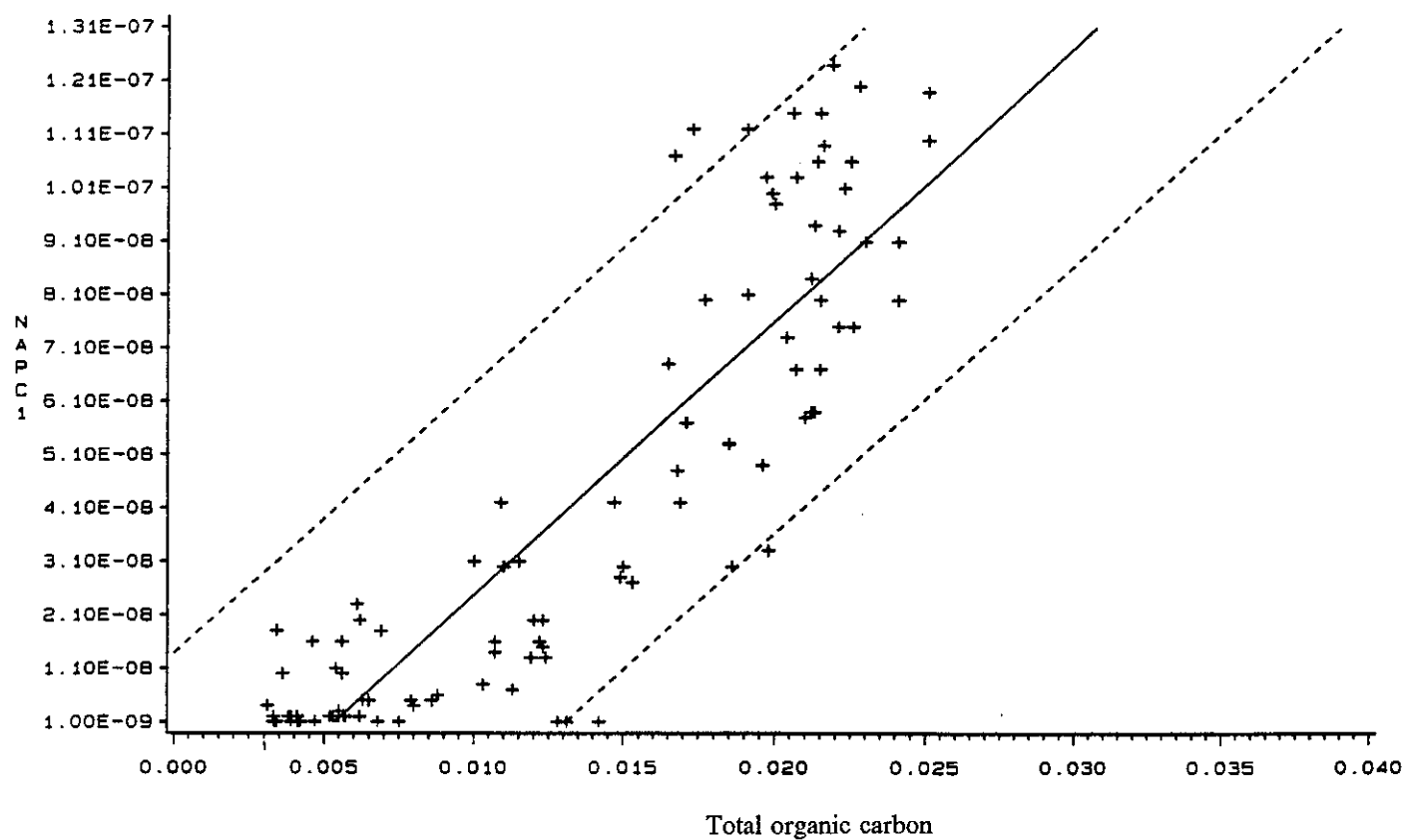


Figure 7.2.1.19 Regression of NAPC1 vs. TOC, for TOC $\geq 0.3\%$.

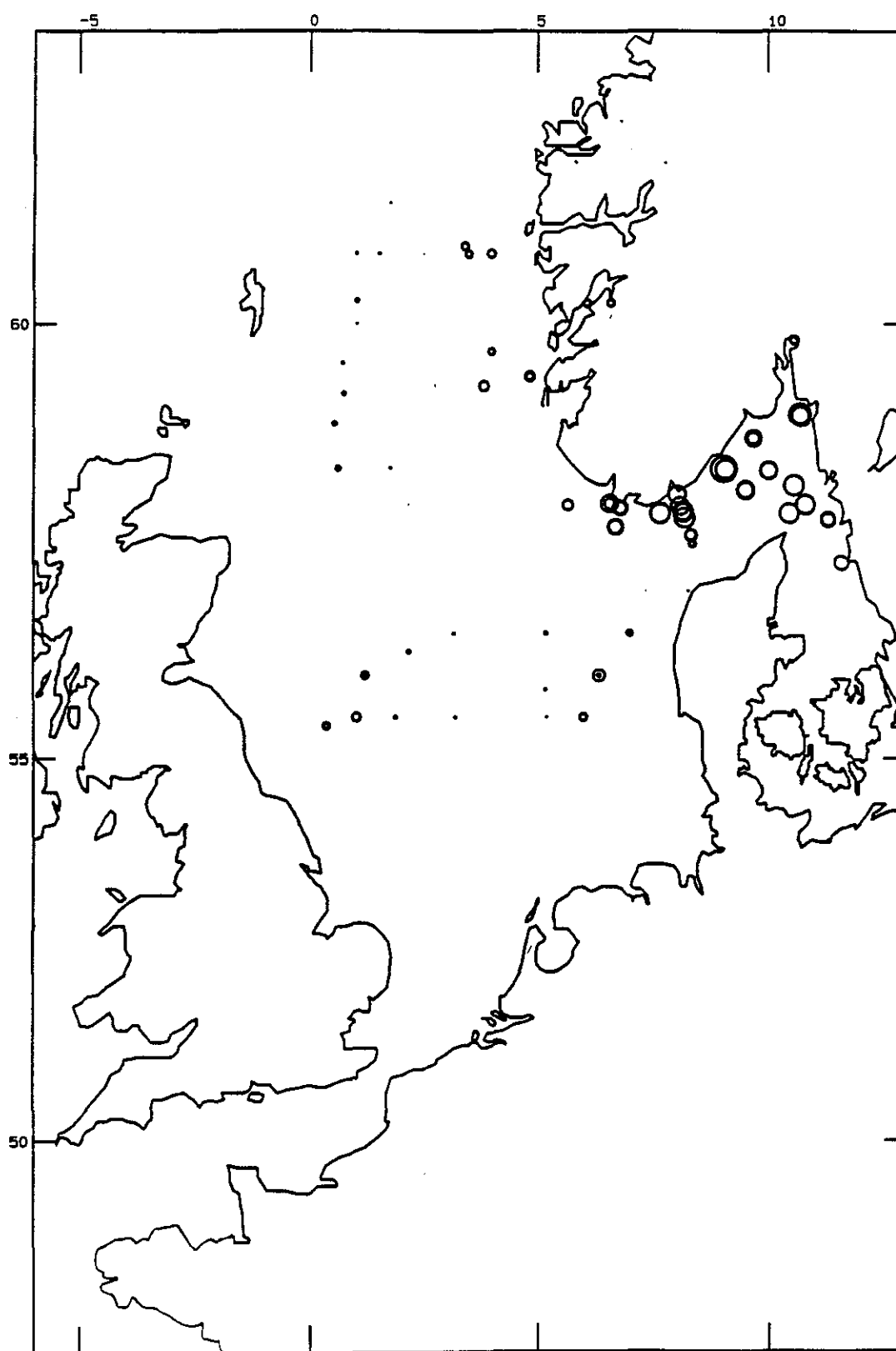


Figure 7.2.1.20 The distribution of mono-alkyl naphthalene (NAPC1) concentrations in North Sea sediments <2000 μm (circle area is proportional to value). The maximum concentration is $98 \mu\text{g kg}^{-1}$.

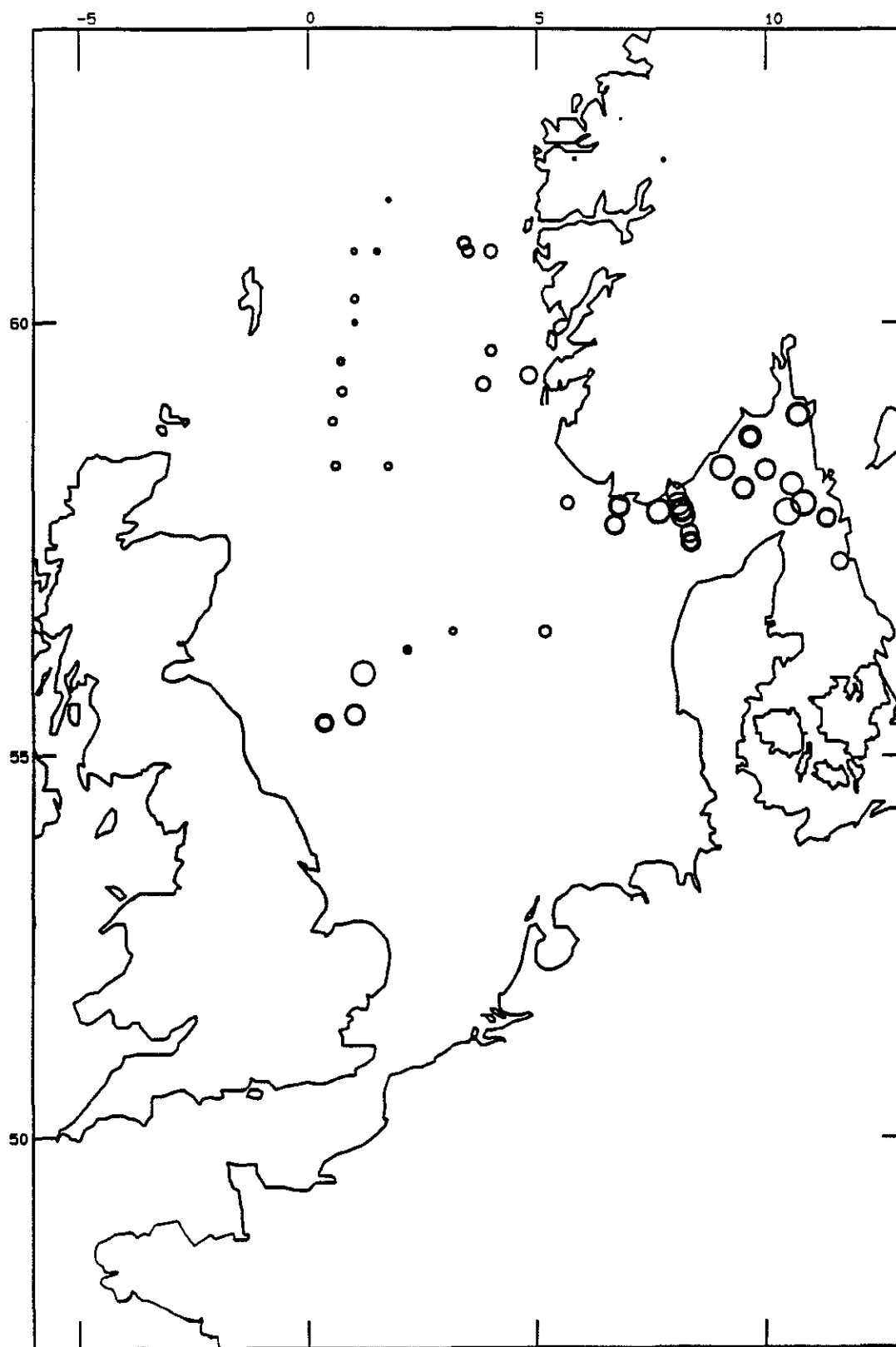


Figure 7.2.1.21 The distribution of NAPC1/TOC ratios in North Sea sediments $<2000\ \mu\text{m}$, with $\text{TOC} \geq 0.3\%$ (circle area is proportional to value).

ANNEX 1

NAMES AND CODES OF LABORATORIES THAT SUBMITTED DATA

Country	Code	Laboratory
Belgium	ECCB	Laboratorium ECCA Klaartestraat 24 B-9710 Zwijnaarde BELGIUM
	IHEB	Institut d'Hygiène et d'Epidémiologie Ministère de la Santé Publique et de l'Environnement Rue Juliette Wytsman 14 B-1050 Brussels BELGIUM
	ISOB	Instituut voor Scheikundig Onderzoek Museumlaan 5 B-1980 Tervuren BELGIUM
	MUMM	Management Unit of the North Sea and Scheldt Estuary Mathematical Models Gulledelle 100 B-1200 Brussels BELGIUM
Denmark	HFLD	now NERI: Miljøstyrelsens Havforureningslaboratorium National Environmental Research Institute Frederiksborgvej 399 P.O. Box 358 DK-4000 Roskilde DENMARK
France	ICNF	IFREMER Centre de Nantes Rue de l'Ile d'Yeu BP 1049 44037 Nantes Cédex 01 FRANCE
Germany	BFGG	Bundesanstalt für Gewässerkunde Kaiserin-Augusta-Anlagen 15-17 D-56068 Koblenz GERMANY
	BSHG	Bundesamt für Seeschifffahrt und Hydrographie Bernhard-Nocht-Strasse 78 D-20359 Hamburg GERMANY
	ISHG	Institut Schumacher Laboratorium für Wasser-, Abwasser- und Ölanalytik Dr. Harald Schumacher (Dipl. Chem.) Sophie-Dethleffs-Str. 4 D-25746 Heide GERMANY

Country	Code	Laboratory
	LWKG	Landesamt für Wasserhaushalt und Küsten Schlesweg - Holstein Saarbrückenstrasse 38 D-24114 Kiel GERMANY
	NLWG	now NLEG: Niedersächsisches Landesamt für Ökologie An der Scharlake 39 D-31135 Hildesheim GERMANY previously NLWG: Niedersächsisches Landesamt für Wasserwirtschaft An der Scharlake 39 D-31135 Hildesheim GERMANY
Netherlands	DGWN	Rijkswaterstaat Dienst Getijdewateren (Public Works Department - Tidal Waters Division) Laboratory Department Nijverheidsstraat 2 P.O.Box 3006 NL-2280 MH Rijswijk NETHERLANDS
	IMWT	Instituut voor Mileuwetenschappen TNO-IMW, Postbus 6011 NL-2600 JA Delft Netherlands
Norway	IMRN	Institute of Marine Research P.O. Box 1870 N-5011 Bergen-Nordnes NORWAY
	NIVA	Norwegian Institute for Water Research P.O. Box 69 Korsvoll N-0808 Oslo 8 NORWAY
	SIIF	Sentral Instituttet for Industriell Forskning Forskingsveien 1 P.O. Box 350 N-Blindern, Oslo 3 NORWAY
Sweden	GUMI	Göteborgs Universitet Maringeologiska institute Box 7064 402 32 Göteborg SWEDEN
	NSLS	Swedish Environmental Protection Agency Naturvårdsverkets Special Analytical Laboratory (NRLS) S-171 85 Solna SWEDEN

Country	Code	Laboratory
	SERI	Swedish Environmental Research Institute P.O.Box 47086 S-40258 Gothenburg SWEDEN
United Kingdom	ALUK	Scottish Office Agriculture and Fisheries Department Marine Laboratory P.O. Box 101 Victoria Road Aberdeen AB9 8DB, Scotland UNITED KINGDOM
	BLUK	Ministry of Agriculture, Fisheries and Food Fisheries Laboratory Remembrance Avenue Burnham-on-Crouch Essex CMO 8HA UNITED KINGDOM
	FRUK	Forth River Purification Board Colinton Dell House West Mill Road Colinton Edinburgh EH13 0PH, Scotland UNITED KINGDOM

ANNEX 2

SEDIMENT EXTRACTION METHOD CODES

Method	Code
(a) Inorganic contaminants:	
Extraction with dilute HCl	HCL
Extraction with acetic acid	HAC
Extraction with 1:1 HNO ₃	HNO
Extraction with HNO ₃ , pressure digestion	HHC
Extraction with aqua regia (HNO ₃ :HCl = 1:3)	AQR
Extraction with a mixture of strong mineral acids without HF (e.g., HClO ₄ and/or H ₂ SO ₄ in addition to HNO ₃)	SAD
'Total' digestion with mineral acids including HF, in open vessels, evaporation of excess HF before analysis	HFO
As HFO above, but with digestion performed in closed vessels (pressurized decomposition)	HFC
As HFC above, but with complexation of excess HF with H ₃ BO ₃	HFB
Alkaline fusion digestion	ALK
Selective chemical extraction of metal species in particulate phases (e.g. by hydroxylamine, oxalate, H ₂ O ₂ , dithionite, ammonium acetate); define procedure(s) in plain language comment record(s)	SCE
(b) Organic contaminants:	
Extraction of organic contaminants by shaking with polar solvents	EXP
Extraction of organic contaminants by shaking with non-polar solvents	EXN
Extraction of organic contaminants by continuous treatment in a Soxhlet or similar apparatus	EXC
Separation of organic contaminants from sediment slurries using water steam distillation	EXH
Other principles of extraction/separation of organic contaminants from sediment samples; define procedure(s) in plain language comment record(s)	EXO
(c) Other:	
Solid suspension technique for determination of total metals	SST
Non-destructive technique for determination of total metals (e.g., proton-induced X-ray emission)	NDT*

*This code is no longer used in the data reporting format.

ANNEX 3

NUMBERS OF SAMPLES FOR WHICH DATA WERE SUBMITTED AND ASSESSED FOR TOTAL CONCENTRATIONS OF METALS IN SEDIMENTS, ACCORDING TO LABORATORY AND METHOD

Table A 3.1 Numbers of samples (N) for which data were submitted.

Analytical Laboratory Code	Extraction Method Code	VARIABLE										
		AL	AS	CD	CR	CU	FE	HG	MN	NI	PB	ZN
		N	N	N	N	N	N	N	N	N	N	N
ALUK	HFB	14	.	14	.	14	14	14	14	.	14	14
BLUK	HFB	361	.	361	361	361	155	325	.	.	361	361
BSHG	HFB	8	.	.	6	7	8	.	8	.	.	8
	HNO	.	.	11	14	14	14	12	14	13	10	14
GUMI	AQR	.	.	.	.	.	.	9	.	.	.	.
	HNO	.	.	9	9	9	.	.	.	9	9	9
HFLD	NDT1	12	12	.	9	12	12	.	12	7	12	12
ICNF	AQR	.	.	3	.	3	.	.	.	.	3	3
	HFO	2	.	2	.	2	.	.	.	.	2	2
	SAD	.	.	.	.	.	.	5	.	.	.	.
IHEB	HHC	.	7	7	7	7	.	7	.	7	7	7
IMWT	HFCA	19	.	19	.	19	.	19	.	.	19	19
ISOB	SAD	.	.	.	.	.	.	34	.	.	.	.
	SST	34	.	34	7	34	.	.	.	7	34	34
LWKG	HCF	.	9	9	9	9	9	8	.	9	9	9
NIVA	HFO	168	.	168	130	168	.	.	.	130	168	168
	HNO	.	.	.	.	.	.	168	.	.	.	.
NLWG	AQR	.	.	34	34	34	34	34	34	34	34	34
SIIF	HFO	.	130	.	.	.	.	.	.	.	.	.
ALL LABS	AQR	.	.	37	34	37	34	43	34	34	37	37
	HFB	383	.	375	367	382	177	339	22	.	375	383
	HFC	.	9	9	9	9	9	8	.	9	9	9
	HFCA	19	.	19	.	19	.	19	.	.	19	19
	HFO	170	130	170	130	170	.	.	.	130	170	170
	HHC	.	7	7	7	7	.	7	.	7	7	7
	HNO	.	.	20	23	23	14	180	14	22	19	23
	NDT1	12	12	.	9	12	12	.	12	7	12	12
	SAD	.	.	.	.	.	.	39	.	.	.	.
	SST	34	.	34	7	34	.	.	.	7	34	34

ANNEX 3 (Cont'd)

NUMBERS OF SAMPLES FOR WHICH DATA WERE SUBMITTED AND ASSESSED FOR TOTAL CONCENTRATIONS OF METALS IN SEDIMENTS, ACCORDING TO LABORATORY AND METHOD

Table A 3.2 Numbers of samples (N) for which data were assessed.

Analytical Laboratory Code	Extraction Method Code	VARIABLE										
		AL	AS	CD	CR	CU	FE	HG	MN	NI	PB	ZN
		N	N	N	N	N	N	N	N	N	N	N
ALUK	HFB	14	.	9	.	14	14	14	14	.	14	14
ALUK	HFB	361	.	360	315	46	155	325	.	.	361	361
BSHG	HFB	8	.	.	6	7	8	.	8	.	.	8
	HNO	.	.	.	.	.	.	12	.	.	.	.
GUMI	AQR	.	.	.	.	.	.	9	.	.	.	.
HFLD	NDT1	12	12	.	.	9	.	.	.	7	12	12
ICNF	HFO	2	.	2	.	2	.	.	.	.	2	2
	SAD	.	.	.	.	.	.	5	.	.	.	.
IHEB	HHC	.	.	.	.	.	.	7	.	.	.	.
IMWT	HFCA	19	.	19	.	19	.	19	.	.	19	19
ISOB	SAD	.	.	.	.	.	.	34	.	.	.	.
	SST	34	.	34	7	34	.	.	.	7	34	34
LWKG	HFC	.	.	.	9	9	9	.	.	9	9	9
NIVA	HFO	168	.	.	130	154	.	.	.	130	154	154
	HNO	.	.	.	.	.	.	154	.	.	.	.
NLWG	AQR	.	.	.	.	.	.	34	.	.	.	.
SIIF	HFO	.	69	.	.	.	.	.	.	.	.	.
ALL LABS	AQR	.	.	.	.	.	.	34	.	.	.	.
	HFB	383	.	369	321	67	177	339	22	.	375	383
	HFC	.	.	.	9	9	9	.	.	9	9	9
	HFCA	19	.	19	.	19	.	19	.	.	19	19
	HFO	170	69	2	130	156	.	.	.	130	156	156
	HHC	.	.	.	.	.	.	7	.	.	.	.
	HNO	.	.	.	.	.	.	166	.	.	.	.
	NDT1	12	12	.	.	9	.	.	.	7	12	12
	SAD	.	.	.	.	.	.	39	.	.	.	.
	SST	34	.	34	7	34	.	.	.	7	34	34

ANNEX 4

CERTIFIED VALUES FOR SEDIMENT REFERENCE MATERIALS

All values in mg kg⁻¹ unless otherwise stated.

	PACS-1	MESS-1	BCSS-1	LISS
Al%	6.47 ± 0.12	5.83 ± 0.20	6.26 ± 0.22	
Fe%	4.87 ± 0.08	3.05 ± 0.17	3.29 ± 0.10	1.76
Cd	2.38 ± 0.20	0.59 ± 0.10	0.25 ± 0.04	0.25 ± 0.9
Cr	113 ± 8	71 ± 11	123 ± 14	71
Cu	452 ± 16	25.1 ± 3.8	18.5 ± 2.7	27.5 ± 0.6
Mn	470 ± 12	513 ± 25	229 ± 15	
Ni	44.1 ± 2.0	29.5 ± 2.7	55.3 ± 3.6	29.2 ± 2.5
Pb	404 ± 20	34.0 ± 6.1	22.7 ± 3.4	37.8
Zn	824 ± 22	191 ± 17	119 ± 12	92.4 ± 4.4
Co	17.5 ± 1.1	10.8 ± 1.9	11.4 ± 2.1	
Hg	4.57 ± 1.6	0.171 ± 0.014	0.129 ± 0.012	0.104 ± 0.012
Li				
As			11.1 ± 1.4	16.6

	SRM-1645	ABSS ¹	CRM 320-85	BEST-1
Al%	2.26 ± 0.04	5.7		
Fe%	11.3 ± 1.2	3.78 ± 14%		
Cd	10.2 ± 1.5	1.11 ± 48%	0.53 ± 0.03	
Cr	29600 ± 2800	82 ± 34%		
Cu	109 ± 19	53 ± 12%	44.1 ± 1.0	
Mn	785 ± 97	388 ± 11%		
Ni	45.8 ± 2.9	42 ± 16%		
Pb	714 ± 28	88 ± 12%	42.3 ± 1.6	
Zn	1720 ± 170	313 ± 8%		
Co	10.1 ± 0.6	14		
Hg	1.1 ± 0.5	0.256 ± 39%	1.03 ± 0.13	0.092 ± 0.009

¹Data from Brüggmann and Niemistö (1987) ± RSD%.

ANNEX 5

RESULTS OF ANALYSES OF REFERENCE MATERIALS FOR VARIOUS METALS BY PARTICIPATING LABORATORIES

Table A5.1 Quality assurance data for aluminium analyses.

Laboratory	Reference material	Certified value (T) %	Reported values (%)		$\left[\frac{T-M}{T} \right] \%$	$\left[\frac{SD}{M} \right] \%$
			Mean (M)	S.D. (SD)		
ALUK	MESS-1	11.03	10.9	0.2	1	2
BLUK	PACS-1	6.47	6.83	0.17	6	2
			6.57	0.14	2	2
BSHG	ABSS-1	5.7	6.4		12	
IMWT	CRM 320/85		8.5			
HFLD	BCSS-1	6.26	6.7	0.7	7	10
ICNF						
NIVA	PACS-1	6.47	6.66	1.14	3	17
	BCSS-1	6.26	6.25	0.663	<1	11
ISOB	MESS-1	11.03	11.9		8	

Conclusion: No laboratories rejected.

Table A5.2 Quality assurance data for cadmium analyses.

Laboratory	Reference material	Certified value (T) mg kg ⁻¹	Reported values (mg kg ⁻¹)		$\left(\frac{T-M}{T} \right) \%$	$\left(\frac{SD}{M} \right) \%$
			Mean (M)	S.D. (SD)		
ALUK	MESS-1	0.59	0.52	0.01	12	2
BLUK	MESS-1	0.59	0.566	0.09	4	16
	MESS-1	0.59	0.548	0.13	7	24
	PACS-1	2.38	2.02	0.22	15	11
BSHG	ABSS-1	1.11	0.944	0.101	15	11
		1.11	0.93	0.112	16	12
IMWT	CRM 320/85	0.53	0.58		9	
HFLD	BCSS-1	0.25	0.26	0.01	4	4
ICNF						
LWKG	LISS	0.25	0.217	0.049	13	23
NIVA	PACS-1	2.38	1.29	0.41	46	32
	BCSS-1	0.25	0.17	0.04	32	24
ISOB ¹	BCSS-1	0.25	0.29		16	

Conclusion: Reject data from LWKG, NIVA.

¹Data from Hovind and Skei (1992).

ANNEX 5 (Cont'd)

Table A5.3 Quality assurance data for copper analyses.

Laboratory	Reference material	Certified value (T) mg kg ⁻¹	Reported values (mg kg ⁻¹)		$\left(\frac{T-M}{T}\right) \%$	$\left(\frac{SD}{M}\right) \%$
			Mean (M)	S.D. (SD)		
ALUK	MESS-1	25.1	23.1	1.0	8	4
BLUK	MESS-1	25.1	24.0	8.0	4	33
	MESS-1	25.1	24.0	2.0	4	8
	PACS-1	452	433	15.0	4	3
BSHG	ABSS-1	53	51.6		3	
	ABSS-1	53	56.1	6.0	6	11
	ABSS-1	53	55.2	2.15	4	4
IMWT	CRM 320/85	44.1	43.2		2	
HFLD	BCSS-1	18.5	20.8	1.99	12	10
ICNF						
NIVA	PACS-1	452	437.8	18.8	3	4
	BCSS-1	18.5	21.6	1.94	17	9
LWKG	LISS	27.5	26.6	3.14	3	12
ISOB	BCSS-1	18.5	19.5		5	

Conclusion: No laboratories rejected.

ANNEX 5 (Cont'd)

Table A5.4 Quality assurance data for mercury analyses.

Laboratory	Reference material	Certified value (T) mg kg ⁻¹	Reported values (mg kg ⁻¹)		$\left(\frac{T-M}{T}\right) \%$	$\left(\frac{SD}{M}\right) \%$
			Mean (M)	S.D. (SD)		
ALUK	MESS-1	0.171	0.16	0.005	6	3
BLUK	BEST-1	0.092	0.112	0.012	22	11
	MESS-1	0.171	0.187	0.044	9	24
	PACS-1	4.57	3.72	0.41	22	11
BSHG	ABSS-1	0.256	0.325	0.0228	27	7
	ABSS-1	0.256	0.320	0.020	25	6
IMWT	CRM 320/85	1.03	1.06		3	
HFLD	BCSS-1	0.129	0.130	0.001	1	<1
	BCSS-1	0.129	0.130	0.001	1	<1
ICNF						
NIVA	PACS-1	4.57	4.70	0.13	3	3
	BCSS-1	0.13	0.17	0.015	31	9
LWKG	LISS	0.104	0.168	0.061	61	36
ISOB						

Conclusion: Reject data from LWKG.

BSHG: Although the means differ from the consensus value by 25–27%, they are well within the range quoted for this material. The data are precise, and have been consistent for at least five years.

BLUK/NIVA: It should be noted that the performance of these laboratories is very close to the criteria applied in this assessment when considering their data.

Note: MESS-1 and BCSS-1 have subsequently been decertified for mercury.

ANNEX 5 (Cont'd)

Table A5.5 Quality assurance data for lead analyses.

Laboratory	Reference material	Certified value (T) mg kg ⁻¹	Reported values (mg kg ⁻¹)		$\left(\frac{T-M}{T}\right) \%$	$\left(\frac{SD}{M}\right) \%$
			Mean (M)	S.D. (SD)		
ALUK	MESS-1	34.0	32.3	0.51	5	2
BLUK	MESS-1	34.0	33.4	4.0	2	12
	MESS-1	34.0	36.1	2.8	6	8
BSHG	ABSS-1	88	82.6		6	
	ABSS-1	88	93.4	5.28	6	6
	ABSS-1	88	93.2	5.46	6	6
IMWT	CRM 320/85	42.3	44		4	
HFLD	BCSS-1	22.7	26.8	3.8	18	14
ICNF						
NIVA	PACS-1	404	332.7	78.4	18	23
	BCSS-1	22.7	19.3	3.26	15	17
LWKG	LISS	37.8	32.9	5.23	13	3
ISOB	BCSS-1	22.7	21.8		4	

Conclusion: No laboratories rejected.

ANNEX 5 (Cont'd)

Table A5.6 Quality assurance data for zinc analyses.

Laboratory	Reference material	Certified value (T) mg kg ⁻¹	Reported values (mg kg ⁻¹)		$\left(\frac{T-M}{T}\right) \%$	$\left(\frac{SD}{M}\right) \%$
			Mean (M)	S.D. (SD)		
ALUK	MESS-1	191	174	18	9	1
BLUK	MESS-1	191	169	14	12	8
	MESS-1	191	167	4	13	2
BSHG	ABSS-1	313	306		2	
	ABSS-1	313	317	10.3	1	3
	ABSS-1	313	318	10.9	2	3
IMWT*						
HFLD	BCSS-1	119	124	6.48	4	5
ICNF						
NIVA	PACS-1	824	843	75	2	9
	BCSS-1	119	113.9	6.85	4	6
LWKG	LISS	92.4	91.2	12.2	1	13
ISOB	BCSS-1	119	116		3	

* IMWT intercalibrated with laboratories in five other countries in 1991 and deviated from the consensus value by 2% with an RSD of 7%, and therefore the data are considered acceptable.

Conclusion: No laboratories rejected.

Table A5.7 Quality assurance data on arsenic analyses.

Laboratory	Reference material	Certified value (T) mg kg ⁻¹	Reported values (mg kg ⁻¹)		$\left[\frac{T-M}{T}\right] \%$	$\left[\frac{SD}{M}\right] \%$
			Mean (M)	S.D. (SD)		
HFLD	BCSS-1	11.1	13.2	1.6	19	12
SIIF A	BCSS-1	11.1	40.0	4.64	260	12
	B	11.1	11.1	1.02	<1	9
LWKG	LISS	16.6	12.7	0.99	23	8

Conclusion: Reject data from LWKG and SIIF (Batch A).

ANNEX 5 (Cont'd)

Table A5.8 Quality assurance data on chromium analyses.

Laboratory	Reference material	Certified value (T) mg kg ⁻¹	Reported values (mg kg ⁻¹)		$\left(\frac{T-M}{T}\right) \%$	$\left(\frac{SD}{M}\right) \%$
			Mean (M)	S.D. (SD)		
BLUK	MESS-1	71	60	3	15	5
	MESS-1	71	58	3	18	5
BSHG	ABSS-1	820	788		4	
HFLD	BCSS-1	123	131.6	37	7	28
NIVA	BCSS-1	123	107	7.38	13	7
ISOB ¹	BCSS-1	123	131.3		7	

Conclusion: Reject data from HFLD.

¹Data from Hovind and Skei (1992).

Table A5.9 Quality assurance data for nickel analyses.

Laboratory	Reference material	Certified value (T) mg kg ⁻¹	Reported values (mg kg ⁻¹)		$\left(\frac{T-M}{T}\right) \%$	$\left(\frac{SD}{M}\right) \%$
			Mean (M)	S.D. (SD)		
HFLD	BCSS-1	55.3	57.8	2.13	5	4
NIVA	BCSS-1	55.3	45.2	4.63	18	10
LWKG	LISS	29.2	28.9	4.8	1	17
ISOB ¹	BCSS-1	55.3	56.7		3	

Conclusion: No laboratories rejected.

¹Data from Hovind and Skei (1992).

Table A5.10 Quality assurance data for manganese analyses.

Laboratory	Reference material	Certified value (T) mg kg ⁻¹	Reported values (mg kg ⁻¹)		$\left(\frac{T-M}{T}\right) \%$	$\left(\frac{SD}{M}\right) \%$
			Mean (M)	S.D. (SD)		
ALUK	MESS-1	513	490	2.5	4	<1
BLUK	MESS-1	513	512	9.2	<1	2
HFLD	BCSS-1	229	313.5	52.7	37	17

Conclusion: Reject data from HFLD.

ANNEX 5 (Cont'd)

Table A5.11 Quality assurance data for iron analyses.

Laboratory	Reference material	Certified value (T) %	Reported values (%)		$\left(\frac{T-M}{T}\right) \%$	$\left(\frac{SD}{M}\right) \%$
			Mean (M)	S.D. (SD)		
ALUK						
BLUK	MESS-1	3.05	3.16	0.06	4	2
HFLD	BCSS-1	3.29	4.075	0.168	24	4
LWKG	LISS	1.76	1.94	0.014	11	1

Conclusion: Reject data from HFLD.

ANNEX 6

CHEMICAL COMPOSITION OF SEDIMENT FINES

Table A6.1 Summary statistics for aluminium.

Units: %					
Fraction	Sample size	Average	Median	Mode	Geometric mean
< 20µm	131	6.94	7.00	6.35	6.86
< 63µm	51	5.53	5.70	5.80	5.32
Fraction	Variance	Standard deviation	Standard error	Minimum	Maximum
< 20µm	0.994	0.997	0.087	4.02	8.51
< 63µm	2.21	1.49	0.208	2.68	10.0
Fraction	Lower quartile		Upper quartile		
< 20µm	6.40		7.66		
< 63µm	4.80		6.20		

Table A6.2 Summary statistics for organic carbon (TOC).

Units: %					
Fraction	Sample size	Average	Median	Mode	Geometric mean
< 20µm	175	4.17	3.94	3.10	3.87
< 63µm	55	2.47	2.39	2.38	2.07
Fraction	Variance	Standard deviation	Standard error	Minimum	Maximum
< 20µm	2.86	1.69	0.128	1.26	11.3
< 63µm	1.67	1.29	0.174	0.063	5.93
Fraction	Lower quartile		Upper quartile		
< 20µm	3.00		5.01		
< 63µm	1.58		2.95		

Table A6.3 Summary statistics for iron.

Units: %					
Fraction	Sample size	Average	Median	Mode	Geometric mean
< 20µm	227	5.39	5.13	3.80	5.11
< 63µm	26	4.28	4.42	3.22	4.09
Fraction	Variance	Standard deviation	Standard error	Minimum	Maximum
< 20µm	3.37	1.84	0.12	2.56	13.3
< 63µm	1.51	1.23	0.24	1.94	6.56
Fraction	Lower quartile		Upper quartile		
< 20µm	4.00		6.37		
< 63µm	3.23		5.11		

Table A6.4 Summary statistics for titanium.

Units: %					
Fraction	Sample size	Average	Median	Mode	Geometric mean
<20 μm	132	0.439	0.430	0.390	0.431
<63 μm	7	0.377	0.385	0.370	0.369
Fraction	Variance	Standard deviation	Standard error	Minimum	Maximum
<20 μm	0.008	0.0896	0.0078	0.210	1.01
<63 μm	0.007	0.0837	0.0316	0.246	0.463
Fraction	Lower quartile		Upper quartile		
<20 μm	0.390		0.480		
<63 μm	0.289		0.459		

Table A6.5 Summary statistics for mercury.

Units: mg kg ⁻¹					
Fraction	Sample size	Average	Median	Mode	Geometric mean
<20 μm	232	0.432	0.330	0.300	0.322
<63 μm	85	0.734	0.290	0.160	0.324
Fraction	Variance	Standard deviation	Standard error	Minimum	Maximum
<20 μm	0.132	0.364	0.0239	0.040	2.10
<63 μm	2.98	1.72	0.187	0.020	13.0
Fraction	Lower quartile		Upper quartile		
<20 μm	0.195		0.530		
<63 μm	0.160		0.520		

Table A6.6 Summary statistics for cadmium.

Units: mg kg ⁻¹					
Fraction	Sample size	Average	Median	Mode	Geometric mean
<20 μm	232	0.862	0.725	0.210	0.630
<63 μm	86	1.52	0.565	2.00	0.670
Fraction	Variance	Standard deviation	Standard error	Minimum	Maximum
<20 μm	0.453	0.673	0.0442	0.100	3.49
<63 μm	8.37	2.89	0.312	0.0667	15.9
Fraction	Lower quartile		Upper quartile		
<20 μm	0.315		1.10		
<63 μm	0.300		1.19		

Table A6.7 Summary statistics for lead.

Units: mg kg ⁻¹					
Fraction	Sample size	Average	Median	Mode	Geometric mean
<20µm	232	122.2	110.0	110.0	107.2
<63µm	89	142.9	56.4	36.0	69.8
Fraction	Variance	Standard deviation	Standard error	Minimum	Maximum
<20µm	3611	60.1	3.95	21.0	292.0
<63µm	167950	409.8	43.4	17.0	3500.
Fraction	Lower quartile		Upper quartile		
<20µm	76.0		158		
<63µm	43.3		88		

Table A6.8 Summary statistics for zinc.

Units: mg kg ⁻¹					
Fraction	Sample size	Average	Median	Mode	Geometric mean
<20µm	231	317	240	180	272
<63µm	93	311	185	121	210
Fraction	Variance	Standard deviation	Standard error	Minimum	Maximum
<20µm	39306	198	13.0	82.0	1450
<63µm	283954	532	55.2	46.0	4550
Fraction	Lower quartile		Upper quartile		
<20µm	180		386		
<63µm	132		268		

Table A6.9 Summary statistics for copper.

Units: mg kg ⁻¹					
Fraction	Sample size	Average	Median	Mode	Geometric mean
<20µm	232	30.0	29.0	30.0	29.2
<63µm	93	47.5	28.0	20.0	33.5
Fraction	Variance	Standard deviation	Standard error	Minimum	Maximum
<20µm	51.2	7.16	0.470	16.0	57.0
<63µm	3036	55.1	5.71	8.00	395.
Fraction	Lower quartile		Upper quartile		
<20µm	25.0		33.0		
<63µm	20.0		47.6		

Table A6.10 Summary statistics for chromium.

Units: mg kg ⁻¹					
Fraction	Sample size	Average	Median	Mode	Geometric mean
< 20 μ m	214	109.	107.	96.0	106.
< 63 μ m	53	80.6	82.0	82.0	76.8
Fraction	Variance	Standard deviation	Standard error	Minimum	Maximum
< 20 μ m	672.	25.9	1.77	52.0	192.
< 63 μ m	595.	24.4	3.35	37.0	139.
Fraction	Lower quartile		Upper quartile		
< 20 μ m	92.0		126.		
< 63 μ m	62.9		93.6		

Table A6.11 Summary statistics for nickel.

Units: mg kg ⁻¹					
Fraction	Sample size	Average	Median	Mode	Geometric mean
< 20 μ m	204	40.0	40.0	46.0	39.3
< 63 μ m	51	30.0	27.2	26.0	28.4
Fraction	Variance	Standard deviation	Standard error	Minimum	Maximum
< 20 μ m	58.8	7.67	0.537	19.3	70.0
< 63 μ m	102.	10.1	1.42	11.0	56.0
Fraction	Lower quartile		Upper quartile		
< 20 μ m	34.0		46.0		
< 63 μ m	22.0		36.6		

Table A6.12 Summary statistics for arsenic.

Units: mg kg ⁻¹					
Fraction	Sample size	Average	Median	Mode	Geometric mean
< 20 μ m	169	52.0	44.0	41.0	41.4
< 63 μ m	27	20.5	18.6	17.4	18.5
Fraction	Variance	Standard deviation	Standard error	Minimum	Maximum
< 20 μ m	1111	33.3	2.56	6.90	193
< 63 μ m	84.5	9.19	1.77	7.50	39.2
Fraction	Lower quartile		Upper quartile		
< 20 μ m	28.0		71.0		
< 63 μ m	12.9		27.8		

Table A6.13 Summary statistics for maganese.

Units: mg kg ⁻¹					
Fraction	Sample size	Average	Median	Mode	Geometric mean
<20 μ m	207	1875	1166	1100	1387
<63 μ m	25	1474	774	771	1045
Fraction	Variance	Standard deviation	Standard error	Minimum	Maximum
<20 μ m	3.42E6	1851	129	349	13440
<63 μ m	3.41E6	1848	370	397	9430
Fraction	Lower quartile		Upper quartile		
<20 μ m	798		2314		
<63 μ m	680		1410		

ANNEX 7

RESULTS OF REGRESSION ANALYSES OF SELECTED PAH COMPOUNDS

	ALL DATA	C org < 0.3 %	C org ≥ 0.3 %
BAP			
Intercept	-1.29×10^{-8}	1.5×10^{-18}	-1.85×10^{-8}
Organic Carbon Content	4.7×10^{-6}	8.6×10^{-16}	5.1×10^{-6}
F	269.046	0.040	182.265
Prob > F	0.0001	0.8439	0.0001
R ²	0.6594	0.017	0.6152
Adj R ²	0.6569	-0.0417	0.6118
N	141	25	116
PA			
Intercept	-1.02×10^8	9.73×10^{-9}	-1.47×10^{-8}
Organic Carbon Content	4.05×10^{-6}	-2.4×10^{-6}	4.3×10^{-6}
F	219.886	0.621	152.987
Prob > F	0.0001	0.4408	0.0001
R ²	0.6321	0.0334	0.5862
Adj R ²	0.6292	-0.0203	0.5824
N	130	20	110
NAP			
Intercept	-9.02×10^{-9}	4.06×10^{-9}	-1.45×10^{-8}
Organic Carbon Content	1.97×10^{-6}	5.38×10^{-7}	2.27×10^{-6}
F	259.413	0.101	251.501
Prob > F	0.0001	0.7582	0.0001
R ²	0.7403	0.0125	0.7564
Adj R ²	0.7375	-0.1109	0.7534
N	93	10	83
NAPC1			
Intercept	-1.58×10^{-8}	4.62×10^{-9}	-2.69×10^{-8}
Organic Carbon Content	4.52×10^{-6}	0.03×10^{-7}	5.1×10^{-6}
F	358.225	0.053	321.248
Prob > F	0.0001	0.8209	0.0001
R ²	0.7554	0.0031	0.7681
Adj R ²	0.7533	-0.0555	0.7657
N	118	19	99

ANNEX 8

ORGANIC COMPOUNDS (EXCEPT CBs AND PAHs) FOR WHICH DATA WERE SUBMITTED

Code	Name	Number of samples	Number with organic carbon content
HCBD	hexachlorobutadiene	5	5
TECB	1,2,4,5-tetrachlorobenzene	5	5
TRCB	1,2,4-trichlorobenzene	5	5
QCB	pentachlorobenzene	5	5
QCNB	pentachloronitrobenzene	5	5
ALD	aldrin	186	146
ISOD	isodrin	26	0
DIELD	dieldrin		
SALDI	sum of aldrin + dieldrin	7	7
CCDAN	<i>cis</i> -chlordane	26	26
TCDAN	<i>trans</i> -chlordane	156	155
OCDAN	oxychlordane	146	145
HCEPT	<i>trans</i> -heptachlorepoxyde	30	5
HEPC	heptachlor	30	5
TNONC	<i>trans</i> -nonachlor	155	154
END	endrin	187	161
ENDA	α -endosulfan	25	0
ENDB	β -endosulfan	24	0
HCHA	α -hexachlorocyclohexane	240	198
HCHB	β -hexachlorocyclohexane	73	35
HCHG	γ -hexachlorocyclohexane	245	197
PCC	polychlorinated camphenes (as toxaphene)	9	9
MBTIN	monobutyltin	18	9
DBTIN	dibutyltin	18	9
TBTIN	tributyltin	18	9
DDEPP	DDE (p,p')	231	191

Code	Name	Number of samples	Number with organic carbon content
DDTOP	DDT (o,p')	190	150
DDTPP	DDT (p,p')	231	191
TDEOP	TDE (o,p') = DDD (o,p')	204	165
TDEPP	TDE (p,p') = DDD (p,p')	220	182
SDDT	sum of DDTs	39	7
METOC	methoxychlor	25	
PCDD	polychlorinated dibenzo-p-dioxins	13	9
PCDF	polychlorinated dibenzo-furans	13	9
TCDD	2,3,7,8-tetrachloro-dibenzo-[b,e][1,4]p-dioxin	13	9
OCS	octachlorostyrene	18	18

