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TECHNICAL REPORT WB/95/28C

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TECHNICAL REPORT WB/95/28C

The geochemistry of sea-bed sediments of the United Kingdom Continental Shelf; the North Sea, Hebrides and West Shetland shelves, and the Malin-Hebrides sea area

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Volume 1

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British Geological Survey

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Summary

The sea area around the United Kingdom is used for a wide range of human activities all of which have a significant impact on the marine environment. The naturally-occurring concentrations of chemical elements in sea-bed sediments may be enhanced by contaminants introduced by input from rivers and the atmosphere and by more localised sources arising from shipping operations, exploitation of oil and gas, and by direct discharges from drainage systems, sewage outfalls, effluents from industry and waste disposal at sea. It is therefore important to identify components of sea-floor sediments which are due to the rocks or older sediments from which they are derived, and those which are introduced into the environment.

This report presents regional geochemical data for a variety of sediment types occurring in a wide range of environments. Samples have been collected offshore of the eastern coast of the UK where major river systems which drain heavily populated and industrialised catchment areas, such as the Thames, Humber and Tyne, flow into the North Sea, and on the shelf west of Scotland where man's activities have had much less impact.

The data presented here provide a baseline for chemical element concentrations in sea-bed sediments against which future work may be assessed. It should therefore be of significance to a diverse range of interests including pollution control, fishing, natural resources, nature conservation, shipping, tourism, recreation, and waste disposal management. In addition the information will be of use to geologists in identifying the source of sea-bed sediments and the underlying glacial deposits.

1 INTRODUCTION

This report presents geochemical data for 31 elements analysed in sea-bed sediments from the North Sea and the UK Continental Shelf to the west of Scotland. The data were collected as part of the British Geological Survey's regional mapping programme funded by the Department of Energy (now incorporated into the Department of Trade and Industry) and the Natural Environment Research Council. The samples were analysed by the Analytical Geochemistry Group of BGS. The data are managed by the Marine Geology and Operations Group as part of its offshore database.

The report includes descriptions of sampling, analytical methods, quality control and data processing techniques. The geochemical data are presented as a series of maps accompanied by summary statistics and a brief description of the geochemical distribution of each element. Interpretation of the data includes the description of anomalous element associations and correlations, and highlights the main features of each distribution map. These summaries are designed to provide a focus for future investigation and interpretation and do not provide an exhaustive appraisal of the data in the context of other work carried out in the offshore environment. Selected geochemical data from published sources is provided for comparison of major and trace element levels.

It is intended that this report will provide a basis for future collaborative projects both within BGS and with external organisations. Projects currently under discussion include collaboration with the BGS Geochemistry Group to produce atlases of combined data in both the onshore and offshore environments. It is hoped also that the data can stimulate co-operation between university and government research organisations with a view to completion of sampling and analysis in areas where data density is low, and in the area to the south and west of England and Wales where no geochemical data exists.

2 HISTORY OF BGS OFFSHORE GEOCHEMISTRY PROGRAMME

In the early 1970's, studies being undertaken in the USA revealed what were thought to be substantial quantities of mercury in tuna fish. This information was widely publicised and highlighted how little information was available on trace metal contents, particularly mercury, of waters and sediments around the British Isles. As a result, the Analytical Chemistry Unit (ACU) of the British Geological Survey (then the Institute of Geological Sciences (IGS)) was asked to investigate the distribution of mercury in waters and sediments in the marine environment.

Investigations began in the tidal reaches of the River Thames where the Port of London Authority collected water samples between Teddington and Southend. The publication of these results (Smith et al., 1971) revealed mercury levels of under 3ppm increasing to 35ppm when calculated on a particulate only basis. This survey was followed by a study of the sediments of the Thames Estuary in conjunction with the City of London Polytechnic. Fresh surface sediments were collected using a cone dredge and historical samples were made available by the British Museum of Natural History. Mercury was again determined and showed correlation with fine grained sediments (less than 63µm); levels of mercury found were very similar in both fresh and historical samples (Smith et al., 1973).

During 1971, IGS began work on the monitoring of sea-bed radioactivity and by collaborating on these surveys the ACU were able to collect sea-bed sediments across the Forth Estuary and southward along the North Sea coast to Flamborough Head. Samples were collected using a Shipek grab and were analysed for copper, lead, zinc, cadmium, manganese, mercury and loss on ignition at 450°C and 1050°C to determine approximate percentages of organic and carbonate carbon. In addition the samples were sieved to provide three size fractions equating to gravel, sand and mud. This survey was supplemented by other work with the Lothians River Purification Board (LRPB), and the results were incorporated into an IGS report (Nicholson and Moore, 1977).

Collaborative fieldwork with the Ministry of Agriculture, Fisheries and Food (MAFF) allowed the survey to extend farther offshore, even across the North Sea into the territorial waters of the near continent. These cruises across the median line were to improve interlaboratory collaboration and standardisation between MAFF and the Netherlands Institute for Sea Research (NIOZ), but there was no opportunity for similar collaboration between NIOZ and IGS. The results of these collaborative projects were presented at a meeting of the International Council for the Exploration of the Sea (ICES) (Nicholson and Moore, 1981).

Meanwhile, co-operation between ACU and the IGS group monitoring sea-bed radioactivity continued, but the areas being monitored were widely separated leading to sporadic sample distribution for geochemical data. At about the same time, ACU were directly granted funds by NERC to organise their own sample surveys and until 1977 continued to collect sea-bed sediments on a ten-mile grid in the North Sea between the Dover Strait and the Firth of Forth. Due to the restricted duration of sampling surveys, and additional weather constraints, an average of about 100 samples were collected each year. Data from these surveys were published in 1985 (Nicholson et al., 1985).

In 1977, the BGS Marine Geology Group, which had recently commenced the Department of Energy funded survey of the UK Continental Shelf, proposed that the two groups amalgamate their offshore sampling programmes. As a result, geochemical sample collection rate and sample density increased significantly, and also had the advantage of providing information which was being routinely obtained by the Marine Geology Group, such as particle-size analysis.

Collaborative surveys between the Marine Geology and Analytical Chemistry groups continued until completion of the regional offshore survey in 1986. Analysis of the samples was completed during 1991 when archive samples were used to improve data density in areas where fewer samples had been collected by early shallow water surveys near the east coast of Scotland.

Geochemical data for approximately 9000 samples now exist for the whole of the UK sector of the North Sea and extends across the northern coast of Scotland to the Hebrides and West Shetland shelves, and as far south as the North Channel between the west coast of Scotland and Northern Ireland. Although sample material exists for the English Channel, Western Approaches and the Irish Sea, only limited geochemical analysis of these samples has been carried out.

3 SAMPLE COLLECTION AND PREPARATION

During the period 1968 to 1986 approximately 30 000 sea-bed sediment samples were collected on the UK Continental Shelf. About 9 000 of these samples have been analysed for 38 geochemical elements, 29 of which are presented in this report.

The samples were collected mainly by Shipek grab which samples approximately 10 to 15cm of surficial material from the sea floor. Sample density varies between areas, however the overall ratio for samples selected for geochemical analysis has been calculated as 1 per 43 square kilometres. Figures 1 and 2 indicate the distribution of geochemical sample sites and a summary of periods of sample collection. Figure 3 shows the BGS 1:250 000 sheet areas; the density of samples per 1:250 000 sheet is given in Table 1. Sample density is generally poor in nearshore areas such as the Thames Estuary and The Wash, and in the Marr Bank, Peterhead, and part of the Moray-Buchan sheet areas to the east of Scotland. Completion of the coverage of geochemical data to the east of Scotland by analysis of archived samples was hindered by the lack of suitable sample material. This was mainly due to insufficient composite material being available due to consumption during particle-size analysis.

This report describes only those samples which were analysed during the course of the regional offshore survey (see Section 1). However, in areas where sample density is low in the central and southern North Sea, earlier work by Nicholson and Moore (1981) and Nicholson et al. (1985) has been taken into consideration in the description of the geochemical distribution of elements which are common to both sets of analysis. The distribution of sample sites analysed by these authors is shown in Figure 4 and their data is summarised in Table 2. No attempt was made to merge these data sets due to the difference in the size fractions of the analysed material between the two surveys: during the earlier work, a portion of the total sample was analysed, whereas the present work is based on the analysis of material finer than 2mm in grain size (see below). The change in the analysed size fraction occurred at the time that the Analytical Chemistry and Marine Geology groups commenced collaboration on the offshore geochemical survey (see Section 2).

Samples from the early survey were initially analysed by Atomic Absorption Spectrophotometry (AAS) for only 5 trace elements (Nicholson and Moore, 1981). The slower rate of sample collection at that time also

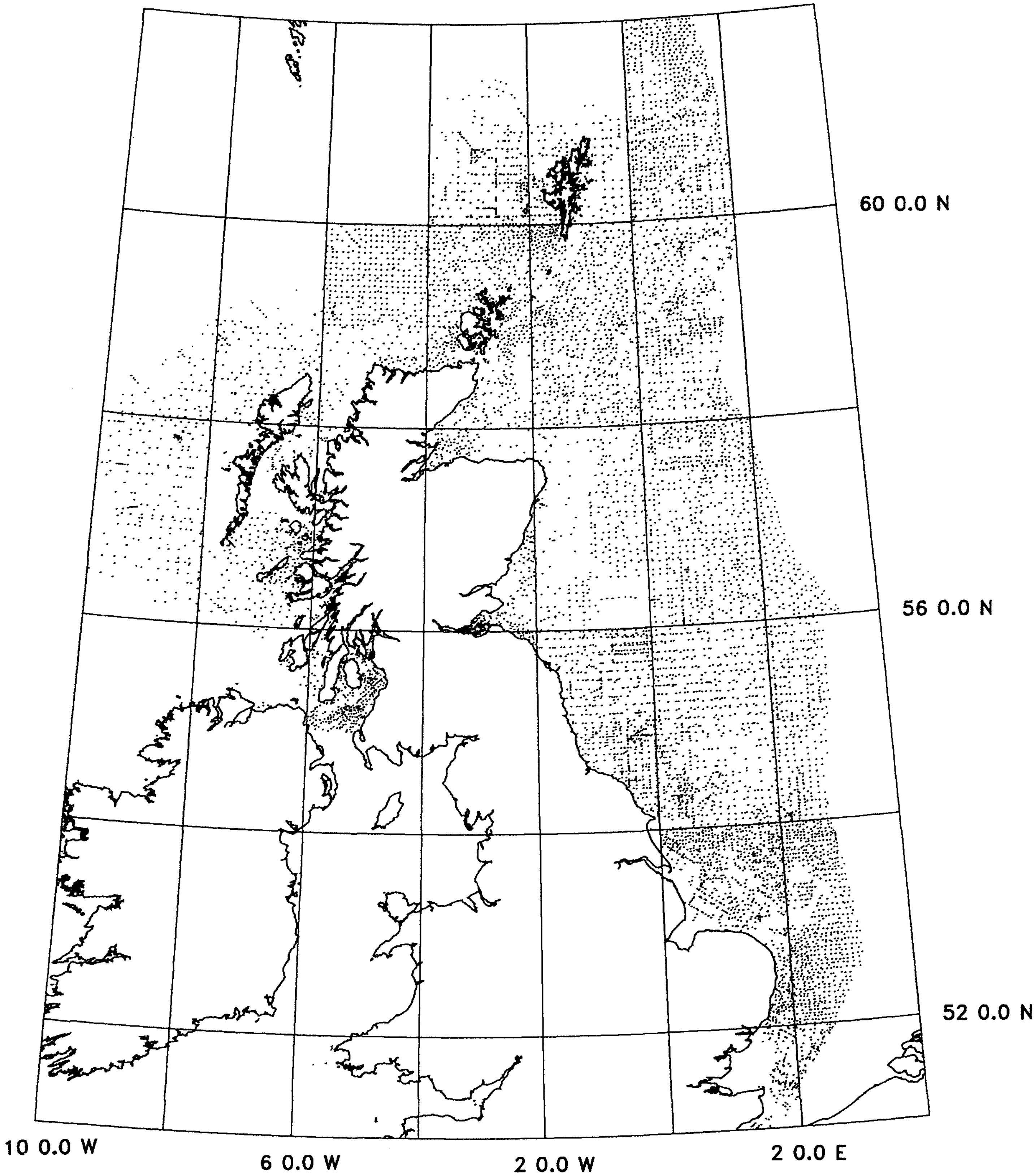


Figure 1 Locations of geochemical sample sites.

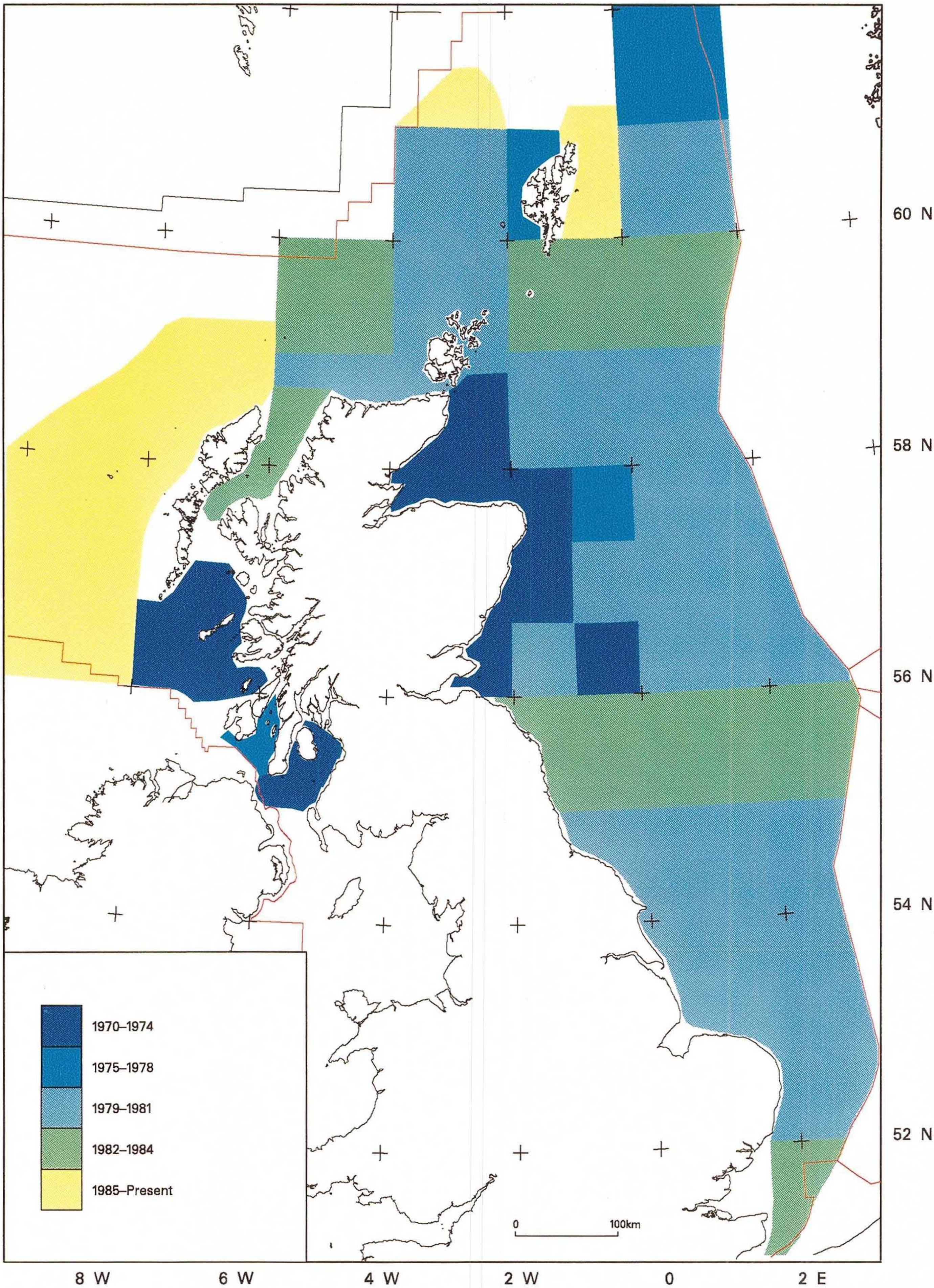


Figure 2 Periods of sample collection

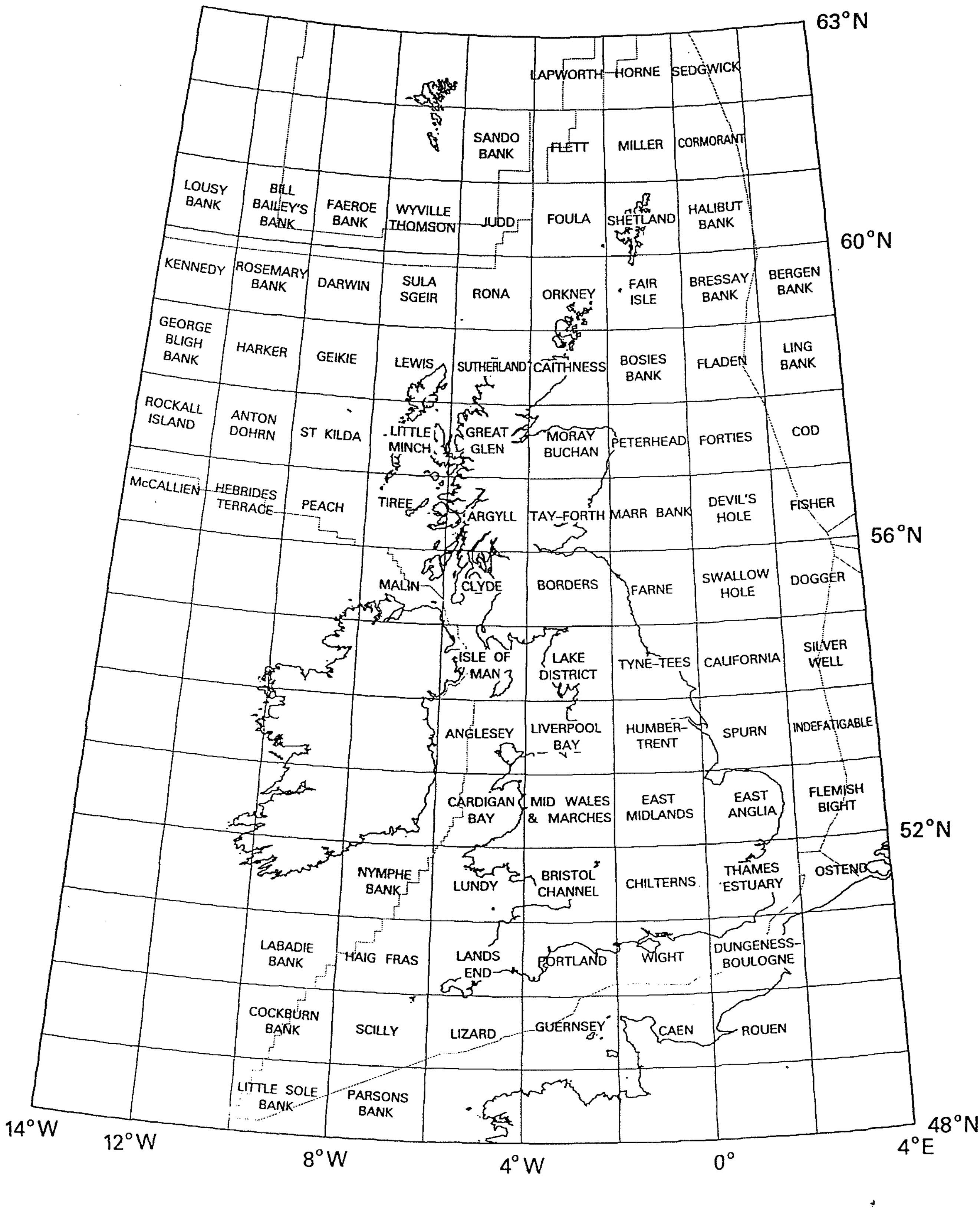


Figure 3 BGS 1:250 000 sheet areas.

1:250 000 sheet area	Sample density (Number of samples/ square kms)
Thames Estuary	1/38
Ostend	1/22
East Anglia	1/19
Flemish Bight	1/20
Spurn	1/21
Indefatigable	1/22
Tyne-Tees	1/19
California	1/36
Silver Well	1/36
Borders	1/10
Farne	1/31
Swallow Hole	1/49
Dogger	1/38
Peach	1/137
Tiree	1/57
Argyll	1/31
Tay-Forth	1/24
Marr Bank	1/84
Devil's Hole	1/55
Fisher	1/44
St Kilda	1/107
Little Minch	1/136
Great Glen	1/45
Moray Buchan	1/23
Peterhead	1/113
Forties	1/66
Cod	1/34
Geikie	1/100
Lewis	1/89
Sutherland	1/112
Caithness	1/45
Bosies Bank	1/39
Fladen	1/35
Rona	1/38
Orkney	1/35
Fair Isle	1/31
Bressay Bank	1/42
Foula	1/40
Shetland	1/75
Halibut Bank	1/30
Flett	1/124
Miller	1/216
Cormorant	1/114
Total area	1/43

Table 1. Geochemical sample density per 1:250 000 sheet area. See Figure 1 for BGS map sheet areas.

allowed the ACU to carry out more detailed particle size analysis prior to chemical analysis. Subsequently, as the collaborative project progressed, it was decided to analyse for a wider range of elements using Direct Reading DC Arc Emission Spectrometry (DRES) which initially increased the number of elements to 26. The samples collected during the early survey were re-analysed by DRES and this data was presented by Nicholson et al. (1985).

Element	Range	Mean
Aluminium (as Al_2O_3)	0.2-21.7%	5.65%
Barium	100-1371ppm	303ppm
Beryllium	0.1-11.5ppm	0.8ppm
Bismuth	1-22ppm	0.6ppm
Boron	2-187ppm	31ppm
Cadmium*	0-7ppm	-
Copper*	0-410ppm	6.2ppm
Chromium	2-160ppm	40ppm
Gallium	0.1-17.8ppm	1.7ppm
Iron (as Fe_2O_3)	0.3-20.9%	1.9%
Lanthanum	1-119ppm	15ppm
Lead*	0-320ppm	21.1ppm
Lithium	1-121ppm	16ppm
Magnesium (as MgO)	0.1-9%	1%
Manganese	100-2916ppm	353ppm
Mercury*	0.01-0.94ppm	0.04ppm
Nickel	1-100ppm	10ppm
Potassium (as K_2O)	0.3-3%	1.2%
Rubidium	8-134ppm	33ppm
Silica	13.8-87.2%	77.3%
Strontium	48-4734ppm	225ppm
Tin	1-202ppm	8ppm
Titanium (as TiO_2)	0.01-1.2%	0.25%
Uranium	0.1-14.9ppm	1.1ppm
Yttrium	1-126ppm	11ppm
Zinc*	5-2249ppm	39.5ppm
Zirconium	1-2124ppm	97ppm

Table 2 Summary of geochemical data presented in Nicholson and Moore (1981)* and Nicholson et al. (1985).

With the wider range of elements, analytical problems were encountered, generally related to calcium-rich samples (see Section 3). To minimise this effect, which was mainly due to abundance of coarse shell fragments in the sea-bed sediments, it was decided to dispose of the gravel fraction (greater than 2mm) of the sediment. This was also a practical consideration, because the increased rate of sample collection resulted in a back-log in particle-size analysis relative to sample preparation for analysis. The complete loss of collectable material from many gravelly or sandy areas of the sea bed precluded use of a finer size fraction. Particle-size analysis and Folk-classification of each sea-bed sample was however carried out on each sample by the Marine Geology

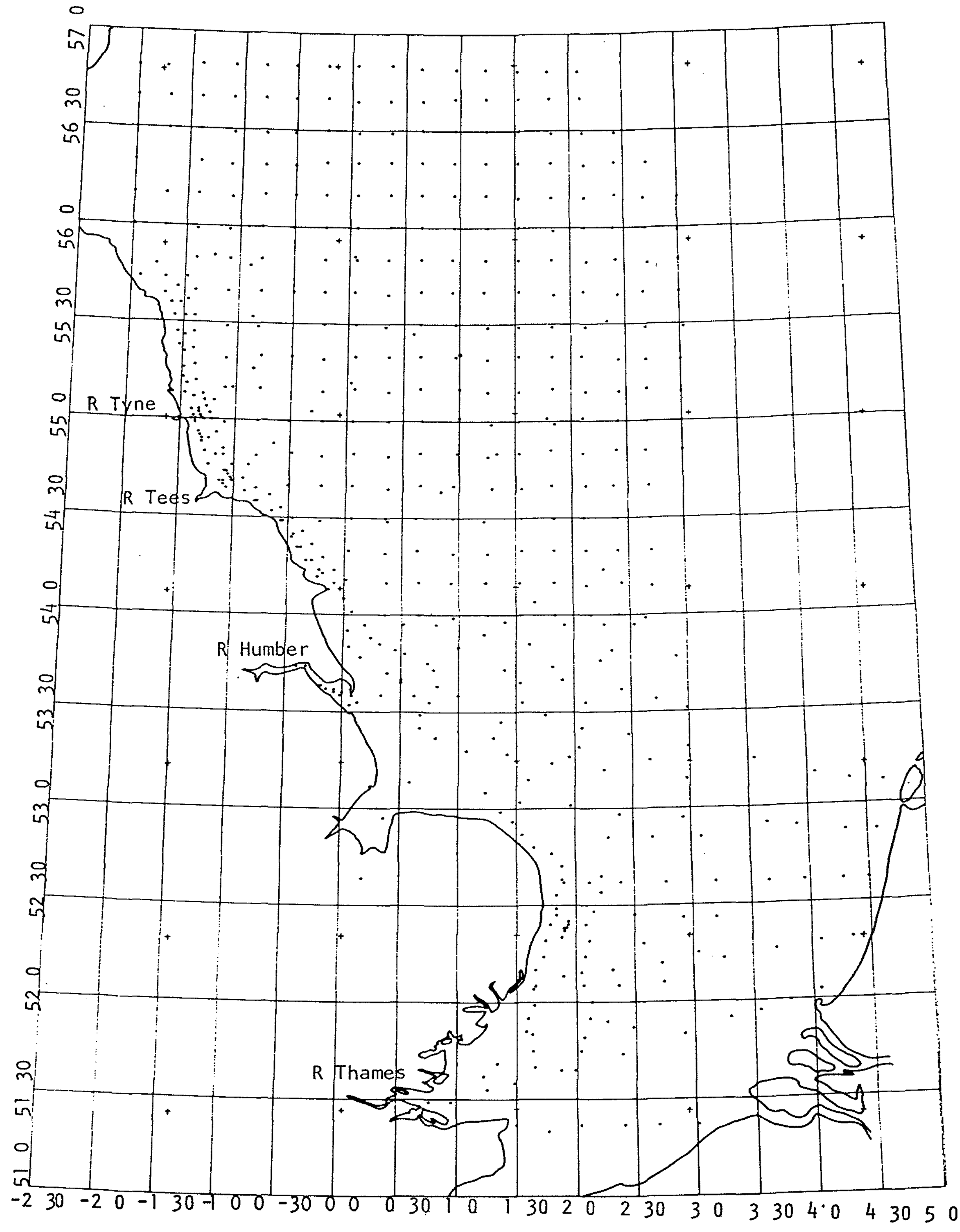


Figure 4 Geochemical sample locations of data presented in Nicholson and Moore (1981) and Nicholson et al. (1985).

Group at a later date.

The samples collected for this survey were prepared for analysis on-board ship. A 50g subsample was taken from the Shipek Grab sample and freeze-dried before being quartered and sieved to less than 2mm. This fraction was then milled to a particle size finer than 50µm in an agate planetary ball mill.

4 CHEMICAL ANALYSIS

Direct Reading Emission Spectrometry

All of the chemical elements reported here, with the exception of U and Hg, were determined by DRES. The spectrometer system used was based on a Jarrel-Ash 1.5 m 'Atomcounter'. The system incorporated 40 channels including an Hg monitor, and was unusual in covering the wavelength range 250-850nm in the first order. The external optics comprised a spherical quartz lens in the arc stand, which projected a 1:1 image of the arc onto a screen used to mask unwanted radiation from the electrode tips. The entrance slit was a 25µm vertical aperture with cylindrical quartz lens and quartz refractor plate. Exit slits with refractor plates were placed on the focal curve of the instrument so that selected wavelengths could pass through to photomultiplier tubes.

The source unit was a custom-built Jarrell-Ash three-phase DC Arc unit, giving continuously variable controlled current in the range 0-25A. It incorporated low and high current ranges, with automatic stepping and trigger ignition. Simultaneous data acquisition for 39 channels was provided by the Jarrell-Ash 65-532 Intensity Ratio Readout system (IRR). The system could accommodate up to 60 channels and performed an intensity ratio comparison between each element channel and, in this work, a reference voltage. The ratio was converted to digital format as an uncorrected measure of element concentration, which was shown on a three-digit readout display. The system included options for automatic background and dark current correction; controls for pre-flush, pre-burn and exposure times; an Hg monitor channel for checking the spectrum profile in stand-by mode; a high voltage power supply and dynode control panels for photomultiplier tube operation, and output for interfacing to a mini-computer.

The IRR system was connected via a custom-built interface (Westinghouse Brake and Signal) to an IBM 1130 computer which was used for calibration, matrix correction and statistical analysis on uncorrected data relayed from the IRR system. The interface also served a Friden flexowriter which was used to input sample identification, to control computer operation, and to output corrected data. The flexowriter, with 210-character line width, provided data for sample identification and 40 channels on one line.

Approximately 3 to 6g of the ground (less than 50µm) sample were ignited at 450°C for 2 hours in porcelain crucibles to destroy any organic matter present in the sample. A 100mg subsample was then mixed with an equal weight of spectroscopic buffer (a 1:1 mixture of sodium fluoride and pelletable graphite containing Eu and Pt

Element	Interference correction (element values set to null where correction applies)
Bismuth	CaO >10% and Bi >2ppm
Chromium	CaO >15% and Cr >10ppm
Cobalt	CaO >15% and Co >5ppm
Lead	CaO >15% and Pb >10ppm
Molybdenum	CaO >10% and Mo >2ppm
Vanadium	CaO >10% and V >5ppm

Table 3 Calcium interference corrections applied to data on the Oracle database

Element	Detection limits
Aluminum	0.5-1%
Barium	1-5ppm
Beryllium	0.3-0.5ppm
Bismuth	4-7ppm
Boron	7-10ppm
Cadmium	0.5-0.8ppm
Calcium	0.5%
Chromium	5-7ppm
Cobalt	2-6ppm
Copper	1-7ppm
Gallium	3-6ppm
Iron	1%
Lanthanum	20-30ppm
Lead	10-20ppm
Lithium	0.3-1ppm
Magnesium	0.1%
Manganese	0.002-0.005%
Molybdenum	5ppm
Nickel	5-7ppm
Niobium	20-25ppm
Phosphorus	0.01-0.3%
Potassium	0.1%
Rubidium	1-3ppm
Strontium	1-2ppm
Titanium	0.06%
Vanadium	9ppm
Yttrium	1-7ppm
Zinc	10-18ppm
Zirconium	30-60ppm

Table 4 Direct-reading emission arc spectrometry: minimum detectable values. For most elements a range of values applies due to changes in calibration during the period of chemical analysis.

as internal standards). A 30mg pellet of the buffered sample mixture was placed in the cup of a preformed electrode which forms the anode of a DC arc and was arced (100 seconds at 12.5A anode excitation - spectrum is detected for the last 99 seconds by the spectrometer) in a flow of argon and oxygen (in the proportion 3:1). No correction was made for loss on ignition.

Due to the high calcium carbonate content of sea-bed sediments, some difficulty was experienced in arcing the samples without ejection of the pellet due to the evolution of carbon dioxide. This problem was solved by providing an axial hole through the electrode to relieve pressure build-up and prevent ejection. Despite this, some samples containing high concentrations of calcium carbonate still caused analytical irregularities and strong interference with several trace elements such as V, Cr, Co, Pb and Bi. These could not be adequately corrected by appropriate spectrometer wavelength selection so a correction factor was applied to these data after they were added to the Oracle database (see Table 3).

Calibration was performed by polynomial regression (Coats, 1974) on data obtained from a series of synthetic reference materials, prepared by a co-precipitated gel technique (Date, 1978) and arced in the same way as the geochemical samples. The lowest levels at which individual results are considered to be reliable for interpretation are listed for each element in Table 4. The reliability of individual results decreases below these quoted levels, but for some elements significant patterns can still be recognised within the context of the complete range of values.

Delayed Neutron Activation

Uranium was determined by the delayed-neutron method. One-gram splits of sea-bed sediment were irradiated in polythene tubes in a thermal neutron flux. The irradiation was carried out using either a Triga Mark 1 reactor at ICI Billingham, operating at a power of 250 kw per hour, or at the HERALD reactor centre, AWRE Aldermaston; samples were irradiated for 30 seconds in a thermal neutron flux of $2.5 \times 10^{12} cm^{-2} sec^{-1}$, or for 1 minute at $4.3 \times 10^{12} cm^{-2} sec^{-1}$ respectively. After an initial post-irradiation decay time of 25 seconds, samples were counted for 45 seconds using an array of six BF_3 tubes. The limit of detection by this method was approximately 0.2ppm.

Flameless Atomic Absorption Spectrometry

Mercury was determined by flameless atomic absorption spectrometry (AAS).

5 QUALITY CONTROL

Geochemical data collected by the Geochemical Survey Group in the production of the BGS Regional

Geochemical Atlas series for the land area of the United Kingdom, are subject to procedures for monitoring data accuracy and precision as described by Plant et al. (1975). A systematic quality control procedure was not in place during the collection and sample preparation stages of the offshore survey. This is largely due to the way in which the offshore survey evolved. Initially the survey involved very few samples, and only a small suite of analysed elements, therefore rigorous sampling quality control systems were not given a high priority.

Sampling and analytical precision of onshore data are calculated using a procedure based on analysis of variance. Duplicate samples were collected a few metres apart at a number of sites and were subsequently split to give four replicates from each site for chemical analysis. Within-site variance and between-site variance is then calculated to provide a general indication of the reliability of the element distribution maps. Although duplicate samples were collected at approximately every tenth sample station to check sampling reproducibility offshore, the practical problems of obtaining a duplicate sample from a non-anchored ship preclude the presentation of analysis of variance tables in this report. However, in most locations there was a good measure of agreement between analyses of duplicate samples, although in a few instances the sample recovered was totally different in visual appearance. The reproducibility of marine samples, even in shallow waters is a generally accepted problem.

An aspect of onshore geochemical quality control procedures which has been applied to the offshore data is the monitoring of long-term analytical drift between batches of samples by analysis of a series of standards representing a range of concentrations for each element. The standards include several stream sediments collected over representative rock types from northern Scotland, three of which were analysed in every batch of 100 samples. As a consequence, offshore samples analysed between 1977-1991 may be monitored by reference to standards submitted within batches of onshore samples analysed during the same period and by the same technique.

To assess changes in element levels between different periods of analysis, the data were loaded to the International Imaging Systems (I^2S) Model 75 image processing system which produces percentile-classified digital maps. Any boundaries within the data which were due to different periods of analysis were eliminated by applying a correction factor based on element concentrations in standard samples. A problem which arises from this procedure is that, as the correction factors applied to each element are unrelated, some of these boundaries are evident on some of the element:element normalisation maps.

6 DATA PROCESSING AND STATISTICAL ANALYSIS

Data processing were performed using software packages and systems running on the NERC Computer Services (NCS) VAX cluster at BGS Keyworth and Edinburgh. The geochemical and locational data were loaded, compiled and merged with the BGS Offshore Database, and are held on the ORACLE relational database

	*Mean muddy sediment	*Mean sandy sediment	*Mean gravelly sediment	*Median sea-bed sediment
Li	26.99	28.3	10.36	9.3
Be	1.17	0.67	0.44	0.7
B	67	33	29	33
Mg	1.51	0.61	1.4	0.87
Al	8.19	4.37	3.36	4.08
P	0.06	0.04	0.09	-
K	1.88	1.03	0.72	1.03
Ca	9.81	6.51	23.2	5.93
Ti	0.46	0.18	0.19	0.17
V	34	24	14	24
Cr	70	34	18	29
Mn	0.04	0.03	0.05	0.027
Fe	3.21	0.94	2.18	1.44
Co	9	5	4	5
Ni	23	7	14	9
Cu	11	1	3	0 (mean=4)
Zn	71	23	34	26
Ga	7	2	3	2
Rb	57	30	23	29
Sr	409	355	1303	237
Y	19	8	11	10
Zr	341	194	141	140
Nb	6	4	11	0 (mean=5)
Ba	471	357	257	317
La	31	18	28	22
Pb	24	15	8	15
Bi	0	0	0	-
Mo	-	-	-	-
U	-	-	-	-

Table 5 Summary of mean concentrations of elements in sea-bed sediments around the UK, and published averages in rocks and marine sediments. All values in parts per million (ppm) except Al_2O_3 CaO, Fe_2O_3, K_2O, MgO, MnO, P and TiO_2 which are in per cent unless otherwise indicated. *Data from this report.

	Mean sands	Mean muddy sands/sandy muds	Mean muds (0-1 cm below sea bed)	Mean muds (18-20 cm below sea bed)
Li	-	-	-	-
Be	-	-	-	-
B	-	-	-	-
Mg	-	-	-	-
Al	0.18	1.24	2.57	3.32
P	0.02	0.08	0.16	0.12
K	-	-	-	-
Ca	0.15	0.3	0.48	0.48
Ti	-	-	-	-
V	5	32	64	78
Cr	4	22	50	56
Mn	70 (ppm)	582 (ppm)	765 (ppm)	669 (ppm)
Fe	0.24	1.37	2.86	3.44
Co	1	6	12	15
Ni	2	15	32	38
Cu	2	13	39	37
Zn	11	58	155	113
Ga	-	-	-	-
Rb	-	-	-	-
Sr	9	32	56	52
Y	-	-	-	-
Zr	-	-	-	-
Nb	-	-	-	-
Ba	14	125	149	148
La	-	-	-	-
Pb	6	22	63	46
Bi	-	-	-	-
Mo	-	-	-	-
U	-	-	-	-

Table 5 (continued) Data from Szczepanska and Uscinowizc (1994).

	*Mean sea-bed sediment	*Mean clay	**Mean sea-bed sediment	***Mean sea-bed sediment
Li	-	-	-	5-38
Be	-	-	-	<1-3
B	32	140	-	37-79
Mg	-	-	-	-
Al	-	-	-	1.39-10.07
P	439 (ppm)	1316 (ppm)	-	-
K	0.99	2.94	-	0.5-2.3
Ca	-	-	-	-
Ti	0.01	0.02	-	0.14-0.55
V	29	-	-	-
Cr	17	56	-	14-53
Mn	637 (ppm)	2720 (ppm)	-	200-2900 (ppm)
Fe	1.59	6.33	-	0.98-6.41
Co	3	-	-	-
Ni	18	-	23	9-23
Cu	7	-	14	-
Zn	44	-	39	-
Ga	-	-	-	2-12
Rb	-	-	-	13-85
Sr	302	111	-	21-400
Y	-	-	-	-
Zr	168	48	-	195-730
Nb	-	-	-	-
Ba	252	568	-	152-860
La	-	-	-	-
Pb	-	-	21	-
Bi	-	-	-	-
Mo	-	-	-	-
U	-	-	-	-

Table 5 (continued) Data from *Cronan (1970); **North Sea Task Force (1993); ***Hirst (1962).

	Crustal mean	Mean basalt	Mean granite	Mean shale
Li	20	12	30	60
Be	3	0.5	5	3
B	10	5	15	100
Mg	4.59	7.52	0.67	2.34
Al	-	-	-	-
P	-	-	-	-
K	2.53	0.97	3.87	3.03
Ca	5.81	10.08	2.24	3.5
Ti	0.95	1.5	0.35	2.0
V	135	250	50	130
Cr	100	200	20	100
Mn	0.095	0.17	0.05	0.085
Fe	8.05	12.3	3.86	6.72
Co	25	48	3	20
Ni	75	150	1	80
Cu	55	100	12	50
Zn	70	100	50	90
Ga	15	18	18	25
Rb	90	30	150	140
Sr	375	450	300	400
Y	33	30	40	35
Zr	165	140	180	180
Nb	-	-	-	-
Ba	425	300	700	600
La	30	10	55	40
Pb	12.5	3.5	20	20
Bi	0.15	0.1	0.2	0.06
Mo	1.5	1	1.5	2
U	2.7	0.5	5	3.5

Table 5 (continued) Data from Turekian and Wedepohl (1961); Taylor (1964).

	*Mean sandstone	*Mean shale	*Mean carbonate	**Mean stream sediment
Li	2.1-17	25-79	0.78-2.6	39
Be	0.8	1.1-1.7	-	2.6
B	18-36	43-110	29-31	40
Mg	0.09-0.21	0.61-1.6	-	2.41
Al	0.43-3.0	4.4-9.2	0.17-2.0	-
P	0.01-0.1	0.03-0.07	0.004-0.06	-
K	0.08-0.66	1.8-5.4	0.12-0.56	2.66
Ca	0.09-0.22	0.13-1.1	-	1.75
Ti	0.008-0.22	0.23-0.57	0.003-0.08	1.17
V	5.3-38	74-400	3.9-40	96
Cr	2-39	62-130	2.7-29	142
Mn	29-300 (ppm)	65-420 (ppm)	83-910(ppm)	0.4 (%)
Fe	0.09-1.9	1.8-4.5	0.11-2.1	8.16
Co	1.6-74	4.8-13	1.3-7.1	27
Ni	1.2-18	21-110	2.3-16	44
Cu	1.2-8.4	13-130	0.84-12	24
Zn	5.2-31	55-82	6.3-24	199
Ga	1.5-10	15-30	2.2-10	17.4
Rb	-	-	-	106
Sr	13-99	90-200	100-990	220
Y	9-22	25-38	8-20	96
Zr	22-170	95-230	6.5-42	1048
Nb	8.8	7.7	-	-
Ba	38-170	220-510	5.6-160	786
La	6-36	29-67	24	47
Pb	5-17	11-24	4-18	52
Bi	-	-	-	1.6
Mo	-	-	0.79	0.5
U	-	-	-	5.2

Table 5 (continued) Data from *Connor and Shacklette (1975). **Data compiled from British Geological Survey, 1987; 1990; 1991; 1993. Values represent an average of approximately 45 000 samples for most elements.

management system.

The point data were then processed using the Interactive Surface Modelling software (ISM) to create surface grid files of each element. The function used generates a smooth, continuous surface passing close to the data points and avoiding abrupt changes in direction. An advantage of the ISM technique is that it closely honours every data point.

The resultant grid matrices were then converted to digital images by FORTRAN programs and loaded to the International Imaging Systems (I^2S) Model 75 image processing system which produces percentile-classified digital maps. These maps were used in assessing quality control adjustments to the data (see Section 5).

The maps presented in this report show the data as a contoured surface. Three dimensional plots of element distribution and concentrations were generated using the BGS CONPLOT software. Class intervals were based on the selection of a threshold value broadly equivalent to the 95 percentile level in conjunction with examination of cumulative frequency histograms for each element. Data below the threshold are divided into nine equal class intervals giving a total of ten classes. The class interval limits can be compared with the 5, 10, 25, 50, 75, 95 and 99 percentile levels in the tables of summary statistics which accompany each histogram.

The geochemical maps are accompanied by tables of summary statistics and frequency distribution histograms showing the statistical distribution of each element. The minimum and maximum values for each element are listed, together with the median, mean and standard deviation. For elements that have particularly high values which skew the distribution shown on the frequency histograms, a second histogram is presented showing the distribution of data below the 99th percentile.

The average concentration of each element in each of the main sea-bed sediment facies (gravels, sands and muds) are presented for comparison with published average crustal values and mean concentrations of elements in igneous and sedimentary rocks in Table 5. Although these values provide a useful reference against which to compare the sea-bed sediment geochemistry a more appropriate comparison is with published data for marine sediments and these are also given in Table 5. In addition, a more detailed analysis of selected areas of muddy, gravelly, sandy and gravelly sandy sediments are summarised in tables in Appendix 1 to allow comparison of average element concentrations in similarly classified sediments from different areas of the shelf. Correlation coefficient matrices have also been generated for each area (see Appendix 1). All statistical data were produced using the SAS software package.

7 DATA INTERPRETATION

Geochemical maps for 31 elements are presented at 1:5 000 000 scale. The distribution of each element is

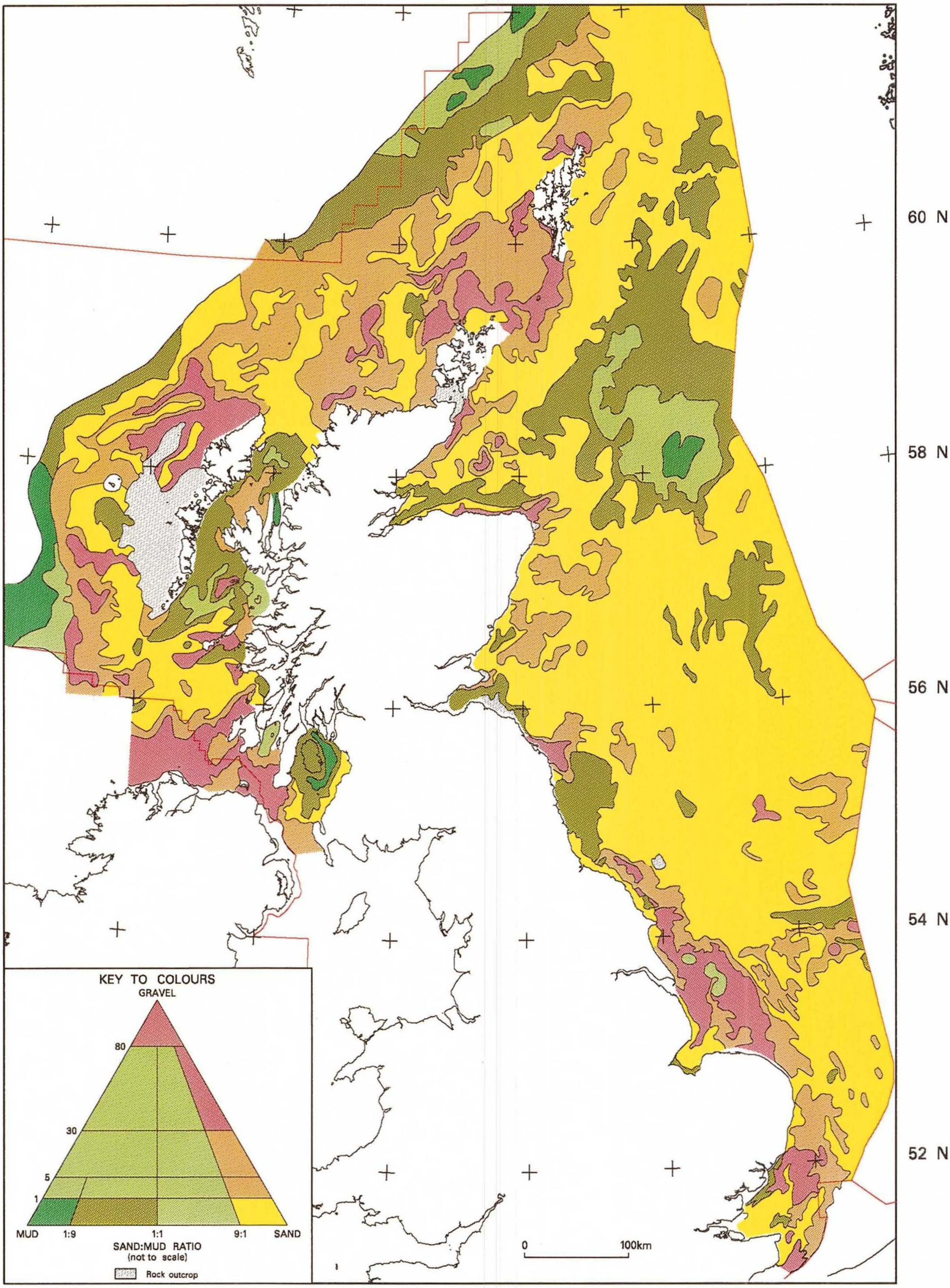


Figure 5 Generalised distribution of sea-bed sediments on the UK Continental Shelf.

described in relation to the classification of surface sediments published in the BGS 1:250 000 Sea Bed Sediment Series and the 1:1 000 000 compilation maps of these data. A simplified version of this map is shown in Figure 5. A transparent copy of this map is also included to allow it to be overlain on the geochemical distribution maps. The sediment classification used is modified after Folk (1954) and is based on particle-size analysis of mainly grab samples collected from the sea bed. The Folk classification has been adapted to include fewer categories of sandy or muddy sediments, while retaining Folk's original categories for sediment with more than 5 per cent gravel. Gravel is defined as grains greater than 2mm diameter. Sand is defined as grains less than 2mm in diameter but greater than 62.5μm, and mud is less than 62.5μm.

A summary of the sea-bed sediments and bedforms on the UK Continental Shelf is presented in an explanatory report which was produced in conjunction with the 1:1 000 000 Sea Bed Sediment compilation maps (Pantin, 1991). This report partly forms the basis of the geological section presented in this report. Further information is presented in the United Kingdom Offshore Regional Report Series produced by BGS (Cameron et al. 1992; Gatliff et al. 1994; Johnson et al. 1993; Andrews et al. 1990; Stoker et al. 1993 and ; Fyfe et al. 1993). Detailed interpretation of the sea-bed sediments is presented on each map in the 1:250 000 series (Figure 3). Reference is also made to internal BGS reports which presented mineralogical analyses of selected sea-bed samples from the offshore sample archive (e.g Dearnley, 1989; 1991; Dangerfield and Tulloch, 1989).

In the geology and geochemistry sections, information is presented on the basis of five regional subdivisions of the UK Continental Shelf. These regions are selected generally to coincide with the descriptions presented in Pantin (1991) and the UK Offshore Regional Report Series. However, the subdivision of the North Sea derived from ICES (1983) and North Sea Task Force (1993) has been taken into account to give a compromise between areas of similar hydrographic, biological, geological and geochemical characteristics. The study area is therefore subdivided into the following areas with boundaries shown on Figure 6: 1. The southern North Sea 2. The central North Sea 3. The northern North Sea 4. The Hebrides and West Shetland shelves 5. The Malin-Hebrides sea area.

As described in Section 6, percentile levels for each element are presented in summary statistic tables. These values can be used to define a background level, and in the discussion which accompanies each element the terms 'background', 'intermediate', or 'moderate' express values within the 25 to 75th percentile range. Values below or above this range are considered to be anomalously low or high respectively. The background concentration may be defined as the concentration of an element that would be found in the absence of human activities (North Sea Task Force, 1993). The background values presented in this report are derived from the complete dataset and therefore contain values due to contamination. However, by selection of a statistically-derived range of concentrations which reflect a wide range of sediment types and a large number of samples, the effect of extreme high or low values is reduced. The average and background values are therefore considered the best estimate of element concentrations in sea-bed sediments on the UK Continental Shelf published to date;

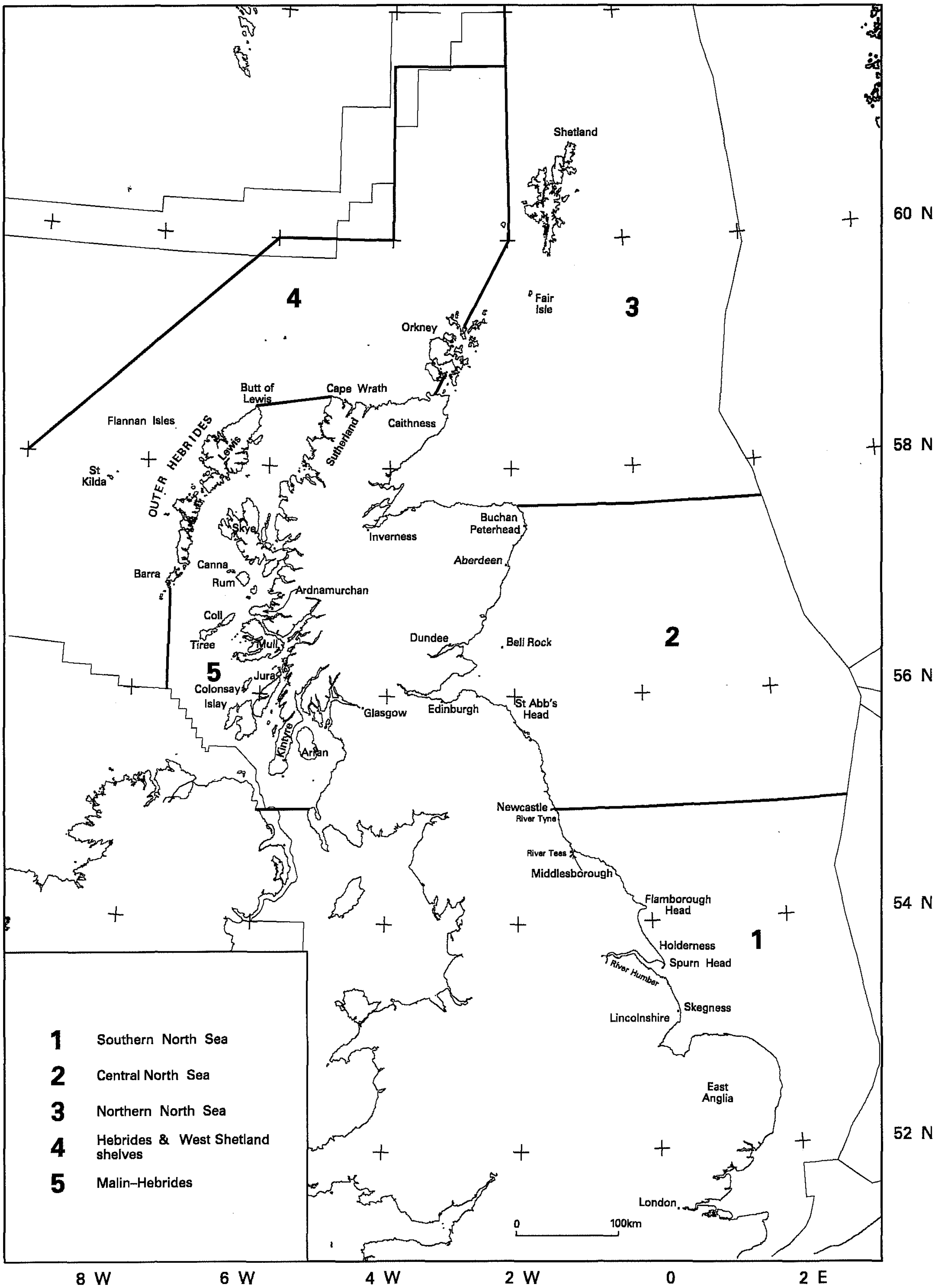


Figure 6 Locality map and offshore regional subdivisions described in the text.

combined with the detailed statistical analysis of different sediment facies presented in Appendix 1, they provide a baseline against which to assess local studies or to monitor changes in element concentrations with time.

Normalisation techniques

One of the major problems in the interpretation of metal concentrations in sea-bed sediments is the differentiation of naturally-occurring levels from those which have an anthropogenic source. The main influence on the distribution of metals in sea-bed sediments is grain size, which determines the surface area to volume ratio of the solid phase in chemical exchange processes (Kester et al., 1983), and the conditions under which sediment is deposited and resuspended. Fine-grained sediments are the most important medium for transporting metals in rivers and seas, whether from natural or anthropogenic sources, and therefore generally have higher metal concentrations than coarse-grained sediments. The analysis of a relatively wide range of grain sizes (clay to very coarse sand) could limit the value of the data in assessing pollution factors, however the application of normalisation procedures helps recognise the various factors which control element distribution patterns.

Some of the common normalisation techniques have been described by Loring and Rantala (1992), who review various granulometric and geochemical approaches that can be used to determine background levels of elements, and to normalise for grain size effects. Natural background levels can be derived either from published values; from direct measurements of texturally and mineralogically similar sediments from areas which are known to be unpolluted; and from sub-surface samples obtained from depths below possible contamination or biological mixing.

Normalisation techniques can be simple to complex depending on the requirements and resources of each investigation. A simple approach would be to compare element concentrations to estimated background values as described above. More complex mathematical normalisation techniques depend on a significant correlation between the element under consideration and the normalising parameter. These include element:grain size and element:element normalisations. In the former, metal values may be plotted against weight percentages of mud (<63μm); this method is of particular value where analyses are not based on selected grain size fraction. The latter technique is often carried out in addition to grain size normalisation. In this approach, a reference metal is assumed to represent a certain mineral fraction, for example Al as a proxy for the granular variations of the aluminosilicate fraction (particularly clays); or a specific mineral group such as the use of Li as a proxy for micas and/or clay minerals. The normalising element must therefore be an important constituent of one or more of the main rock-forming minerals in the area under investigation, and reflect their granular variability in the sediments. Finally, multi-element normalisation in which element concentrations, grain size, carbonate and organic carbon contents have been measured, allows the inter-relationships between the variables to be established in the form of a correlation matrix. From such a matrix, the most significant parameters can be determined and used for normalisation.

In this report, maps of each element normalised to Li are presented. Li is selected because of its greater analytical accuracy than Al; it is also considered a better indicator of fine-grained sediments. In a study of the geochemistry of sea-bed sediments in the eastern English Channel (Ridgway et al., 1993), Li showed the strongest correlation with the mud fraction. To assist further in interpretation, correlation coefficient matrices of element data have been generated for selected areas of varying sea-bed sediment facies (Appendix 1). These data also indicate that Li has a stronger correlation with other geochemical elements across a wide range of grain sizes when compared to Al. Furthermore, Loring (1990), investigating the granulometric normalisation of trace metal data in estuarine and coastal sediments, concluded that normalisation to Li may demonstrate a universal application to silicate sediments and considered it superior to Al for the normalisation of metals in high-latitude sediments derived mainly from the glacial erosion of crystalline rocks, and equal or superior to Al for those derived from non-crystalline rocks. This is a consequence of Li being incorporated in fine-grained aluminosilicate metal-bearing minerals, but not in the Al-rich but metal-poor feldspars that occur throughout the grain-size range of such sediments. Li also has the advantage of not being significantly influenced by anthropogenic inputs.

The correlation matrices also provide a basis for selection of other normalisation factors. For instance, the normalisation of data to Mn in areas where trace metals show a strong correlation with Fe and Mn due to adsorption by secondary hydroxides, is useful in distinguishing natural and contaminant metal sources from those related to secondary sorption effects. Note that the key to the normalised maps is similar to those showing single element distribution, with the purple colour at the lowest end of the range and red at the top. No data values are therefore presented, as it is the relative variation in this data and not the absolute values which are considered important. Frequency histograms of each normalised distribution were investigated before selecting the plotting intervals to compensate for the effect of extremely high ratios.

Although normalising factors can assist in data interpretation, it is necessary to consider the effect of geochemical variation due to differences in sediment provenance. For example, parts of the area to the west of Scotland are characterised by some of the highest levels of elements such as Fe, Ni, Cr, and Ti due to the derivation of sediments from basic igneous rocks. Here, normalising factors based on grain-size parameters alone would identify these element levels as anomalous. Since these are natural anomalies, to differentiate anomalous values which may be related to contamination requires a different set of normalising parameters and background values specific to this area.

It is worth noting also that if the area west of Scotland was considered to fulfil the criteria for the calculation of background values, in that it is likely to be the least polluted area under investigation, values for some heavy metals would not highlight the significance of anomalous concentrations of these elements in the nearshore areas of the North Sea. Kersten et al. (1988) used such a technique to calculate heavy metal enrichment factors in the North Sea based on the composition of sediment fines at the shelf edge off the Hebrides. Appendix 1 shows however that the average concentrations of elements such as Cr, Ni and Co are as high at the shelfbreak as they

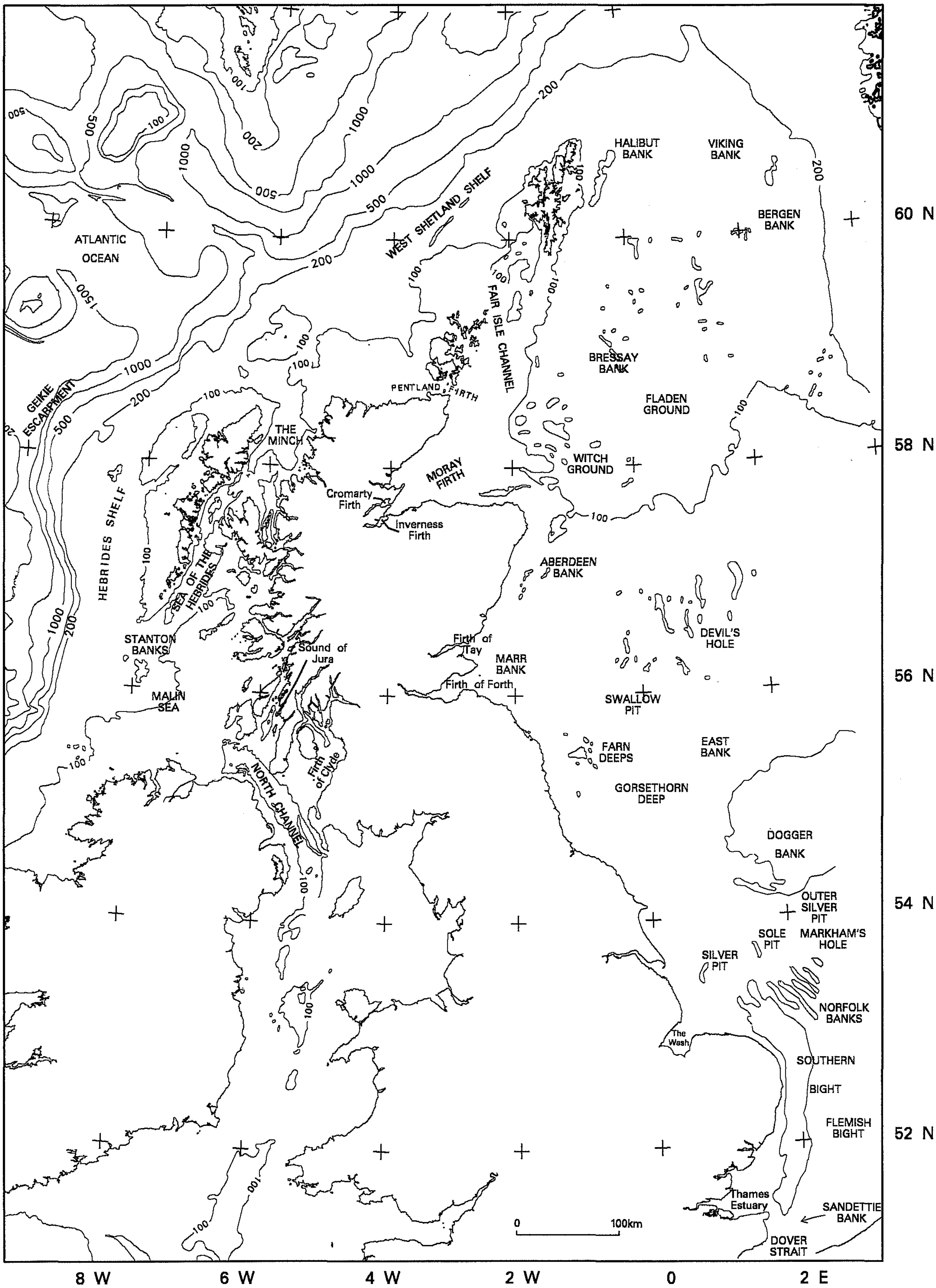


Figure 7 Generalised bathymetry

are off the estuaries of the Tyne, Tees and Forth. Assessment of geochemical data in areas of different provenance is considered a necessary part of future work on the offshore geochemical data.

8 PHYSICAL OCEANOGRAPHY

Descriptions of the processes which influence the input and movement of sediments in the seas around Britain occur in several publications including Hill (1973), Lee (1980), Otto (1983), Reid at al. (1988), Pantin (1991), and North Sea Task Force (1993). Properties discussed in these reviews include: the influence of sea-floor topography; water mass characteristics such as salinity and temperature; stratification and fronts; wave action, tidal currents and water circulation. Some of the important features which affect sea-bed sediment geochemistry are summarised here.

Several water mass classifications exist for the sea area around the UK, based on properties such as temperature, salinity or stratification. Lee (1980) proposed a classification into six water masses which formed the basis of subdivisions used by the ICES study group (ICES, 1983) and the North Sea Task Force (1993). Those which are most relevant to this report are 1. Atlantic water 2. Channel water 3. Northern North Sea water 4. Central North Sea water 5. Southern North Sea water 6. Scottish Coastal water. Sea-bed topography is important in relation to circulation and vertical mixing of these water masses. A generalised bathymetry map is presented in Figure 7 and a schematic representation of the general circulation in the North Sea is shown in Figure 8.

Tidal, wave-induced, wind-driven and oceanic currents all affect the Hebrides and West Shetland shelves, whereas oceanic currents predominate on the adjacent slopes and basin floors. A persistent, northerly or north-easterly flowing oceanic current caused by the circulation of relatively warm and saline Atlantic water follows the upper slope and outer shelf to the north of Shetland before passing southwards along the Norwegian Trench to form the major flow into the North Sea. The current probably extends down to depths of between 400 and 600m on the slope, and to about 800m in the Norwegian Sea. Occasionally some of this water may pass southwards into the northern North Sea close to the eastern coast of Shetland. To the north-east of the Wyville-Thomson Ridge a flow of somewhat smaller transport follows the 100 metre contour across the West Shetland Shelf and part of it diverges to the south-east where it enters the northern North Sea between Shetland and Orkney as the Fair Isle Current. This flow is an admixture of coastal and Atlantic water that crosses the northern North Sea along the 100 metre contour as the Dooley Current before entering the Skaggerak.

There is also a deeper-water, southerly-returning current which affects the lower slope and basin floor to the north-west of Scotland. This is caused by the flow at depth of relatively cold and dense water from the Norwegian Sea into the Atlantic (Kenyon, 1986).

Most areas of the North Sea are vertically well mixed in the winter months. In late spring, a thermocline is

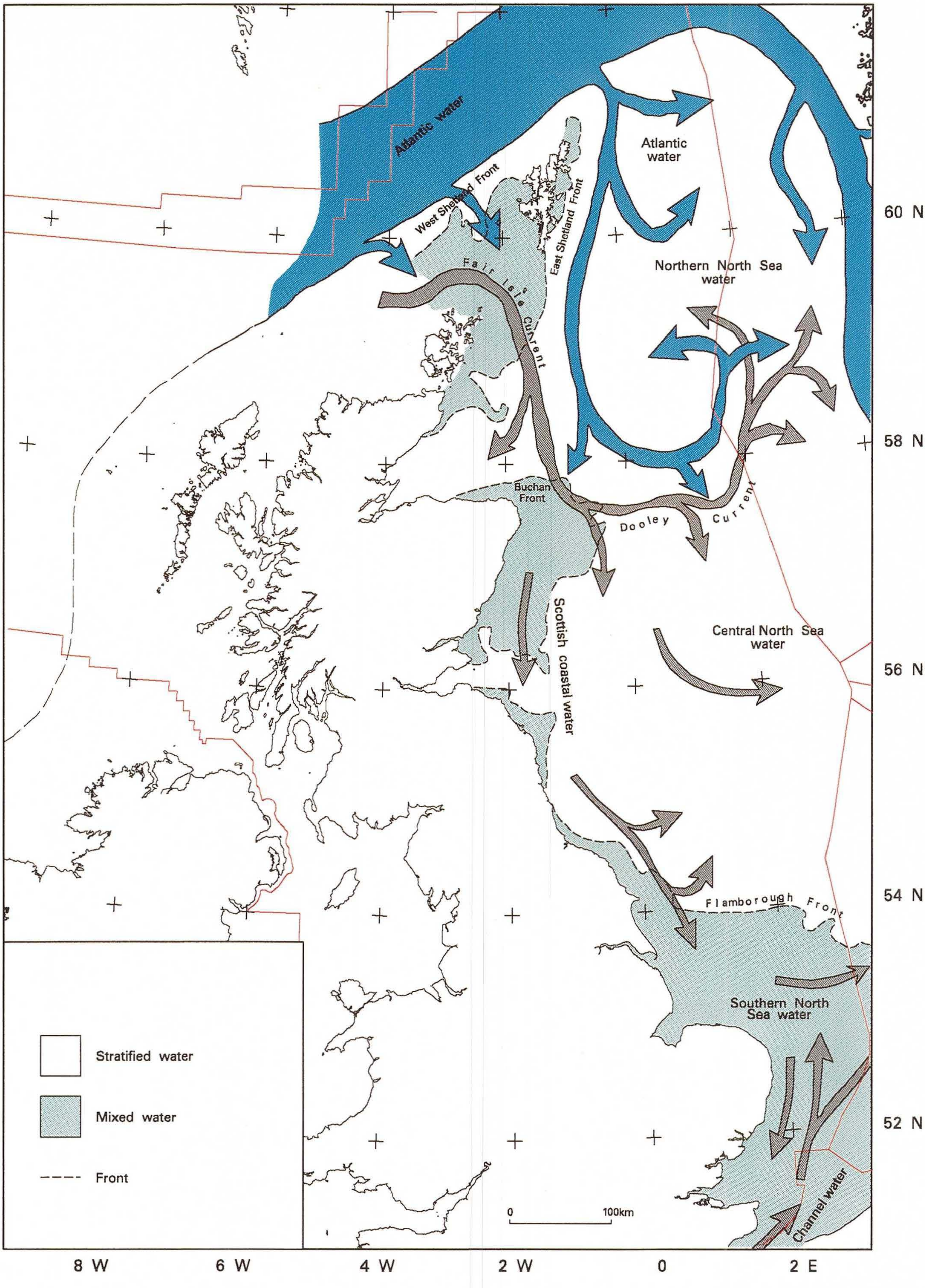


Figure 8 General circulation in the North Atlantic and the location of fronts between water masses. After North Sea Task Force (1993) and Reid et al. (1988).

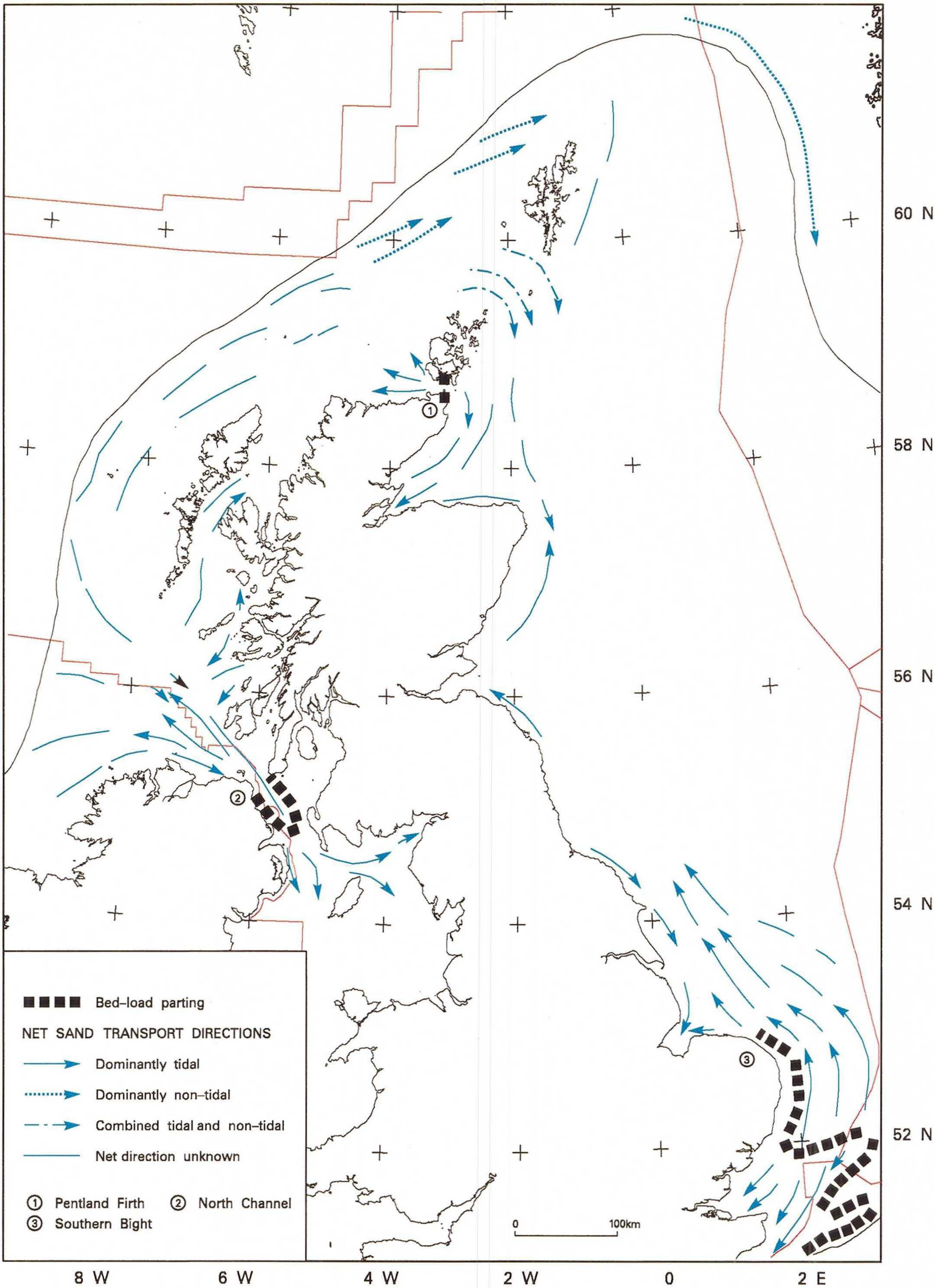


Figure 9 Net sand transport directions and locations of bed–load partings. After Johnson et al. (1982).

established which separates a lower and upper layer. Thermal expansion of the surface layer reduces its density producing a self-stabilising stratification. In autumn, the increasing number and severity of storms in addition to seasonal cooling of the surface layer, destroy the thermocline and mix the upper and lower layers. The shallow parts of the southern North Sea remain well mixed throughout the year owing to strong tidal action.

The boundaries between well-mixed and stratified water masses are marked by thermal fronts which are characterised by increased variability in water properties. These fronts are important as they may restrict horizontal dispersion. Figure 8 shows that a continuous sequence of fronts extend from Shetland to the mainland of Scotland. An area of mixed water with a frontal boundary (the Buchan Front) extends from Dundee to Fraserburgh off the north-east coast of Scotland. A variable sequence of coastal fronts and upwelling develops south of Edinburgh to Flamborough Head. From here a clear boundary with the mixed waters of the southern North Sea, the Flamborough Front, passes eastward, and to the north of this a complicated pattern of fronts and upwelling mark the position of the Dogger Bank and other shallow features in this area.

In the southern North Sea, the water body originates from North Atlantic water and freshwater run-off in different admixtures. The Atlantic water enters through the Dover Strait from the English Channel and moves erratically towards the Skaggerak along the coast of continental Europe.

The North Sea has only one outflow. It commences in the Skaggerak and with additions from the Baltic Sea and Norwegian coastal water, leaves the North Sea as the Norwegian Coastal Current.

The whole of the north-west European Continental Shelf is affected by tides and thus tidal currents. These currents, either alone or superimposed on wave action, have a significant effect on sediment movement. For example, tidal currents are the most energetic force in the North Sea, stirring the entire water column in most of the southern North Sea and English Channel. In certain areas the frontal region between coastal and offshore waters is much reduced during neap tides relative to spring tides. The exchange of suspended particulate matter (SPM) between coastal and offshore waters is therefore reduced during spring tides and the SPM remains in coastal waters. During storms, the resuspension and vertical dispersion of bottom sediments due to waves and currents is a process that affects most of the North Sea with the exception of the deepest parts. A review of waves, tides and storm surges is given in Pantin (1991) and Figure 9 summarises some of the main features of the hydrodynamic regime, which affect sand transport on the UK Continental Shelf. The local effects of tides and currents on sediment distribution is discussed in Section 9.

9 SEDIMENT INPUT AND TRANSPORT

Suspended sediment is supplied to the UK Continental Shelf by the water masses described in Section 8 and additional inputs from rivers, coastal erosion, sea-floor erosion, the atmosphere and primary production of organic matter. Suspended matter originates from the weathering and erosion of sediments, soils and rocks, as well as from anthropogenic sources (see below), and consists of a variety of components including mineral particles (e.g clay minerals, quartz and feldspar), aggregates of mineral particles and organic matter. These components are often coated with hydrous Fe and Mn oxides or by organic substances which to a large extent affect the interaction process between solids and dissolved components. Grain size affects the conditions under which sediment is deposited and resuspended and also determines the surface area to volume ratio of the solid phase which is important in chemical exchange processes with the aqueous phase (Kester et al. 1983).

Natural inputs

Suspended matter has been found to consist largely of particles smaller than 60 to 70 μm (Eisma, 1981). Material coarser than suspended matter, sand and gravel, is supplied to the North sea in only limited quantities. Sand reaches the sea from rivers only during exceptional conditions or, together with gravel, from cliff erosion. The relative contributions of the major components of suspended particulate matter vary considerably from the shallow southern parts of the North sea to the deeper central and northern areas. Virtually all sand and gravel on the sea floor around the UK dates from the Pleistocene or early to middle Holocene. During storms, larger particles can be temporarily held in suspension in the shallower parts of the southern North Sea where the sea-bed sediments are predominantly sandy, but this material is soon redeposited during calmer weather.

In general, the metal concentration of particulate matter is higher than that of the same metal dissolved in water (Kersten et al.,1988) as suspended material tends to accumulate trace metals preferentially. The relative enrichment of metals in the sediment particulate phase makes it the most appropriate matrix for assessing both natural and anthropogenically introduced levels of metals in the marine environment. The analysis of metals in sea-bed sediments, as the final sink for all material entering the marine environment, also has the advantage of integrating inputs with time.

All the processes of transfer of material from land to waters are constrained by the removal of reactive elements onto particles. Depending on the composition and adsorption characteristics of the suspended matter, and environmental factors such as pH and Eh, redistribution of trace metals takes place during transport and deposition of suspended matter particularly during diagenesis of the deposited sediment. Particulate organic matter, clay minerals and the oxides and hydroxides of Fe and Mn represent the most important substrates for trace metal scavenging (Gibbs,1973). Most of the sediment on the sea bed around the UK consists of sandy sediments with low organic matter content over which frequent flushing of bottom water occurs. Such conditions create well-oxygenated sediments and positive redox potentials in the upper few centimetres of the sediments. Exceptions are estuaries, some near-shore deposits or around oil platforms. (North Sea Task Force, 1993).

The distribution of suspended matter in the UK sector of the North Sea shows the highest concentrations in the

Southern Bight. High concentrations occur where a large gyre is present nearshore or where resultant transport directions meet (Eisma and Kalf, 1987). Concentration of suspended matter nearshore is partly related to the predominance of flow parallel to the coast with a relatively small component at right angles to the coast, so that suspended matter nearshore will tend to stay nearshore. Further concentrations of suspended matter in a shoreward direction is related to nearshore water circulation. The nearshore water usually has a lower salinity and therefore lower density than water offshore. Nearshore water therefore tends to flow seaward along the surface and offshore water flows shoreward along the sea floor (Eisma and Irion, 1988). Suspended sediment flowing offshore along the surface and settling will therefore tend to be returned to the shore.

Eisma (1981) considered the main sources of suspended matter in the southern North Sea to be rivers and coastal erosion. River systems that discharge into the North Sea alone have a total catchment area of 850 000 km^2 (North Sea Task Force, 1993) and are estimated to supply 4.8 million tonnes of material per year (Eisma and Irion, 1988). Supply of mud from erosion of cliffs varies around the UK coastline but in areas such as East Anglia and the Holderness Peninsula an estimated input of 0.7 million tonnes per year (McCave,1973) is more than the combined supply of the rivers Thames and Humber (0.3 million tons per year) according to Veenstra (1970). In coastal areas, wind-induced and tidal currents, and/or wave action, induce stresses on the sea-floor and resuspend sea-bed sediments into the water column where they may be transported and redeposited elsewhere. Resuspension and estuarine run- off is the predominant source of clays and oxides in suspended matter.

Erosion of the sea floor is more difficult to assess, however Eisma and Irion (1988) have estimated a yearly supply to the North Sea of about 13.5 million tonnes. Numerical models have made it possible to simulate suspended particulate matter deposition and erosion areas of the North Sea (Figure 10; North Sea Task Force, 1993). Gossé (1977) estimated that up to 2.4 million tons per year may be supplied from the Flemish Banks by erosion; the eroded material is lost from the area and is assumed to be removed in suspension. Eisma (1981) noted indications of sea-floor erosion off East Anglia.

In the deeper central North Sea, erosion of sea-bed sediments affects the composition of suspended matter much less. In areas of nondeposition, organic material derived from plankton and pollutants may be the most important heavy metal removal mechanism. Reworking of what is left after decomposition will result in burial of at least part of the pollutants supplied to the sea floor in this way. This type of deposition whereby organic matter is accumulated in coarse-grained bottom sediments, is going on in the Fladen Ground and the Great Fisher Bank in the northern North sea (Eisma, 1981). Here only a very small amount of deposition has taken place during the Holocene, but radiocarbon data indicate the deposition of more recent organic material and reworking of the top 10-15 cm by bioturbation or trawling.

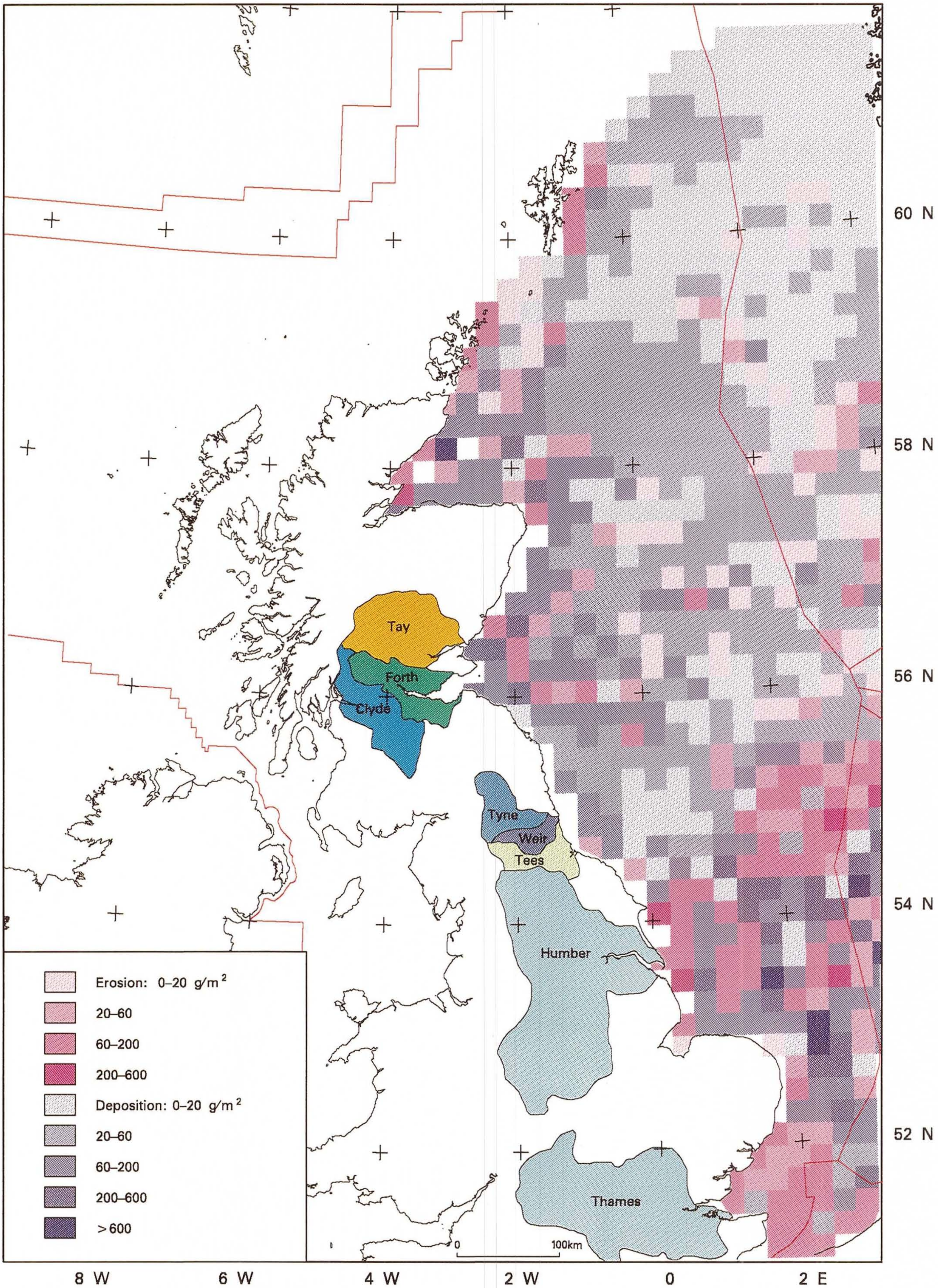


Figure 10 Erosion and deposition of sediments in the North Sea and catchment areas of major rivers. After North Sea Task Force (1993).

Anthropogenic inputs

Anthropogenic sources of metals which enter the seas around the UK are derived from a wide range of human activities such as industry, agriculture and the production of domestic waste. Material is introduced into the marine environment by diffuse inputs, such as by rainfall and atmospheric fall out, and by direct sources such as discharges of sewage sludge, sewage effluents or industrial effluents via river systems from land, dumping at sea, discharges from offshore installations and shipping.

Atmospheric inputs

Atmospheric inputs to the North Sea are still highly uncertain, although research indicates that they are in the same order of magnitude as inputs by rivers, dumping and discharges (Van Aalst, 1988). Particles injected into the atmosphere by man-made activities include those derived from industrial processes, fuel combustion and solid waste incineration. Van Jaarsveld et al. (1986) and van Aalst (1988) published data on atmospheric inputs to the North Sea; their maps of cadmium, arsenic, lead and zinc deposition show that the highest concentrations of each element within the study region occur mainly in the southern North Sea near the coast of England and south of 53°N.

Riverine inputs

Riverine inputs comprise those from main rivers, tributary rivers, and coastal areas. The catchment areas of the rivers Thames, Humber, Tyne, Wear, Tees, Forth, Tay and Clyde (Figure 10) are locally densely populated, highly industrialised and intensively farmed, and are therefore among the largest sources of contaminants and nutrients entering the marine environment around the UK.

Fine-grained sediments (less than 63 μm) are important as the medium by which many adsorbed contaminants are carried from river to estuary to coastal zone and then to the sea. Contaminated particulate matter mix with natural particles and therefore follow the same transport paths. It is not possible to estimate how much of the riverine inputs are retained within estuaries and how much reaches the open sea. Riverborne metals entering an estuary can be affected by a change in pH, chlorinity, turbidity maximum and formation of new particulate matter (Salomons, 1980).

Dispersion of contaminants depends largely on whether they are transported in suspension, where they can be widely dispersed and mixed, or along the river bed with coarser-grained sediments and deposited locally. The settlement of contaminated material on the sea bed is an important process that reduces the net (dissolved plus particulate) concentration of a contaminant in sea water. However, the sink can be a subsequent source releasing contaminants back into the sea water as a result of remobilisation of sediment during storms or by leak of pore waters (North Sea Task Force, 1993). Contaminated particles can also be exchanged against uncontaminated sediment in sea-bed deposits; reworking of surface deposits through the sediment column, for example by benthic organisms or human activities such as trawling, can lead to contamination of older deposits. The sea bed exchange process may determine the long term mean concentrations in sea water for many contaminants irrespective of inputs from other sources. Kremling (1983) and Nolting (1986) have shown that this process controls elevated concentrations of dissolved Cu, Ni, Cd and Zn near the southeastern English coast and in the Scottish shelf region, probably to a greater extent than freshwater inputs.

Although fine-grained particles generally have the highest concentrations of adsorbed contaminants because of their large surface area, some contaminants may adhere to sand grains particularly when coated with organic matter or Fe and Mn hydroxides. Relatively pure sands may also contain an admixture of fine particles that have settled in the pore space between the sand grains. In this way, sands may also have high concentrations of contaminants. The areas where suspended matter is being deposited, particularly those near to sources of contamination, are primarily the area where adsorbed contaminants are concentrated.

The introduction of organic material by rivers is also considered to be important as organic particles have very high sorption capacities and are able to remove metals dissolved in sea water. This process has most influence on geochemical patterns near river estuaries, but more generally high concentrations of elements such as Zn in the southern North Sea may be related to accumulation of organic matter derived not only from the rivers of the UK but to those of Continental Europe, such as the Rhine. The wide distribution of high Zn concentrations in both fine and coarse-grained sediments suggests that the organic matter occurs not only in association with clay particles, but also in the pore spaces of coarser-grained sediments.

Waste inputs

Dumping

The types of waste dumped into the North sea can be divided into three categories: industrial waste, sewage sludge, and dredged material. Industrial waste covers a variety of types such as waste from metal extraction, phosphogypsum waste from the production of fertilisers, colliery waste, fly ash, rock, tailings and sediments. In addition, materials such as concrete, scrap iron and cables and wire, as well as ships containing waste such as military munitions, are known to be dumped at sea. The amount of waste dumped in the North Sea has decreased in the last few years, from about 4.1 million tonnes in 1987 to about 2.8 million tonnes in 1990 (North Sea Task Force, 1993). The incineration of chemical waste at sea started in 1969 in the North Sea and ceased in 1991. Specifically, incineration is designed for the destruction of liquid organochlorine wastes. Since 1979, the burning area in the North Sea was located to the east of Dogger Bank.

Sewage sludge is dumped at 8 sites along the east coast of Scotland and England between the rivers Thames and Forth. The bulk of metal contaminants in sludge remain bound to very small particles (< 10 μm) within the sludge (Chapman 1986) and most organic contaminants also concentrate in the particulate fraction. Statistics for 1981 show that, as a proportion of total inputs to the North sea, sewage sludge provides a relatively small contributor of metals compared with river, atmospheric and dredge spoil inputs (Hill et al. 1984). The UK is committed to a programme to phase out the disposal of sewage at sea by the end of 1998.

Material dumped at sea consists principally of dredged material removed to keep navigation channels clear or during construction of new harbours or other coastal engineering projects. Because this dredged material is derived from such areas of extensive human activity the quantities of contaminants contained within these sediments may be considerable (North Sea Task Force, 1993).

Offshore installations

The offshore oil and gas industry has become a major economic activity in the North Sea since the late 1960's. Major oil developments have been in the northern part of the UK sector whereas gas deposits are mainly exploited in the southern North Sea. Quality status reports (Quality Status Report, 1987; North Sea Task Force, 1993) indicated that offshore oil and gas installations introduce hydrocarbons and heavy metals into the sea mainly via cuttings from oil or water based drilling muds. Accidental spills result in relatively minor amounts of oil entering the North Sea. The UK sector of the North Sea has about 150 platforms in production with about 5800 kilometres of pipeline to transport oil and gas (1991 figures; North Sea Task Force, 1993).

Shipping

Most of Europe's largest ports are situated on North Sea coasts and rivers (e.g Rotterdam, Antwerp and Hamburg) consequently some of the busiest shipping routes in the world, such as the Dover Strait, occur within the study area. Estimates of waste discharges from shipping are difficult to assess, however observations of oil slicks by aerial surveillance flights during 1990 and 1991 found that the majority occurred in the shipping corridor between Dover Strait and the north-west coast of Europe (North Sea Task Force 1993).

10 GEOLOGY

Sea-bed sediment distribution

The sea-bed sediments of the UK Continental Shelf (Figure 5) are mostly derived from underlying Quaternary deposits. Consequently the proportion of mud or sand in surface sediments is largely dependant on the composition of the older deposits. In some areas tidal currents or wave action may prevent deposition over relict

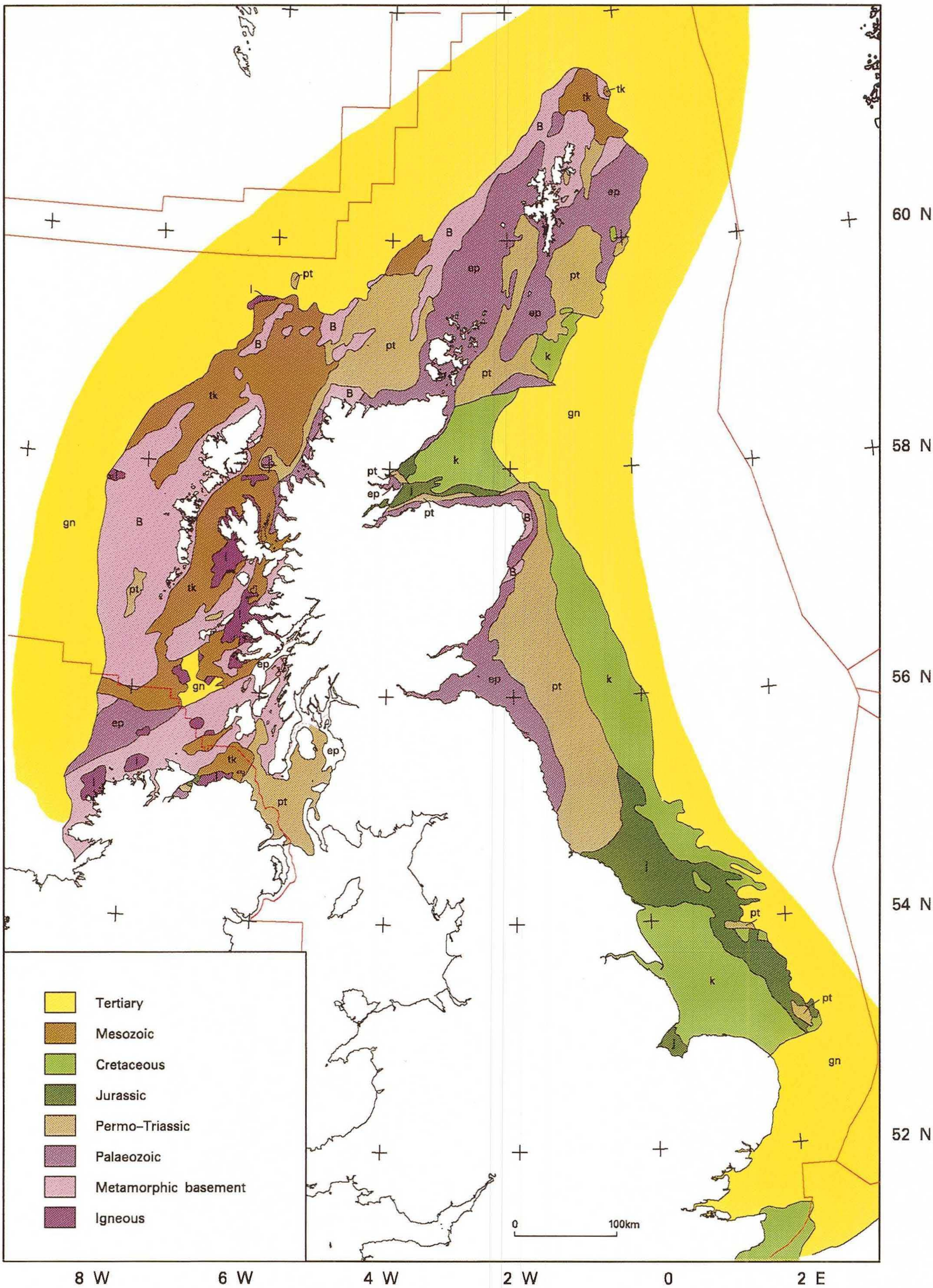


Figure 11 Generalised pre-Quaternary geology of the UK continental Shelf.

coarse-grained sediments or winnow the fine-grained material to leave a coarse-grained lag deposit. The following discussion also shows that some sea-bed sediments are derived by direct erosion of pre-Quaternary rocks therefore a summary of their distribution is presented in Figure 11.

Southern North Sea

Coastal erosion has been an important source of sediment to this region throughout the Holocene. The present coastline of eastern England south of Flamborough head is dominated by low cliffs of unlithified Pleistocene or Tertiary formations which are receding at a rate of as much as 2m/year along the Holderness coast (Valentin, 1971). North of Flamborough Head, coastal erosion of relatively resistant Mesozoic formations is much slower (Jago, 1981).

The major rivers of eastern England presently input only silt- and clay-sized sediment into the southern North Sea, although their competence to transport sediment may have varied throughout the Holocene.

Gravelly sediments are widespread in the region, but despite strong tidal currents, they are generally not transported any significant distance at present. The distribution of gravelly sediments therefore reflects processes no longer active offshore, including glacial, fluvioglacial, fluvial and coastal processes. A small biogenic contribution to the gravel fraction may be made locally, mostly by mollusc shells. The largest area of gravelly sediments occurs between the north Norfolk coast and Flamborough Head. These sediments are thin, and rest on an erosional surface of till or, at or near the coast, on a bedrock of chalk. In places the gravel is overlain by sand, for example at Norfolk Banks. In the area of chalk outcrop, the gravel is probably derived from sea-floor erosion, as samples contain pebbles of chalk and flint. Elsewhere, the gravels are of mixed lithology, including flint, but are dominated by Carboniferous sandstone and limestone, together with igneous rocks believed to have been derived from the Cheviots in north-east England (Veenstra, 1971). In general the lithological assemblage indicates derivation from Palaeozoic formations of north-east England and southern Scotland. These gravels have arisen as lag deposits derived from glacial deposits (Robinson, 1968; Veenstra, 1971).

Gravel-size sediment may also be derived by coastal erosion of Late Pleistocene tills, however the source sediments contain only minor amounts of gravel. Gravel derived from coastal erosion between Spurn Head and Flamborough Head is transported southwards by longshore drift to form the sand and shingle spit of Spurn Head, and may also be transported offshore (De Beer, 1964).

Patches of gravel on Dogger Bank and to the south of the Outer Silver Pit have a similar composition to those to the west, and are similarly believed to be derived from Late Pleistocene glacial deposits (Veenstra, 1969).

Gravelly deposits also occur on the sea floor off eastern East Anglia and in the Dover Strait. Off Great

Yarmouth, the gravelly sediments rest unconformably on Pleistocene deposits, but farther south in the Outer Thames Estuary they rest on Tertiary formations. Considerable variation in pebble lithology is seen in this area, but flint is the dominant component. Quartz and quartzite are locally common, especially in the north. Most of the gravels originate from reworking by marine transgression of deposits resting on the early Holocene land surface.

Other gravel components show a relationship to the underlying geology. In the Dover Strait, rounded chalk pebbles are numerous and, in the vicinity of the Paleocene outcrop, very well-rounded, small, black flint pebbles derived from Tertiary pebble beds are common. Gravels from areas underlain by the London Clay Formation contain large cobbles of calcareous mudstone derived from septarian concretions. In an area east of Orfordness, the gravels contain rounded phosphorite pebbles reworked from Pliocene lag deposits (Balson, 1989).

Sandy sediments dominate much of the sea floor in the region. Much of the sand is mobile under present-day hydrodynamic conditions, and therefore its distribution relates to modern sand-transport processes. However, the heavy mineral content of the sands does show significant geographical variation reflecting a variety of sources (Baak, 1936). Sand may also be derived from pre-existing glacial deposits, and a large sand-wave field in the Southern Bight may be derived from an early Holocene Rhine-Meuse estuary complex (Nio, 1976). At present, rivers input very little sand to the North Sea, the main input being from coastal erosion. An important contribution comes from the Norfolk coast between Weybourne and Happisburgh where sediment derived from cliff erosion is transported to the west and south-east along the beaches by longshore drift, with dominant transport to the east. Sand derived from coastal erosion may also be transported offshore along a complex transport path to maintain offshore sandbanks tens of kilometres from the shore (Stride, 1988) although this has not been proven.

Sediment budget calculations suggest that coastal erosion from the Norfolk coast is of the same volume as sediment deposited in nearshore banks (Clayton et al.,1983) and also confirm that the Sizewell-Dunwich Banks, which are connected to the coast at Thorpe Ness, are mainly derived from coastal erosion. The sand fraction in the sediments is mainly medium-grained. Finer-grained sand occurs in the mouths of estuaries such as The Wash, Humber and Outer Thames. Very fine-grained sands are found within sea-bed depressions such as the Outer Silver Pit.

Muddy sediments have a restricted distribution occurring mostly in the coastal zone. Most mud-size material is held in suspension and is principally derived from inflow through the Dover Strait. Mud derived from coastal erosion mostly remains in the nearshore zone and is deposited in estuaries. The large offshore depressions of the Outer Silver Pit and Markham's Hole are thought to have acted as sediment traps since early Holocene times (Zagwijn and Veenstra, 1966; Eisma, 1975), although it is not clear how much of the Holocene fill was deposited as intertidal flat sediments prior to the onset of marine conditions. Various rates of deposition have been calculated for this area, however Eisma and Kalf (1979) pointed out that the concentrations of suspended material are low in the vicinity of the Outer Silver Pit, perhaps indicating that most of the mud was deposited during the early Holocene.

Muddy sediments in nearshore areas, such as off Great Yarmouth, may be due to the influence on the nearshore zone of the turbidity maximum of the River Yare (McCave, 1981). Alternatively, the mud may originate from local erosion of early Holocene estuarine muds exposed on the sea floor as found by Lees (1982) farther south.

The sea-bed sediments of the report area have a low carbonate content, mostly less than 10 per cent (Figure 12; Pantin, 1991), reflecting the dominance of glacigenic sources. Unlike the area north and west of Scotland (see below), carbonate-rich skeletal sediments are not found in regions of rocky or gravelly substrates. This is partly due to dilution by lithic sediment, but is also due to the briefer time-span for Holocene marine deposition in the southern North sea, and possibly to lower carbonate production rates.

Areas of high calcium carbonate values in sea-bed sediments of the region are commonly derived from older carbonate-rich sediments.

Central North Sea

Gravelly sediments cover about 10 per cent of the sea bed in this area. Gravelly sand forms most of this facies which may contain locally developed patches of gravel and sandy gravel as winnowed lag deposits. These sediments are restricted mainly to an arcuate zone of submarine banks around the southern, western and northern margins of the area notably in the vicinity of the Farne Islands and the offshore banks east of Scotland, particularly the Marr and Aberdeen banks. Although the gravel on banks consists mostly of lithic clasts derived from erosion of underlying morainic material, the sediments include much biogenic material, since these banks are centres of carbonate production.

Sands are the predominant sediment type in the central North Sea where they cover about 80 per cent of the sea bed. They occur in a wide range of water depths and form a significant component of other sediments in the area both on topographic highs and in depressions. Within the Firth of Forth, sandy sediments are restricted to water depths of less than 20m, and on the north side of the Forth they have a dark colour due to the presence of material derived from coastal coal tips (Thomson, 1978). Off north-east England, the sandy sediments are restricted to small patches bordered by gravelly sediments in the north and muddy sediments in the south and east. Fine-grained sands occur in areas of muddy sediments and also in the south-east towards Dogger Bank.

The carbonate content of the sand fraction is generally less than 10 per cent. In areas of gravelly sand nearshore, and on submarine banks, the carbonate content is significantly higher (over 80 per cent locally) because of the

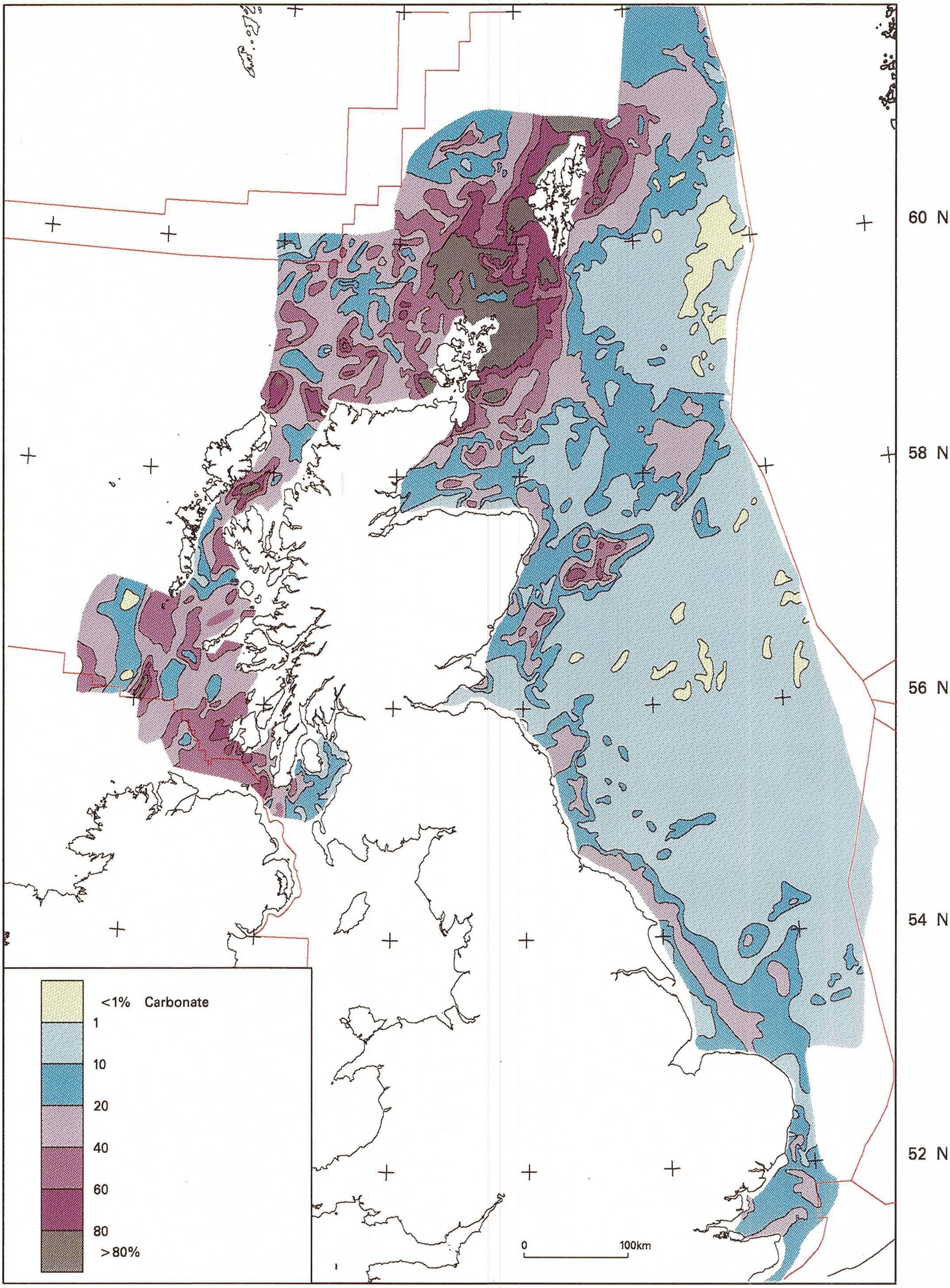


Figure 12 Distribution of carbonate in sea–bed sediments. After Pantin (1991).

relatively high biogenic production and in-situ degradation.

Muddy sediments, of which muddy sand is the most widespread, cover about 10 per cent of the sea bed in the region. Muddy sand is found in a wide range of water depths, commonly in association with muddier sediments or gravelly sediments with significant amounts of mud. Away from the coast, it is found extensively in water depths of between 90 and 100m. It also occurs within isolated linear deeps such as those in the vicinity of Devil's Hole, in the Swallow Hole, and in the Gorsethorn Deep.

Significant deposits of muddy sediment occur within the coastal zone between the Tyne Estuary and the Farne Islands, where muddy sands extend as far as 50km offshore, and also in the vicinity of the firths of Forth and Tay. Although there are bathymetric deeps in these areas which act as traps for fine-grained sediment, the mud occurs extensively beyond the deeps reflecting a relative abundance of mud-grade material derived from land and/or underlying Pleistocene and Holocene deposits.

Northern North Sea

The sea floor in this area is covered by a thin layer of unconsolidated terrigenous and biogenic sediment which generally does not exceed a few decimetres in thickness. The cover is absent locally, exposing either bedrock, Pleistocene deposits or a coarse-grained lag deposit. Most of the terrigenous material is derived from the underlying Quaternary and early Holocene deposits, whereas the bulk of the biogenic sediment has accumulated during the Holocene. Coastal erosion is not an important sediment source, and fluvial supply is limited to the southern and south-western shore of the inner Moray Firth. The fluvial sediment input into the Moray Firth has been calculated to be a minimum of 140 000 tonnes/year and may reach as much as 460 000 tonnes /year (Reid and McManus,1987). At least 50 per cent of this material is peat. Much of the fluvial input contributes to major coastal sediment accumulation in such areas as the Cromarty, Dornoch and Beauly firths.

Sand-grade sediment is predominant within the region. Gravel mainly occurs on the Orkney-Shetland Platform and on isolated highs east of Shetland. Mud is mostly restricted to bathymetric lows far offshore, to enclosed deeps, and to the inlets around Shetland.

In this area, an extensive coarse, lag deposit was formed prior to and during the early Holocene marine transgression. This deposit and others formed during the Holocene have been reworked during the Holocene and the present distribution of sea-bed sediments reflects either modern hydraulic conditions or the last active sedimentological processes. Studies suggest that the rate of sedimentation is very low with little net sedimentation during the Holocene, although Johnson and Elkins (1979) estimated a depositional rate of the order of 5 to 6 cm per thousand years in topographic depressions. Low Holocene sedimentation rates are implied for the Fladen Ground (Erlenkeuser, 1979). Much higher rates are recorded in the carbonate production zone north-east of

Orkney and this appears to be the only clearly identifiable Holocene input to sea-bed sediments in this area.

Areas of rock outcrop extend locally from the coast of Scotland as well as occurring in isolated zones south of Fair Isle, south-east of Orkney and off Tarbat Ness and Lossiemouth. Pleistocene and older sediments that crop out on the sides of some enclosed deeps include Neogene limestone trawled from the Fladen Deeps (Newton, 1916).

Gravelly sand and sandy gravel occur extensively to the north of Shetland, on the Orkney-Shetland Platform, and on upstanding areas east of Shetland. These are generally shallow water areas (less than 110m) where currents have resulted in the erosion and transportation of sediments. Quaternary deposits are largely thin or absent resulting in large areas of patchy rock outcrop. The sediments generally contain a high proportion of biogenic carbonate material. Gravelly sand and sandy gravel also form relatively small isolated patches on Bressay Bank, Viking Bank and Halibut Bank. Subtle differences in topography appear to determine gravel content in these areas. There is also a large area of gravel off the mouth of the River Spey at Lossiemouth, otherwise gravel is restricted to small patches near the north-west coast in the Moray Firth. The sandy gravels off Buchan are predominantly lithic and have a wide range of lithologies which may be derived from erosion of glacial deposits (Owens, 1980) or from the River Spey (Reid and McManus,1987). A tongue of well-sorted sandy gravel extends 30km north-eastward from Rattray Head where strong currents have removed finer sediment.

Sand deposits occur in a wide range of water depths and exhibit significant regional variations in grain size, sorting and carbonate content. These variations reflect a spectrum of environments, from relatively high energy around Orkney and Shetland where there are sources of carbonate material, to low energy farther offshore with relatively little sediment input. Sand occurs extensively to the east of the Orkney-Shetland Platform and Shetland. A broad irregular swathe extends from 50km east of Fair Isle to 50km east of Peterhead. Sand also forms the sea bed on the flanks of several banks and in much of the inner part of the Moray Firth.

Muddy sand occurs mainly as large irregular patches in water depths between 120 and 160m, such as to the west of Viking Bank and in the Witch Ground Basin. The sand fraction in these sediments is relatively rich in carbonate material, probably due to preferential accumulation of foraminiferal tests due to low hydraulic activity (Owens, 1981). It may also reflect enhanced biogenic carbonate production in the vicinity of pockmarks (Hovland and Judd, 1988). The finest grained sediments, the sandy muds and muds, occur mainly in the Witch Ground and Fladen Ground basins and are also found in isolated deeps nearshore. The clay mineralogy of the Fladen and Witch Ground sediments is dominantly illite (45-60 per cent), with lesser amounts of chlorite, montmorillonite and kaolinite (Elkins, 1977).

Hebrides and West Shetland shelves

In general, sand and gravel-rich sediments are predominant on the shelf whereas mud-rich sediments are found on the adjacent slope. Carbonate-rich deposits occur mainly in the vicinity of bedrock and gravel substrates on the inner and middle shelf; sediments on the outer shelf have low carbonate content.

Approximately 10 per cent of the sea bed on the shelf in this area consists of uncovered bedrock. Most is Precambrian basement but Tertiary igneous rocks occur in the vicinity of St Kilda and Devonian sedimentary rocks crop out on the Orkney-Shetland Platform.

Sediments containing significant amounts of gravel are common and the lithic fraction occurs in a wide variety of grain sizes and lithologies. In many areas, especially on topographic highs, the lithic clasts form lag deposits which are either exposed at sea bed or covered by a thin layer of finer-grained mobile sediment. On the shelf west of Barra, lithic and sandy gravels occur mainly on the summits and leeward sides of banks on the outer shelf and on slopes leading towards the shoreline on the inner shelf. Cobble beds have been observed in the region of the shelfbreak south-west of Barra. In deeper waters, the gravel is more sandy with irregular patches of pebbles, and isolated cobbles and boulders which have been observed down to a depth of 900 m on the slope north-west of St Kilda. The lithic gravels and bedrock outcrop form a favourable environment for calcareous fauna which make a significant contribution to the gravel fraction in many regions. A major high-latitude centre of carbonate production occurs between Orkney and Shetland, estimated to be four times greater than that of the shelf as a whole. Radiocarbon dating indicates that the carbonate material has been accumulating throughout the Holocene, which supports the observation of mixing of older stained and abraded fragments with younger material of fresher appearance.

Throughout the Holocene, sand-grade sediment has been reworked, sorted and transported by bottom currents. On the shelf, sand is transported away from areas of high hydraulic energy, mainly topographic highs, which are therefore characterised by gravelly deposits, to lower-lying sea floor where currents are weaker. The redeposition of sand-grade sediment is apparent on the inner and middle shelf where sand-rich sediments form relatively abundant sheet-like deposits. On the current-swept outer shelf, sand commonly occurs as mobile, thin patches overlying coarser-grained lag and Pleistocene deposits. The carbonate content of the sand fraction on the shelf and upper slope consists mainly of biogenic debris broken down by bioerosion and hydraulic action. Typical concentrations in the sand fraction are within the range 25 to 50 per cent but can occur up to 100 per cent in areas of high carbonate production such as between Orkney and Shetland.

Muddy sediments are rare on the shelf. Exceptions are in sea lochs and sheltered coastal sites, or in bathymetric depressions on the inner shelf. By contrast, mud is widespread on the slope where there is a progressive increase in mud content with increasing water depth. Muddy sediments on the shelf occur within basins which have been partially infilled with soft late Pleistocene to Holocene muds. At these locations, superficial sediments are indistinguishable from the underlying deposits - a similar relationship also exists on the slope. It is likely that some deposition of fine-grained sediment has continued within basins on the shelf throughout the Holocene due to the reduction in current action compared with the surrounding, elevated sea bed.

The carbonate content of muddy sediments is generally between 20 and 40 per cent. These result from the bioerosion and maceration of biogenic debris either produced locally or derived from surrounding areas.

Bedform orientation and bottom currents indicate that the main transport paths are probably aligned along the shelf or parallel to the land, although locally complex transport patterns are indicated by detailed studies. There is no evidence for transfer of sediment from the outer shelf to the slope. On the Hebrides Shelf, coarse-grained, carbonate-rich sediment is being transported in the nearshore vicinity of the Sound of Harris. Farther north, such sediments are being transported around the Butt of Lewis and into The Minch. Net sediment transport by tidal currents west of Shetland is generally towards the north. Between Orkney and Shetland, carbonate rich sediments are probably being transported towards the south-east and into the North Sea.

On the slope, bedforms are thought to result from along-slope transport of sand-grade material by ocean currents.

Malin-Hebrides

The sea-bed topography in this area is the most variable of any on the UK shelf. The sediments are largely derived from the underlying Pleistocene deposits, the strong tidal currents over most of the area having prevented the deposition of fine-grained sediments. Sediment transport into the area is largely restricted to fluvial input or bioclastic debris swept into the area around the Butt of Lewis.

Gravelly sediments occur mainly in shallow water areas such as around the Shiant Islands, Stanton Banks, Blackstones Bank and south-west of Mull, Tiree, Coll and Canna. The sea-bed sediments in the southern part of the Malin Sea are predominantly gravelly due to the strong currents, and tend to have a high carbonate content.

In the North Channel, between Kintyre and Northern Ireland, bottom currents are of sufficient strength to erode and transport sandy sediment. The area is therefore largely floored by bare rock with gravel pavements. Poorly sorted muddy and gravelly sands cover much of the sea bed in The Minch, Little Minch and the Sea of the Hebrides, whereas well-sorted lithic sand occurs north of a line between the Butt of Lewis and Cape Wrath. Carbonate shell banks in the northern Minch are thought to be produced locally , however coastal shell sands to the north of Lewis appear to have been transported from the shelf west of the Outer Hebrides.

Widespread sandy sediments occur around the Blackstones Bank becoming gravelly towards the south. Within the Firth of Clyde, sandy sediments are largely restricted to shallow nearshore areas although south-westwards they accumulate near the edge of the North Channel.

Muddy sediments occur mainly in deep-water areas and in shallower more-sheltered locations. Their distribution locally correlate with late and postglacial Quaternary clay deposits. In The Minch, muddy sediments occur in deep-water locations off Stornoway, in the Sound of Raasay and in the Inner Sound. They also occur in a basin in the central part of The Minch and in some sheltered lochs and bays. A zone of muddy sediments extends from Skye southwestwards to the Sea of the Hebrides. Muddy sediments occur to the west of both Tiree and Mull, in the Firth of Lorne and in sea lochs. The only muddy sediments in the Malin Sea occur in the Sound of Jura where they overlie late Quaternary clays. Muddy sediments are widespread in the Firth of Clyde.

Large areas of rock platform are exposed due either to positive topography or to strong bottom currents preventing deposition of sediment. The principal areas of rock outcrop are the North Channel, Stanton Banks, Blackstones Bank, Hawes Bank and to the west of Canna, Tiree, south-west Mull and Islay. These rock platforms have many gullies which trap mainly biogenic sands. The most significant zone of rock outcrop is the North Channel where any glacial deposits have been removed and all superficial deposits are mobile.

Sediment provenance

The following summary is principally extracted from Pantin (1991) who described the provenance of the terrigenous mud, sand and gravel, and the carbonate fractions of the sediments. Information on the lithic fraction and heavy mineral content of selected sediments is also given: this is derived mainly from three internal BGS reports; Dearnley (1989); Dangerfield and Tulloch (1989) and Dearnley (1991).

Mud fraction

Chemical weathering of rocks to generate clay minerals is a slow process in north-west Europe both at the present time and during the earlier Holocene and Pleistocene times. The provenance of the mud fraction of sea-bed sediments on the UK shelf is mostly the reworked remains of non-resistant muddy formations on landmasses and the continental shelf. Principal sources include glacial tills and exposed Mesozoic and Tertiary muddy formations. The main processes which supply mud to the marine environment have been described above. A generalised map of the Pre-Quaternary geology of the UK land area and continental shelf is shown in Figure 11.

The regional distribution of clay minerals in the North Sea and to the west of the UK is dominated by illite with subordinate concentrations of chlorite, kaolinite and smectite (Johnson and Elkins, 1979; Cronan, 1970). According to Griffin et al. (1968), there is no evidence for in situ formation of illite in the marine environment, and its abundance in marine sediments is considered to reflect supply from continental sources. Biscaye (1965) found illite to be the most abundant mineral in the less than 2 μm fraction of Atlantic sediments and considered this to reflect the high concentrations of micas in many rock types in the surrounding land areas, the widespread abundance of illite in many soils, and its relative resistance to chemical weathering. The clay mineral assemblage of the UK Continental Shelf is therefore likely to reflect the mineral composition of the source rocks from which the sediments are derived.

Fine-grained sediments derived from erosion of muddy Tertiary and Quaternary sediments occur in the Minch. Muds deposited by large rivers occur in the estuaries of the rivers Forth, Clyde, Tyne, Tees, Humber and Thames. The erosion of muddy cliffs along the coast of Holderness and East Anglia has been discussed above. Soft muddy Mesozoic formations along the coast of Yorkshire will also contribute significant quantities of mud although the association with nearby muddy deposits is clear only in a few places. Where muddy sediments occur close to an evident source, it may be assumed that the rate of supply exceeds the rate of removal. Some of the mud will inevitably escape to be dispersed across the shelf by residual water currents and by eddy diffusion to mix with particulate matter from North Atlantic inflow and atmospheric fall out.

The most widespread deposition of mud on the shelf occurs in low-energy zones where tidal current and wave action on the sea bed is weak. These areas include the Fladen Ground Basin.

Mud in nearshore areas, which are affected by tides and wave action, is probably deposited at slack tide during periods of unusually weak wave action and in the presence of a high concentration of mud.

Any mud that bypasses the depositional zones and arrives at the shelfbreak without being recirculated by North Atlantic inflow will be diffused or advected across the shelf edge onto the slope. Accumulation of muddy sediments occurs along the shelfbreak between the Malin Sea and the area north-west of Shetland.

Sand fraction

Sands on the UK Continental Shelf have both varied ultimate provenance and immediate provenance. Ultimate provenance derives from unconsolidated or semi-consolidated Mesozoic, Tertiary and Quaternary formations together with fragments of lithified rocks broken down by mechanical weathering, or by abrasion due to coastal wave action or river transport. Immediate provenance consists of presumably Quaternary sands deposited by fluvial, glacial, proglacial, periglacial and marine processes. The mineral composition of the sand fraction has not yet been studied systematically, however various regional studies are available.

In the Sea of the Hebrides, according to Binns et al. (1974), quartz is the dominant constituent of the terrigenous sand fraction, accompanied by minor amounts of authigenic glauconite and pyrite, which occur within foraminiferal tests. Near the coast of Mull, a sand sample contained 3 per cent magnetite, presumably derived from the basaltic rocks of the island. Lovell (1979) found that the sands offshore of Mull were relatively rich in quartz whereas those near the coast are rich in basaltic rock fragments.

Owens (1981) showed that quartz was the dominant constituent of the sand fraction in sediments east of Aberdeen. Feldspar and lithic fragments also formed the main proportion of the sands and accessory minerals included garnet, glauconite, chlorite and amphibole. The angularity of the sand grains indicate derivation from glacial deposits.

Dearnley (1989) studied the sand fraction of 20 samples from the central and northern North Sea. He found that the major mineral and lithic fragment content of the samples consists dominantly of quartz, plagioclase and potassium feldspar, together with variable lithic fragments of mainly igneous and metamorphic origin. A significant feature is the geographical distribution of samples containing relatively abundant and predominantly basic igneous rock fragments. Fragments of dolerite with pyroxene and plagioclase form an assemblage which extends from the Firth of Forth in a south-easterly direction towards the Dogger Bank. There are close petrographical similarities between these fragments and the igneous rocks of the Old Red sandstone and Carboniferous suites of the Midland Valley of Scotland. North of the Firth of Forth, these varieties were found to be rare or absent which suggested to Dearnley that the concentration subparallel to the coast and widening southwards to Flamborough Head was due to general sediment drift in this direction. To the north, and farther offshore east of this zone, sediments were finer grained and basic igneous rock fragments are sparse. The sands here consist mainly of quartz, sodic-plagioclase and potassium feldspar with pyroxene, garnet and opaque oxides. Based on distinct types of quartz, these sediments were considered to have a mainly metamorphic source, but with a significant content of igneous quartz. The Dalradian and Moine metamorphic rocks of the Scottish Highlands and Shetland were concluded to be the most likely source. This was supported by the relatively frequent occurrence of schistose fragments with chlorite, muscovite, biotite and, more rarely, garnet.

A later study by Dearnley (1991) incorporated the results of his earlier work and included an additional 60 samples from the northern North Sea and shelf area west of Scotland. New information from the area between Orkney and Shetland extending to Northern Ireland showed that the sand fraction of the sea-bed sediments contain abundant detrital fragments of a wide variety of basic igneous rocks ranging up to more than 30 per cent of the fraction. Again the major lithic and mineral fragment content is dominated by quartz, plagioclase and potassium feldspar, but many of the samples contain significant proportions of gabbro, dolerite, and basaltic lithic fragments. In The Minch region from County Antrim to Lewis, fragments of fresh dolerite are common. It was inferred that these fragments must be derived from the Tertiary igneous rocks of Antrim, Mull, Ardnamurchan, Morvern, Rum, Canna and Skye. BGS offshore maps also indicate that Tertiary basic and ultrabasic igneous rocks occur offshore of Mull, Skye and at Blackstones Bank.

Element	Range	Mean
Aluminium	0.2-11.0%	4.04%
Barium	24-624ppm	304ppm
Beryllium	0.1-3.2ppm	1.08ppm
Boron	8-111ppm	35ppm
Calcium	0.26-61.95%	18.42%
Chromium	3-415ppm	50ppm
Cobalt	3-17ppm	8ppm
Gallium	0.2-12.6ppm	3.5ppm
Iron	0.1-7.07%	1.8%
Lithium	3.6-54.2ppm	11.4ppm
Magnesium	0.04-3.05%	1.14%
Nickel	2-49ppm	15ppm
Niobium	1-65ppm	17ppm
Potassium	0.24-2.85%	1.11%
Rubidium	4.3-81ppm	31ppm
Strontium	60-3022ppm	628ppm
Titanium	0.04-0.79%	0.23%
Vanadium	11-81ppm	40ppm
Yttrium	2-27ppm	12ppm
Zinc	1-178ppm	33ppm
Zirconium	11-885ppm	178ppm

Table 6 Summary of geochemical data presented in Dearnley (1991).

To the west of the Outer Hebrides, many samples contain fragments of amphibolite and plagioclase-amphibolite with grains of hornblende. These are similar in all respects to the typical Lewisian basic orthogneiss of the Outer Hebrides.

Metamorphic source areas are indicated for many sea-bed samples around Shetland, where fragments of hornblende-epidote schist, mica schist and quartzo-feldspathic epidote schist are relatively common.

To the south-east of Orkney and Shetland, the content of basic igneous rocks as lithic fragments is considerably less than found in The Minch. These sands largely comprise hornblende, garnet, pyroxene and opaque oxides. To the south, this assemblage is characterised by increased content of garnet and opaque oxides but a much reduced proportion of hornblende.

Dangerfield and Tulloch (1989) examined a subset of the samples selected by Dearnley between 54°N and 59°N and analysed the heavy mineral content of the fine and very fine sand-grades. The principal minerals in both fractions are magnetite, ilmenite, other opaque iron oxides, garnet, amphibole, biotite and zircon. The minor minerals were grouped as 'minor acid igneous minerals' (tourmaline, monazite, apatite, rutile, and andalusite), and 'minor metamorphic minerals' (epidote, chlorite, kyanite, staurolite and zoisite). They reinforced the conclusion of Dearnley that a 'plume' of material derived principally from basic igneous rocks of the Midland

Valley extends along the coast from the River Forth to Flamborough Head. Magnetite and ilmenite also occurred in relatively high proportions in the Moray Firth. Garnet, amphibole and other minerals derived from metamorphic or acid igneous rocks occur in low concentrations along the coastal zone with higher content in sediments farther offshore, particularly off north-east Scotland.

Baak (1936) studied the transparent heavy minerals in the sea-bed sediments of the southern North Sea. He found that in all parts of the area sediments contained garnet, epidote, and amphibole but was able to divide the sediments into five groups depending on the presence or absence of certain other minerals. Of those that occur within the UK sector, a group lying between Norfolk and Northumbria characterised by the presence of augite were ascribed a northern English or Scottish origin; sands occupying a limited area north-east of Kent characterised by augite and saussurite were thought to be derived from the Rhine. A Tertiary-derived group found in two limited areas off the Essex and Durham coasts were mainly characterised by zircon and rutile and were derived from local Tertiary deposits.

Gravel fraction

Offshore processes which move gravel-grade material are such that the immediate source of gravel on the shelf must be fairly restricted, consisting almost entirely of Pleistocene gravel formations. These include beaches from previous sea levels together with fluvial, glacial, glaciofluvial, proglacial, periglacial and glaciomarine sediments. Source lithologies range from gravels, through sandy gravels, to gravelly sands from which the finest sediment has been winnowed out.

Borley (1923) records a wide range of sedimentary, igneous and metamorphic rock types among the gravel clasts of the southern North Sea sea-bed sediments. Flint is an important constituent. Glacial transport from the north (Scotland or Scandinavia) is the most likely origin for the crystalline rock types although derivation from western sources (Wales or Cumbria) or the local reworking of pebbly Permo-Triassic beds, cannot be ruled out.

Robinson (1968), working off the coast of Lincolnshire, noted that local rock types such as chalk are rare. Flints are more common, being a more durable rock, but do not represent more than 15 per cent of the gravel fraction. The majority of the gravel clasts are far-travelled, and presumably represent glacial erratics. The commonest lithologies appear to be derived from the Palaeozoic of northern England and southern Scotland.

Aluminium

11 GEOCHEMISTRY

Aluminium

Southern North Sea

Al_2O_3 values are generally low in sediments of the southern North Sea with the exception of sands and gravels in the area between Silver Pit and the Outer Silver Pit where Al_2O_3 values average 3.72% and are associated with increased levels of MgO, Fe_2O_3, MnO, P, Zn, and to a lesser extent Cu, Pb and Ni. These sands form part of the Indefatigable Grounds Formation which is a thin (generally 0.2-2.0 m) veneer of gravelly sand and sandy gravel overlying till. The sands have a mean grain size of less than 400 μm.

Muddy sands infill deep depressions in the sea bed, such as Markham's Hole. Here, high Al_2O_3 concentrations (average 6.48%) occur with increased levels of elements of clay mineral association such as B, Li and Rb, in addition to those enhanced in the surrounding gravelly sediments. High Al_2O_3 values occur near the coast between Spurn Head and off the coast of Lincolnshire as found by Nicholson et al. (1985).

Central North Sea

In the central North Sea, the highest Al_2O_3 values occur in areas of muddy sediment extending from the Tees Estuary northwards (average 8.41%). Nearshore, Al_2O_3 is associated with high values of B, Ba, Co, Cr, Cu, Fe_2O_3, K_2O, La, Li, MgO, MnO, Ni, P, Pb, Rb, TiO_2, Y, Zn and Zr. Nicholson et al. (1985) also reported high Al_2O_3 values with a similar element association off the Tyne and Tees estuaries.

Farther offshore Al_2O_3 is decreasingly associated with Co, Fe_2O_3, La, MgO, MnO and TiO_2 in muddy sands within a sea-bed depression known as the Farn Deeps. Al_2O_3 is also high (average 8.47%) over muddy sands in the Gorsethorn Deep where it is associated with increased levels of B, K, Li and Rb.

In the northern part of the region in the Devil's Hole, Marr Bank, and southern Forties sheet areas (Figure 3), Al_2O_3 concentrations in sandy sediments contrast markedly with those of similar sediments in the southern North Sea. Whereas to the south Al_2O_3 values are uniformly low, in the central North Sea they are mainly intermediate to high. Al_2O_3 is commonly associated with high concentrations of TiO_2, and to a lesser extent Cr and Zr in these sediments. This suggests that Al_2O_3 distribution is controlled by heavy minerals in the sand fraction rather than its more usual occurrence in association with elements which concentrate in clay minerals. Element concentrations therefore reflect significant compositional variation between the sands of the central and southern North Sea and may signify changes in sediment provenance.

The map of normalised Al/Li also shows a major change in the geochemistry of sediments across a boundary extending from the Firth of Forth south-eastward to the Dogger Bank/Outer Silver Pit area. This boundary also corresponds to a change in mineralogy of sediments in the North Sea (Dearnley, 1991) and is therefore a significant feature of the region.

The muddy sands of the Devil's Hole do not have significantly different Al_2O_3 concentrations to those of the surrounding sands, which may be attributed to their derivation from underlying pre-Holocene sediments.

Northern North Sea

The extensive area of muddy sediment of the Fladen Ground and Witch Ground basins, and areas of fine-grained sediments in the Moray Firth and the Halibut Bank 1:250 000 sheet area, each have intermediate to high Al_2O_3 concentrations. The highest values occur in the muds of the Witch Ground Basin (average 9.92%) where Al_2O_3 is associated with high concentrations of B, Ba, Cr, Cu, K_2O, Li, MgO, Ni, Rb, TiO_2 and Y. Al_2O_3 values generally decrease with distance from the centre of this basin and, in the more sandy sediments, element associations reflect the composition of heavy minerals. For example, a group of high normalised Al/Li values near the Viking Bank suggests a similarity in mineral composition between the sands of this area and those of the central North Sea north of 56°N.

In the area between Orkney and Shetland Al_2O_3 values are uniformly low (average 0.41% in gravel; 0.69% in gravelly sand) reflecting the predominance of shell debris in these sediments.

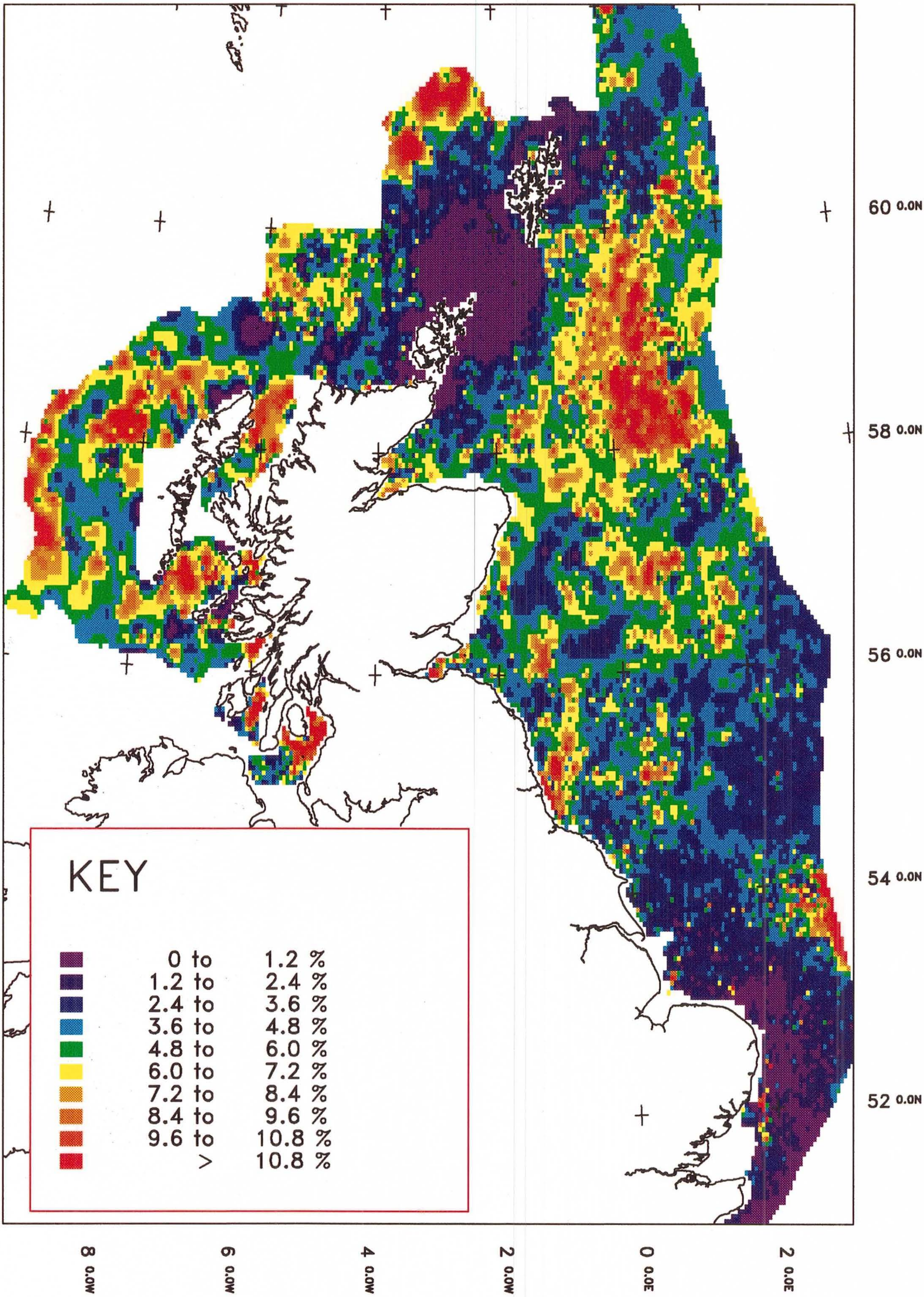
Hebrides and West Shetland shelves

Al_2O_3 values are intermediate to high in most of the sediments in this area, with the exception of sands. The highest values occur in mud along the Geikie Escarpment at the shelfbreak (average 8.55%) where the element association is typical of fine-grained sediments. Intermediate values generally occur in the gravels of the region (average 5.46%) and form noticeably linear patterns extending from the Outer Hebrides and the rock platform offshore. One such group of anomalous Al_2O_3 values extends from west of the Flannan Isles to St Kilda and westward to the shelf edge. The element association in this area has generally high concentrations of Cr, Cu, Fe_2O_3, Ni and TiO_2 which indicates derivation of these sediments from either basic or ultrabasic igneous rocks or possibly metamorphosed igneous rocks.

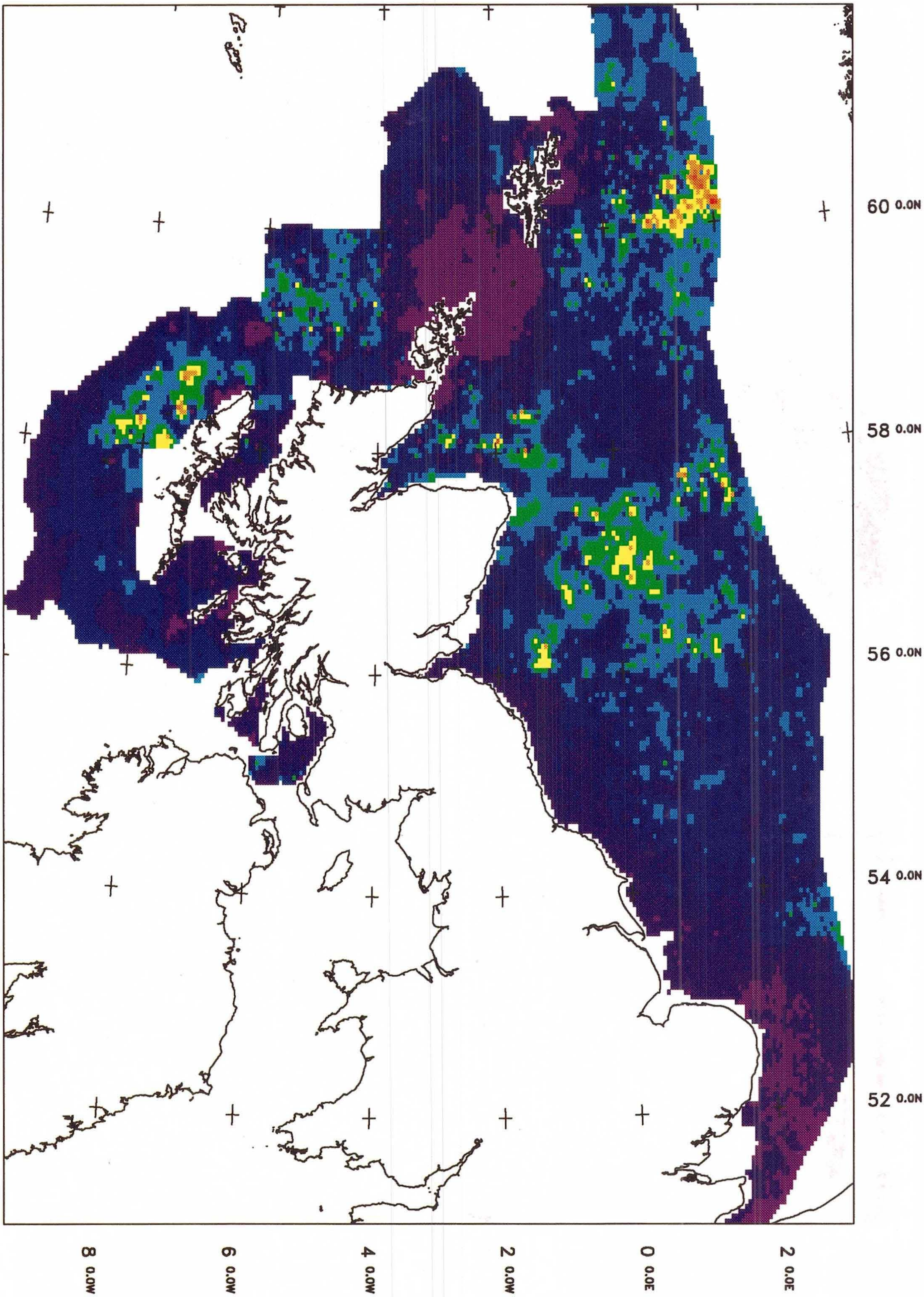
Malin - Hebrides

Al_2O_3 values are generally high in the fine-grained muds and sandy muds of The Minch, Sea of the Hebrides (average 7.98%), Sound of Jura (average 12.3%) and Firth of Clyde (average 11.7%). They are associated with a wide range of increased levels of elements such as B, Ba, Cr, Cu, Fe_2O_3, K_2O, La, Li, MgO, Ni, Pb, Rb, TiO_2 Y, and Zn, which can be attributed to the variety of potential source rocks within the area. These include the Tertiary basic, ultrabasic and granitic rocks of Skye, Mull, and Arran; the basement gneisses of Lewis and the west coast of Scotland; the Moine psammites and pelites of the western Highlands; and in Argyllshire and the Firth of Clyde area, Dalradian schists and Carboniferous sedimentary rocks. High Al_2O_3 values are common in the coarser sediments in the vicinity of Skye which suggests that the Tertiary basic igneous rocks of the island provide the source for much of the sediment in this area.

ALUMINIUM IN SEA-BED SEDIMENT



ALUMINIUM NORMALISED TO LITHIUM



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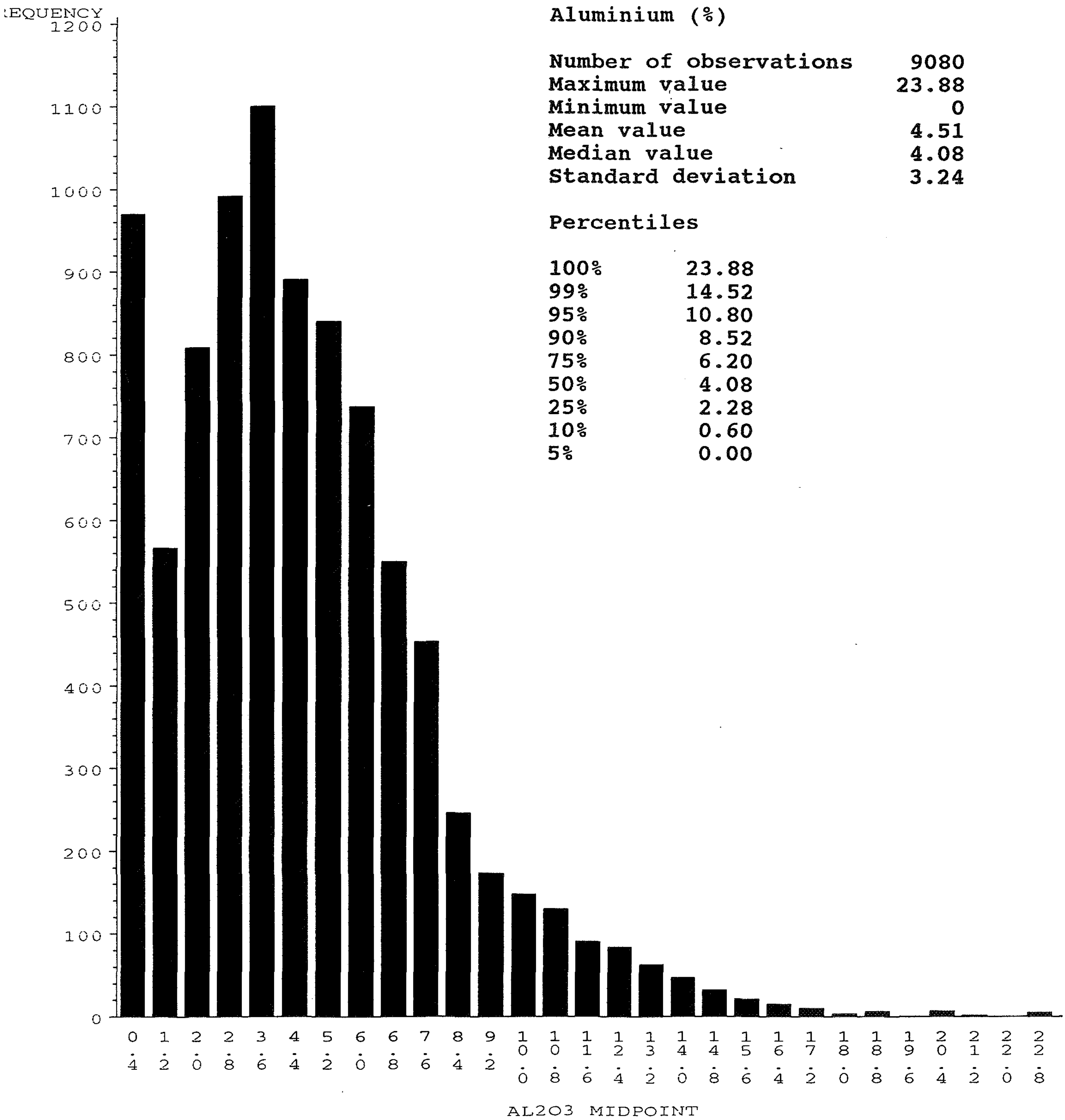


STATISTICS

Aluminium (%)

Number of observations	9080
Maximum value	23.88
Minimum value	0
Mean value	4.51
Median value	4.08
Standard deviation	3.24

Percentiles

100%	23.88
99%	14.52
95%	10.80
90%	8.52
75%	6.20
50%	4.08
25%	2.28
10%	0.60
5%	0.00

Barium

Barium

Southern North Sea

Ba values are generally low in sediments of the southern North Sea with the exception of areas of muddy sediment in the Outer Thames Estuary, Flemish Bight and the Markham's Hole/ Outer Silver Pit area. High Ba concentrations (average 409ppm) also occur in an area of sandy gravels and gravels near the coast of Holderness to the north of Spurn Head, where they are commonly associated with increased values of Fe_2O_3, MnO, Co and Zn which suggests that they are related to co-precipitation with hydrous Fe-Mn oxides. Nicholson et al. (1985) reported a maximum Ba value of 1371ppm in a sample with the highest Zr value recorded from the Humber Estuary. They considered the association with Zr to confirm the likely derivation from the heavy coal trade in the estuary, but noted the common occurrence of 'detrital' elements such as Ba, Zr, Cr and TiO_2 in the sea-bed sediments of the North Sea.

Central North Sea

High Ba concentrations occur in muddy sediment of the Farn Deeps (average 485ppm) and Gorsethorn Deep (average 475ppm). Both areas have high concentrations of elements associated with clay minerals such as Al, B, and Li, however they are relatively low compared to other areas of muddy sediments. In the Farn Deeps, Ba is most strongly correlated with Al_2O_3, K_2O and Rb, whereas in the Gorsethorn Deep, Ba is strongly correlated with Co, La and to a lesser extent Al_2O_3, K_2O, Fe_2O_3 and Ga. Nicholson et al. (1985) found that all significant Ba correlations in the North Sea were with other elements present in fine-grained sediments ie Al, K, Cr and Rb, although none of the correlations were strong, demonstrating the widespread association of Ba with all types of sediment. These authors considered Ba most likely to concentrate in clay minerals as detrital barite.

Ba is comparable with Al_2O_3 in that it is also high in much of the sandy and gravelly sediment of the region. The similarity between maps of normalised Al_2O_3/Li and Ba/Li suggests that the distribution of both elements is largely influenced by the same factors. Anomalous Ba values in coarse-grained sediments can be partly explained by high concentrations of feldspar or other potassium-rich silicates, and the map of Ba normalised to K_2O shows that this is a major influence on Ba distribution. However, the widespread use of barite-based drilling muds in the hydrocarbon industry suggests that some of the highest Ba values may be attributable to dispersion from production platforms. Although these muds are heavy and not thought to be distributed far from drilling rigs, transportation by ship may lead to broader dispersal.

Northern North Sea

Like other elements which concentrate in, or are strongly adsorbed by clay minerals, Ba values are generally intermediate to high over the extensive areas of muddy sediments of the northern North Sea. The strong correlation between Ba, K_2O and Rb and maps of Ba/Li and Ba/K_2O suggest that the muds contain a significant amount of clay minerals derived from potassium-rich (probably due to K-feldspar) rocks, or fine-grained mica. The distribution maps of K_2O and Rb show that these elements are closely correlated with fine-grained sediments. Ba may substitute for K in the interlayer position of illite group minerals (Cronan, 1970), however according to Rankama and Sahama (1950) some Ba may be adsorbed onto clays from seawater and enter into exchange positions. In some areas, the abundance of shell debris may be a contributory source of Ba (Cronan, 1970), however the carbonate-rich sediments of the Orkney-Shetland Platform have relatively low Ba concentrations (average 91ppm).

Ba values are generally high in the fine-grained sediments of the Moray Firth (average 484ppm), where they are associated with high concentrations of K_2O, Rb, and Y and therefore may be due to clay minerals derived from feldspathic rocks. A similar association of elements occurs in coarser sediments to the north which supports the suggestion that feldspar is one of the main constituents of the sediments in the Moray Firth.

Hebrides and west Shetland Shelves

High Ba values occur in areas of sandy and gravelly sediments to the north-west of Lewis. These sediments are not commonly associated with any other trace element although high Al_2O_3 values occur in many of the samples. Fe_2O_3 and MnO values are also generally low in this area therefore the high Ba values cannot be explained by the occurrence of clay minerals or co-precipitation with secondary hydroxides. The most probable influence on the geochemistry of these sediments is the composition of lithic fragments or heavy minerals derived from granulitic gneisses of north Lewis. A narrow range of Ba values (350-600ppm) in stream sediments derived from Lewisian gneiss of the Outer Hebrides has been reported, but rocks have higher concentrations (average 790ppm in grey gneiss; Institute of Geological Sciences, 1983). High Ba values over gravelly sediments north-east of Rona may also be indicative of provenance.

Intermediate Ba values are associated with the muddy sediments along the edge of the shelf (average 383ppm). South-west of Barra, background levels of Ba associated with Al_2O_3, Cr, Fe_2O_3, Ni, MgO, MnO and TiO_2, are evidence of precipitation of Fe and Mn hydroxides, and heavy mineral concentrations in predominantly sandy and gravelly sediments in shallow water near Stanton Banks.

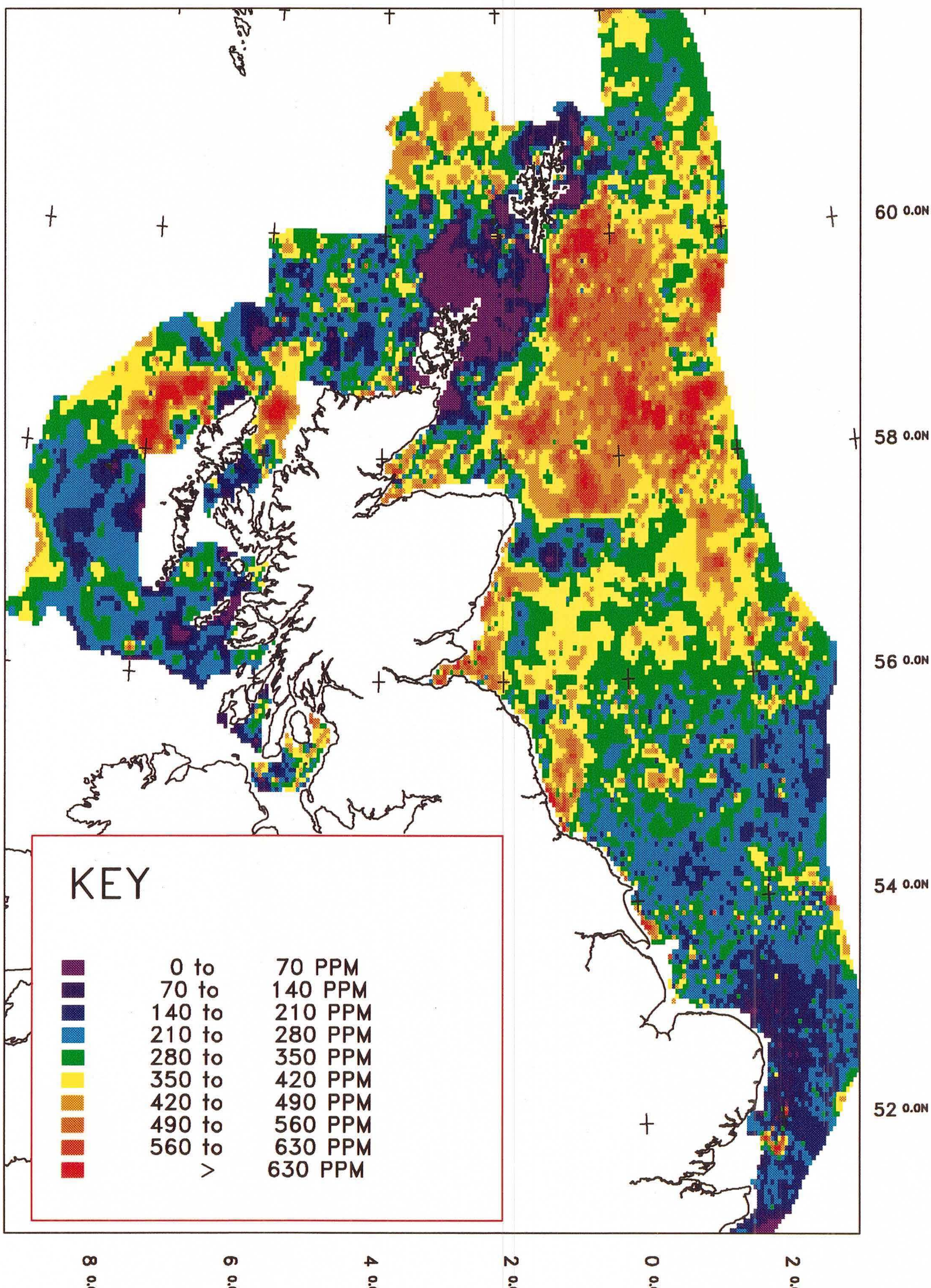
Malin - Hebrides

High Ba values occur in the northern Minch where they are associated with fine-grained sediments and elements of clay-mineral association. Ba concentrations decrease southward in The Minch in muddy sediments around Skye then increase to high levels between Tiree and Barra. This pattern, and the localised occurrence of high

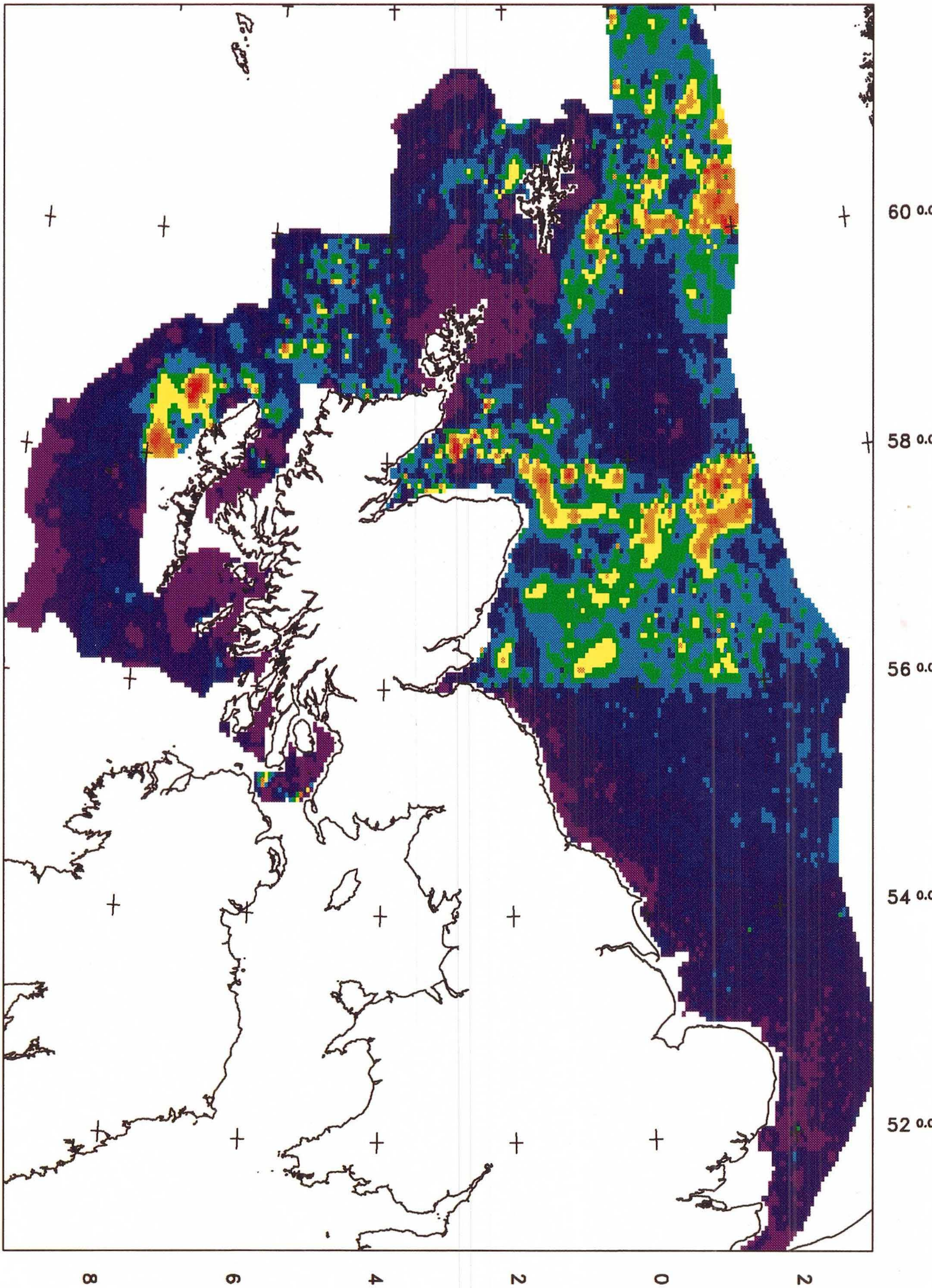
Ba values north-west of Lewis mentioned above, suggest that Ba is a good indicator of marine sediments derived principally from Lewisian, Moine or Torridonian rocks, in contrast to those from mainly basic igneous rocks around most of Skye. Ba concentrations are also high in the muddy sediments of the Firth of Clyde (average 509ppm).

In gravels and sands to the south of the Mull of Kintyre, where Ba values average 348ppm, Ba is most strongly correlated with K and Pb, and is negatively correlated with Mn. Although Mn values are also high in this area, the correlation indicates that Ba occurs in K-bearing minerals such as feldspar in the lithic gravel fraction of the predominantly shelly gravels.

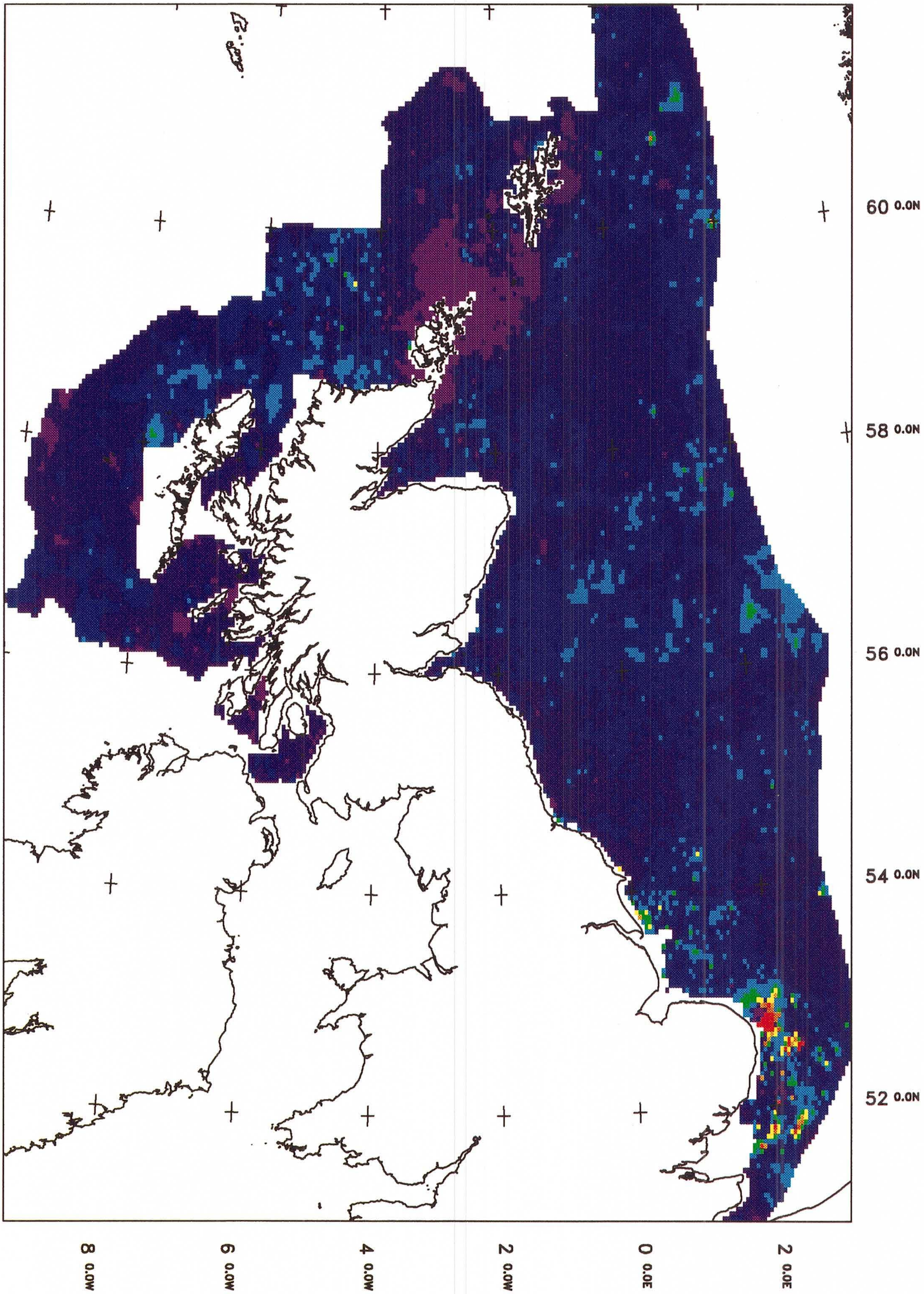
BARIUM IN SEA-BED SEDIMENT



BARIUM NORMALISED TO LITHIUM



BARIUM NORMALISED TO POTASSIUM



BARIUM

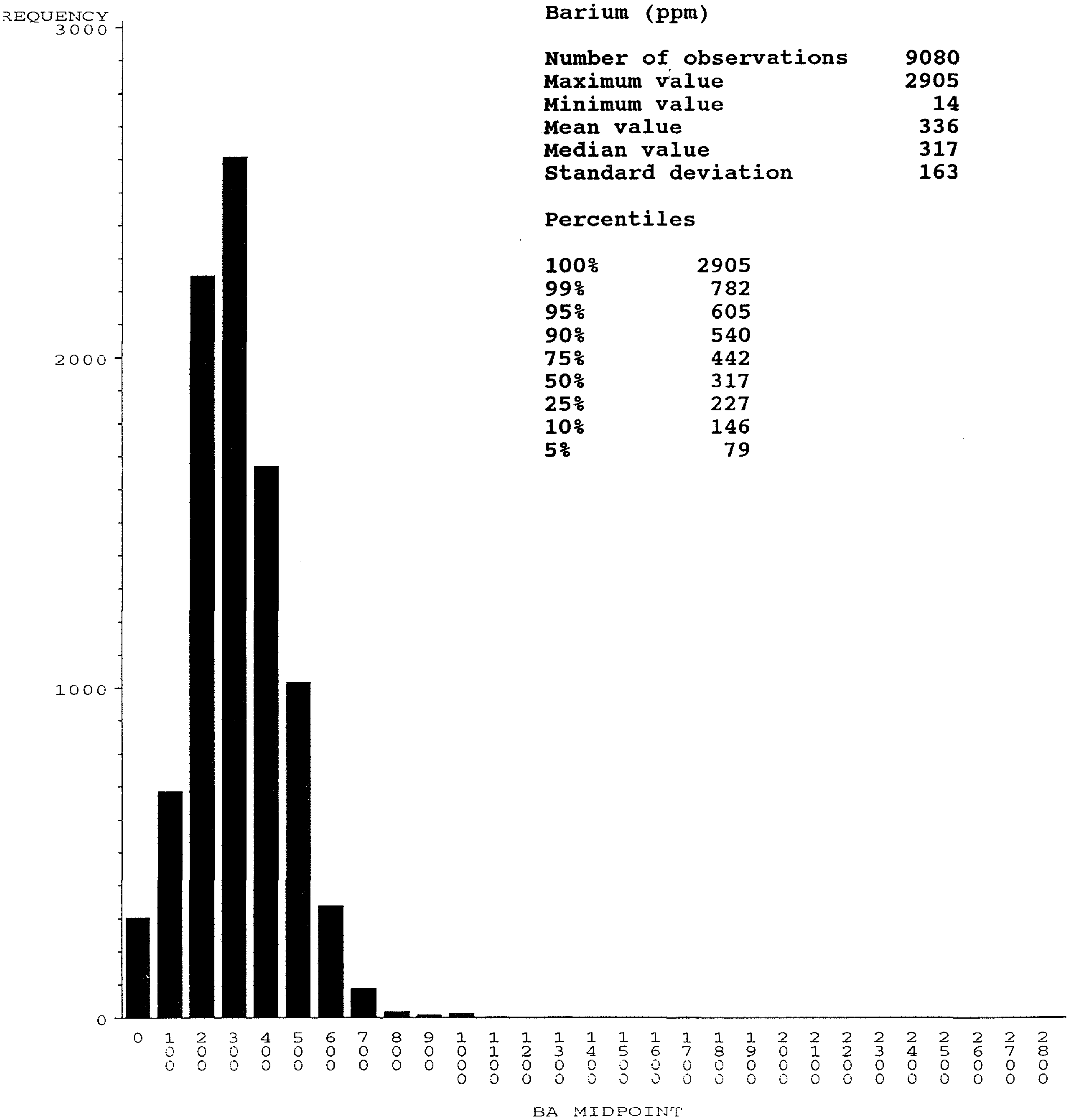
STATISTICS

Barium (ppm)

Number of observations	9080
Maximum value	2905
Minimum value	14
Mean value	336
Median value	317
Standard deviation	163

Percentiles

100%	2905
99%	782
95%	605
90%	540
75%	442
50%	317
25%	227
10%	146
5%	79



Beryllium

Beryllium

Be shows a very restricted concentration range, many (approximately 25 per cent) of the values occurring below the practical limits of detection (0.3-0.5ppm).

Southern North Sea

Be values are generally intermediate or low reflecting the predominantly sandy and gravelly composition of sea-bed sediments in this area. Higher concentrations occur in sands from the deeper waters of the Southern Bight (average 0.89ppm compared to an overall average of 0.7ppm for sands in the area). Be is not strongly associated with other elements, however weak positive correlations with Al_2O_3, Ba, K_2O, La and Rb suggests that these sands may contain a higher interstitial mud content than sands elsewhere. High Be values occur in muddy sediments in the Outer Thames Estuary (average 1.2ppm); near the coast of East Anglia (average 1.5ppm); the Flemish Bight and in the vicinity of Markham's Hole/Outer Silver Pit (average 1.1ppm). The last area is also characterised by high levels of Be and elements such as Cr, TiO_2 and Zr in coarse-grained sediments which implies that Be may be present in detrital minerals. The only significant correlation between Be and other elements reported by Nicholson et al. (1985) was a weak positive correlation between Be and La in samples from the North Sea. These authors concluded that high Be values near the coast of southern England may be due to derivation from iron-rich strata.

Central North Sea

The highest Be concentrations occur in muddy sands including those in the Firth of Forth (average 2.1ppm), north of the Tees Estuary (average 1.7ppm) and the Farn Deeps (average 1.5ppm). Occurring predominantly with elements of clay mineral association, the high levels of Be found in these sediments may reflect derivation from Carboniferous sedimentary sequences containing coals or, in the Tyne-Tees area in particular, from colliery waste dumped offshore. Mining and industrial activities in the catchment areas of these rivers may also have contributed to the mobilisation of Be (British Geological Survey, 1993). Farther offshore, groups of high Be values occur throughout the area of sandy sediments. Dearnley (1991) reported Be values up to 3.2ppm in sands characterised by a garnet/opaque oxide assemblage. Petrographic studies (Dangerfield and Tulloch, 1989) revealed that sandy sediments from the central North Sea contained particularly high proportions of minerals derived from an acid igneous source (tourmaline, monazite, zircon). Be, like rare earth elements, B and Zr, behaves incompatibly in igneous processes and is thus likely to concentrate in the weathering products of granites.

High Be values are also associated with muddy sands in the Gorsethorn Deep (average 1.2ppm) and Devil's Hole area (average 1.0ppm). The map of normalised Be/Li shows that high values in the central and southern North

Sea occur in areas with high Cr/Li, TiO_2/Li and Zr/Li ratios, supporting the suggestion that Be distribution is controlled by detrital mineral content rather than clay minerals. High normalised Be/Li values in sands to the north of 60°N imply a similar control.

Northern North Sea

In the northern North Sea, as elsewhere, high Be values are associated with fine-grained sediments such as those in the nearshore areas of the east coast of Scotland, including the Moray Firth (0.8ppm). High Be concentrations also occur farther offshore in the muddy sediments of the Fladen Ground/ Witch Ground basins (average 0.9ppm in muddy sands; 1.2 ppm in muds), and the Halibut Bank area to the north (average 1.0ppm). A group of high Be values in sands and gravelly sands extending north-east from the coast at Peterhead may be evidence of a high concentration of mica in these sediments, probably derived by weathering of granites in the north-east of Scotland. Dangerfield and Tulloch (1989) reported biotite contents between 8.1 and 60 per cent in the fine-grained fraction of sands from this area.

Be concentrations are low in the carbonate-rich gravels between Orkney and Shetland (average 0.1ppm).

Hebrides and West Shetland Shelves

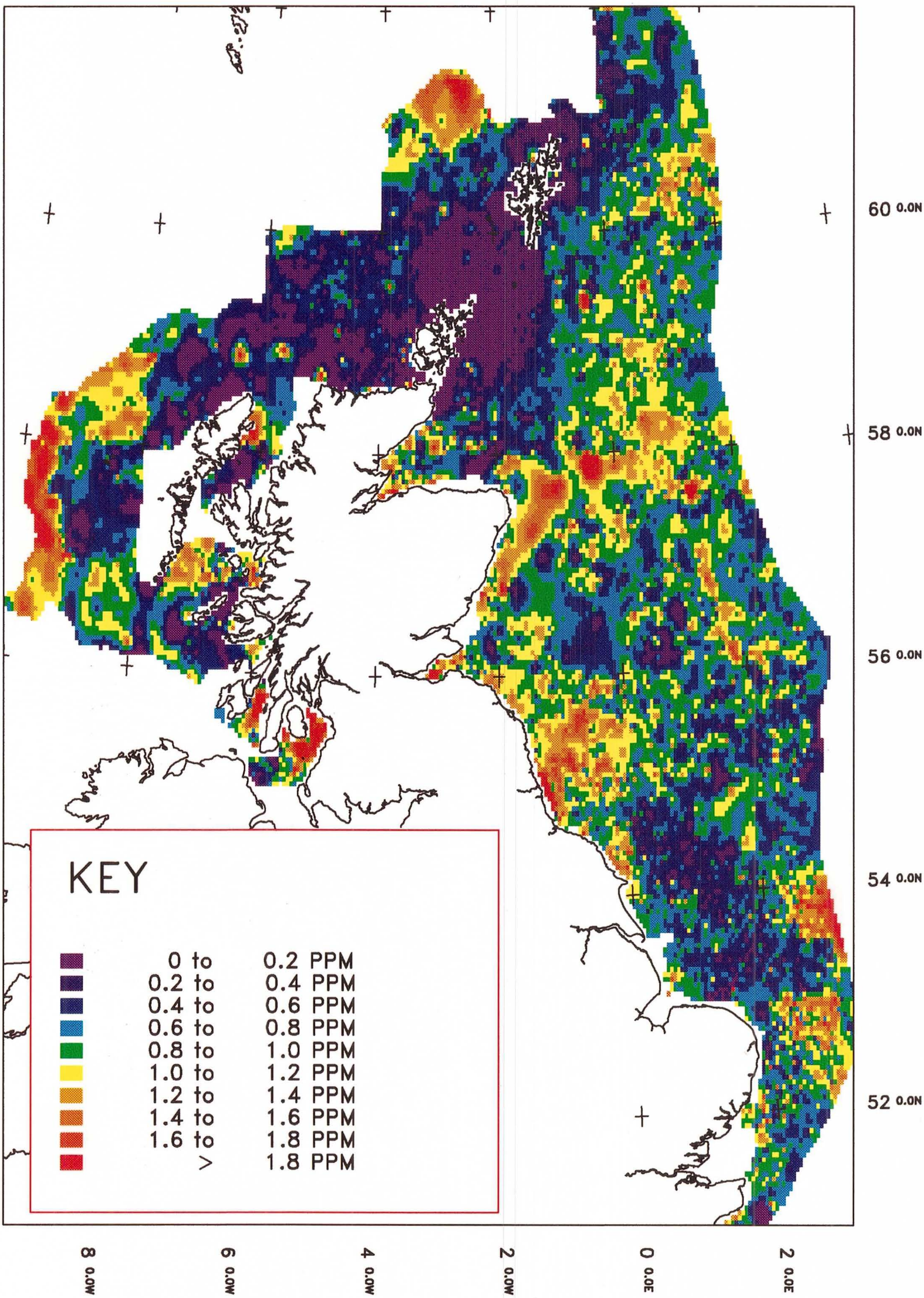
Be values are generally low throughout most of the outer shelf with the exception of fine-grained sediments at the shelfbreak. Be concentrations along the shelfbreak average 1.0ppm north of Rona, to 1.3ppm at the edge of the Hebrides Shelf.

Malin - Hebrides

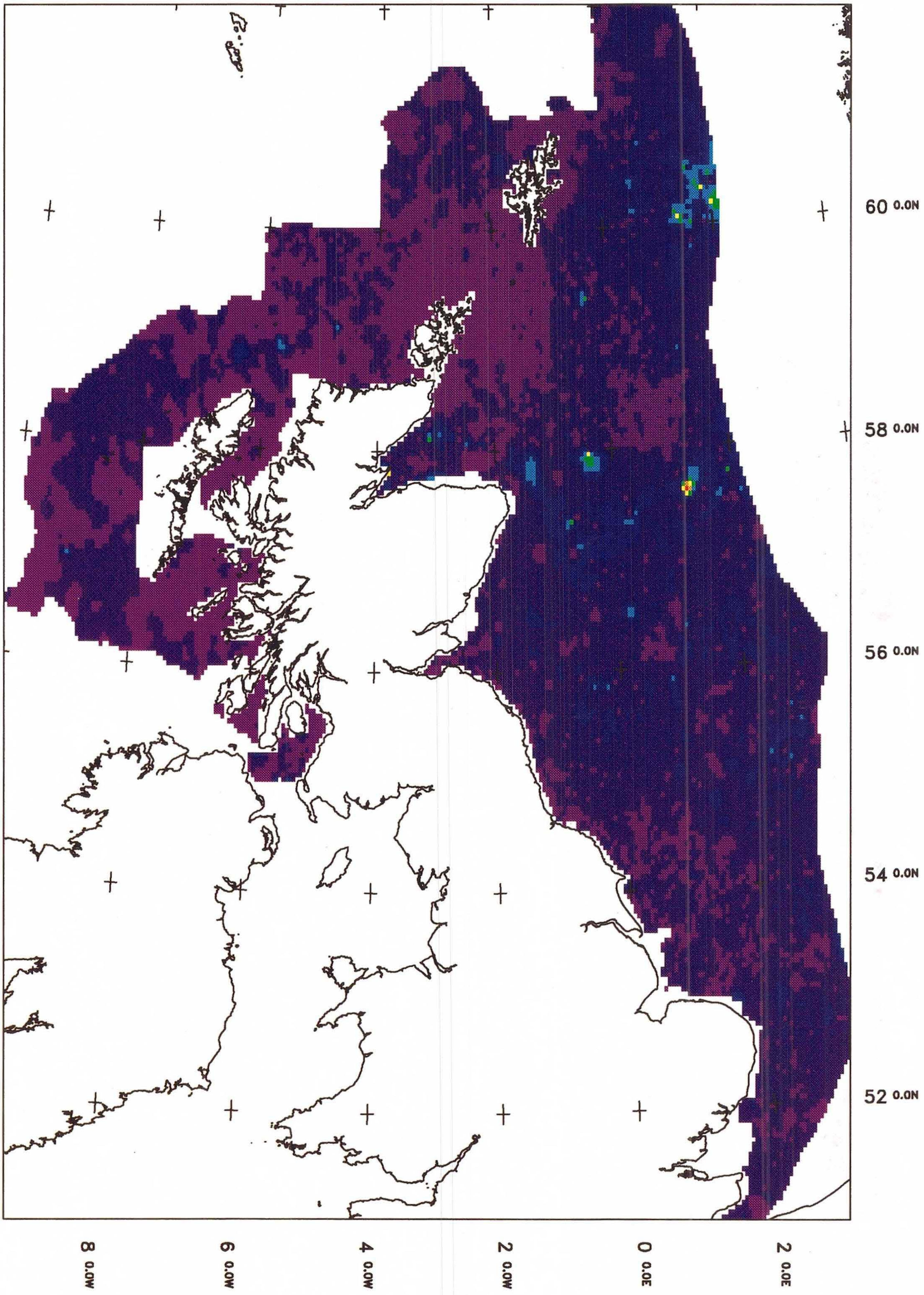
The highest Be concentrations in this area occur in the fine-grained sediments of the Firth of Clyde (average 1.9ppm). Like the area offshore of the Tyne-Tees estuaries this may reflect argillaceous sediments and coals in Carboniferous sedimentary rocks from which the sea-bed sediments and underlying Pleistocene deposits are partly derived, although high organic or clay contents would give a similar pattern.

Elsewhere, Be values are generally low with the exception of three areas of fine-grained sediments near Stornoway; north-west of Coll and Tiree; and in the Sound of Jura (average 1.7ppm). As these are predominantly sandy muds or muds, Be occurs mainly in clay minerals, although high Be concentrations may also be evidence of a relatively high mica content. In the Sound of Jura, this would be consistent with derivation from micaceous schists of the Dalradian Supergroup in Argyllshire, where phyllites and quartzites have been shown to have high Be concentrations (4-7ppm; British Geological Survey, 1993).

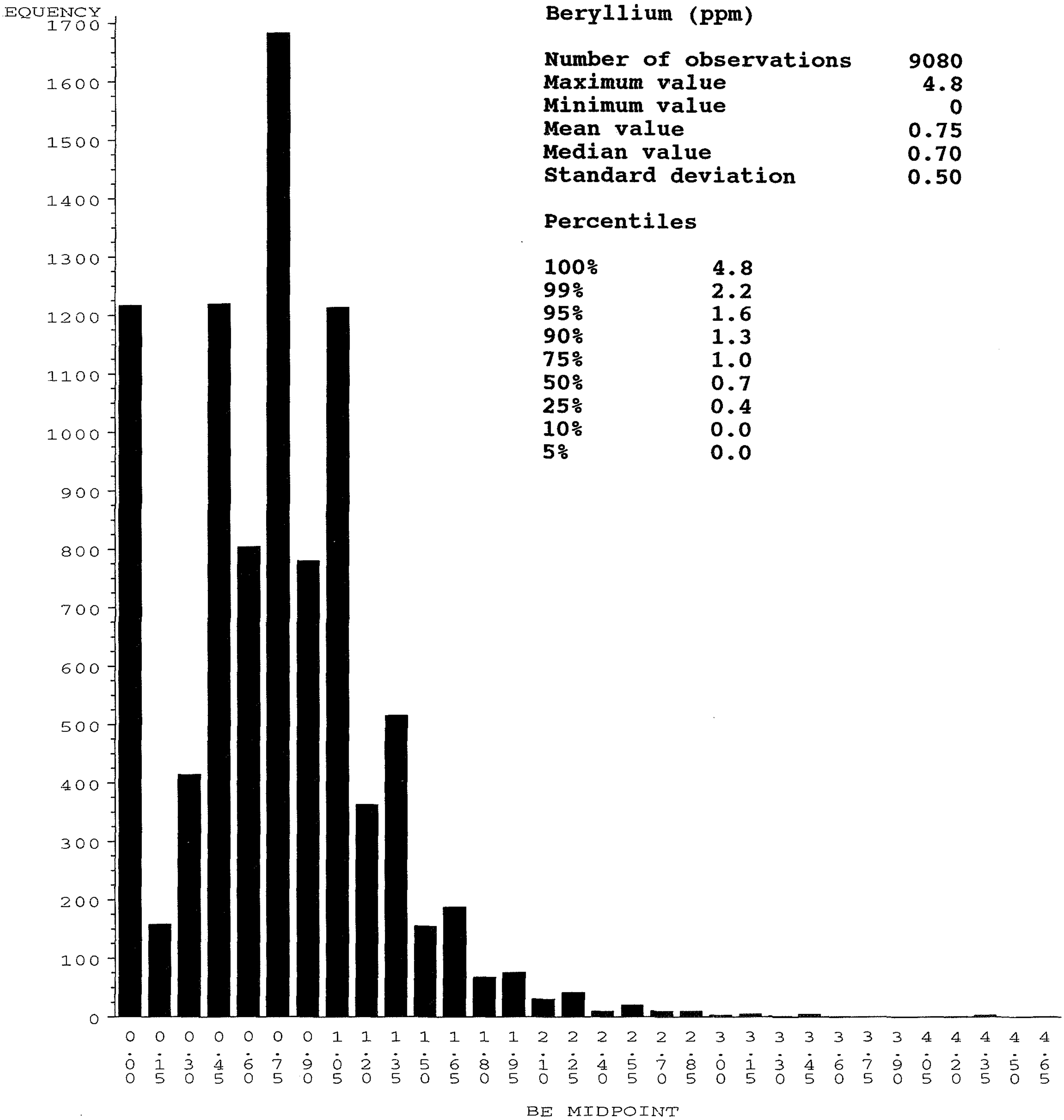
BERYLLIUM IN SEA-BED SEDIMENT



BERYLLIUM NORMALISED TO LITHIUM



BERYLLIUM



STATISTICS

Beryllium (ppm)

Number of observations	**9080**
Maximum value	**4.8**
Minimum value	**0**
Mean value	**0.75**
Median value	**0.70**
Standard deviation	**0.50**

Percentiles

100%	**4.8**
99%	**2.2**
95%	**1.6**
90%	**1.3**
75%	**1.0**
50%	**0.7**
25%	**0.4**
10%	**0.0**
5%	**0.0**

Bismuth

Bismuth

Bi is found mainly in metalliferous minerals such as galena and bismuthinite and occurs in common rock-forming minerals only as a trace constituent. Bi, being closer in ionic size to Pb than Fe or Zn, substitutes primarily in galena rather than pyrite or sphalerite. In silicates there is possibility that Bi substitutes for Ca therefore it may be expected to be enriched in plagioclase rocks (e.g. basalts) rather than acid rocks. It is also possible that Bi substitutes for Ca in the mineral apatite. The Bi content of the common silicate minerals is expected to be less than 1 ppm. As the ionic radius of Bi is close to that of some of the rare earth elements, particularly Y some degree of covariation may exist between these elements. Very little data is available for Bi in sedimentary rocks although a wide spread of concentrations has been recorded for arenaceous rocks. A distinct enrichment is noted in organic-rich sediments such as coal and black shales. Ash deposits derived from coal burning may contain particularly high Bi concentrations.

Nicholson et al. (1985) found that virtually all of their Bi results were below the detection limit and therefore no satisfactory distribution map could be generated. They found a weak positive correlation with elements found in clay minerals and the heavy metals, and the highest concentrations of Bi in or near the east coast estuaries in all types of sediment.

In this study, Bi values are also mostly below the analytical detection limit however, groups of slightly higher values can be identified on the distribution map. Appendix 1 gives average Bi values in areas of muddy, gravelly and sandy sediment and show that in only two areas of muddy sediment, between the Tyne and Tees estuaries, and in the Firth of Clyde, are there significantly high Bi values. There are no strong regional correlations between Bi and other elements in these areas, however investigation of individual high values show some interesting patterns.

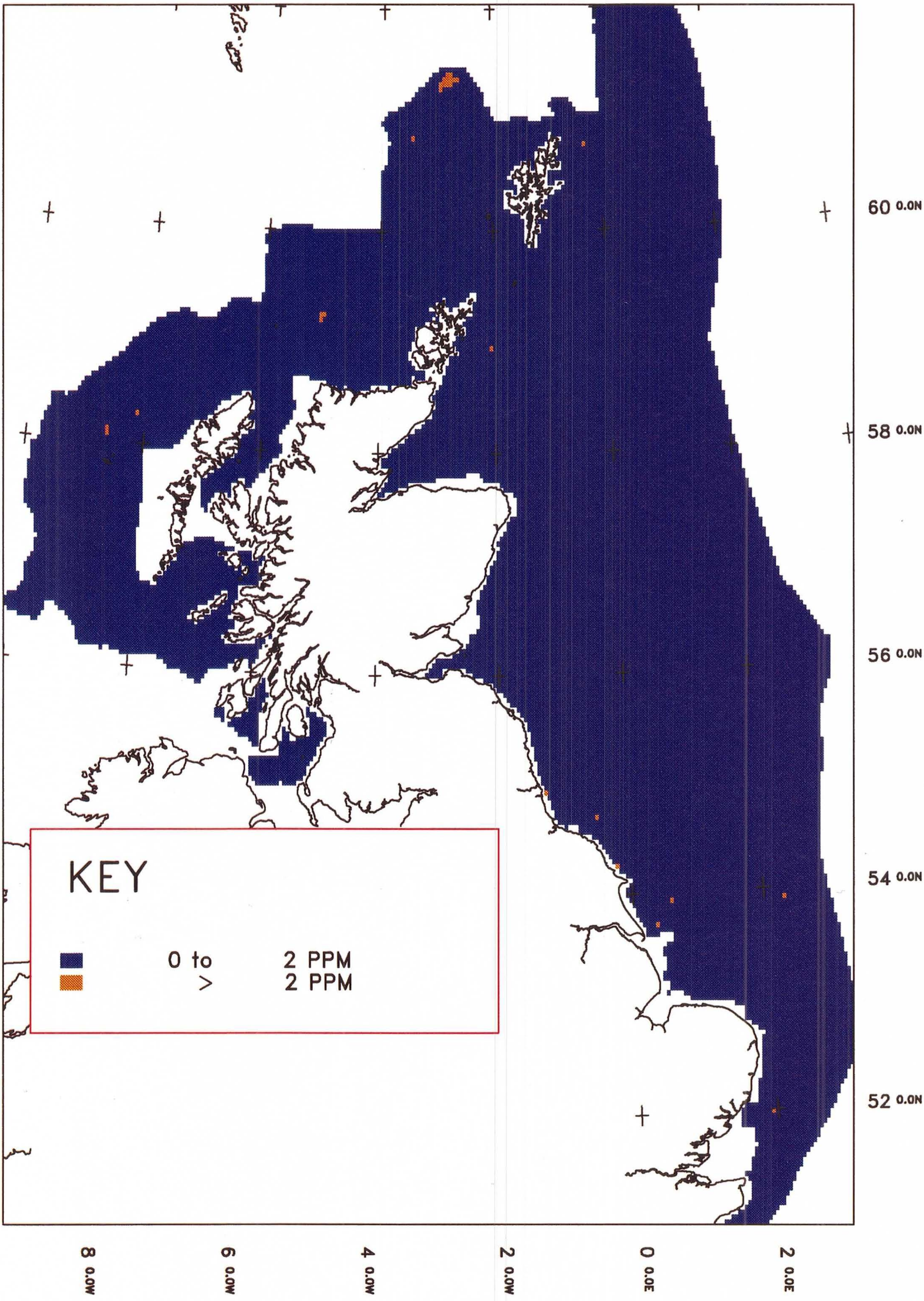
In the central and southern North Sea, high Bi values (up to 8ppm) are always associated with high concentrations of Pb (up to 109ppm) and Zn (up to 500ppm). The location of most of these samples close to the coast and near the estuaries of the Thames, Humber, Tyne and Tees suggests that these are entirely due to contamination, although off north-east England it is possible that these are related to estuarine discharged epigenetic ore minerals and their smelting products from the Pennine Orefield.

The highest Bi value recorded (17ppm) occurs to the west of Orkney. A Ca interference correction has been applied to the Bi data (see Section 3) and samples in this area have generally high CaO levels which tend to obscure the natural Bi distribution pattern. However, the high Bi in this particular sample is unexplained as it is not strongly associated with other elements and has a CaO value slightly below the threshold for Ca correction.

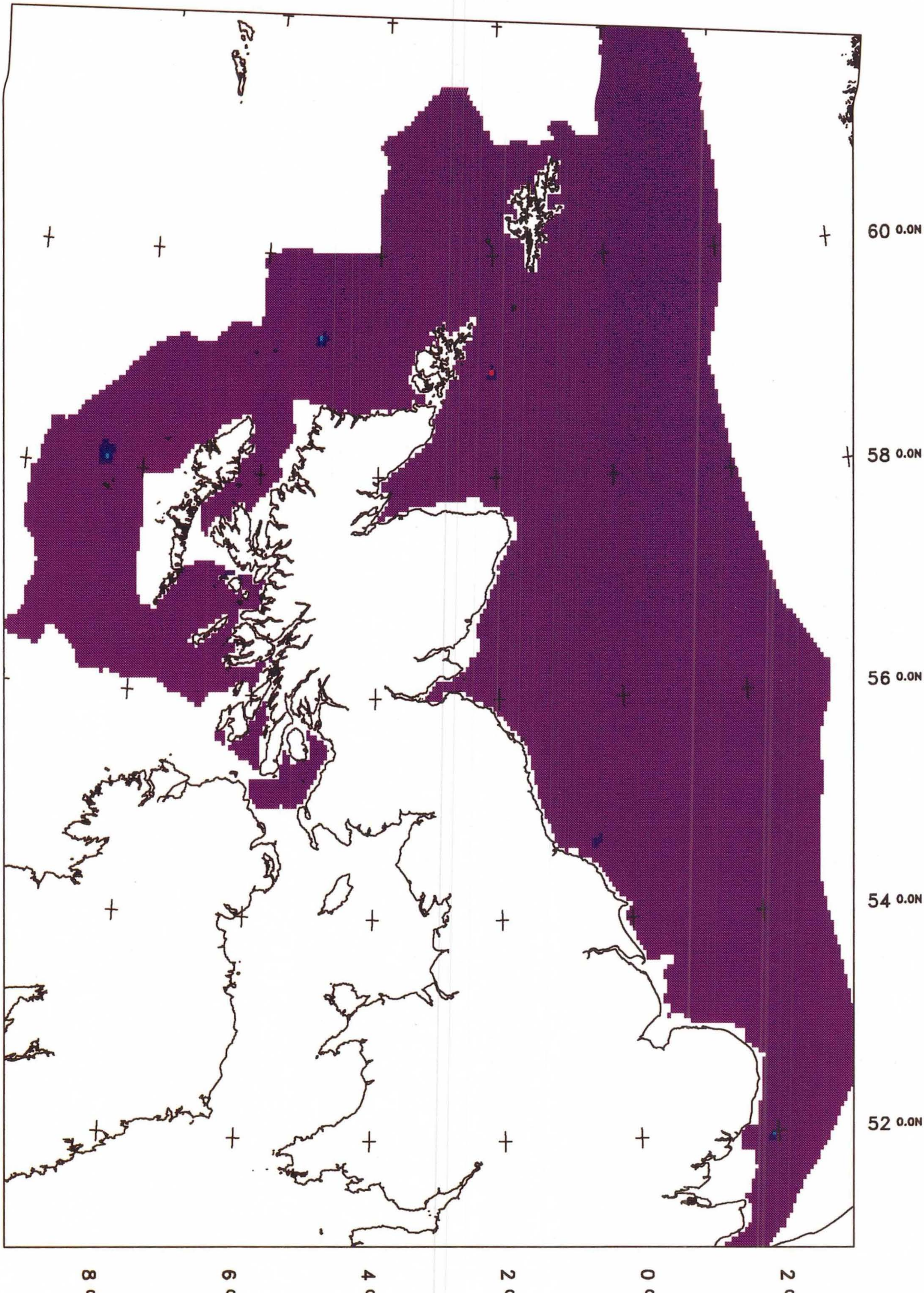
On the Hebrides and West Shetland shelves, three areas of high Bi values occur. The area due north of Cape Wrath can be explained by a similar factor to that of the sample west of Orkney discussed above. The group of high Bi values (up to 8ppm) near the shelfbreak north-west of Shetland and to the north of St Kilda both occur in areas of high Cu, Pb and Zn and are particularly conspicuous on maps of normalised Cu/Li and Zn/Li. The more northerly area consists of muddy sediments with regionally high levels of most trace elements, however the samples with high Bi concentrations have Cu and Zn values above the 99th percentile value for each element. Concentrations of these elements are also considerably higher than average values in fine-grained sediments at the shelfbreak farther south (Appendix 1). Although this may be related to variations in source-rock geochemistry, the absence of high Bi values elsewhere on the shelf, and the high normalisation ratios suggest that there are contaminants present in these sediments, although the possible source is unknown.

The group of samples north of St Kilda occur in sand and gravelly sand. This area also shows regional enhancement of several of the transition metals, which can be explained by the concentration of heavy minerals in the coarse-grained fraction of the sediments (see Titanium Section). However, one sample with high Bi concentration also has a Zn value of 238ppm, considerably higher than the regional average. As previously mentioned, this area is distinguished by high normalised Zn/Li and Cu/Li data suggesting possible contamination. Proximity to the island of St Kilda, used to monitor the testing of missiles fired from the Outer Hebrides, may explain the source of these anomalies.

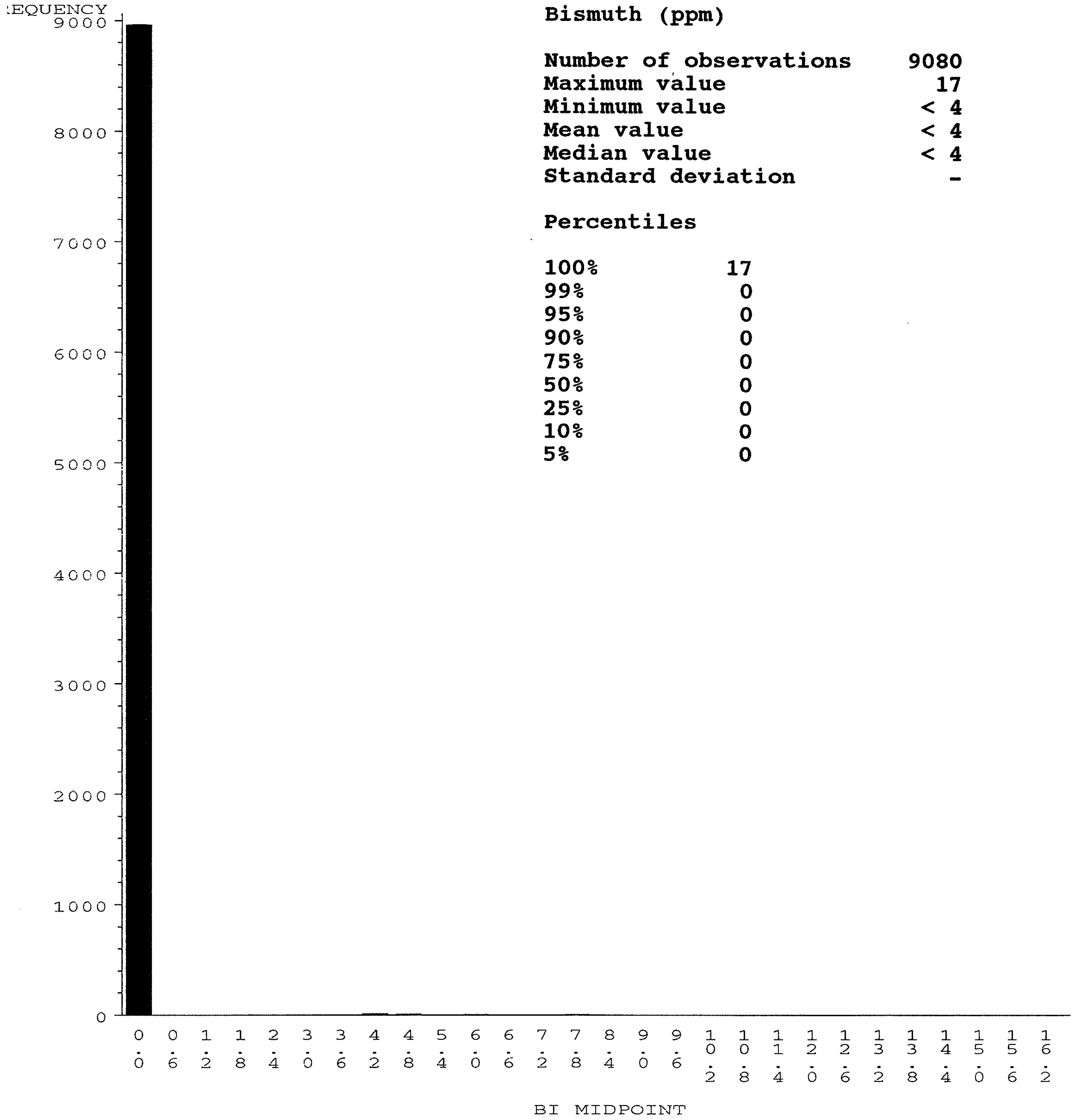
BISMUTH IN SEA-BED SEDIMENT



BISMUTH NORMALISED TO LITHIUM



BISMUTH



STATISTICS

Bismuth (ppm)

Number of observations	**9080**
Maximum value	**17**
Minimum value	**< 4**
Mean value	**< 4**
Median value	**< 4**
Standard deviation	**-**

Percentiles

100%	**17**
99%	**0**
95%	**0**
90%	**0**
75%	**0**
50%	**0**
25%	**0**
10%	**0**
5%	**0**

Boron

Boron

Southern North Sea

B values are generally low in the sands and gravels of the area (average 31ppm and 26ppm respectively). Groups of high values are associated with muddy sediments in the Outer Thames Estuary (average 65ppm) and offshore of the estuaries of the rivers Stour and Orwell (average 63ppm), where they correlate with other elements of clay mineral association. Intermediate levels occur in the fine-grained sediments of the Markham's Hole/Outer Silver Pit area (average 44ppm), and in areas where coastal erosion supplies sediment to the marine environment, such as near the coast of Holderness and offshore of Skegness (average 52ppm).

Nicholson et al (1985) attributed the high levels of B found in the North Sea to minerals such as tourmaline and glauconite which are common constituents of marine sediments, noting that glauconite is being formed in some areas of the sea bed at the present time.

Central North Sea

High B values occur in muddy sediments near the coast between Spurn Head and St Abb's Head and in the Firth of Forth (average 162ppm). The occurrence of high B values in all sediment types in the coastal zone (e.g average B concentration offshore of the Tyne-Tees estuaries in gravel - 51ppm; mud - 49ppm) indicates that clay minerals are uniformly distributed throughout the area, including the pore spaces in coarse-grained sediments. In the areas of highest B concentrations such as in the Firth of Forth and offshore of the Tyne-Tees estuaries, B may also be adsorbed on organic matter. Farther offshore, to the north and east of the Tyne, intermediate to high B values reflect the occurrence of fine-grained sediments in depressions in the sea bed such as the Farn Deeps (average 69ppm), Swallow Pit, Gorsethorn Deep (average 45ppm) and the Outer Silver Pit. The muddy sediments of the Devil's Hole area have similar B levels (average 49ppm).

Intermediate values in sands (average 32ppm) and gravelly sands (average 31ppm) on Dogger Bank are comparable with sandy sediments elsewhere (Appendix 1). However, the normalised map of B/Li shows B enrichment in this area unrelated to grain size factors. Elements such as Cr, Zr and TiO_2 indicate that the sediments in this area contain a high proportion of minerals resistant to weathering; B enrichment may therefore indicate the presence of B-carrying minerals such as tourmaline. A similar process may account for the high B/Li ratios in sands near the Scottish coast east of Peterhead.

Northern North Sea

Comparison of the B distribution map with the sea-bed sediment map presented in Figure 5, shows that intermediate to high B values accurately define all areas of fine-grained sediment in this region. These include the Witch Ground and Fladen Ground basins (average 90ppm in muds); Bressay Bank; and in areas around the Bergen and Viking Banks (average 40ppm). Of the clay minerals, B is mainly incorporated into illite either in the crystal lattice or by sorption. The high levels in the fine-grained sediments of the North Sea in general suggest that illite is the principal clay mineral component of these sediments. B values may be further enhanced in the Fladen Ground by adsorption on organic matter (see Section 9).

The coarse-grained sediments of the area generally have low to intermediate B levels (Appendix 1), however normalised B/Li values show that sandy sediments south of Viking Bank and east of Bressay Bank, are enriched in B. B is not strongly correlated with other elements in any of these areas and, like the coarse-grained sediments farther south on Dogger Bank, B enrichment may indicate high concentrations of minerals such as tourmaline or mica. The lowest B values on the shelf occur in the carbonate-rich gravelly and sandy sediments of the Orkney-Shetland Platform.

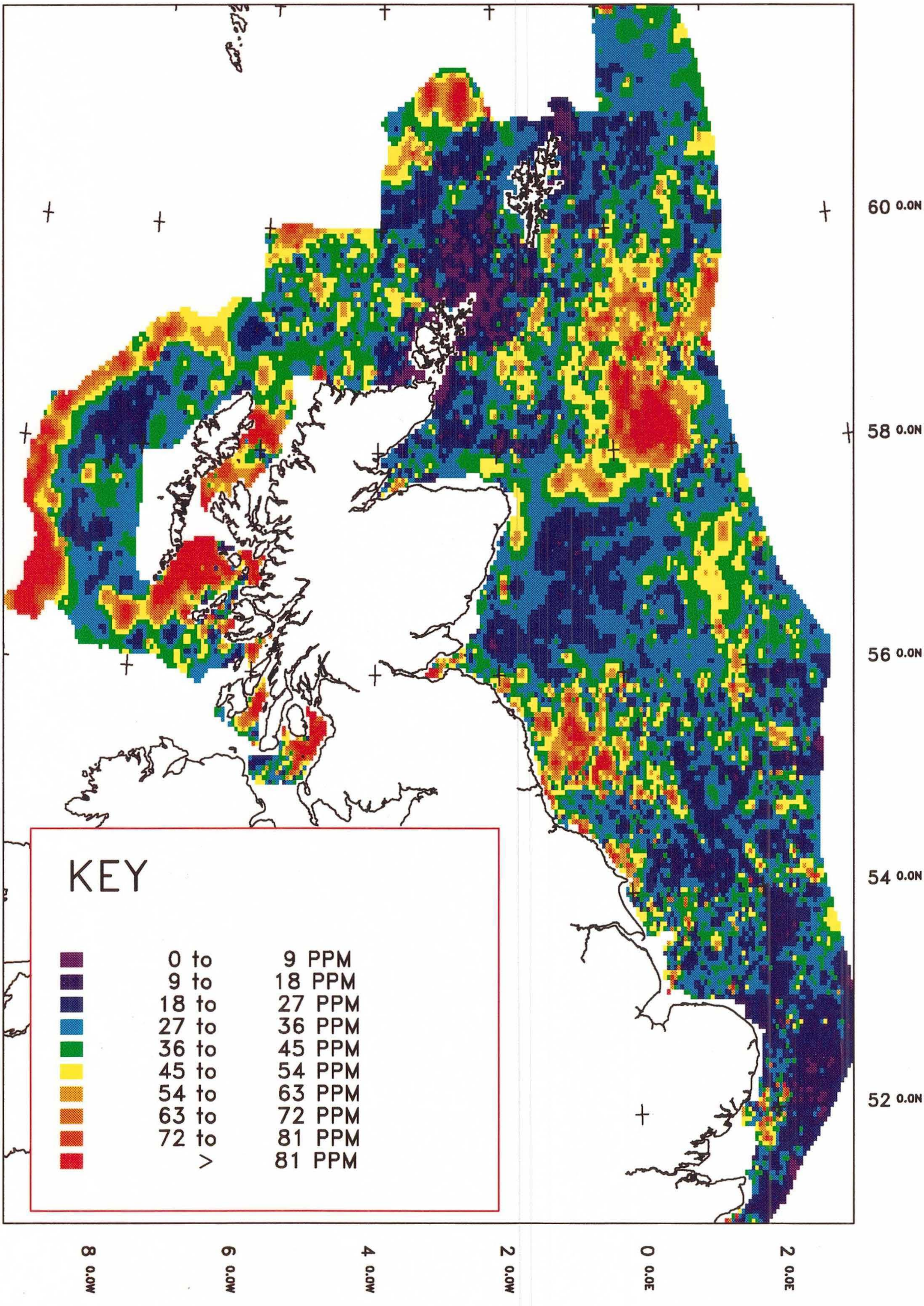
Hebrides and West Shetland shelves

B concentrations are generally low to intermediate on the West Shetland Shelf with similar average values in gravel (39ppm), gravelly sand (41ppm), and sand (39ppm). The highest values in the area occur in muddy sediments at the shelfbreak (average 72ppm north-west of Shetland; average 76ppm west of the Outer Hebrides). Gravel, gravelly sands, and sands on the Hebrides Shelf have comparable B concentrations to those farther north on the West Shetland Shelf (average 31ppm, 31ppm and 35ppm respectively).

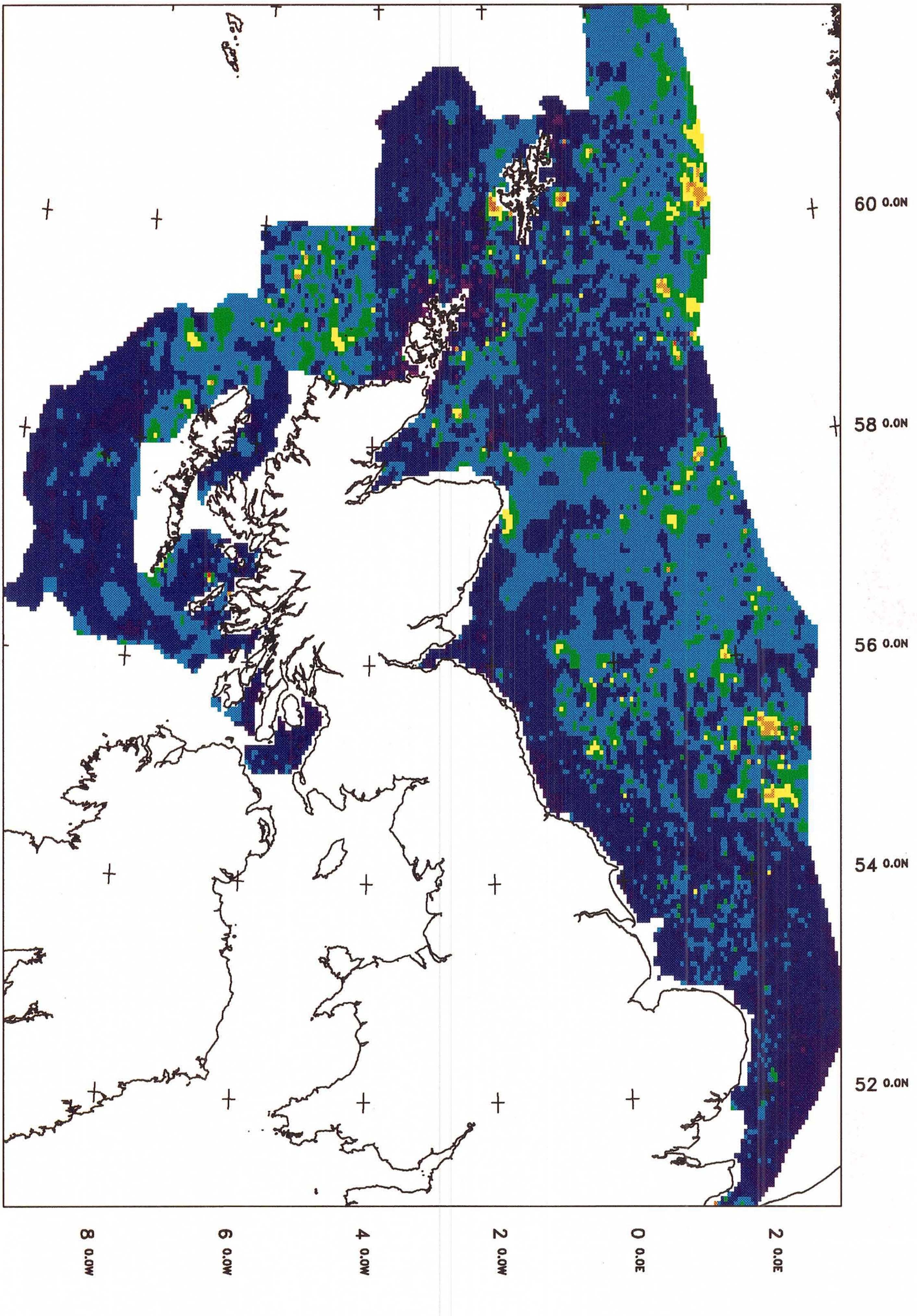
Malin-Hebrides

High B concentrations in The Minch and Sea of the Hebrides (average 83ppm), Sound of Jura (average 91ppm) and Firth of Clyde (average 87ppm), reflect the predominantly clay-rich nature of the fine-grained sediments of the region, as indicated by the normalised data. Low to intermediate values occur in sands in The Minch/Sea of the Hebrides (average 41ppm) and Firth of Clyde (average 38ppm), and in gravels in the North Channel south of the Kintyre Peninsula (average 28ppm).

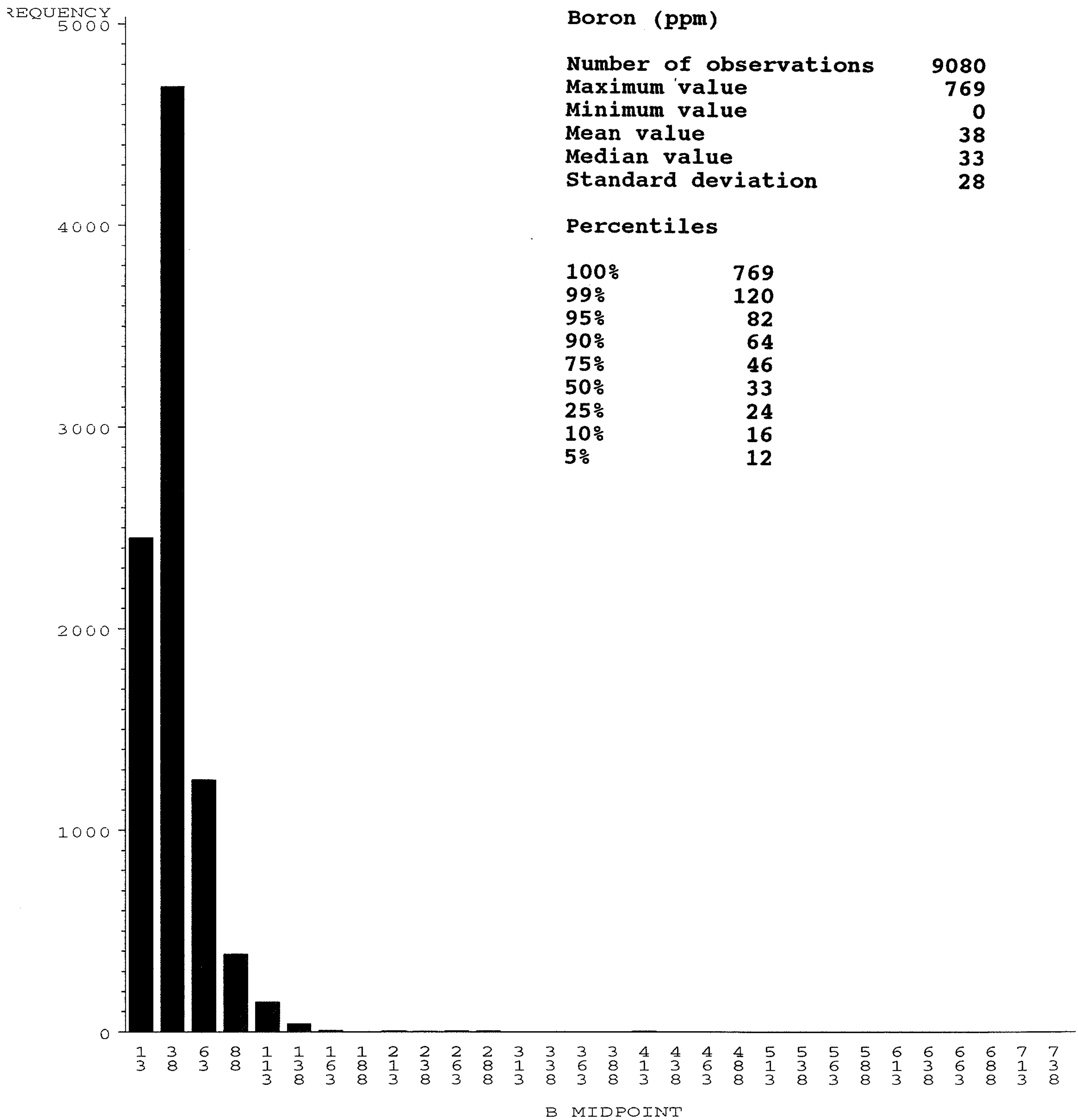
BORON IN SEA-BED SEDIMENT



BORON NORMALISED TO LITHIUM



BORON



STATISTICS

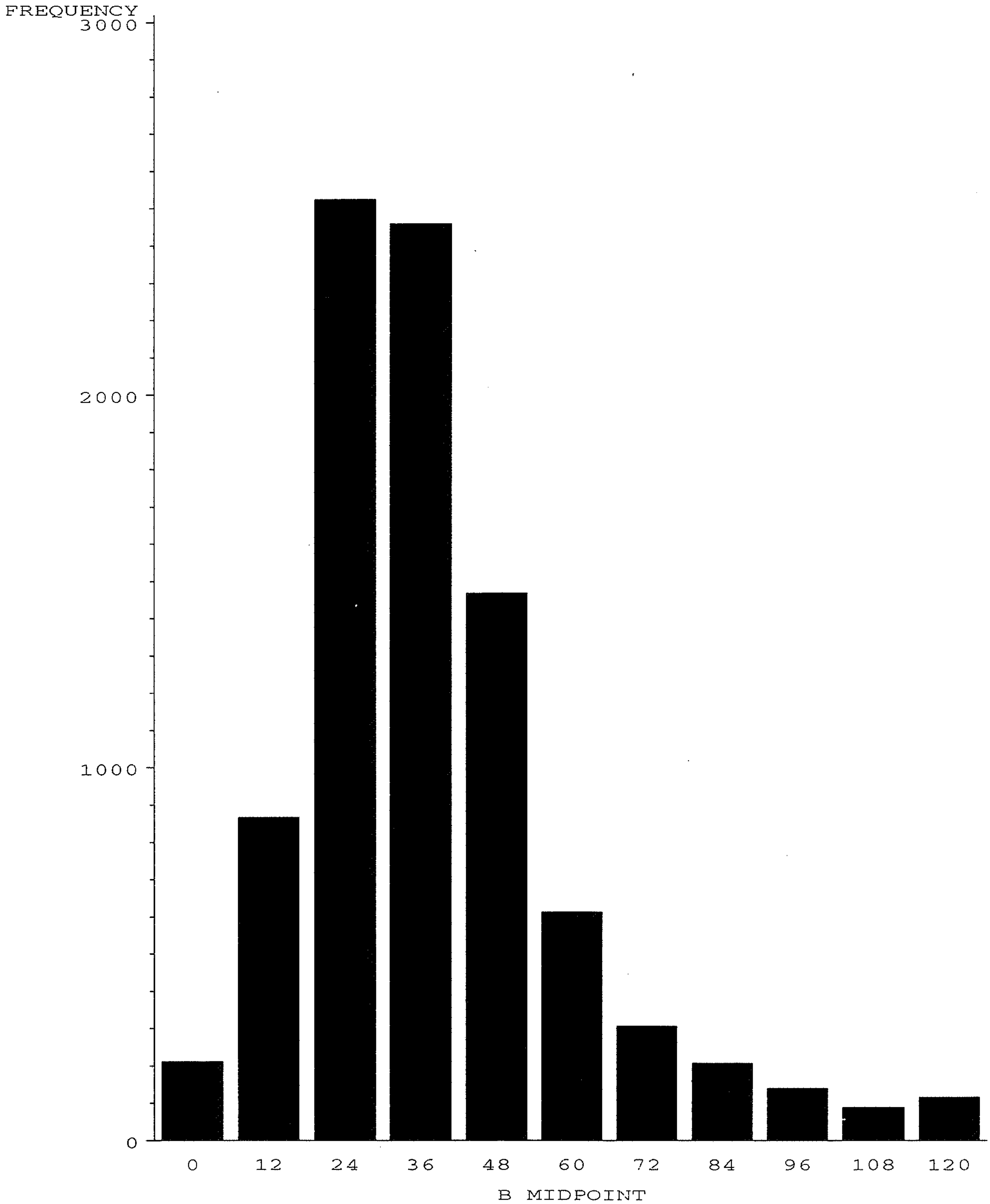
Boron (ppm)

Number of observations	9080
Maximum value	769
Minimum value	0
Mean value	38
Median value	33
Standard deviation	28

Percentiles

100%	769
99%	120
95%	82
90%	64
75%	46
50%	33
25%	24
10%	16
5%	12

BORON



FREQUENCY
3000
2000
1000
0
0
12
24
36
48
60
72
84
96
108
120
B MIDPOINT

Cadmium

Cadmium

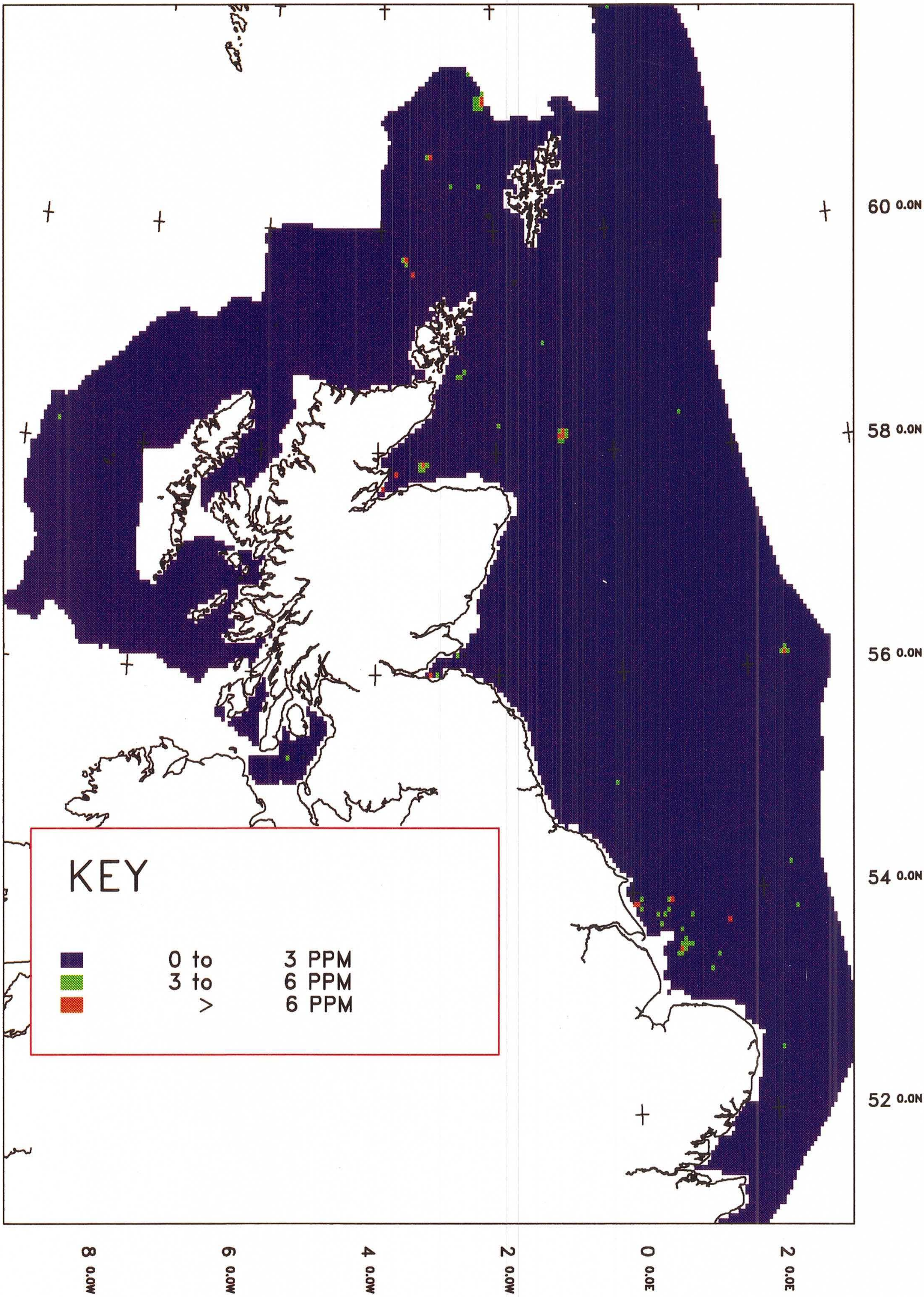
Approximately 65 per cent of analysed samples contain less than 0.5 ppm Cd (the lowest detection limit during the period of analysis by DRES). In addition, data manipulation during the production of the Cd distribution map indicated that values in the range from detection limit to 3 ppm are spurious. The map presented here therefore displays data in 3ppm class intervals which clearly identifies samples with high Cd concentrations.

The majority of high Cd values occur in the southern North Sea off the Humber Estuary, the Firth of Forth and the Moray Firth. In the southern area, the high Cd concentrations occur mainly in coarse-grained sediments with greater than 10 per cent carbonate. Nicholson and Moore (1981) observed the higher Cd concentrations in their survey occurring along the eastern coast of the UK in fine to coarse-grained sediments. They also noted a substantial correlation between Cd and loss on ignition at 1050°C , a measure of the carbonate content of the sediment, and the coarse-grained sediment fraction which contains a large proportion of shell debris in samples. Although Kukal (1971) noted the tendency for Cd to be precipitated with $CaCO_3$, Mullin and Riley (1956) found extremely low concentrations of Cd in calcareous shell (0.003-0.08ppm) and Recent marine sediments with the exception of manganese nodules.

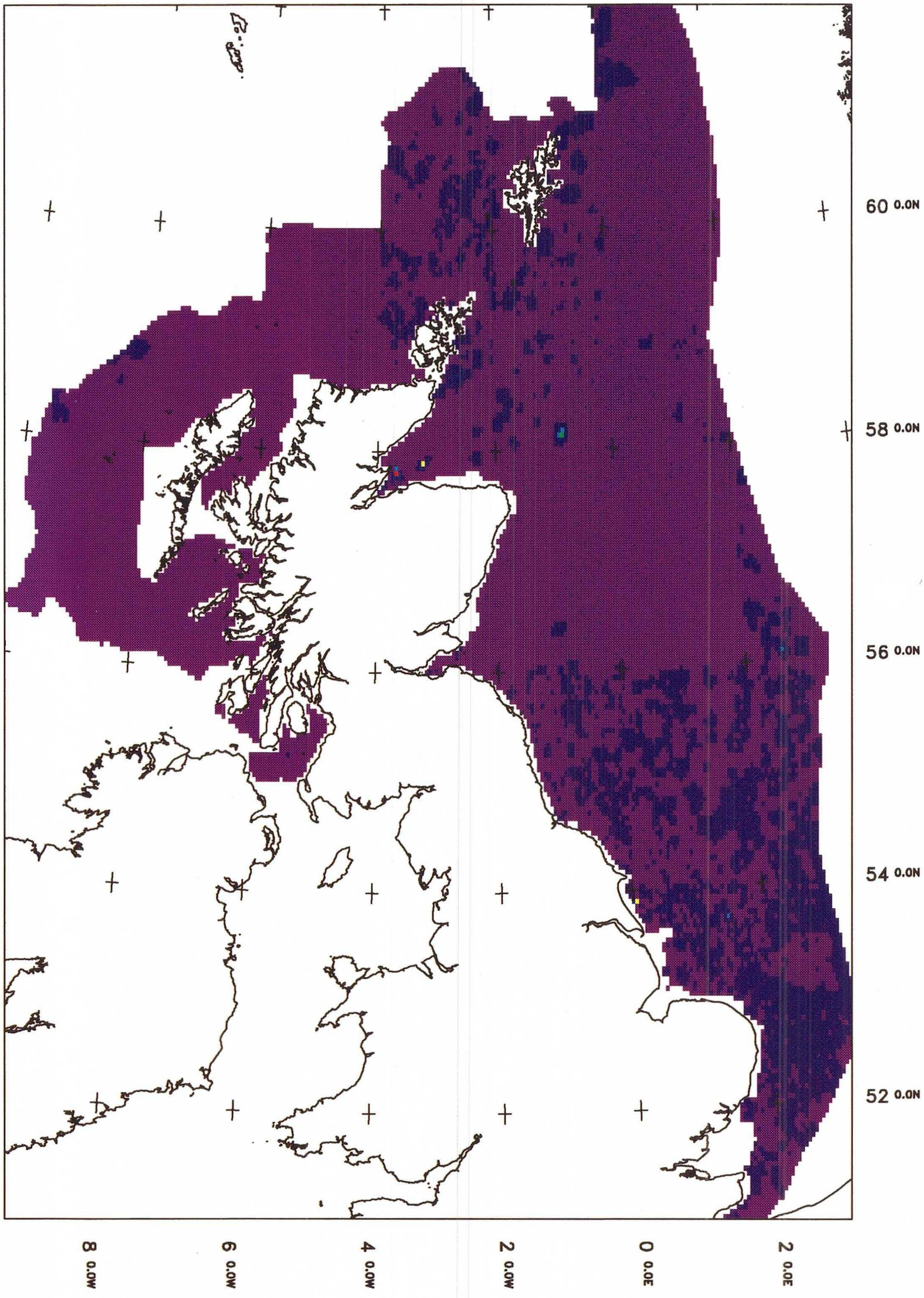
Cd occurs predominantly in the dissolved phase in the marine environment (Kersten et al., 1988), which would explain the generally low concentrations in sea-bed sediments. Burt et al (1992) noted that dissolved concentrations of Cd are high whereas they are less markedly anomalous in sediments. North Sea Task Force (1993) also found predominantly low Cd values in sediments from the North Sea (10 -380µg/kg) with the highest values in this range occurring in the Humber Estuary and the north-east coast of England.

Cd contamination has been noted in a number of areas around the UK coast, particularly along the coast of Cumbria (Langston and Pope, 1991) and in the River Severn/Bristol Channel (Abdullah et al., 1972; Nickless et al., 1972). As Cd occurs in a number of industrial waste materials it seems likely that high values near the coast are due to contaminants introduced into the marine environment by river transport, whereas those farther offshore may reflect contamination from shipping or the hydrocarbon industry.

CADMIUM IN SEA-BED SEDIMENT



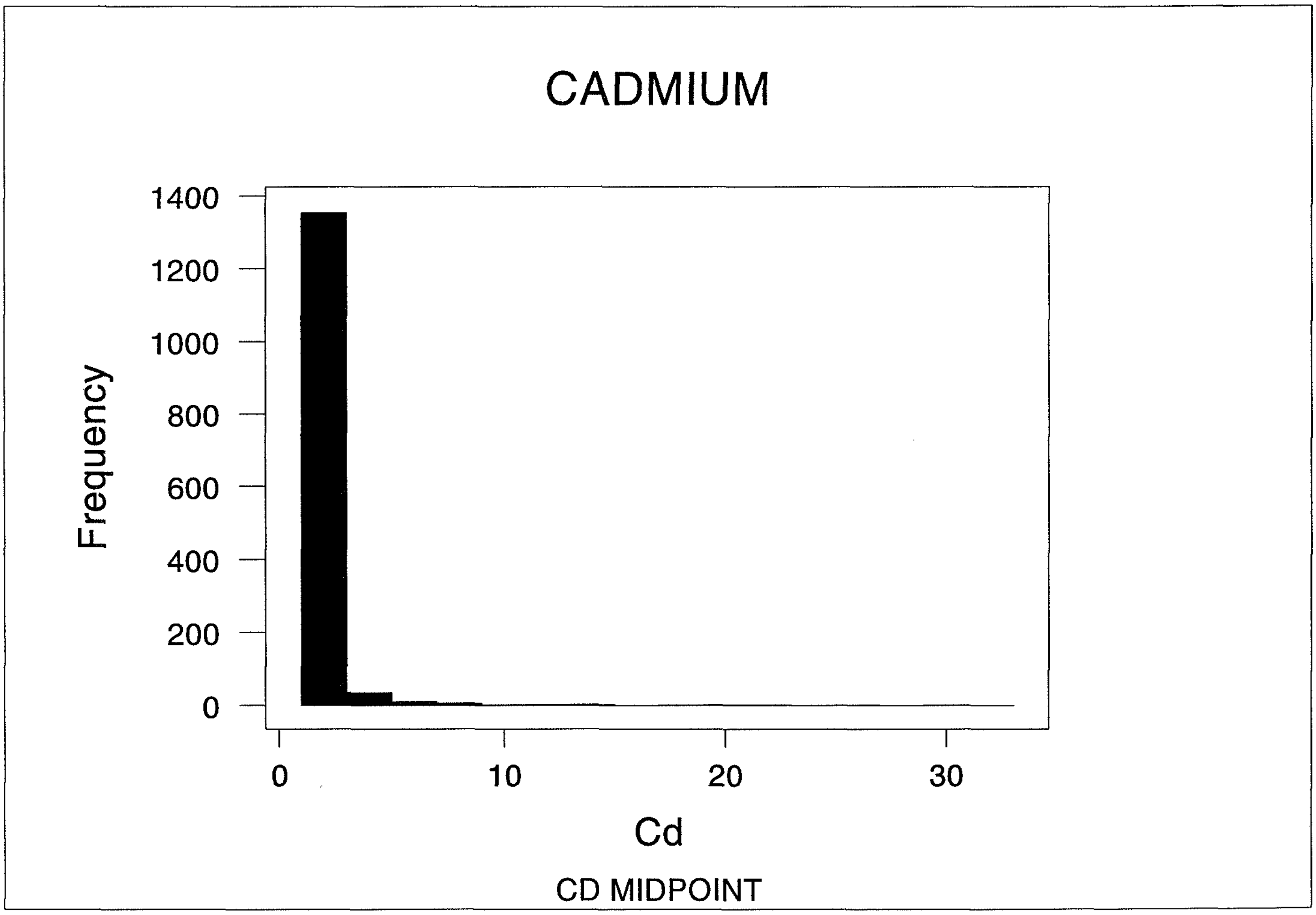
CADMIUM NORMALISED TO LITHIUM



STATISTICS

Cadmium (ppm)

Number of observations	8994
Maximum value	30.5
Minimum value	0
Mean value	0.33
Median value	0
Standard deviation	0.944



Calcium

Calcium

Southern North Sea

CaO values are generally low throughout the region. High concentrations up to 30.8% occur in gravels in the eastern Dover Strait (average 22.9%) indicating derivation from Cretaceous chalk exposed on the sea bed within the Strait (Figure 11). The highest CaO concentrations south-east of Spurn Head also occur in gravelly sediments (average 20.8%), although muddy sediments in this area have generally high concentrations compared to fine-grained sediments elsewhere (average 14.66%). BGS maps of the area show areas of high carbonate content in gravels and sands which represent modern shell material in areas of slow sedimentation. The highest values may also reflect Carboniferous limestone fragments, which are one of the main components of the gravels (Spurn 1:250 000 Sea Bed Sediments sheet; Figure 3). Sands in the southern North Sea have a low average CaO concentration of 2.13%.

Central North Sea

CaO concentrations are uniformly low in the central North Sea (average 1.39% in sandy sediments) with the exception of muddy sediments in the coastal zone between Flamborough Head and the Tees Estuary (average 10.49%) which, like the area off Spurn Head to the south, reflects sediment derived from cliff erosion. A small group of increased values also occur in gravelly sediments around the Farne Islands. These sediments have relatively low biogenic carbonate concentrations in the gravel fraction (Farne 1:250 000 Sea-Bed Sediments sheet), therefore CaO values may indicate gravels derived from Carboniferous calcareous rocks which crop out at sea bed around the islands. Throughout most of the central and northern North Sea, CaO values are low in sandy (average 8.41%), gravelly and muddy sediments. Areas of higher values occur in the Marr Bank and Peterhead 1:250 000 sheet areas, particularly on the Aberdeen Bank (average 17.51%). As would be expected, high CaO values coincide with high total carbonate in samples from these areas (Figure 12). These high concentrations occur on submarine banks, indicating that they are areas of carbonate production and in situ degradation, whereas deeper sediments contain little carbonate material.

Northern North Sea

Part of the most extensive area of high CaO values in the area surveyed around the UK, occur in gravelly sediments on the Orkney-Shetland Platform (average 38.79%). Here, CaO is associated with intermediate to high concentrations of MgO, Sr, La and Co, although it is not strongly correlated with any of these elements. Comparison with Figure 12 shows that the area delineated by high CaO values is broadly similar to an area of high carbonate in sea-bed sediments. This is due to the accumulation of sandy and gravelly sediments composed mainly of comminuted macroscopic shells and foraminifera in an area of strong tidal currents. Johnson and

Elkins (1979) also found high Ca concentrations in sediments from the northern North Sea which they considered were due to the presence of foraminifera and other calcareous shell debris.

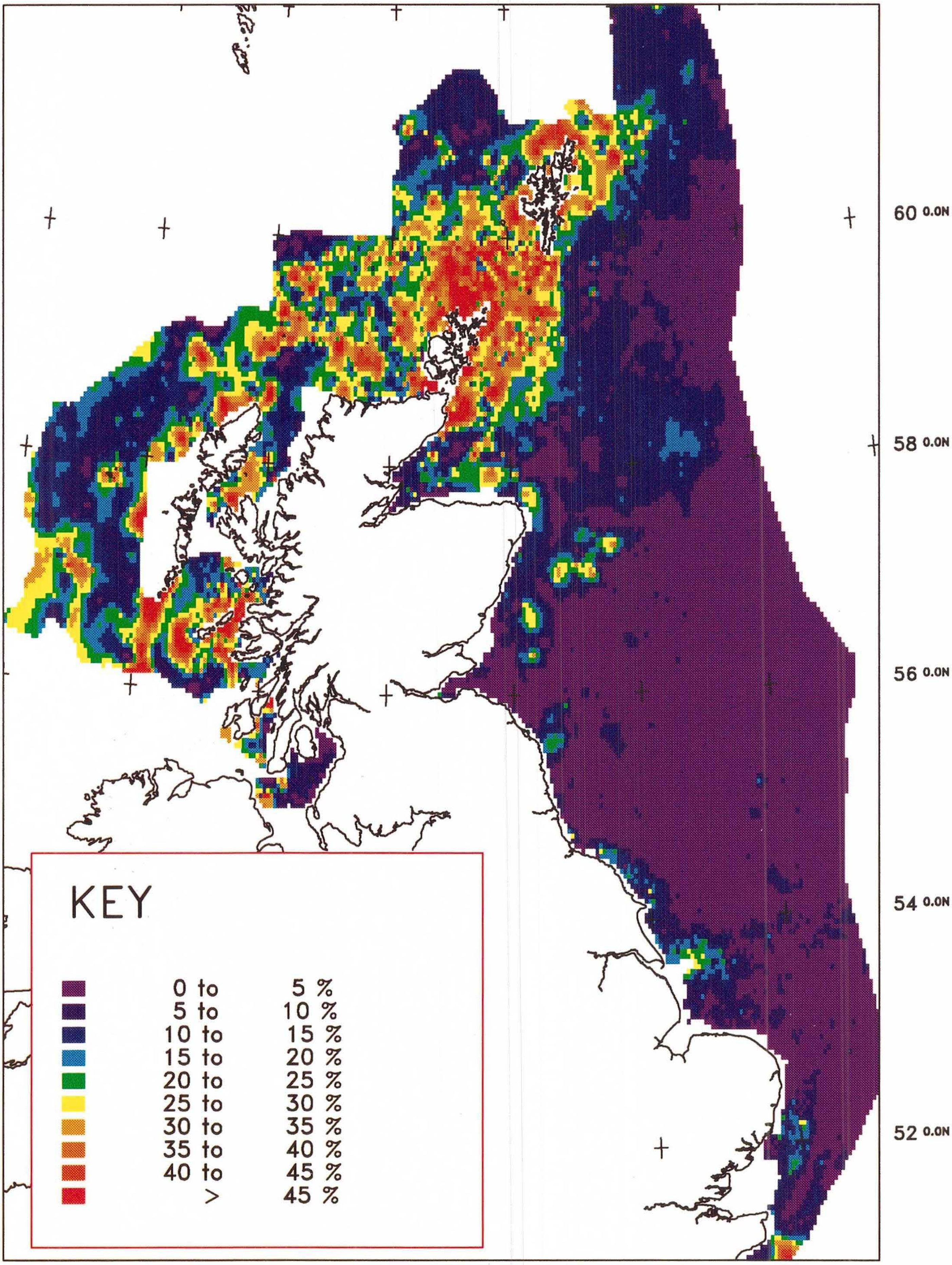
Hebrides and West Shetland shelves

Several groups of high CaO values occur in this region and, like the area between Orkney and Shetland, are commonly associated with sandy (average 19.31%) and gravelly (average 23.77%) sediments and increased concentrations of MgO, Sr and Co. A study of the carbonate-rich deposits of this area by Allen (1983) indicated that the sand fraction in these sediments consists mainly of fragments of barnacles and bivalves.

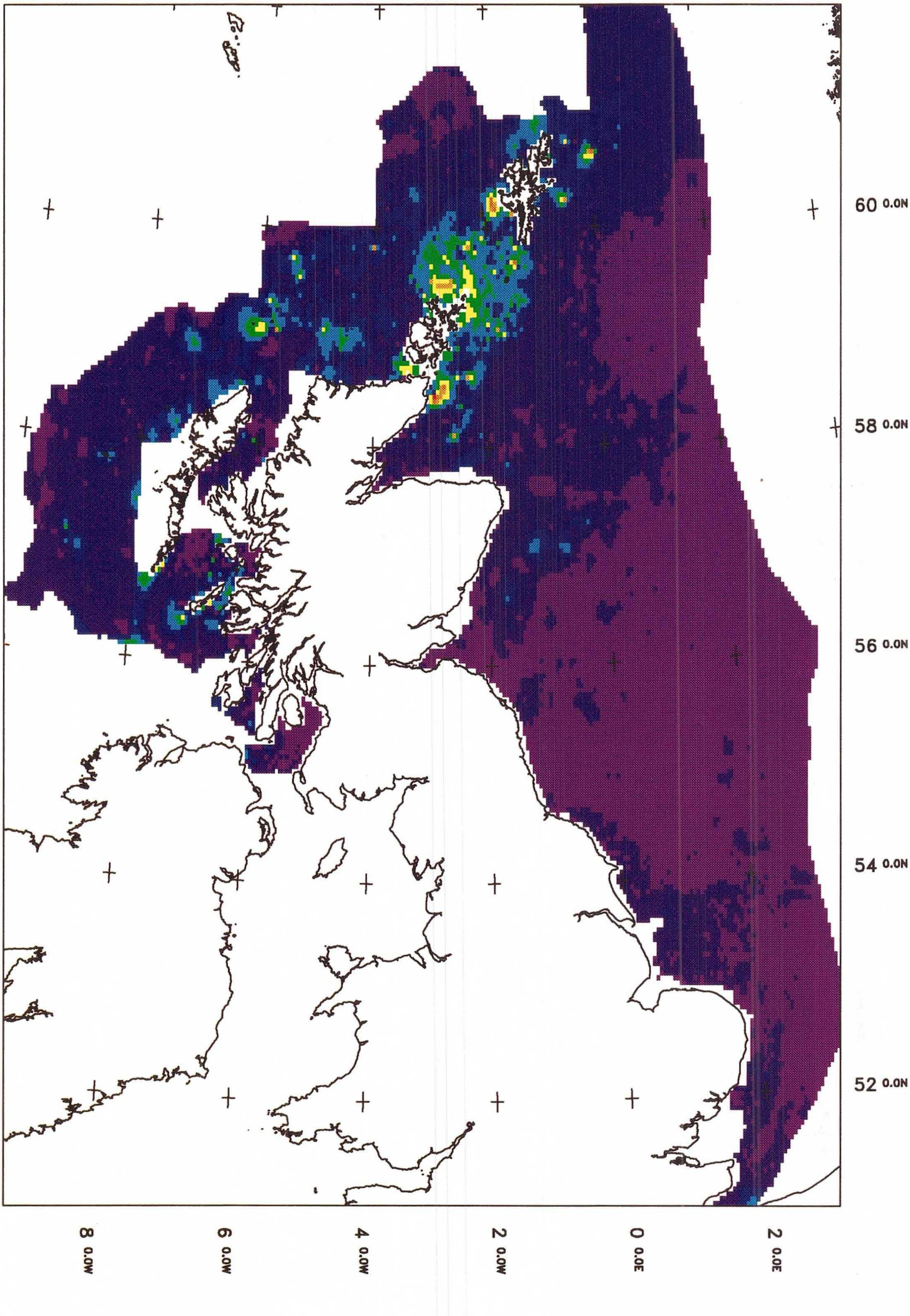
Malin - Hebrides

High CaO values occur in three main areas to the north of Skye; around Coll and Tiree; and in the North Channel between Kintyre and Northern Ireland. Once again these occur mainly in coarse-grained sediments in areas with high current strengths. Associated elements include MnO which suggests that mixing of the water column occurs in these areas causing precipitation of Fe-Mn hydroxide coatings on the surface of shell fragments. Pendlebury (1974), working in the Malin Sea, observed that bivalves and barnacles are the most abundant components of the sand fraction in sediments from this area.

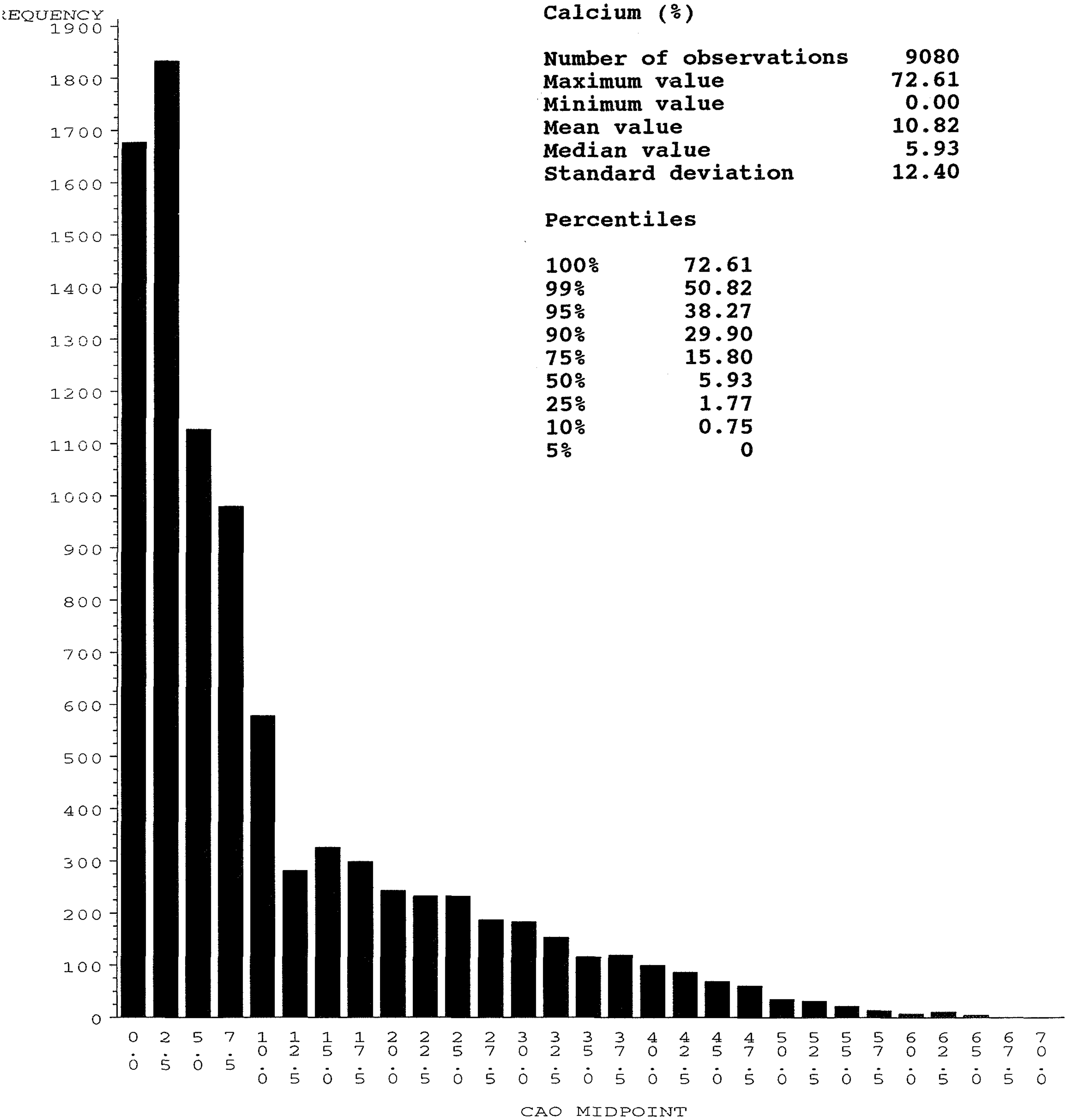
CALCIUM IN SEA-BED SEDIMENT



CALCIUM NORMALISED TO LITHIUM



CALCIUM



STATISTICS

Calcium (%)

Number of observations	9080
Maximum value	72.61
Minimum value	0.00
Mean value	10.82
Median value	5.93
Standard deviation	12.40

Percentiles

100%	72.61
99%	50.82
95%	38.27
90%	29.90
75%	15.80
50%	5.93
25%	1.77
10%	0.75
5%	0

Chromium

Chromium

Southern North Sea

Cr values are generally low throughout most of the southern North Sea (average 19ppm in sandy sediments - 4 to 19ppm in areas of gravelly sand). High values occur in the Outer Thames Estuary (average 57ppm) and off the coast of East Anglia (average 77ppm) and are associated entirely with sediments classified as muddy sandy gravels. The association with high Li, B and Rb and the absence of Cr in sandy and gravelly sediments suggests that it occurs mainly in the mud fraction; this is confirmed by normalised Cr/Li data. As Cr primarily occurs in minerals resistant to weathering, it is likely therefore that it is adsorbed onto clay minerals or organic matter.

Nicholson et al. (1985) reported negative correlations between Cr and the gravel and sand fractions of sea-bed sediments in the North Sea, and poor positive correlations with Fe, Mg and Mn which indicated that Cr was not included in oxide coatings or the structure of ferromagnesian minerals. Intermediate to high Cr values to the north-east of Skegness also occur in muddy sandy gravel. Intermediate Cr values occur in the Markham's Hole area where they are associated with both fine and coarse-grained sediments. This suggests that Cr occurs in both clay minerals and detrital minerals in the sandy sediment of this area.

Central North Sea

Groups of high Cr values are widespread across the region and occur in a variety of sediments. The largest group is associated with muddy sand off the Tyne-Tees estuaries (average 88ppm), extending northwards to the Farn Deeps (average 73ppm). Cr is strongly correlated with all elements with the exception of Zr and P in the former area, and most strongly with Co, Ga, V and TiO_2 in the Farn Deeps; normalised Cr/Li data indicate that grain-size is the main control on Cr distribution. High Cr concentrations also occur along the east coast of Scotland, including the Firth of Forth (average 156ppm).

Farther offshore, high Cr concentrations occur in sands and gravelly sands, particularly in the Dogger Bank area (average 60ppm in gravelly sands), where it is associated with high Zr and to a lesser extent TiO_2. The sediments on Dogger Bank are derived from underlying glacial deposits (Dogger Bank Formation). These deposits have features of a proglacial water-laid body with input from meltwater streams flowing from both northerly and southerly directions. The occurrence of high Cr and TiO_2 values indicate the accumulation of resistate heavy minerals, such as magnetite and ilmenite, which have survived glacial transport from areas of basic or ultrabasic igneous rocks, or metamorphic or sedimentary rocks containing clasts derived from these lithologies. Nicholson et al. (1985) also noted high Cr in nearshore muds and a correlation with TiO_2 and Zr in sands in the central North Sea, which they attributed to Cr in lattice positions in degraded clay minerals and detrital minerals respectively.

Elsewhere, high Cr concentrations also occur in gravelly sands on Marr Bank (average 48ppm), probably indicating the presence of detrital heavy minerals. Like the Dogger Bank area, these sediments are derived from the underlying Quaternary (Marr Bank Formation) deposits and are of a similar age to the glacial sediments of Dogger Bank. The distribution of intermediate to high Cr values between the Firth of Forth and Dogger Bank supports the conclusion of Dearnley (1991) - see Section 10 - although it is more probable that the mineralogy and geochemistry reflects the derivation of the underlying Pleistocene deposits from the Scottish Highlands rather than to general sediment drift of surface sediments from this direction .

A high Cr value (630ppm) in sand south of Aberdeen Bank is the most prominent feature of the normalised Cr/Li map; as the sands around this area have much lower Cr concentrations, this value is probably due to contamination. High Cr concentrations also occur in the fine-grained sediments of the Devil's Hole area (average 64ppm).

Northern North Sea

In this region, the distribution of high Cr values is mainly related to the occurrence of fine-grained sediments in the Fladen Ground and Witch Ground basins (average 87ppm in muds). Cr may occur in the lattices of the illite group minerals (Frohlich, 1960; Hirst, 1962), however the regional enrichment of Cr in this area may indicate that it occurs in sand- and clay-size detrital minerals such as chromite, magnetite and ilmenite. A sample with a value of 380ppm Cr in the south-west of the Cormorant 1:250 000 sheet area is thought to be contaminated.

Hebrides and West Shetland shelves

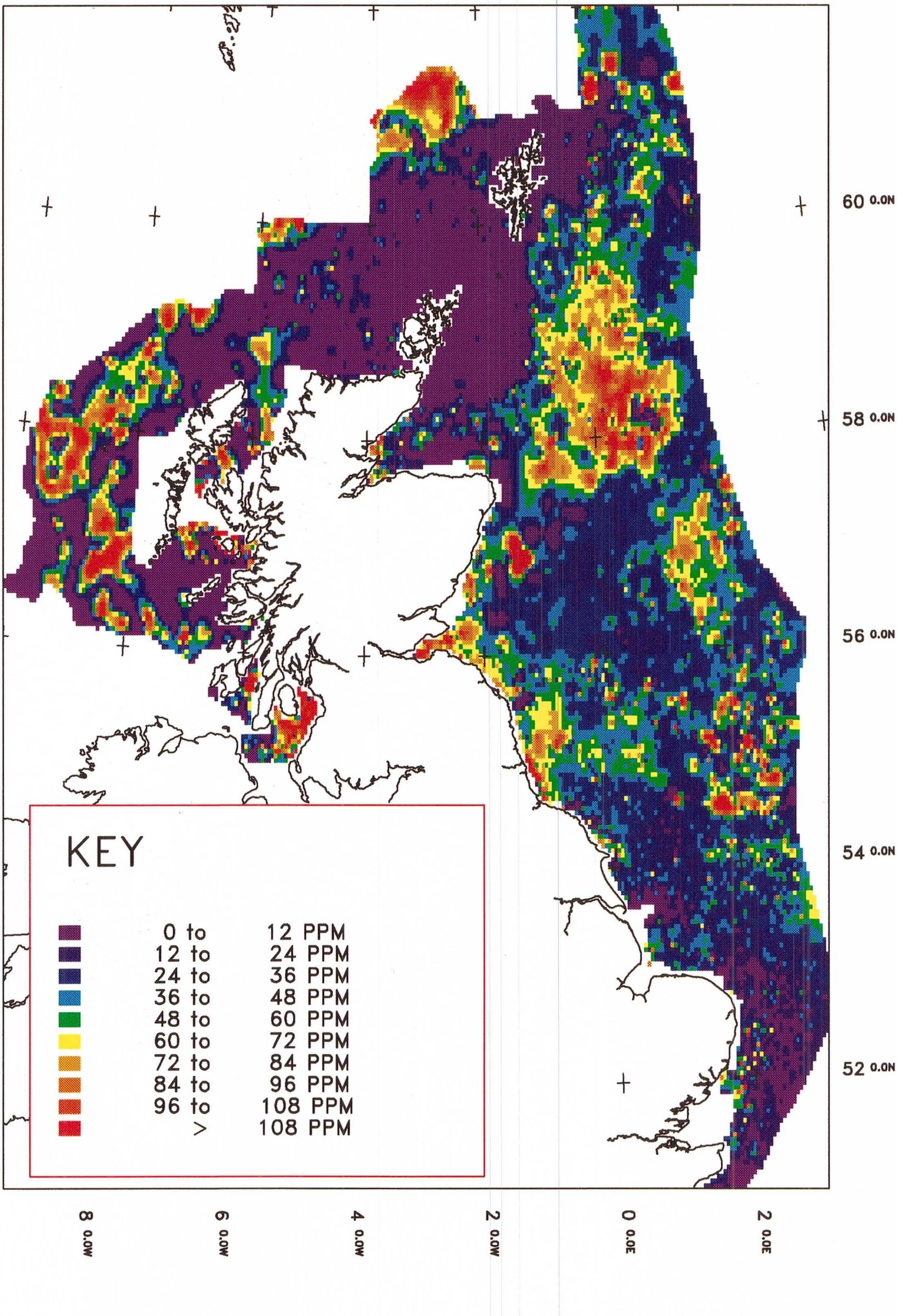
Low Cr values occur throughout most of the north-western shelf although it should be noted that correction to compensate for Ca interference during analysis has a significant affect in this area (see section 4). Where Cr values are unaffected by this correction, Cr values are generally high. Dearnley (1989) recorded Cr values greater than 80 ppm in the sand fraction of several samples from the Orkney-Shetland Platform and Hebrides and West Shetland shelves which confirms that the analytical adjustment for Ca does mask the real distribution of Cr in these areas. High levels of Fe_2O_3, MgO, TiO_2, Cu and Ni are commonly associated with Cr anomalies, reflecting the influence of Tertiary basic igneous rocks throughout the region. The widespread occurrence of this element association over both fine-grained and coarse-grained deposits on the outer shelf indicate that most sediments contain some proportion of lithic fragments derived from basic igneous lithologies.

Malin-Hebrides

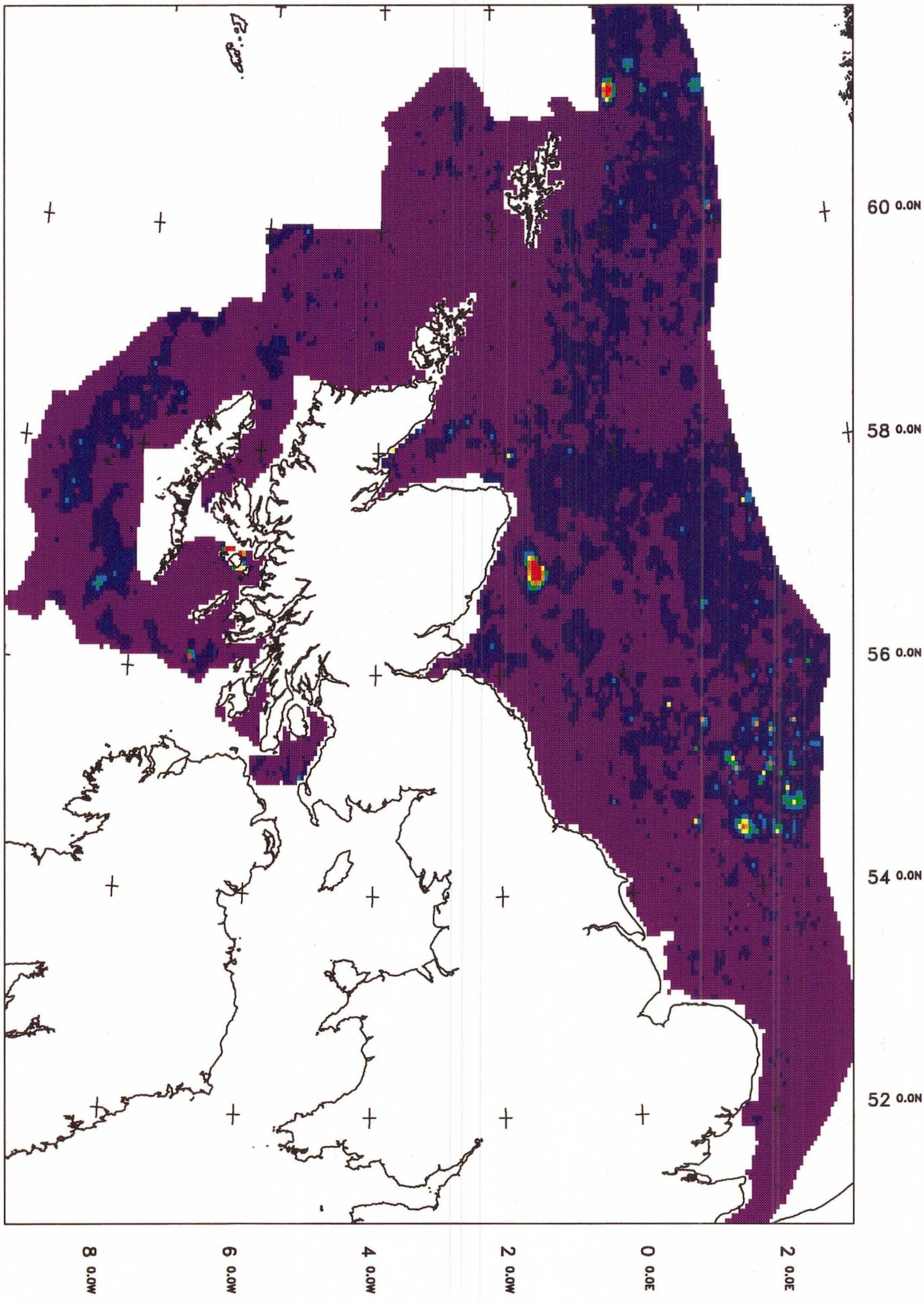
As on the outer shelf, Ca interference correction obscures the Cr distribution pattern in this area. Analysis of sand fractions by Dearnley (1989) confirm that high Cr values do occur throughout the region. Sediments in the Minch and Sea of the Hebrides are mainly derived from the underlying Pleistocene deposits and the association of Cr with high Fe_2O_3, MgO, TiO_2, Ni and Cu reflects the derivation of much of these deposits from the Tertiary igneous rocks of Mull and Skye. Normalised Cr/Li data show a group of high values around the island of Rum where a study by Gallagher et al (1989) indicated the presence of 70 000 tonnes of chrome spinel averaging 32 per cent Cr_2O_3 at a grade of nearly 1 per cent in the topmost sands south of the island.

Intermediate to high Cr values in the vicinity of Blackstones Bank may reflect sediment derived from the ultrabasic rocks of the igneous centre in this area. High Cr values occur in fine-grained sediments in the Sound of Jura (average 98ppm) and Firth of Clyde (average 135ppm) and are related to adsorption on clay minerals or organic matter. The sewage dump at Garroch Head in the Firth of Clyde has resulted in an area of anomalous geochemistry (Halcrow et al.,1973) and has created a biomass centre which contributes to the organic matter input to the estuary. Burt et al. (1992) also found high levels of Cr at the Garroch Head dump site and the Clyde Estuary in general, and established that the sediments in this estuary, and that of the Tees, had the highest levels of anthropogenically derived Cr within the study area.

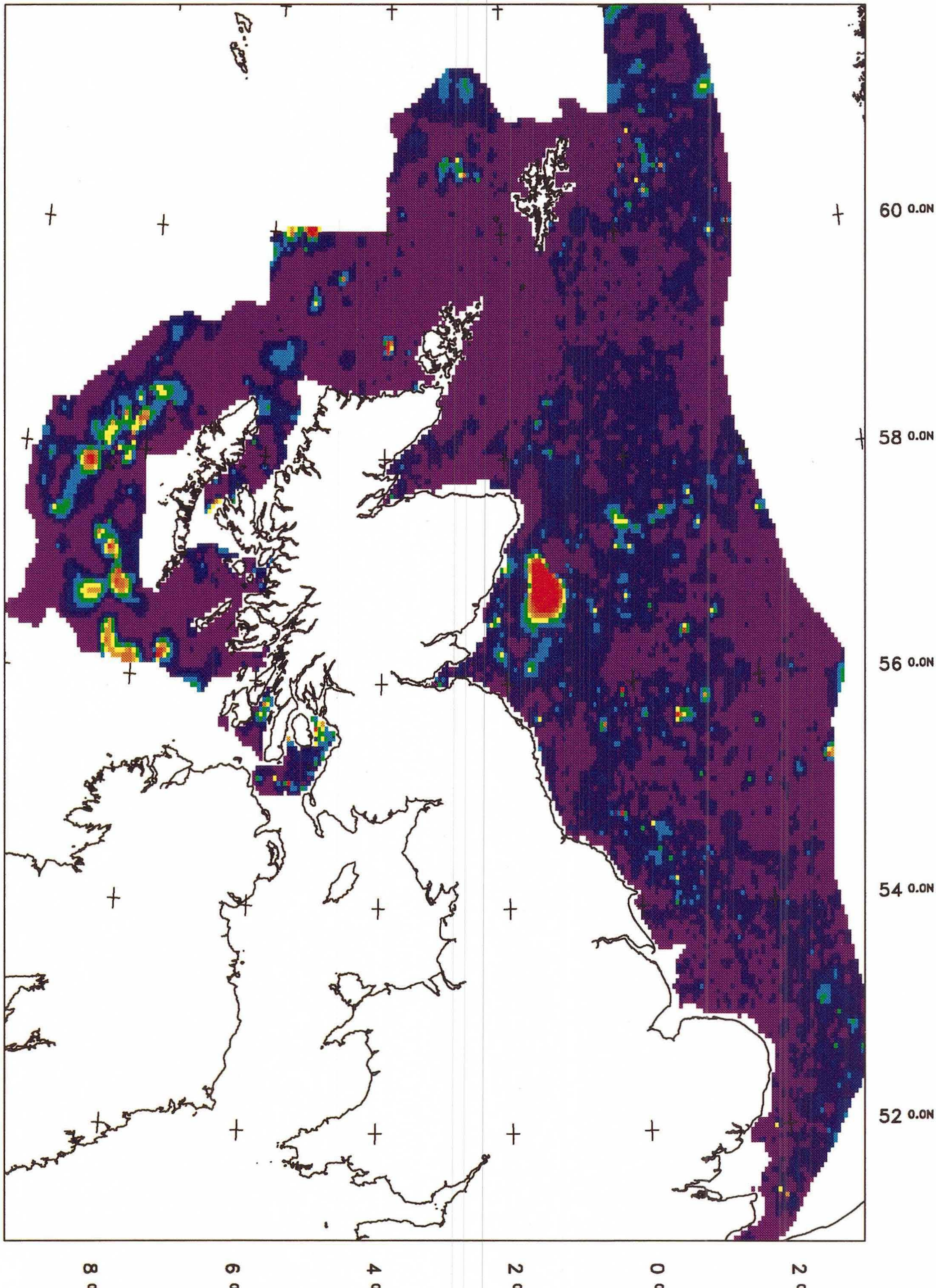
CHROMIUM IN SEA-BED SEDIMENT



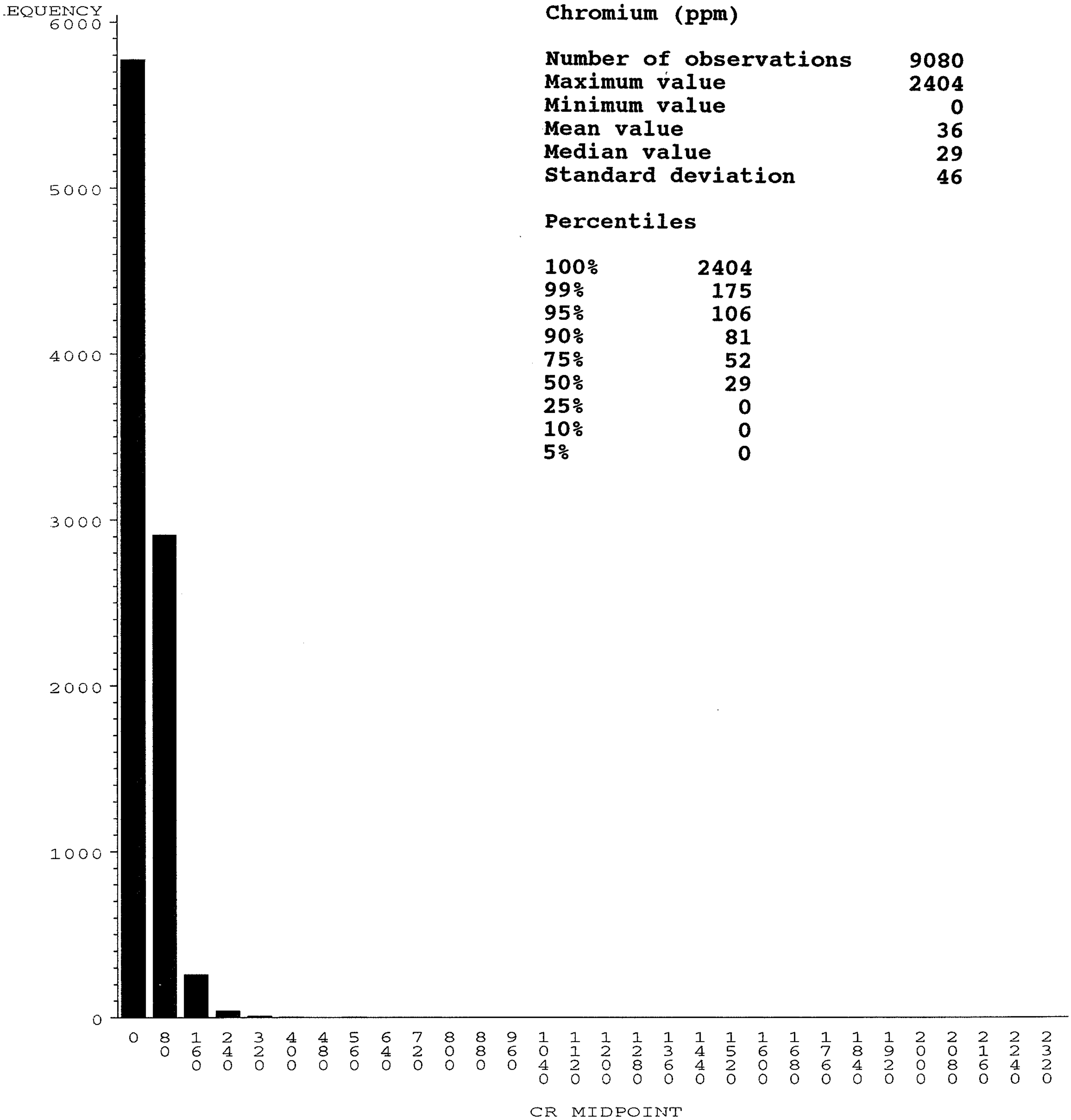
CHROMIUM NORMALISED TO LITHIUM



CHROMIUM NORMALISED TO ZIRCONIUM



CHROMIUM



STATISTICS

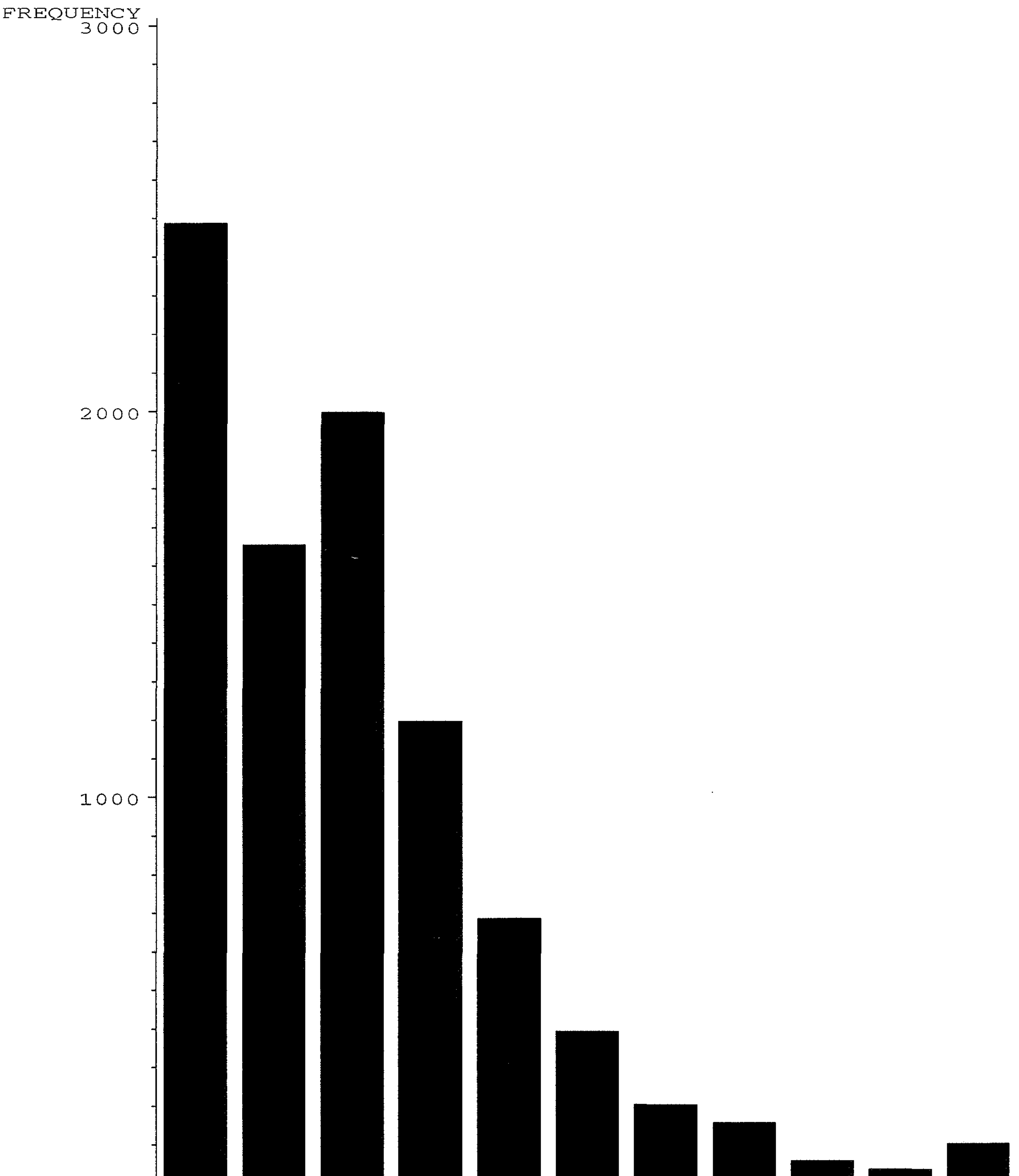
Chromium (ppm)

Number of observations	9080
Maximum value	2404
Minimum value	0
Mean value	36
Median value	29
Standard deviation	46

Percentiles

100%	2404
99%	175
95%	106
90%	81
75%	52
50%	29
25%	0
10%	0
5%	0

CHROMIUM


FREQUENCY
3000
2000
1000
0
0
18
35
53
70
88
105
123
140
158
175
CR MIDPOINT

Cobalt

Cobalt

Southern North Sea

Co concentrations are generally low to intermediate in the sandy sediments of the region (average 7ppm). High Co values occur in gravelly sediments in the Dover Strait (average 14ppm). Elsewhere, Co values are generally higher in gravelly and muddy sediments near the coast of East Anglia and between Flamborough Head and Norfolk. In the nearshore zone, Co is most strongly correlated with Cr and Pb which suggests that it is concentrated in lithic fragments or clay minerals derived from basic or ultrabasic igneous rocks, however the association with Pb may indicate that Co is partly related to contamination derived from the estuaries of the rivers Humber and Thames. In each of these areas, but particularly in the Dover Strait, the effect of co-precipitation with Fe-Mn hydroxides may also be an important control on Co distribution. The map of normalised Co/MnO indicates that this process is less influential in deeper waters of the Southern Bight.

The highest Co values occur in muddy sediments near the coast between Flamborough Head and the Tyne Estuary. Like the nearshore gravels farther south, Co is most strongly correlated with elements such as Cr and Pb, however a wider range of elements associated with clay minerals are also correlated.

Fine-grained sediments farther offshore in the Markham's Hole/Outer Silver Pit area have similar Co levels (average 8 ppm) to the surrounding sands and have significantly lower Co concentrations than muddy sediments in the Outer Thames Estuary.

Central North Sea

Co concentrations in sandy sediments of the area are generally low to intermediate similar to those of the southern and northern North Sea. High Co values occur in fine-grained sediments of the Firth of Forth (average 16ppm), where once again they are strongly correlated with Cr and Pb, and in the sandy and gravelly sediments near the near the east coast of Scotland. In the latter area, Co is associated with Ni and Cr suggesting that these sediments contain a proportion of lithic fragments or clays derived from basic igneous rocks such as those of the Midland Valley of Scotland.

An unusual feature of the normalised Co/Li and Co/MnO maps is a group of high ratios in the Devil's Hole area. As Co values are generally low (less than 4ppm) in these muddy sediments, it suggests that it is anomalously low concentrations of Li and Mn relative to Co which produces this pattern. Correlation matrices for the area (Appendix 1) show that Co is mainly negatively correlated with other elements with the exception of Cu, La, Ni, Pb and Zr. In an area of otherwise uniform Co distribution, this association could indicate that the sea-bed depression of Devil's Hole has accumulated concentrations of heavy minerals or possibly contaminants.

Several authors, including Cronan (1970) and Moore (1968) have noted that Co is largely associated with accessory minerals in sea-bed sediments and Cronan (1970) also noted that in coarse-grained sediments derived from reworked glacial debris, Co levels are similar to those in muddy sediments due to concentration of detrital minerals. A similar explanation would account for the narrow range of Co values in sea-bed sediments around the UK.

Northern North Sea

In this area, and to the west of Scotland, Co concentrations are masked by the calcium interference correction applied to the analytical data (see Section 4). Samples of sand from the area have intermediate to high Co concentrations (average 8ppm) as shown by Dearnley (1991). In association with high Cr, Cu, Ni, V and Zn values, Dearnley related this pattern to a contour of 15 per cent basic igneous rock fragment content in these sands.

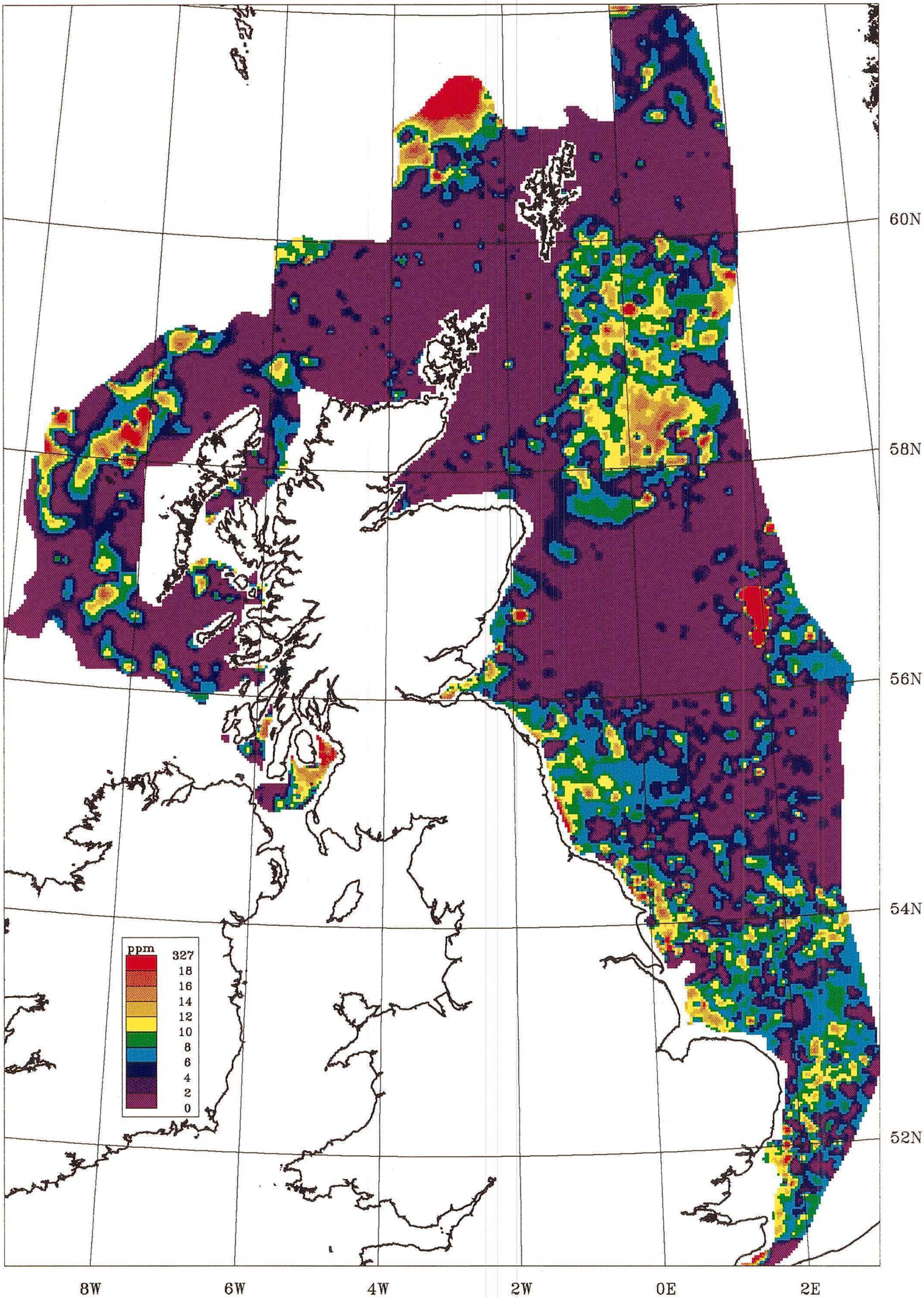
Hebrides and West Shetland shelves

Co distribution is obscured by Ca interference correction, however where unaffected the values are similar to those reported by Dearnley (1991) in sands from the west of Scotland. Intermediate to high values are typical of all sediment types due to the influence of Tertiary basic igneous rocks in the area but also possibly to basic Lewisian gneiss derived from the Outer Hebrides. A group of high normalised Co/Li values in the area north of St Kilda are associated with elements such as Cr, Fe_2O_3 and TiO_2 and indicate concentrations of heavy minerals such as magnetite and ilmenite which are a common component of basic and ultrabasic igneous rocks.

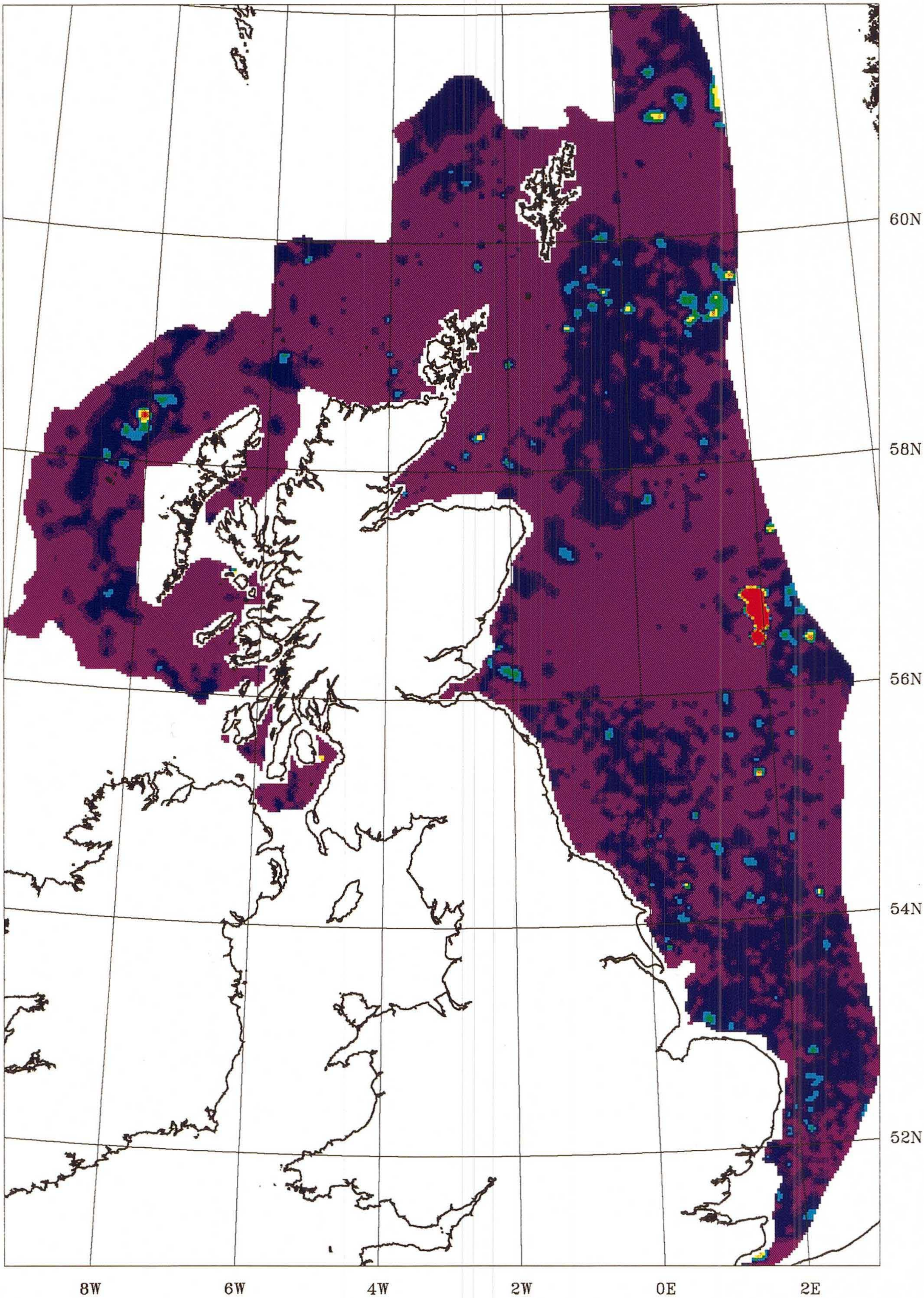
Malin-Hebrides

The highest values of the area occur in fine-grained sediments in the Firth of Clyde (average 16ppm) and the Sound of Jura (12ppm). In both areas, the rocks from which the Quaternary and Recent sediments of the sea bed are derived, have considerably higher levels of Co concentration (British Geological Survey, 1993). In the former area, however, it is probable that high Co levels are partly related to contamination.

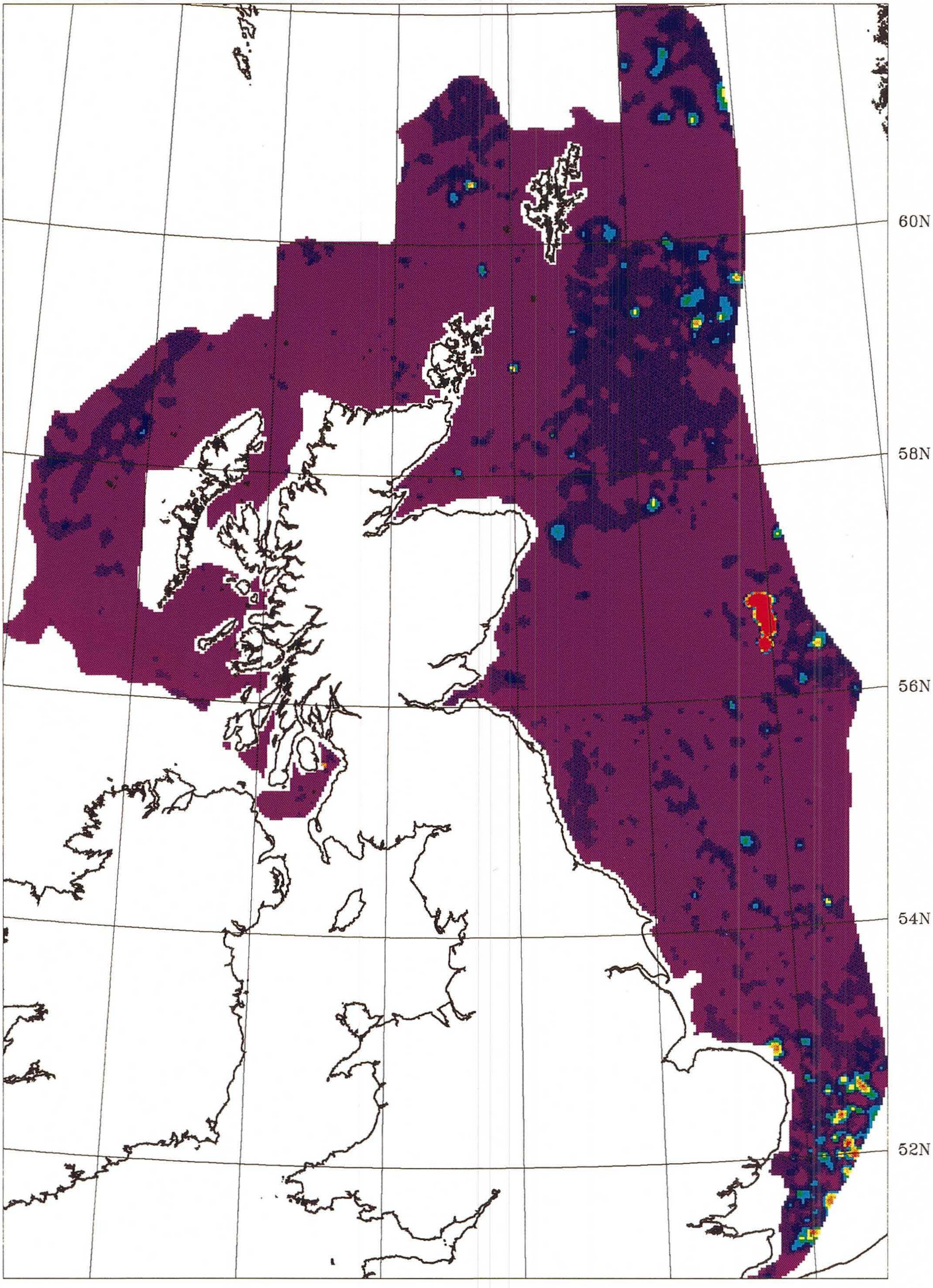
COBALT IN SEA-BED SEDIMENT



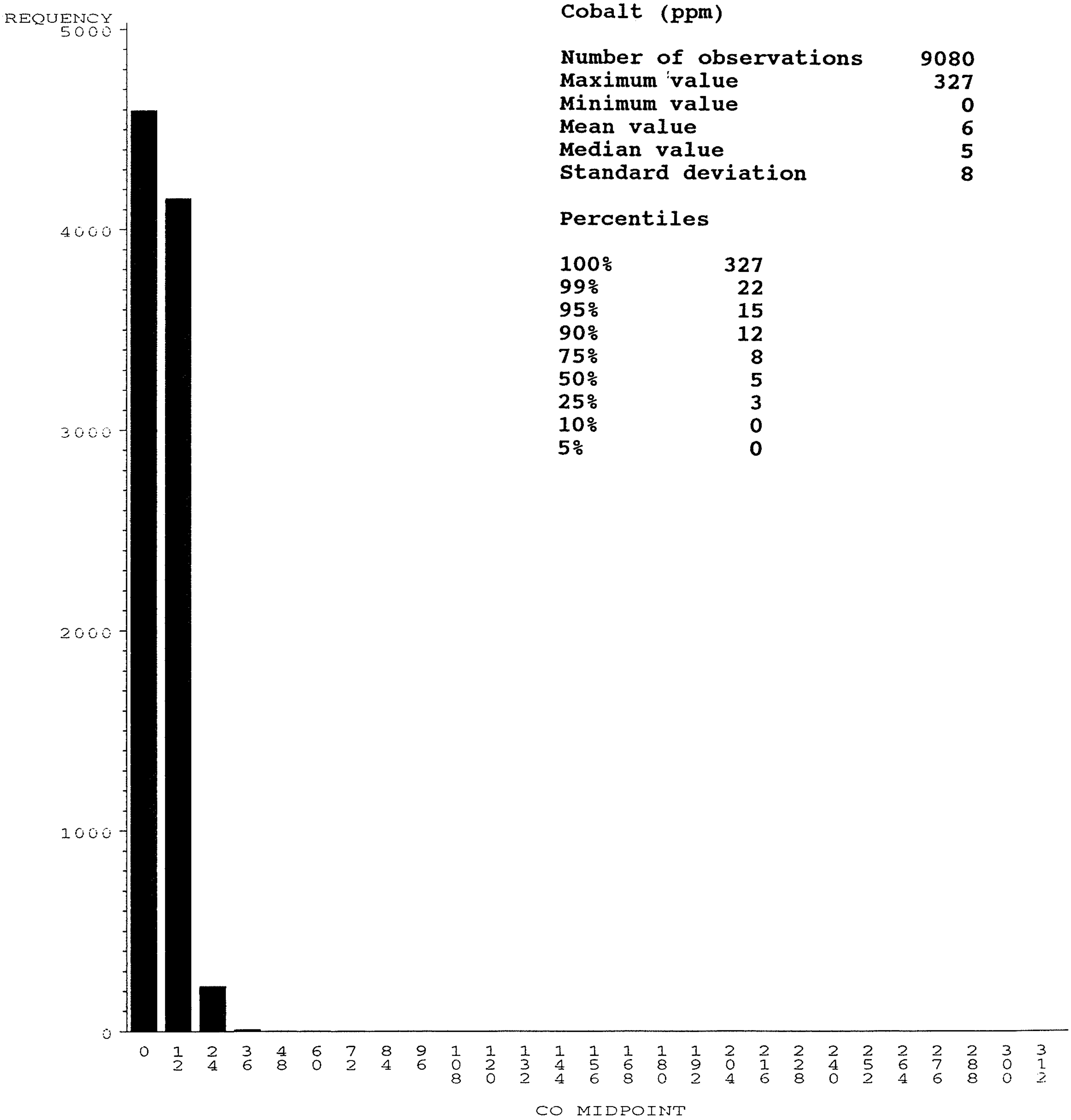
COBALT NORMALISED TO LITHIUM



COBALT NORMALISED TO MANGANESE



COBALT



STATISTICS

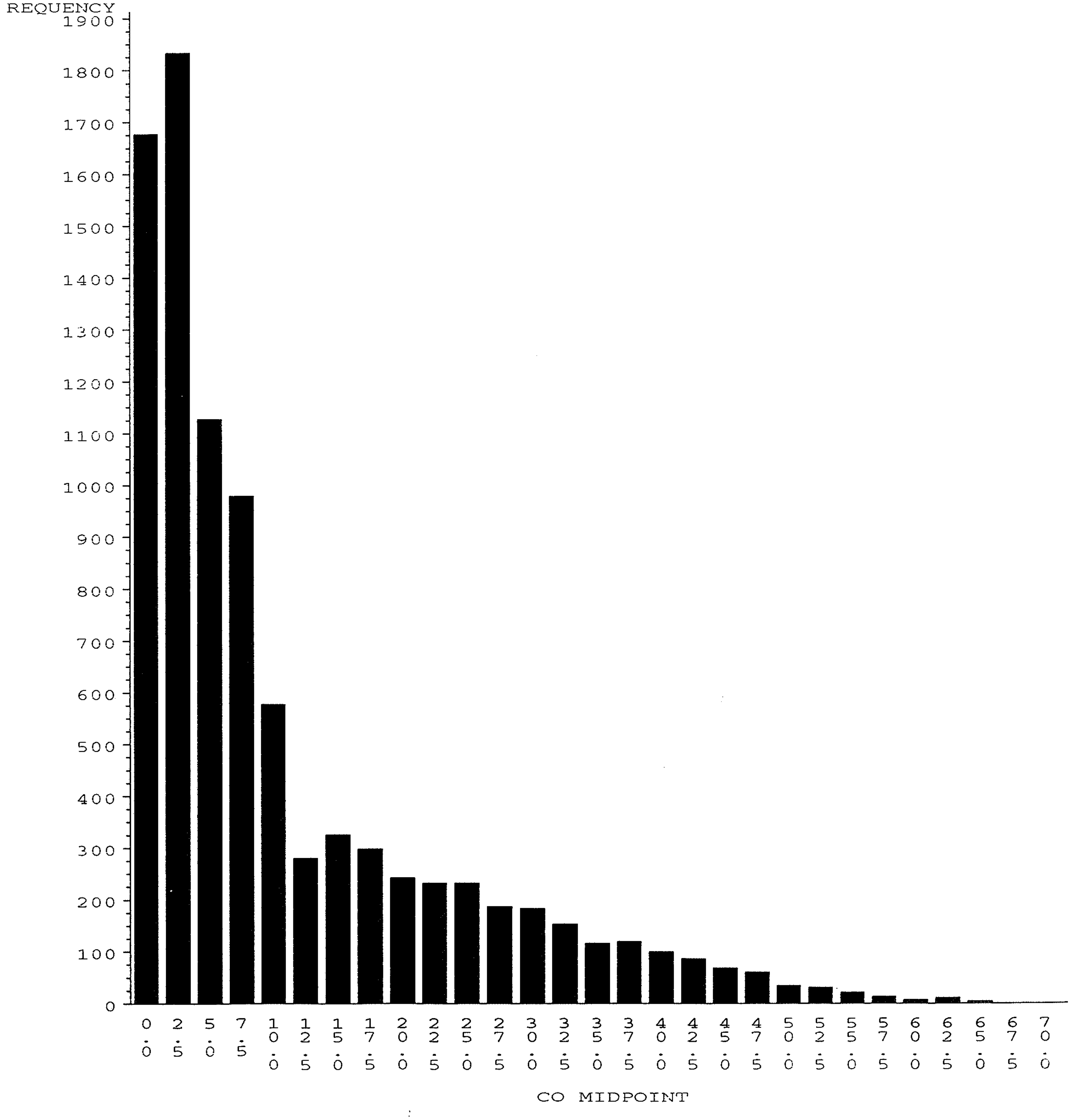
Cobalt (ppm)

Number of observations	9080
Maximum value	327
Minimum value	0
Mean value	6
Median value	5
Standard deviation	8

Percentiles

100%	327
99%	22
95%	15
90%	12
75%	8
50%	5
25%	3
10%	0
5%	0

COBALT



REQUENCY
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
0.0 2.5 5.0 7.5 10.0 12.5 15.0 17.5 20.0 22.5 25.0 27.5 30.0 32.5 35.0 37.5 40.0 42.5 45.0 47.5 50.0 52.5 55.0 57.5 60.0 62.5 65.0 67.5 70.0
CO MIDPOINT

Copper

Copper

Southern North Sea

Cu values are generally low in the sea-bed sediments of the southern North Sea with the exception of the Outer Thames Estuary, Markham's Hole and offshore of the coast of East Anglia and Lincolnshire. In each of these areas, intermediate to high Cu concentrations are mainly associated with fine-grained sediments (average 21ppm; 6ppm; 28ppm and 10ppm respectively). However, each area also has high Cu values in samples from sandy or gravelly sediments commonly in association with high concentrations of Pb, Zn and to a lesser extent Ni suggesting that some of these values may be related to contamination.

In the area of highest Cu concentrations in the region, off the coast of east Anglia, North Sea Task Force (1993) also reported high Cu normalised to Al. Nicholson and Moore (1981) found that Cu values were less than 2ppm in sands from the southern North Sea , comparable with the results of this study, and took this to indicate the virtual absence of detrital minerals of the heavy metals (including Pb and Zn). They also considered that some of the Cu may be found in the lattices of clay minerals in the fine-grained sediments, although more probably that the greater proportion is adsorbed onto clay minerals, clay/organic complexes, or organic debris; a good correlation between Cu, Pb, Zn and loss on ignition at 450°C (an approximate measure of organic material content) was observed. Nicholson and Moore concluded that the high concentrations of Cu (and associated elements) nearshore were consistent with river-borne derivation for the metal-enriched silt fraction.

Central North Sea

High values of Cu occur along a restricted zone nearshore between Spurn Head and St Abb's Head (e.g. average 29ppm in muddy sediments between Flamborough Head and the Tees Estuary) and in muddy sediments in the Firth of Forth (average 39ppm). The area of high Cu values in the coastal zone also has high levels of elements associated with clay minerals. The wider occurrence of high Cu values in coarse-grained sediments associated with high Fe, Ni, Pb and Zn suggests that some at least can be related to metallic contamination in all size fractions of the nearshore sediments, although the elements are more probably adsorbed on clay or organic particles in the pore spaces of sandy and gravelly deposits.

North Sea Task Force (1993) reported high values of Cu normalised to Al off the English coast near the Tyne, Tees, and Humber estuaries. Natural mineralisation in the catchment areas of the rivers Tyne and Tees was though to be the source of some of the Cu found in the sediments. The highest average Cu concentration found in this study occurs in muddy sediments offshore of the Tyne-Tees estuaries (41ppm). This is significantly higher than in fine-grained sediments farther offshore such as in the Farn Deeps (average 20ppm) and Gorsethorn Deep (average 6ppm) and would appear to confirm Cu enrichment in the nearshore zone due to contamination. Farther offshore a group of high values in the Marr Bank area in gravelly sands, and a high Cu value of 158ppm in sandy sediment due east of the Forth Estuary, are not associated with high values of other elements and are therefore probably due to contamination. The presence of groups, and point values, of high Cu/Li ratios in this area and throughout the North Sea are a good indication of areas of probable contamination.

Northern North Sea

An area of Cu values above background, extending from the east coast of Scotland to the Fladen Ground Basin, may indicate sediment derived from the Dalradian metasediments of north-west Scotland but possibly reflect some input of sediment derived from the basic/ultrabasic complexes of the east Grampians. Intermediate to high Cu values (average 10ppm in mud) in the Fladen Ground Basin and in the Moray Firth (average 10ppm) are typical of fine-grained sediments found elsewhere on the UK shelf. In the Inner Moray Firth, however, high Cu/Li ratios suggest that some values are related to contamination.

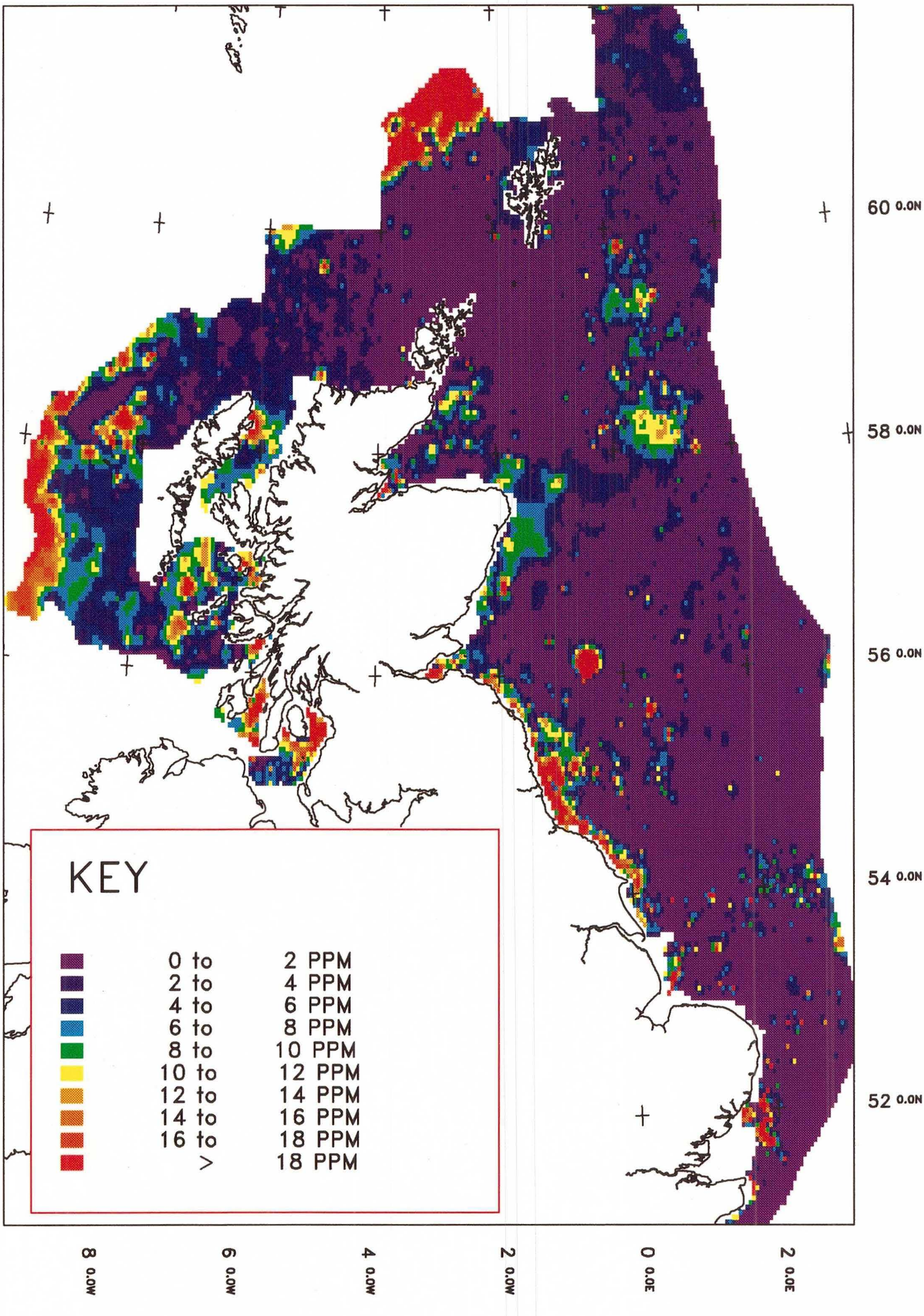
Hebrides and West Shetland shelves

Cu values are generally low throughout this region with the exception of muddy sediments which occur at the shelfbreak. Here, high Cu is associated with high concentrations of elements which occur in clay minerals and Cu values average 12ppm to the north-west of Shetland and 15ppm farther to the west of the Hebrides Shelf. The high Cu/Li values in the more northerly of these two areas results from low Li concentrations. This is due to there being more sandy muds in this area compared to the finer-grained sediments at the shelfbreak farther south. A group of high values in the area around St Kilda are associated with increased levels of MgO, Cr, Ni, TiO_2 and Zn and probably reflect detrital minerals derived from the basic igneous rocks of the island.

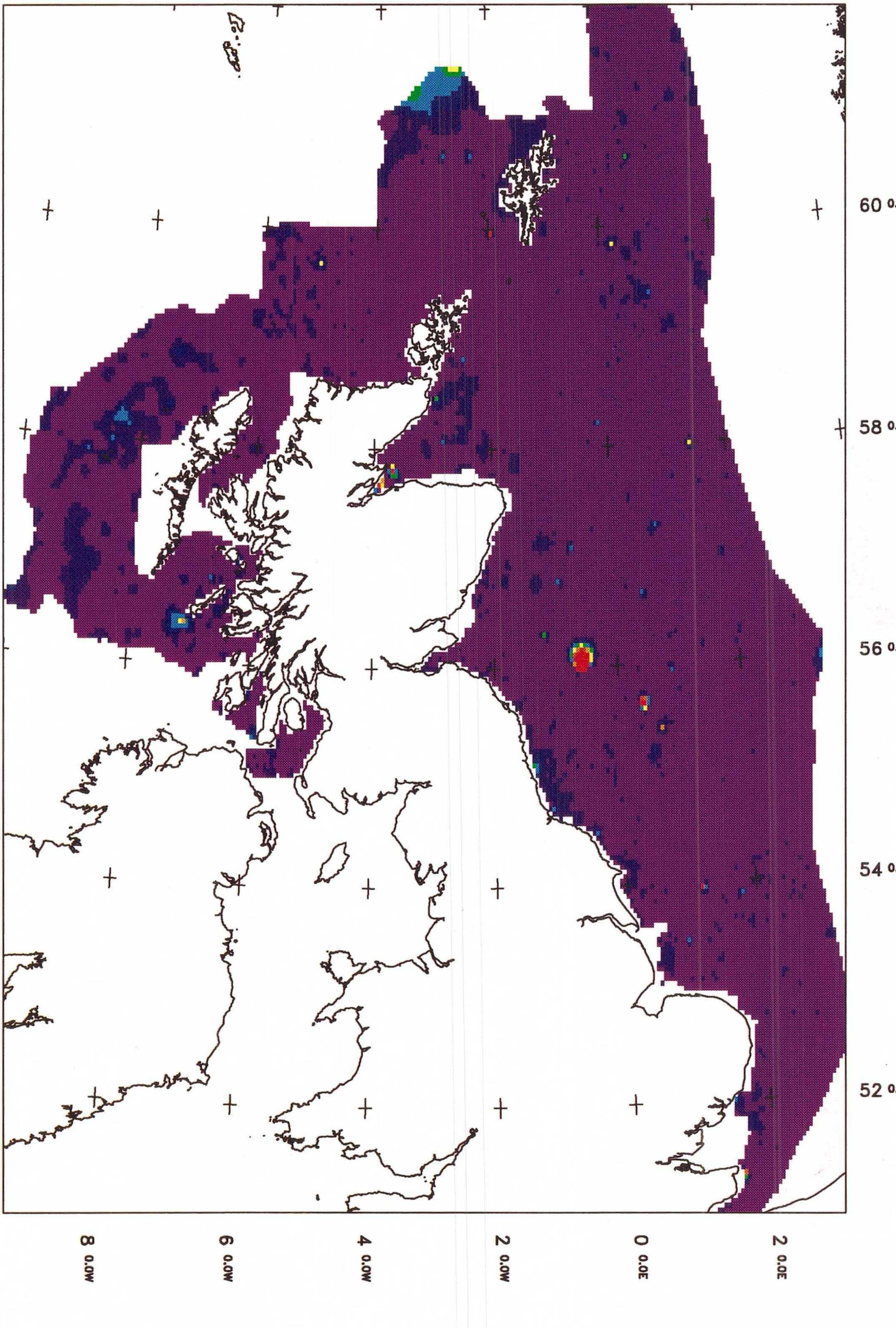
Malin-Hebrides

High Cu concentrations occur in fine-grained sediments (average 11ppm) in The Minch and Sea of the Hebrides in association with elements which indicate derivation from the Tertiary igneous rocks of the islands of Skye, Mull, Rum and Canna. The muddy sediments of the Sound of Jura and Firth of Clyde both have high Cu concentrations (average 21ppm in each area). Heavy metals such as Pb and Zn, which show a weak to strong positive correlation with Cu (Appendix 1), also occur in high concentrations in the Clyde Estuary and are therefore considered to be partly related to contaminants and adsorption on organic matter.

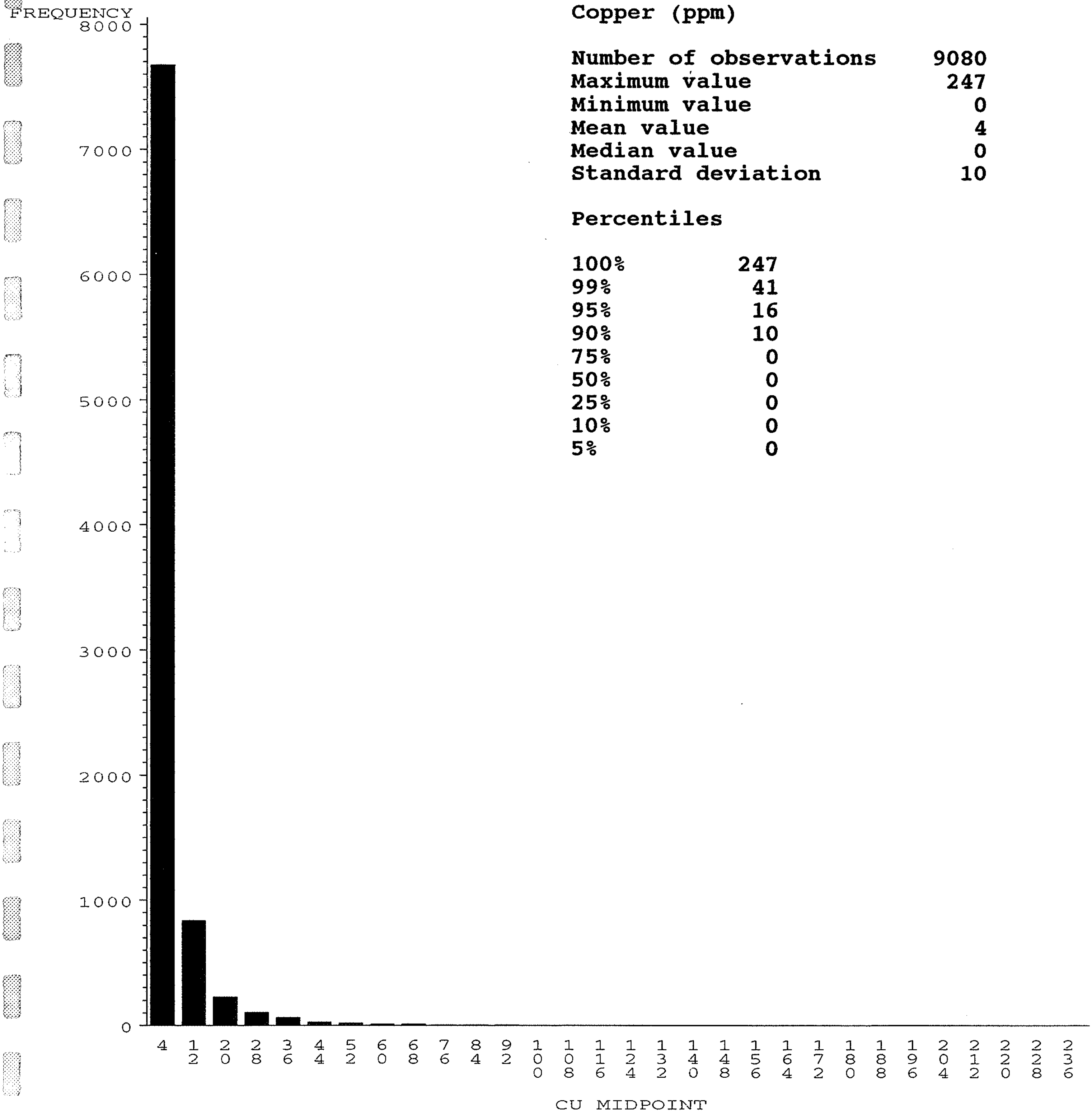
COPPER IN SEA-BED SEDIMENT



COPPER NORMALISED TO LITHIUM



COPPER



STATISTICS

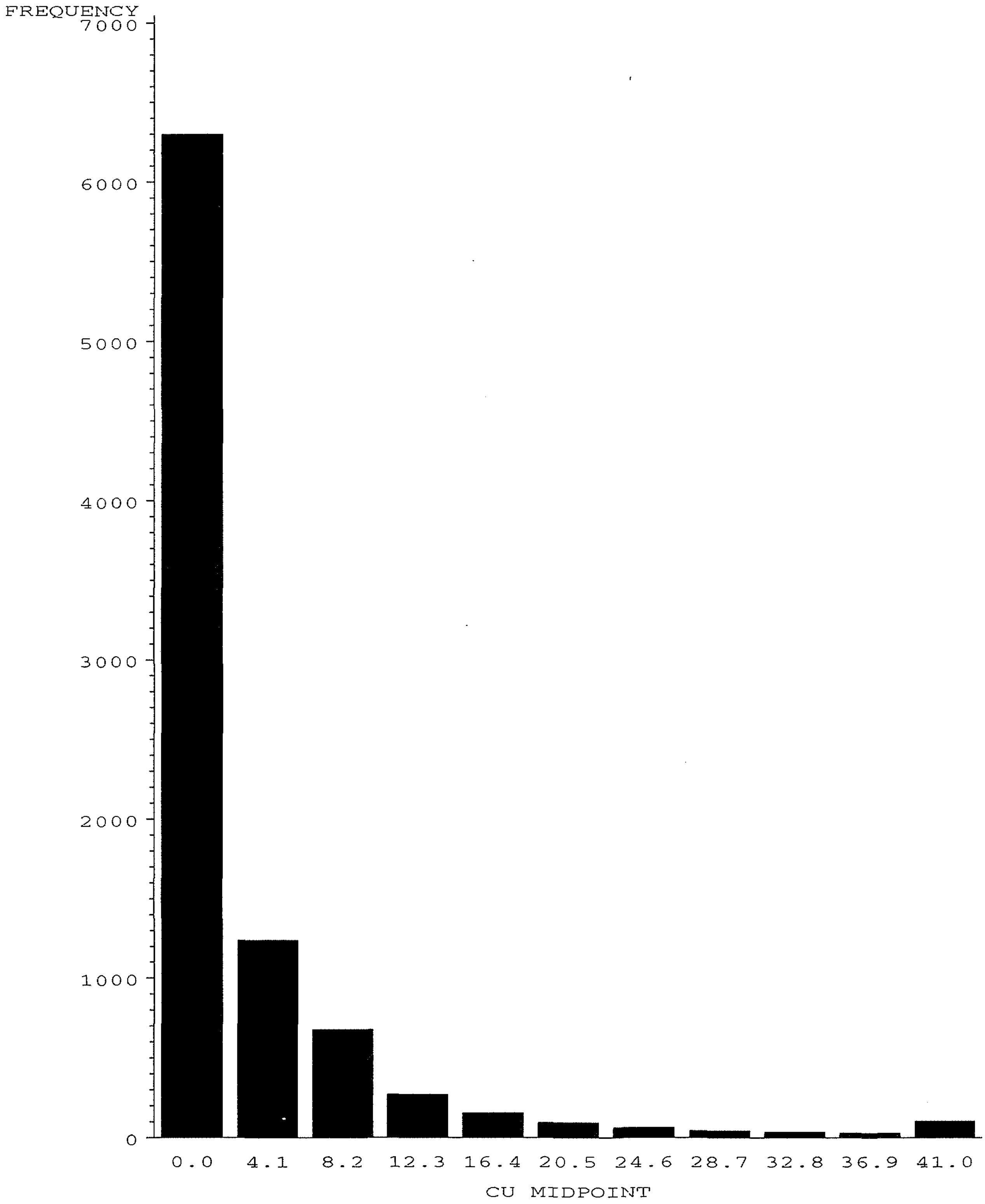
Copper (ppm)

Number of observations	**9080**
Maximum value	**247**
Minimum value	**0**
Mean value	**4**
Median value	**0**
Standard deviation	**10**

Percentiles

100%	**247**
99%	**41**
95%	**16**
90%	**10**
75%	**0**
50%	**0**
25%	**0**
10%	**0**
5%	**0**

COPPER


FREQUENCY
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5000
4000
3000
2000
1000
0
0.0
4.1
8.2
12.3
16.4
20.5
24.6
28.7
32.8
36.9
41.0
CU MIDPOINT

Gallium

Gallium

Southern North Sea

Ga values are generally low in sandy and gravelly sediments in the region. As the distribution of Ga closely follows that of Al, the highest concentrations occur in fine-grained sediments where clay minerals are the main component. Hirst (1962) found that much of the Ga in sediments from the Gulf of Paria was found to be replacing Al in kaolinite with lesser amounts in illite and montmorillonite, Intermediate to high values therefore occur in the muddy sediments off the coast of East Anglia (average 6ppm) and in the Outer Thames Estuary (average 5ppm). Slightly increased Ga values occur in the Markham's Hole area although the average concentration is low (3ppm). Nicholson et al. (1985) reported the highest Ga concentrations in inshore samples with a high mud (less than 63μm) component, and a strong correlation between elements found in clay-forming minerals, particularly Li and Rb. The correlation matrices in Appendix 1 also show this to be the case in this investigation.

Central North Sea

The highest Ga values occur near the coast of north-east England in muddy sediments (average 8ppm) and in the Firth of Forth (average 18ppm). Intermediate to high Ga values also occur in fine-grained sediments farther offshore in the Farn Deeps (average 6ppm), the Gorsethorn Deep (average 4ppm) and the Devil's Hole (average 4ppm).

Northern North Sea

Intermediate to high Ga values characterise all muddy sediments of the area including those of the Fladen and Witch Ground basins (average 9ppm in mud). Some areas of sandy sediment, for example in the vicinity of Viking Bank, also have intermediate Ga concentrations possibly reflecting increased amounts of detrital feldspar in the sand fraction. High values in the gravelly sediments of the Orkney-Shetland Platform may indicate precipitation with Fe or Al hydrous oxides as coatings on shell fragments.

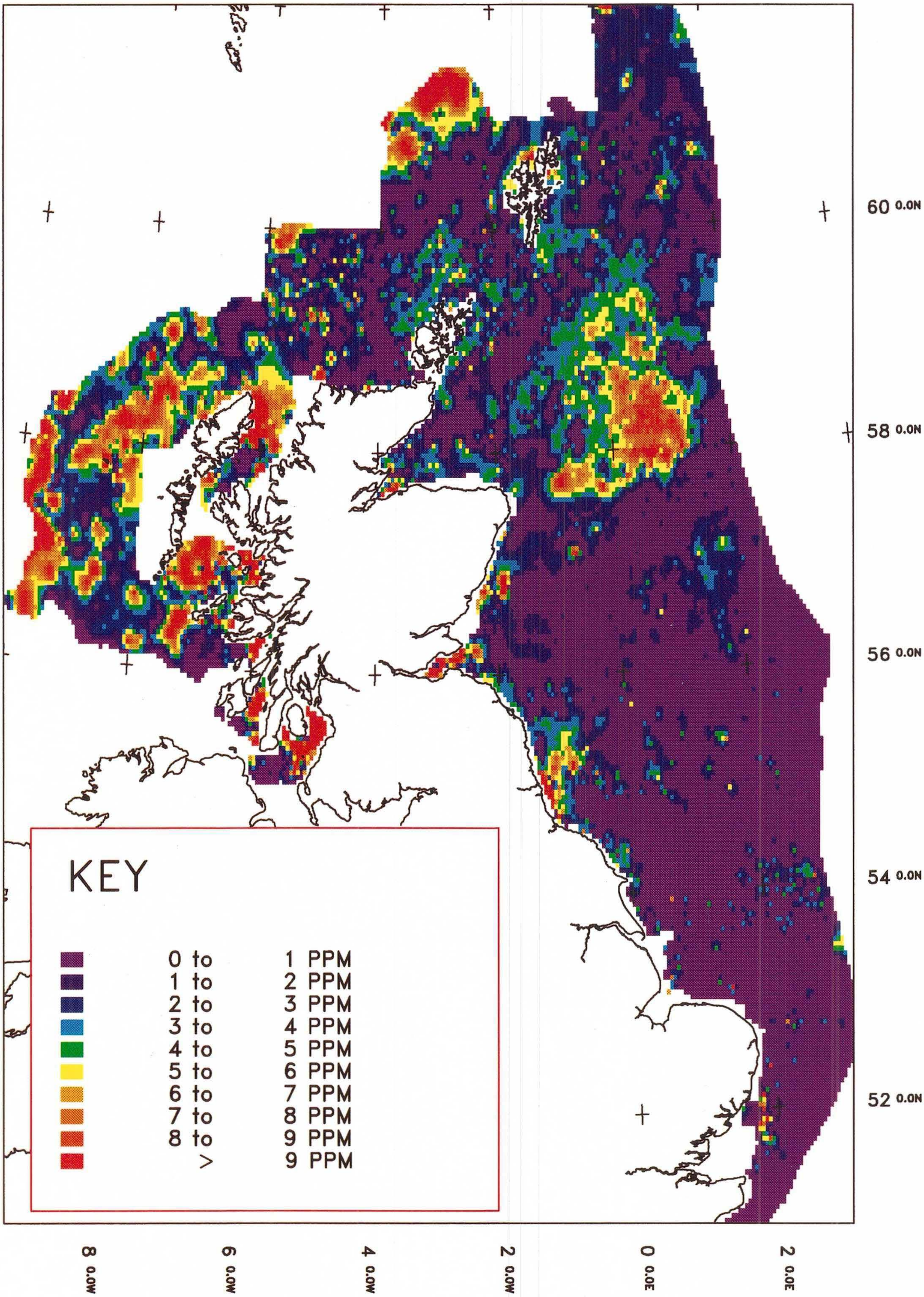
Hebrides and West Shetland shelves

The most areally extensive group of high Ga concentrations occurs on the Hebrides Shelf where gravelly (average 7ppm) and sandy sediments (average 4ppm) have Ga levels comparable with finer-grained sediments elsewhere. The normalised Ga/Li data show that Ga distribution in this area does not follow that of clay minerals in fine-grained sediments and is therefore likely to reflect Ga-bearing minerals, such as feldspar. High Ga values related to its concentration in clay minerals is reflected in the muddy sediments at the shelfbreak (average 9ppm west of the Outer Hebrides).

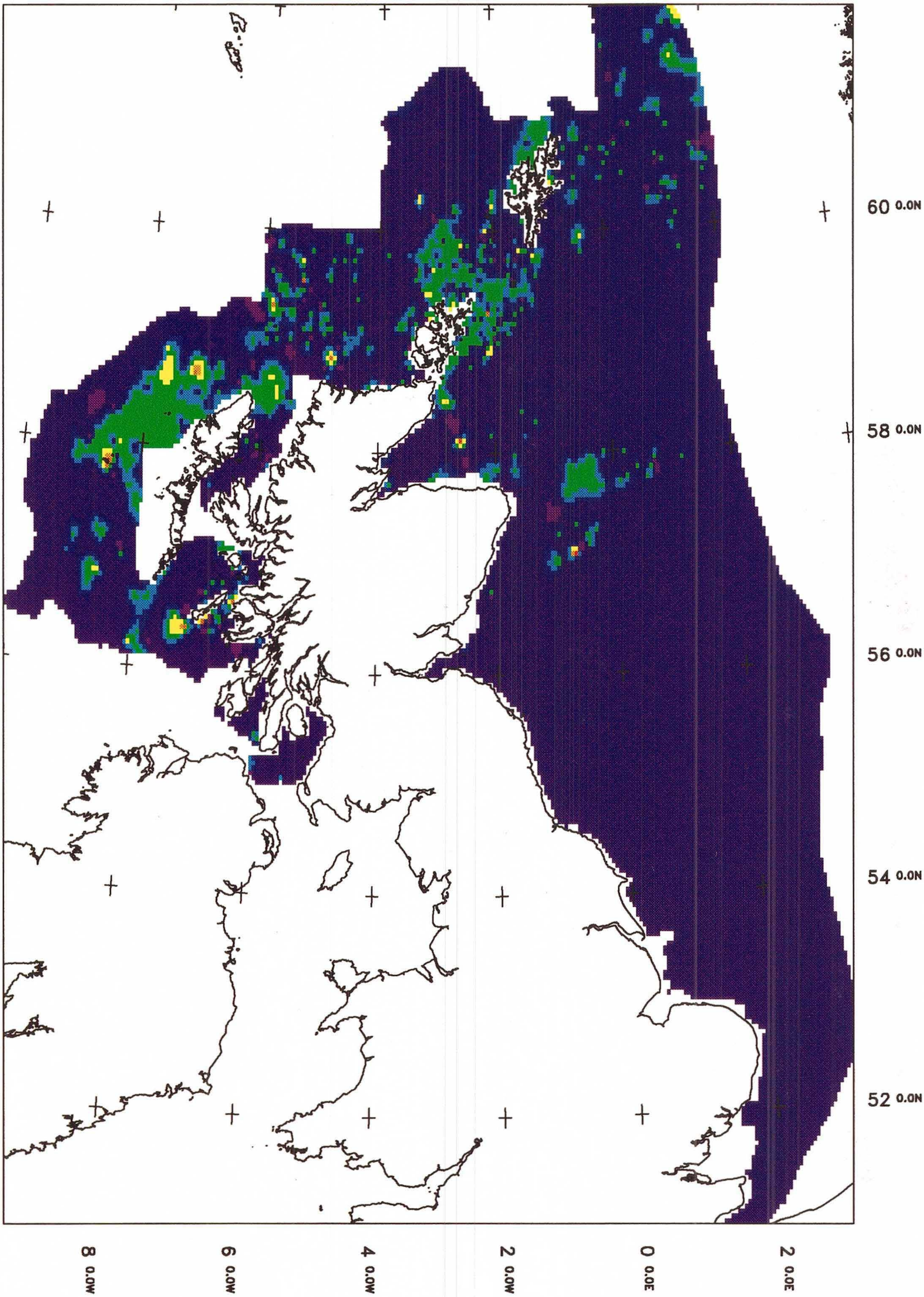
Malin-Hebrides

Ga distribution in this area also demonstrates both types of geochemical behaviour seen on the outer shelf. Fine-grained sediments in the Minch and Sea of the Hebrides (average 8ppm); Sound of Jura (average 15ppm) and the Firth of Clyde (average 16ppm) all have high Ga concentrations. Groups of high values also occur in coarse-grained sediments as indicated by the Ga/Li map around the island of Coll and Tiree.

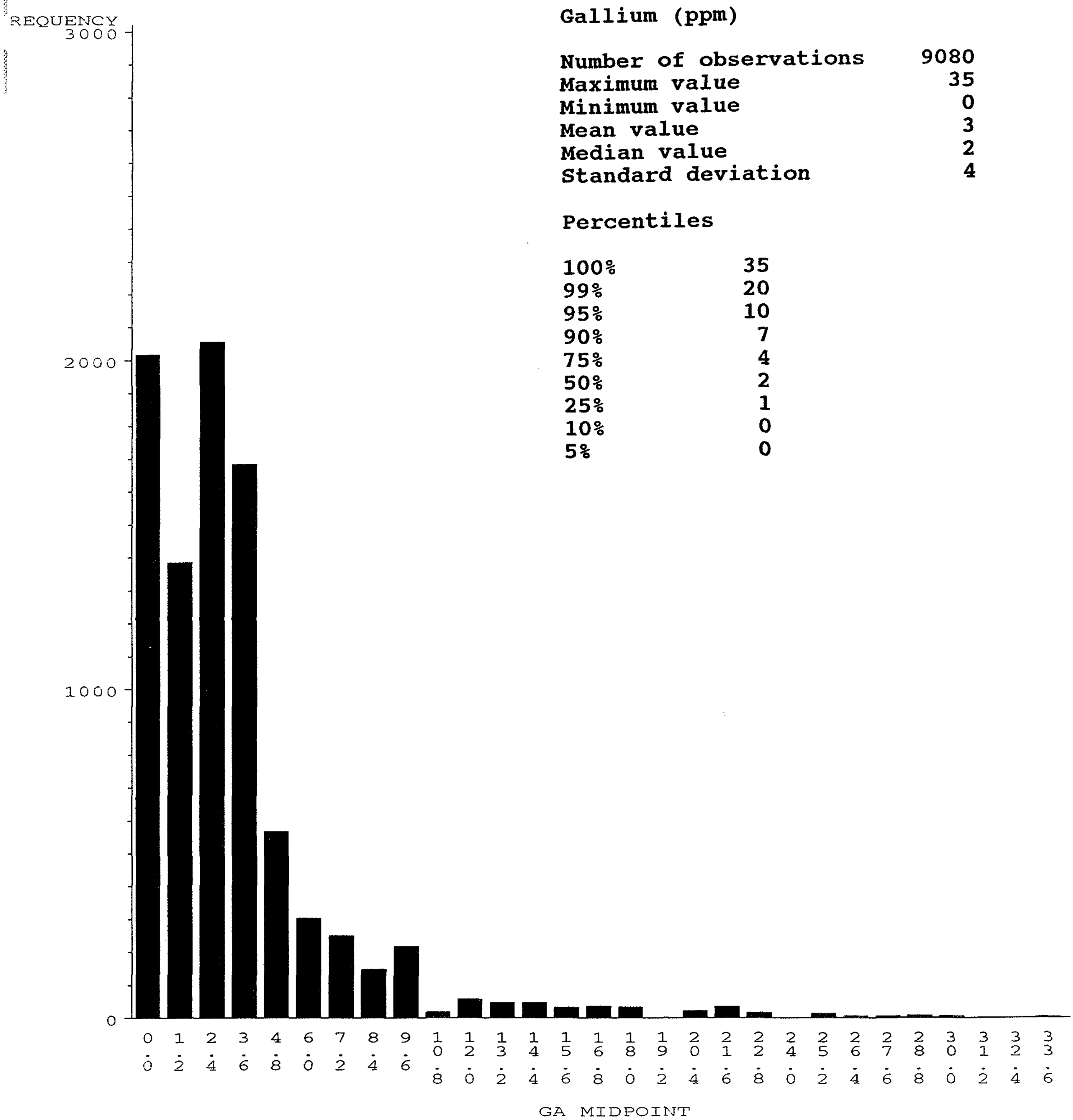
GALLIUM IN SEA-BED SEDIMENT



GALLIUM NORMALISED TO LITHIUM



GALLIUM



STATISTICS

Gallium (ppm)

Number of observations	9080
Maximum value	35
Minimum value	0
Mean value	3
Median value	2
Standard deviation	4

Percentiles

100%	35
99%	20
95%	10
90%	7
75%	4
50%	2
25%	1
10%	0
5%	0

Iron

per cent magnetite and 28.2 per cent other opaque iron oxides in a sand sample from this area.

Northern North Sea

Intermediate Fe_2O_3 values in the Fladen Ground Basin (average 2.91% in mud) are typical of clay and organic-rich fine-grained sediments. Elsewhere, Fe_2O_3 values are low in sands of the area (average 0.33% north of 58°N).

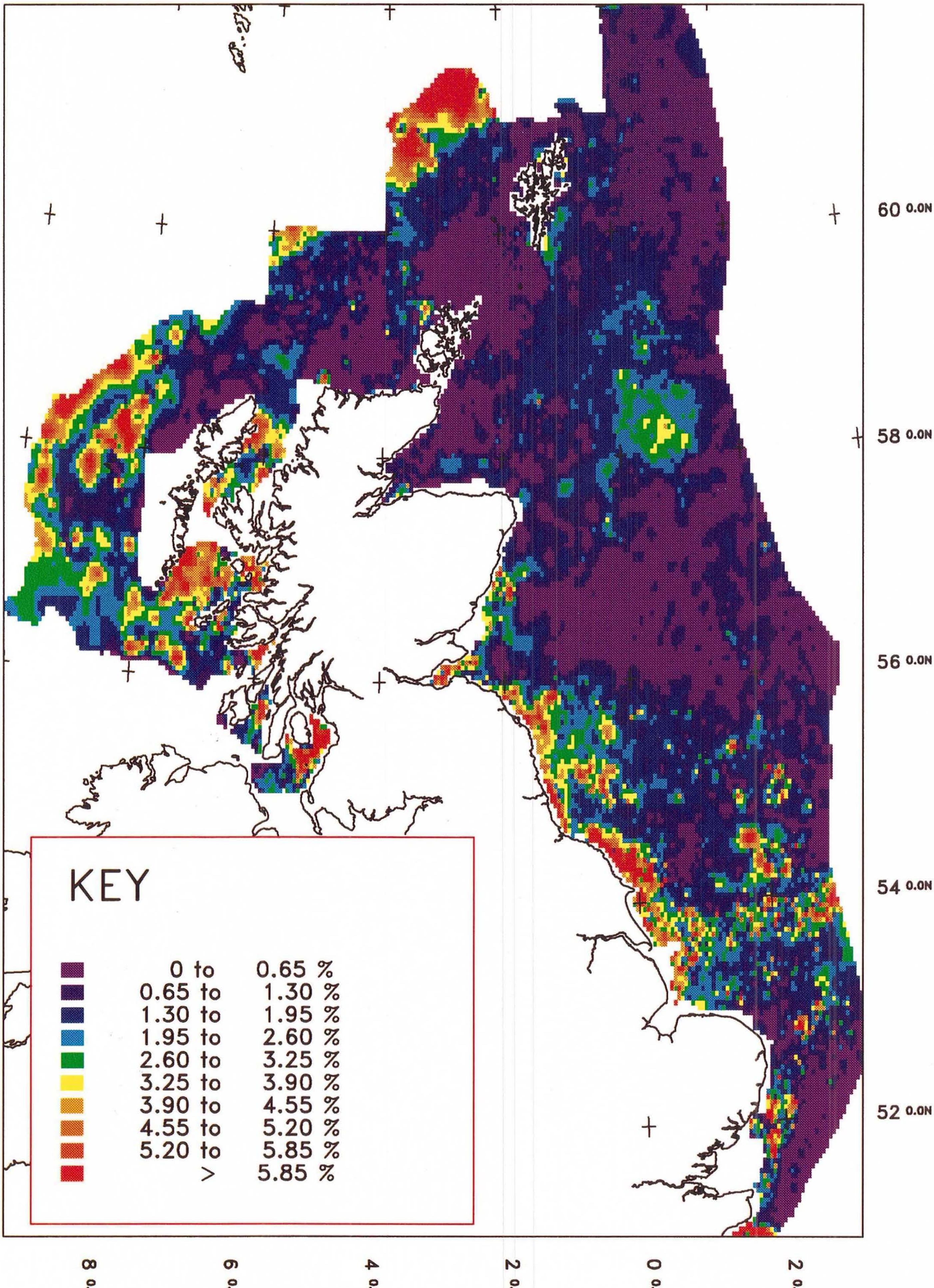
Hebrides and West Shetland shelves

Fe_2O_3 values are generally low throughout the shelf north of Scotland, however high values near Orkney, Shetland and north-west of Cape Wrath are due to precipitation of Fe-Mn hydroxides. Dearnley (1991) reported more than 15% basic igneous rock derived material in the sand fraction of samples from this area, although Fe concentrations were generally less than 1%. High Fe_2O_3 values at the shelfbreak occur in fine-grained sediments (average 4.58% north-west of Shetland; 4.2% west of the Outer Hebrides). High Fe_2O_3 concentrations also occur in coarse-grained sediments in shallow waters such as the Stanton Banks. Here, Fe_2O_3 is associated with high MnO and probably reflects local mixing of the water column due to current action over topographic highs on the sea bed, giving rise to precipitation of Fe-Mn hydroxides. On the outer shelf, in the vicinity of St Kilda, high Fe values in association with Cr, Ni, Ti and Zn probably indicate local derivation from the basic igneous rocks which crop out on the St Kilda Platform.

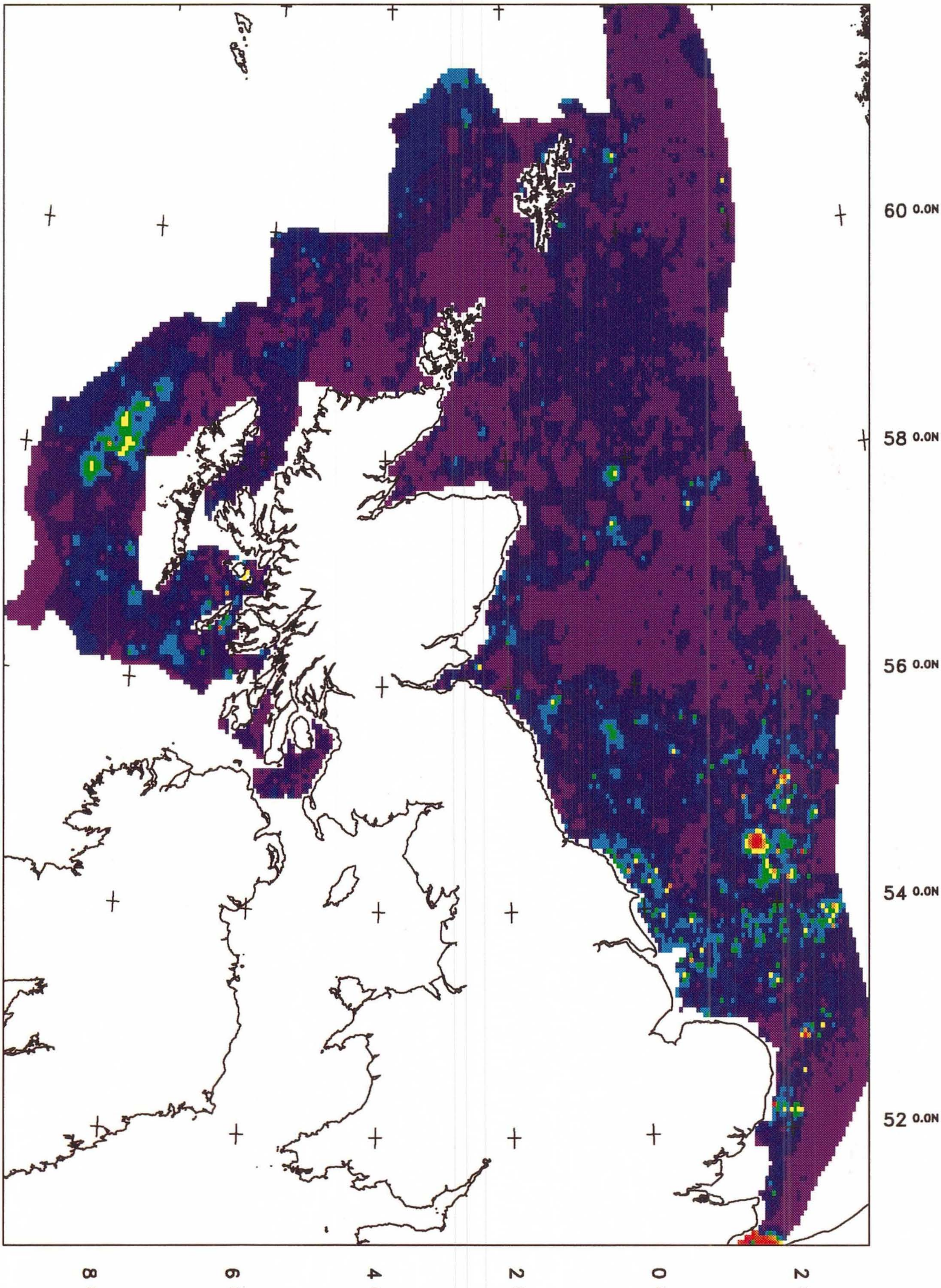
Malin-Hebrides

High Fe_2O_3 values throughout the area are associated with regionally high MnO concentrations. However, the association of Fe_2O_3 with Al_2O_3, Cu, MgO, Ni, TiO_2 and Zn is evidence of the influence of Tertiary basic igneous rocks in The Minch (average Fe_2O_3 concentration of 4.26% in muddy sediment). High Fe_2O_3/Li ratios around Rum, Coll and Tiree probably indicate concentrations of heavy minerals nearshore (see Chromium section). Off the coast of Argyll, and in the Firth of Clyde, high Fe_2O_3 values (average 5.53% in the Sound of Jura; 6.97% in the Clyde Estuary) occur in fine-grained sediments with a high content of clay and organic matter. The Fe_2O_3 concentration of these sediments may also reflect high Fe levels in Dalradian and Carboniferous lithologies (British Geological Survey, 1993) from which the underlying Pleistocene sediments are derived.

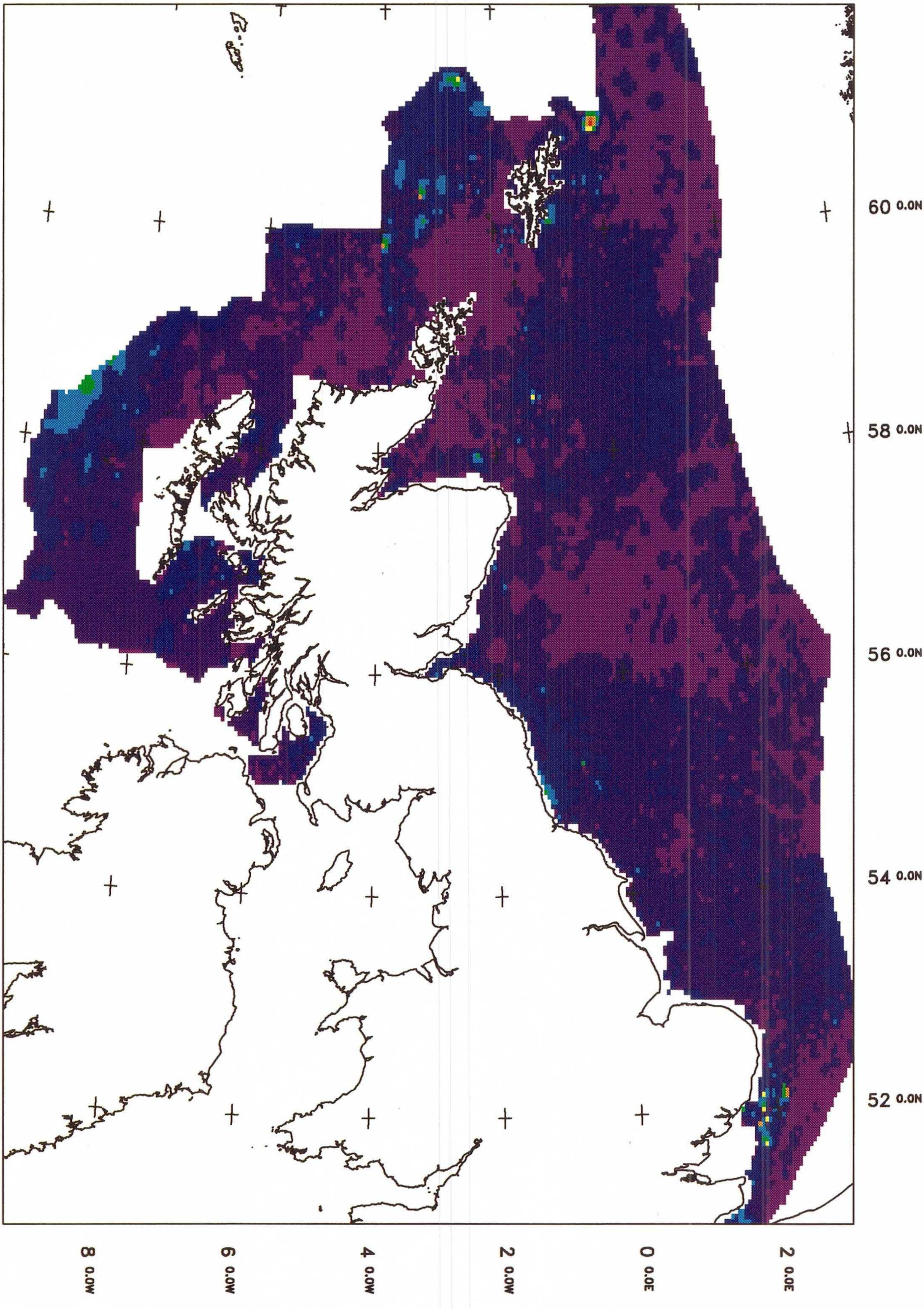
IRON IN SEA-BED SEDIMENT



IRON NORMALISED TO LITHIUM



IRON NORMALISED TO MANGANESE



IRON

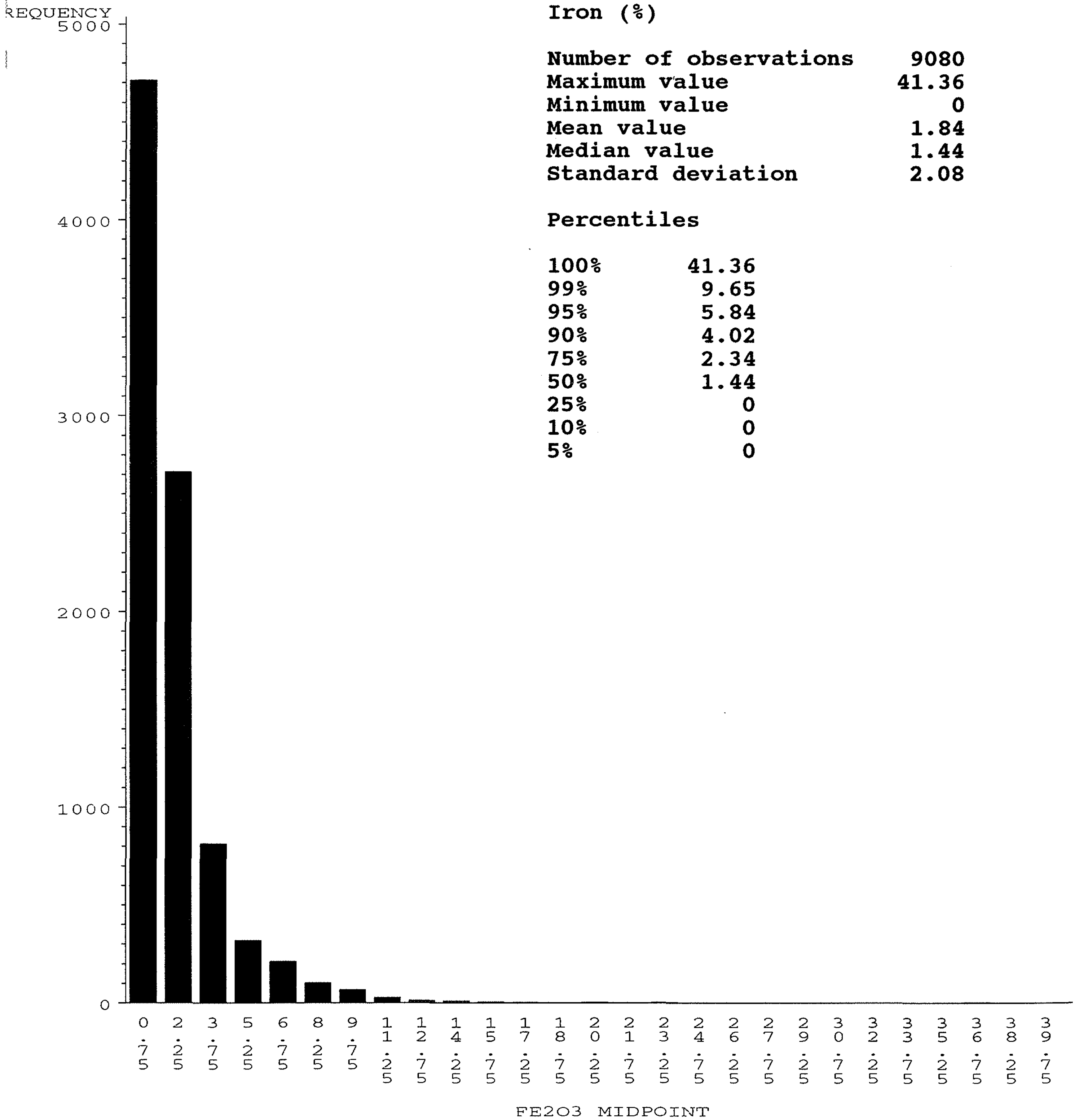
STATISTICS

Iron (%)

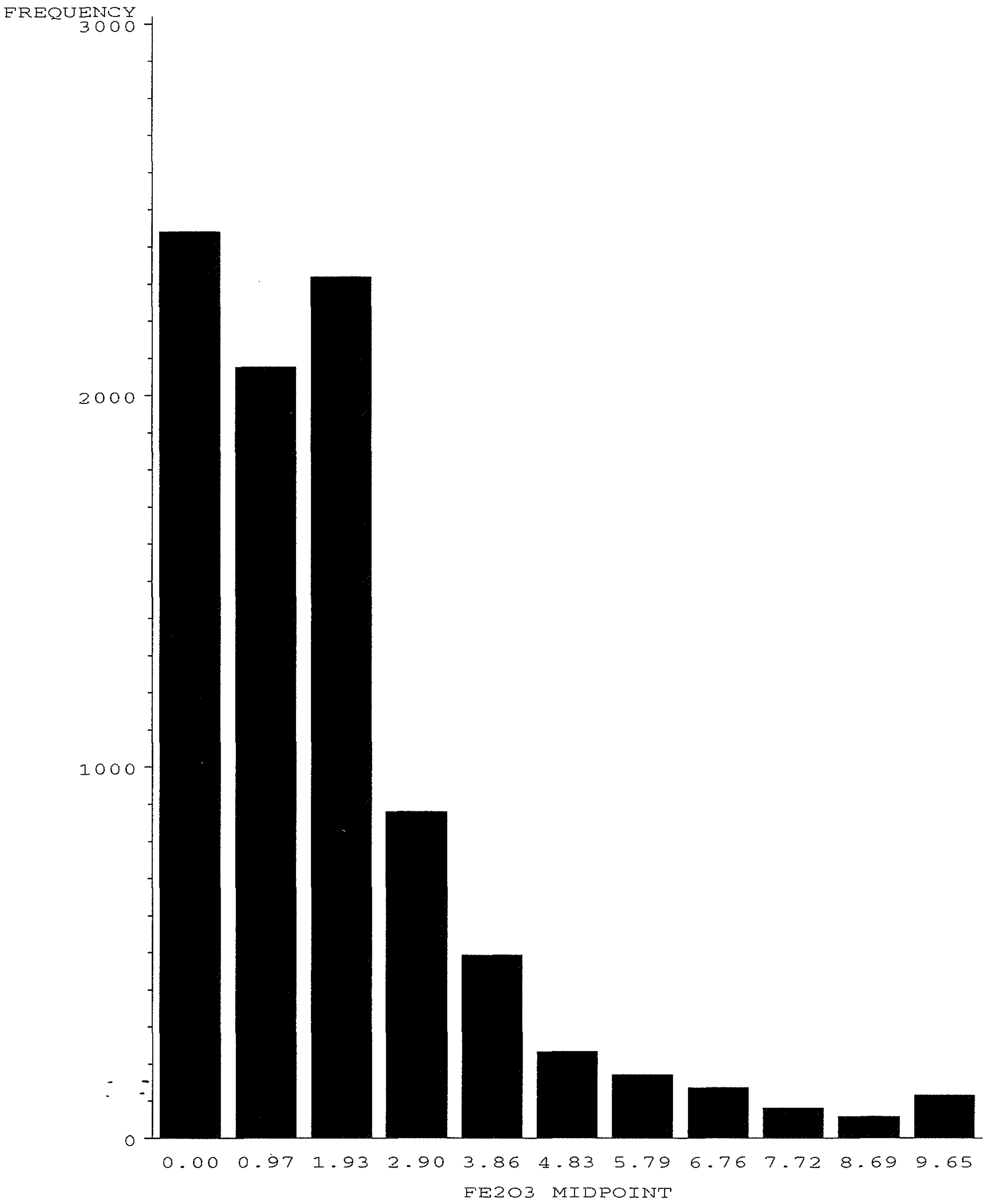
Number of observations	9080
Maximum value	41.36
Minimum value	0
Mean value	1.84
Median value	1.44
Standard deviation	2.08

Percentiles

100%	41.36
99%	9.65
95%	5.84
90%	4.02
75%	2.34
50%	1.44
25%	0
10%	0
5%	0



IRON



FREQUENCY
3000
2000
1000
0
0.00
0.97
1.93
2.90
3.86
4.83
5.79
6.76
7.72
8.69
9.65
FE2O3 MIDPOINT

Lanthanum

Lanthanum

Southern North Sea

La values are generally lower in sands and gravelly sands than in gravelly and muddy sediments. Correlation matrices indicate that La is associated with elements of clay-mineral association in fine-grained sediments whereas in coarse-grained sediments it is concentrated by several different processes. These include detrital minerals (e.g. monazite) where it correlates with Cr and Zr, shell or carbonate rock fragments where correlated with Ca and Sr, or it may be precipitated with Fe-Mn hydroxides. The highest La values in the region occur in fine-grained sediment off the coast of East Anglia (average 31ppm) and in the Markham's Hole/Outer Silver Pit area. Slight increases in La concentrations occur in sandy gravels on banks in the central part of the southern North Sea. According to Nicholson et al. (1985), La distribution in the southern North Sea is related to that of coarse-grained sediment. These authors found correlations between La, U, Sr, Y, Be and carbonate content suggesting association with the Ca content in shell debris or carbonate rocks. A marked correlation with Be was thought to arise from Fe/Mn coatings on coarse particulate matter.

Central North Sea

High La values occur in muddy sediments near the coast between the Tees and Tyne estuaries (average 40ppm) and southward along the coast to Flamborough Head (average 37ppm). This may reflect their derivation from Carboniferous (Westphalian) and Permian sedimentary rocks in the catchment areas of these two rivers, as La concentrations are high in stream sediments derived from these lithologies (British Geological Survey, 1993). The highest La concentrations occur in the Firth of Forth (average 54ppm) and the catchment area of the River Forth also consists mainly of Carboniferous sedimentary rocks.

Farther offshore intermediate La values (average 21ppm in gravelly sands; 17ppm in sands) occur in the Dogger Bank area, suggesting that La-bearing resistate minerals such as monazite, occur in an area of heavy mineral enrichment (see Chromium, Iron, Titanium and Zirconium sections). A slight increase in La/Li ratios on the Dogger Bank, and sands to the north with similar intermediate to high La values, suggest detrital minerals form a significant proportion of these sediments (see below). Intermediate La concentrations in nearshore gravelly sands along the east coast of Scotland (average 26ppm) may also be explained by concentrations of detrital minerals. Sandy sediments near the median line both north and south of the Fladen Ground Basin have intermediate to high La concentrations which, like the sands farther south, may signify the occurrence of detrital minerals. Dangerfield and Tulloch (1989) noted monazite concentrations up to 2% in the fine sand fraction of samples from the Fisher 1: 250 000 sheet area, and the highest concentrations of minor 'acid igneous' minerals of all samples from the North Sea.

Northern North Sea

La values vary over a wide range in the northern North Sea with high concentrations occurring in fine-grained sediments in the Fladen Ground Basin (average 39ppm). The largest group of high La values (average 48ppm) occurs in shell-rich sandy gravels on the sea bed between Orkney and Shetland. The strong correlation between La and Ca suggests that La is incorporated into the shells of marine organisms. This may also explain the intermediate values (average 24ppm) on the Aberdeen Bank which is also an area of high Ca concentration. As noted above, Nicholson et al. (1985) reported a strong correlation between La and Ca which they related to association with shell debris or carbonate rocks.

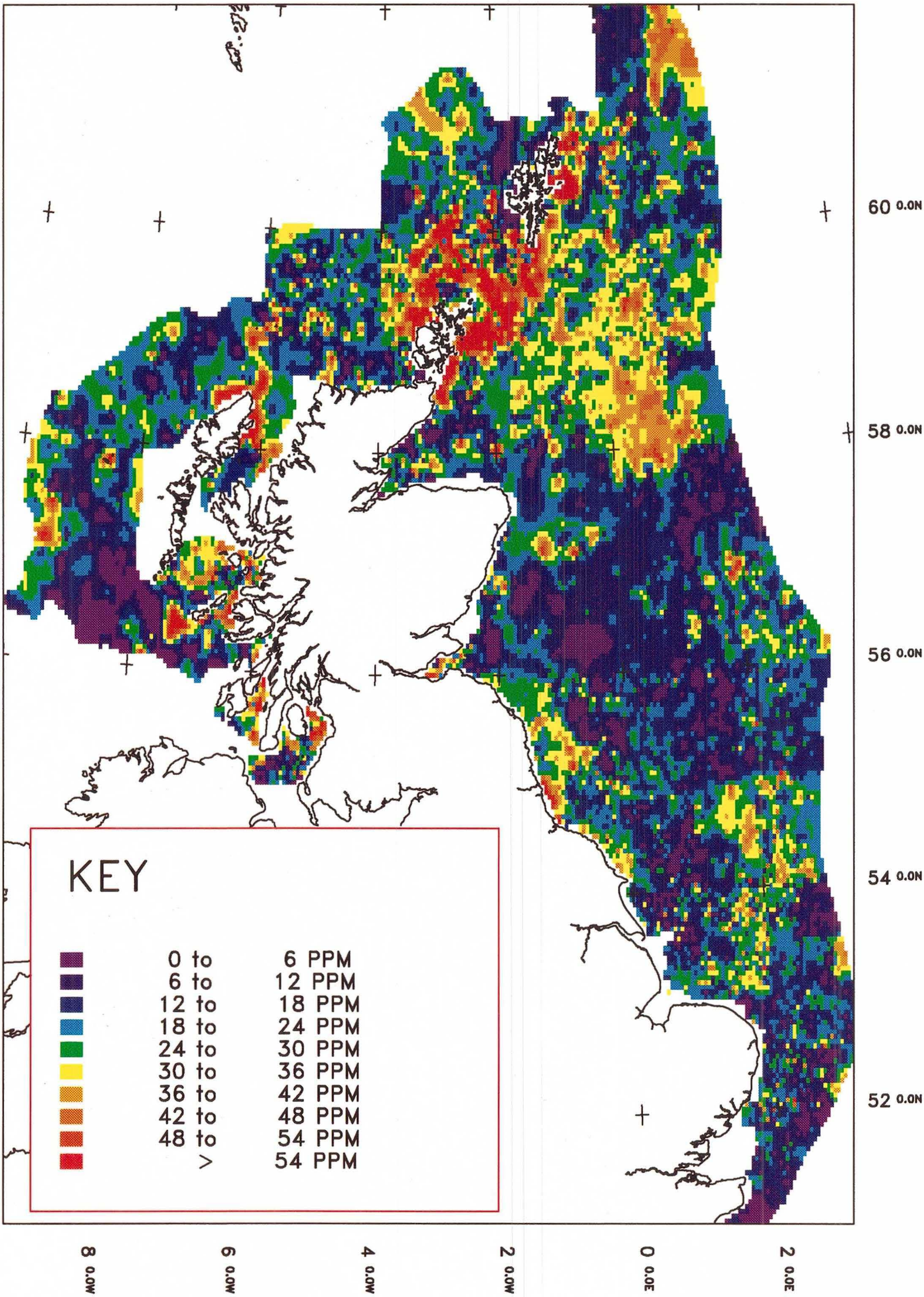
Hebrides and West Shetland shelves

La values decrease westward from the Orkney-Shetland Platform across the West Shetland Shelf, where average values in sands, gravelly sands and gravels are similar (21-24ppm). High La values around the north coast of Lewis and north-west of Cape Wrath occur in association with high Ca concentrations and are due to shell-rich sediments. A group of high La values around St Kilda suggests local accumulation of heavy minerals derived from the Tertiary igneous rocks of the St Kilda Platform. Muddy sediments at the shelfbreak have intermediate to high La values (average 28ppm west of the Outer Hebrides).

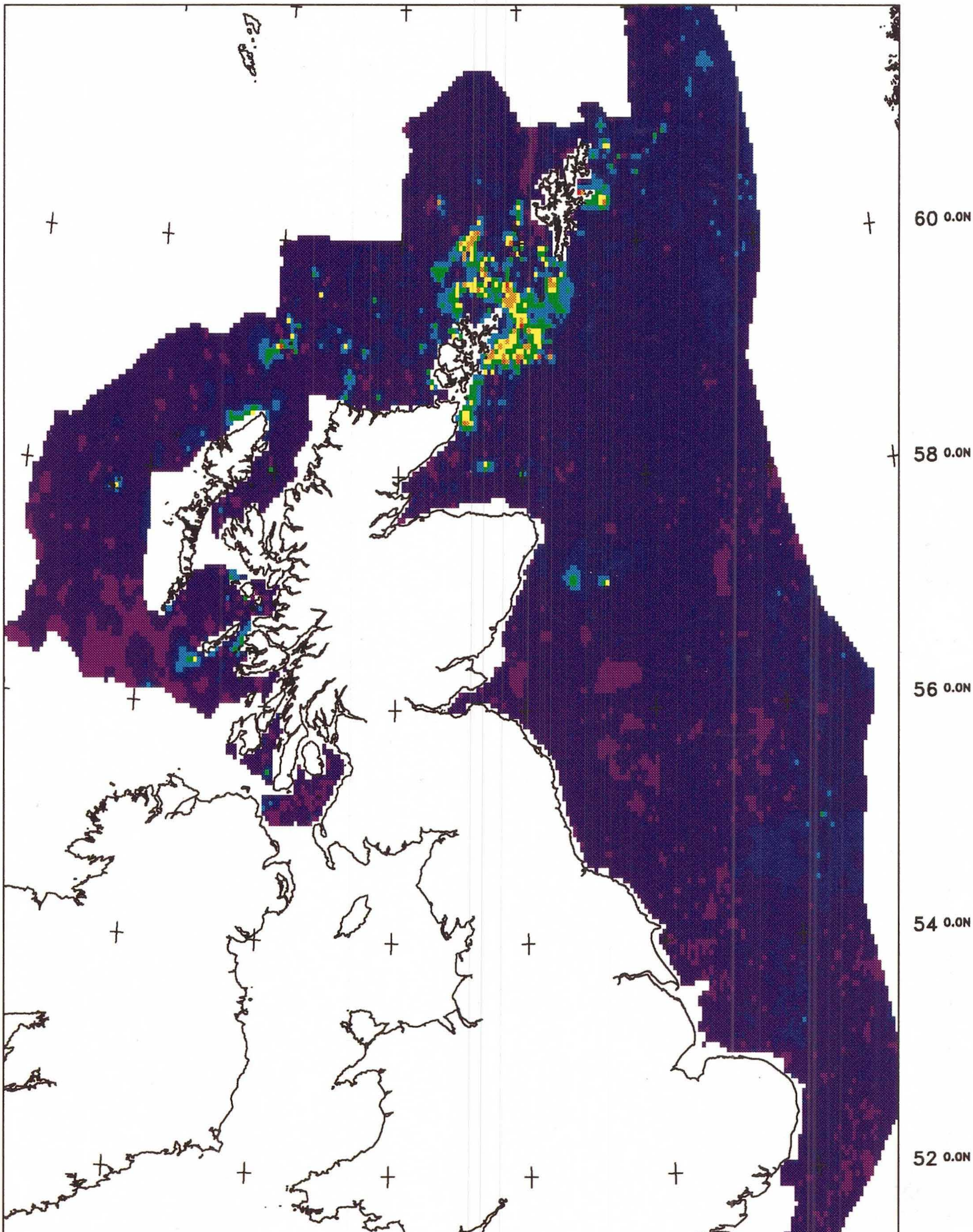
Malin-Hebrides

A group of intermediate La values in coarse-grained sediments south-west of Tiree, in an area with high Cr, Fe, and TiO_2 concentrations, suggests local accumulation of heavy minerals. Other groups of higher La values in the region occur in fine-grained sediments in the Sound of Jura (average 37ppm) and Firth of Clyde (average 32ppm). High La values in the latter area occur mainly around Arran and probably reflect derivation of sediment from the light rare earth element enriched Tertiary granite of the island (British Geological Survey, 1993).

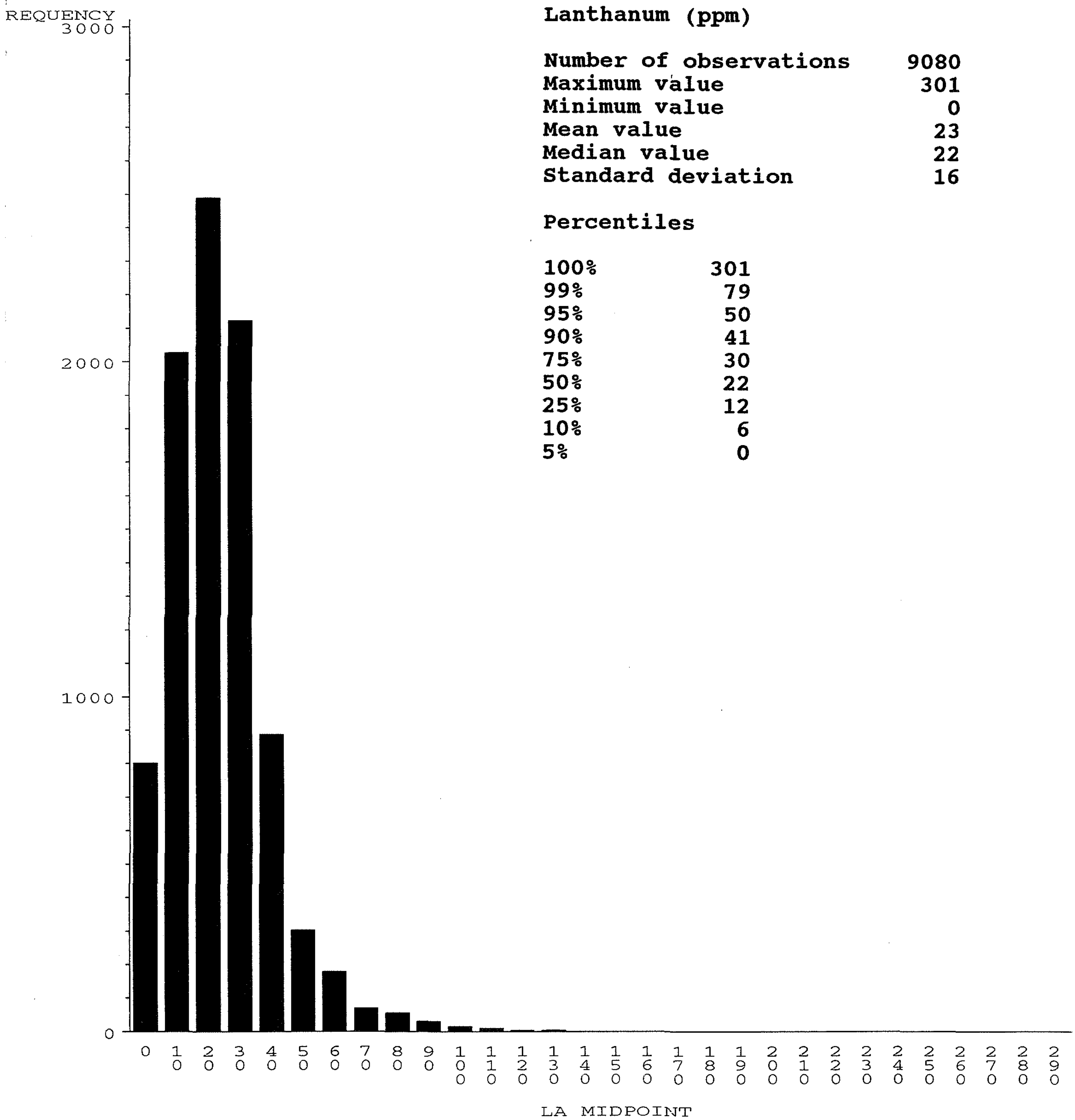
LANTHANUM IN SEA-BED SEDIMENT



LANTHANUM NORMALISED TO LITHIUM



LANTHANUM



STATISTICS

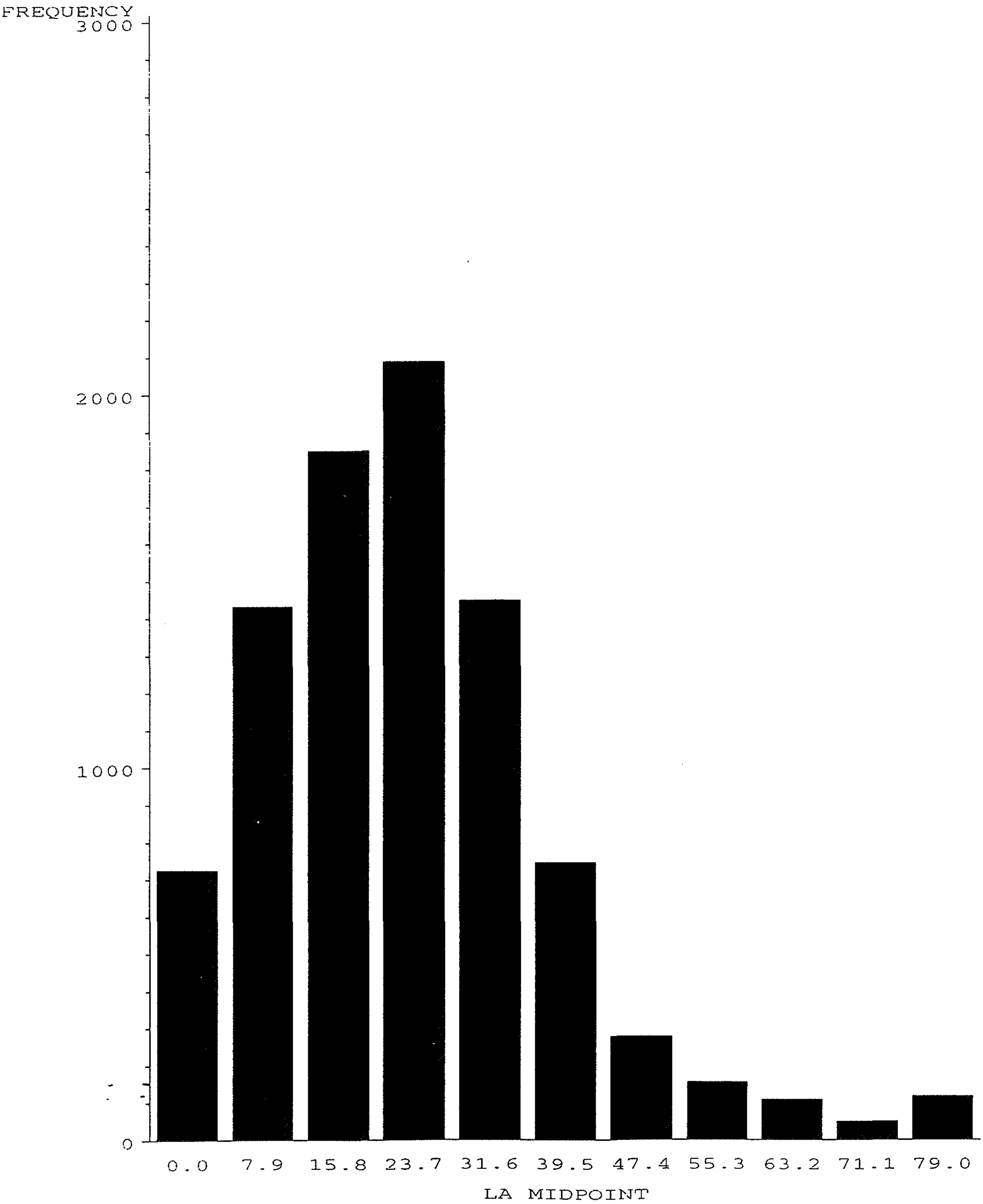
Lanthanum (ppm)

Number of observations	9080
Maximum value	301
Minimum value	0
Mean value	23
Median value	22
Standard deviation	16

Percentiles

100%	301
99%	79
95%	50
90%	41
75%	30
50%	22
25%	12
10%	6
5%	0

LANTHANUM



FREQUENCY
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1000
0
0.0
7.9
15.8
23.7
31.6
39.5
47.4
55.3
63.2
71.1
79.0
LA MIDPOINT

Lead

Lead

Southern North Sea

Pb values are generally higher near the coast than in the sandy and gravelly sediments farther offshore. Intermediate values nearshore in coarse-grained sediments of the Dover Strait (average 21ppm), and offshore of Skegness (average 22ppm), are not significantly higher than Pb concentrations in muddy sediments (e.g. average 21ppm in the Outer Thames Estuary; 29ppm off the coast of East Anglia).,The high Pb/K_2O values off the coast of East Anglia indicate that in this area, Pb occurs mainly in the fine-grained fraction of the sediments. Farther offshore, the fine-grained sediments of the Markham's Hole area have similar Pb concentrations to those nearshore (average 20ppm) however they are higher than Pb values in the surrounding sands. The highest Pb values in the region occur as part of a continuous zone along the east coast of the UK between Spurn Head and Aberdeen (see below).

Central North Sea

High Pb values occur mainly in fine-grained sediments near the coast (average 65ppm between Flamborough Head and the Tees Estuary; 58ppm offshore of the Tyne-Tees estuaries). Nicholson and Moore (1981) found a clear association between fine-grained coastal sediments and high concentrations of Pb, Cu and Zn, the maximum in each case being found in samples from the Tyne Estuary. Kersten and Klatt (1988) reported low concentrations of Pb near the coast except for an area off the north-east coast of England. Some of the highest Pb values which they recorded occurred in an elongate area off the Tyne and Tees estuaries, but north of the Humber. Webb (1978) pointed out that the mineralized catchment areas of these rivers gave rise to sediments with anomalously high metal content, especially of Pb. Kersten and Klatt (1988) calculated heavy metal enrichment factors and found that the highest factor for Pb also occurred in an area off the north-east coast of England. Furthermore Burt et al. (1992) found high Pb in sediments from the Tyne and Wear estuaries and noted that the use of leaded petrol makes it inevitable that, particularly in urban areas, most estuarine sediments are contaminated with Pb. The occurrence of high values of Pb normalised to Li, K_2O and Cr (as an indicator of a transition metal which occurs mainly in heavy mineral concentrations) in the coastal area between the Humber and Tees estuaries, suggests that these are mainly due to contamination.

North Sea Task Force (1993) reported a range of 1.7 to 288ppm Pb (average 21ppm) for sediments in the North Sea. In the UK sector, the highest values were associated with rivers draining industrialised catchments such as along the northeast coast of England and the Humber and Thames estuaries.

The zone of high Pb levels near the eastern coast of England continues northward suggesting that Pb concentrations are enhanced by sediment input from the industrialised catchments of the rivers Forth and Tay.

Pb values in the Firth of Forth (average 64ppm) are comparable with those offshore of the Tyne and Tees estuaries. Although the catchment area of the River Tay is less industrialised than the other major rivers of the east coast of the UK, industrial activity in the cities of Dundee and Perth, and dumping of sewage sludge in the vicinity of Bell Rock, may contribute to high metal contents in the coastal zone. Nicholson and Moore (1985) observed a strong correlation between Pb and organic material content, and adsorption onto clay/organic complexes or organic debris is thought to be an important factor in the enhancement of Pb values in all river estuaries around the UK.

Farther offshore, Pb values are generally higher than in the central and southern North Sea. An overall increase in elements such as Al, Ba, K_2O and Rb in this area suggests that these sediments contain a higher proportion of potassic aluminosilicates, such as mica and K-feldspar, both of which are primary carriers of Pb. Comparison of maps of Pb/Li and Pb/K_2O confirm that Pb is mainly associated with K_2O in most of the central and southern North Sea. Fine-grained sediments in the Devil's Hole area have intermediate Pb levels (average 24ppm).

In the central North Sea on the Dogger Bank and Great Fisher Bank, North Sea Task Force (1993) reported high Pb concentrations in the fine fraction of sea-bed sediments. Pb normalised to Al showed a uniform distribution, indicating that there are both land-based and atmospheric sources. BGS geochemical data indicate that Pb concentrations in sands on the Dogger Bank are generally low (average 9ppm), although there is a slight increase in gravelly sands (average 12ppm) and in sands to the north of the Dogger Bank towards the Fisher Bank area (average 14ppm). Kersten and Klatt (1988) in a study of 122 sea-bed sediments from the Dover Strait to 60° N, found high values of Pb in the Fisher Bank area between 2° and 6°E and north of 56° N. Since this area is not affected by waste discharges or dumping, the authors considered atmospheric input as a possible source of Pb.

Northern North Sea

Pb concentrations in fine-grained sediments of the Fladen Ground Basin (average 18ppm), while higher than the surrounding sands, are significantly lower than in muddy sediments nearshore. Although intermediate levels of Pb in muddy sediments of the Moray Firth (average 17ppm) would suggest sediments with low metal contributions from contaminants, the maps of Pb normalised to Li, Cr and K_2O each indicate Pb enrichment in this area. As this pattern also occurs for Cu and Zn, it seems probable that sediments derived from the industrialised Inverness and Cromarty firths contain some contaminants.

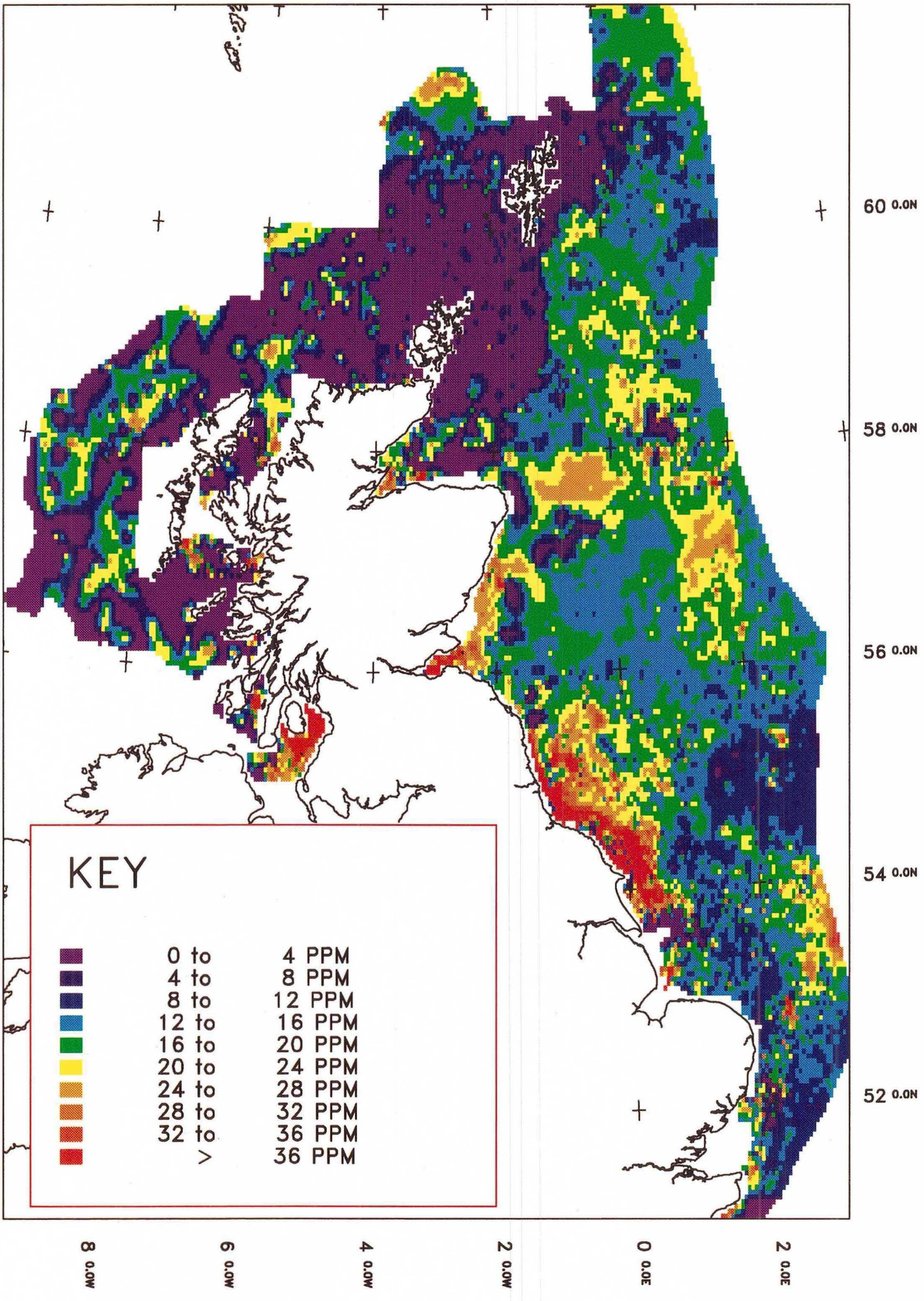
Hebrides and West Shetland shelves

Pb analyses in the area are affected by correction for Ca interference and therefore do not give an accurate representation of Pb values in the sea-bed sediments of the region. Where the Ca correction has not been applied, the sediments appear to have similar Pb concentrations to those of the northern North Sea. Pb values are broadly similar in both fine- and coarse-grained sediments suggesting that widespread occurrence of ferromagnesian minerals derived from the basic igneous rocks of the region is the dominant influence on Pb distribution.

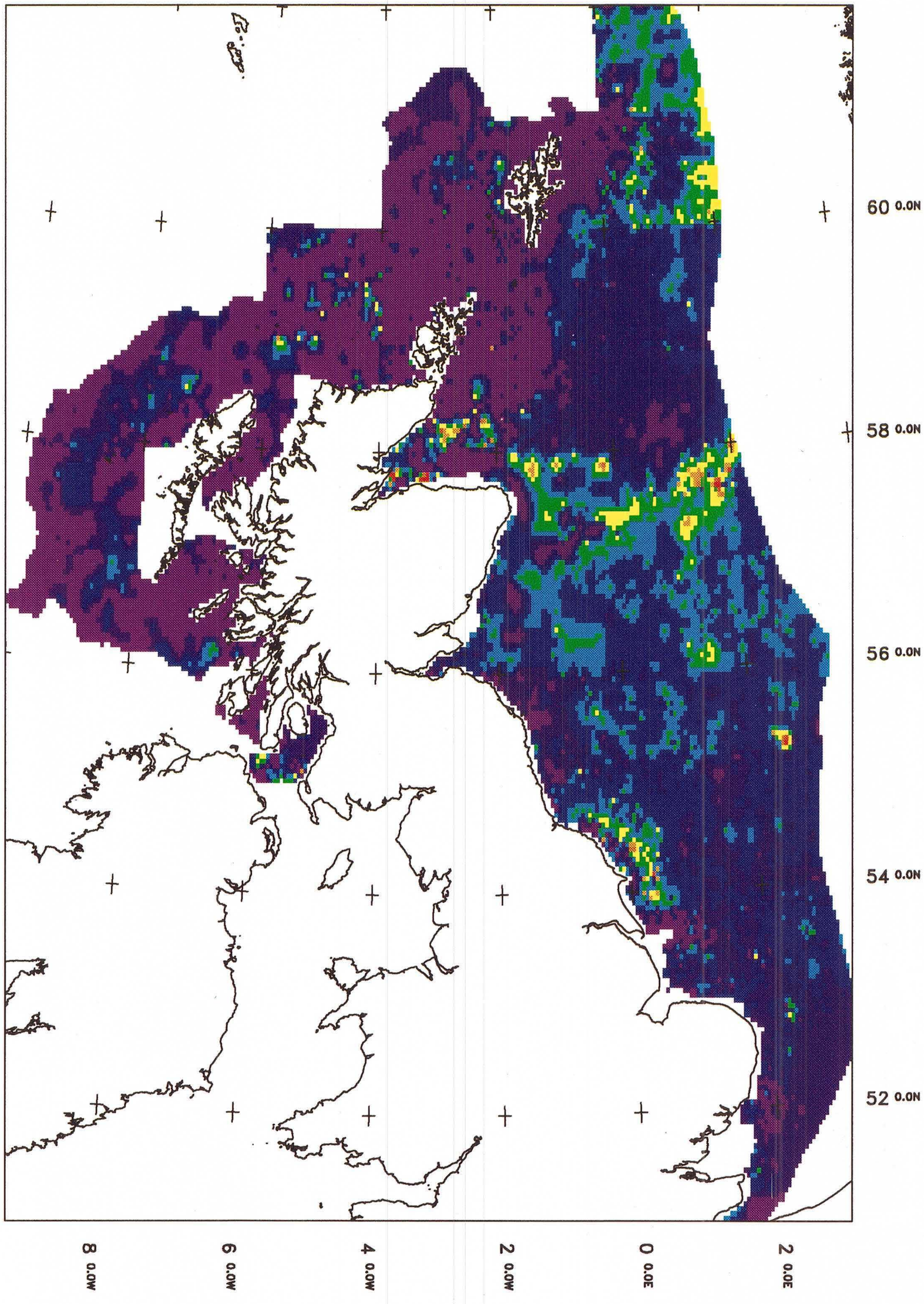
Malin-Hebrides

Although Ca interference corrections also largely obscure the Pb distribution pattern in this region, the highest values are seen to occur mainly in fine-grained sediments where Pb is adsorbed on clay minerals. Sediments containing lithic fragments derived from Tertiary granitic rocks may influence some of the high Pb values found in The Minch. Dearnley (1991) noted the occurrence of granophyric fragments similar to those of the Skye granites in several samples within this area. The highest Pb values in the area occur in fine-grained sediments in the Sound of Jura (average 25ppm) and the Firth of Clyde (average 59ppm). Like the industrialised rivers of the east coast, Pb concentrations in the Clyde Estuary are enhanced due to contamination, such as by dumping of sewage waste, at Garroch Head which increases adsorption of Pb on organic debris. This is demonstrated by comparing Pb values in the Firth of Clyde with those in the Sound of Jura, which in relation to other trace metals which are not enhanced by contamination, have similar levels to those of the Clyde Estuary.

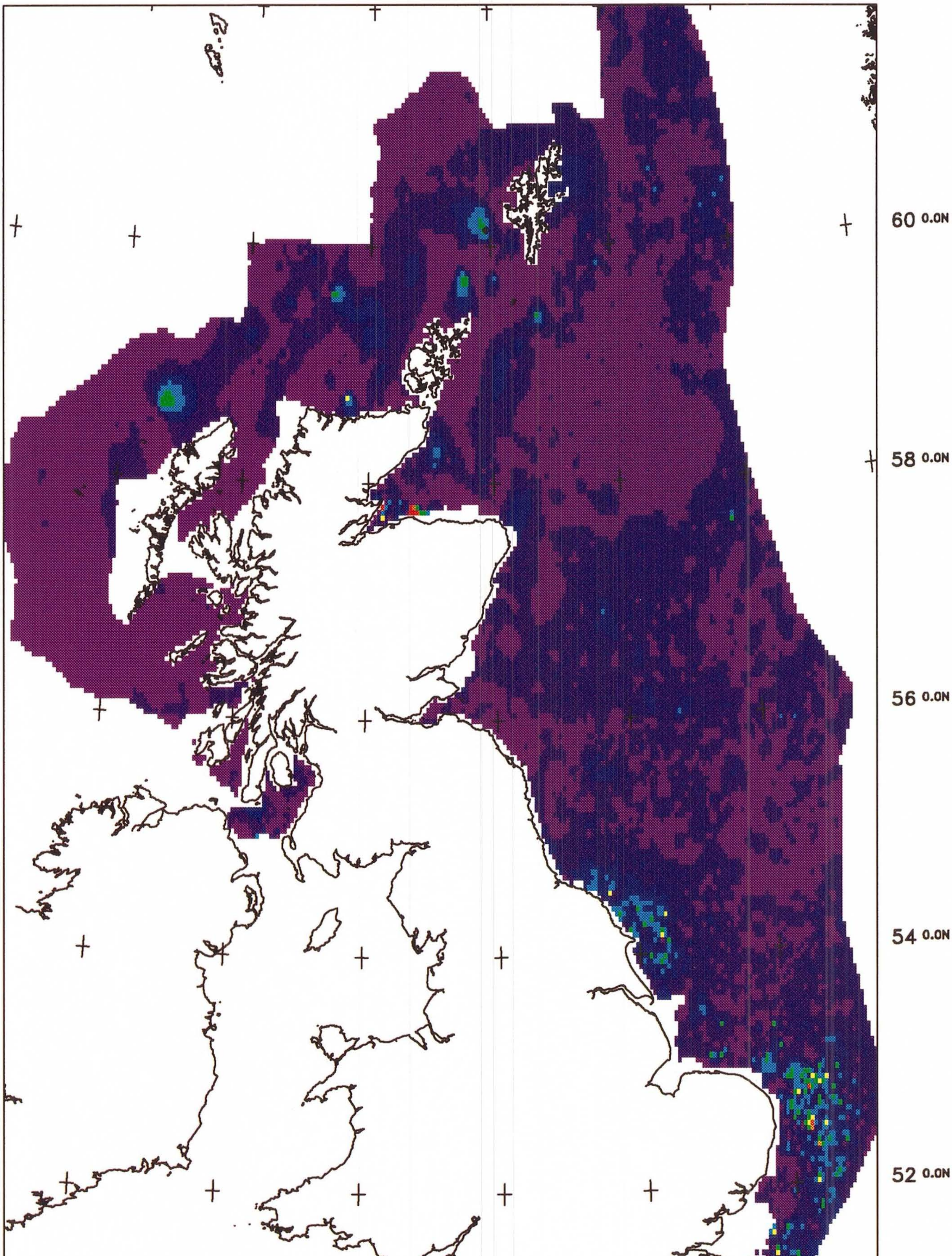
LEAD IN SEA-BED SEDIMENT



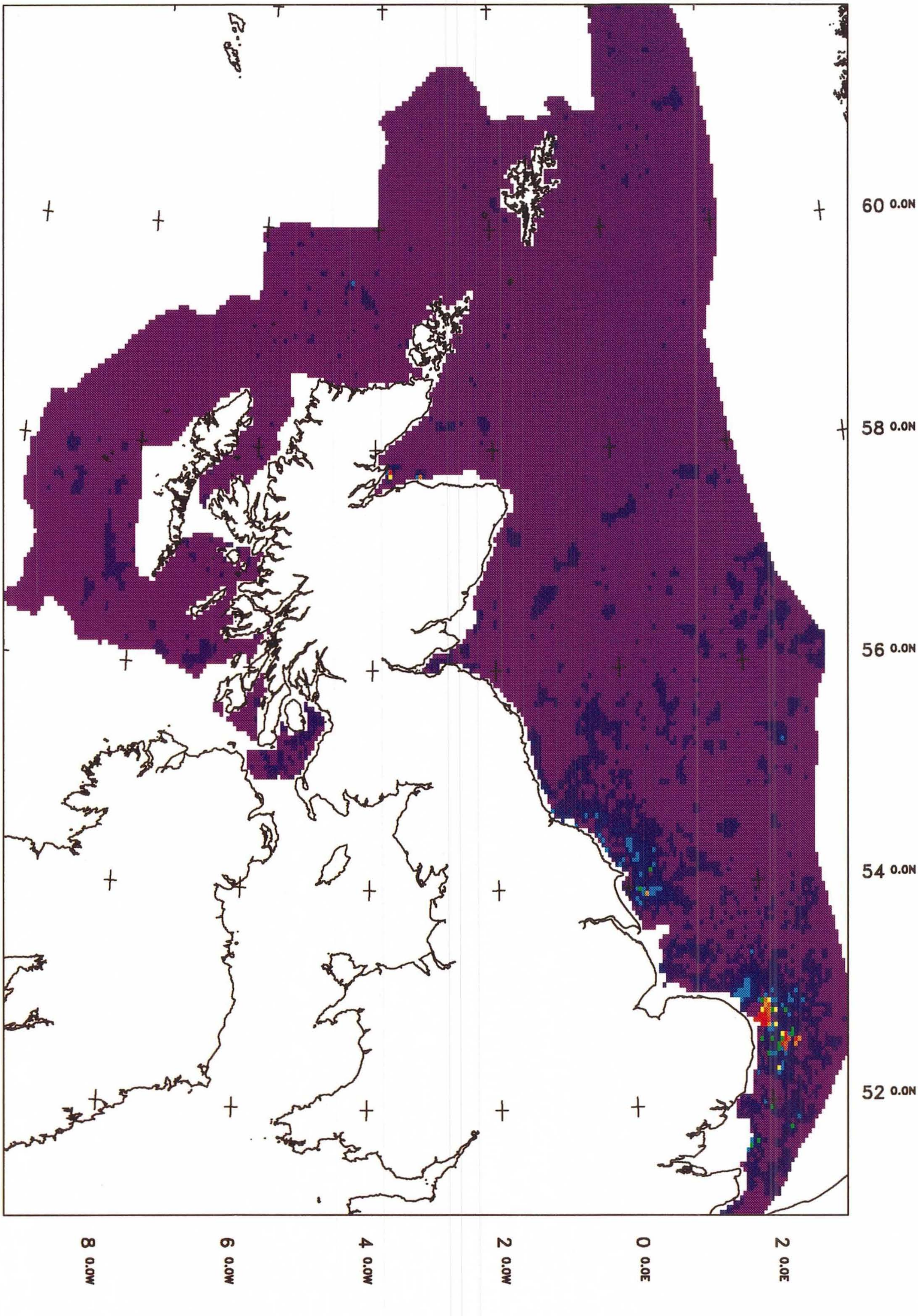
LEAD NORMALISED TO LITHIUM



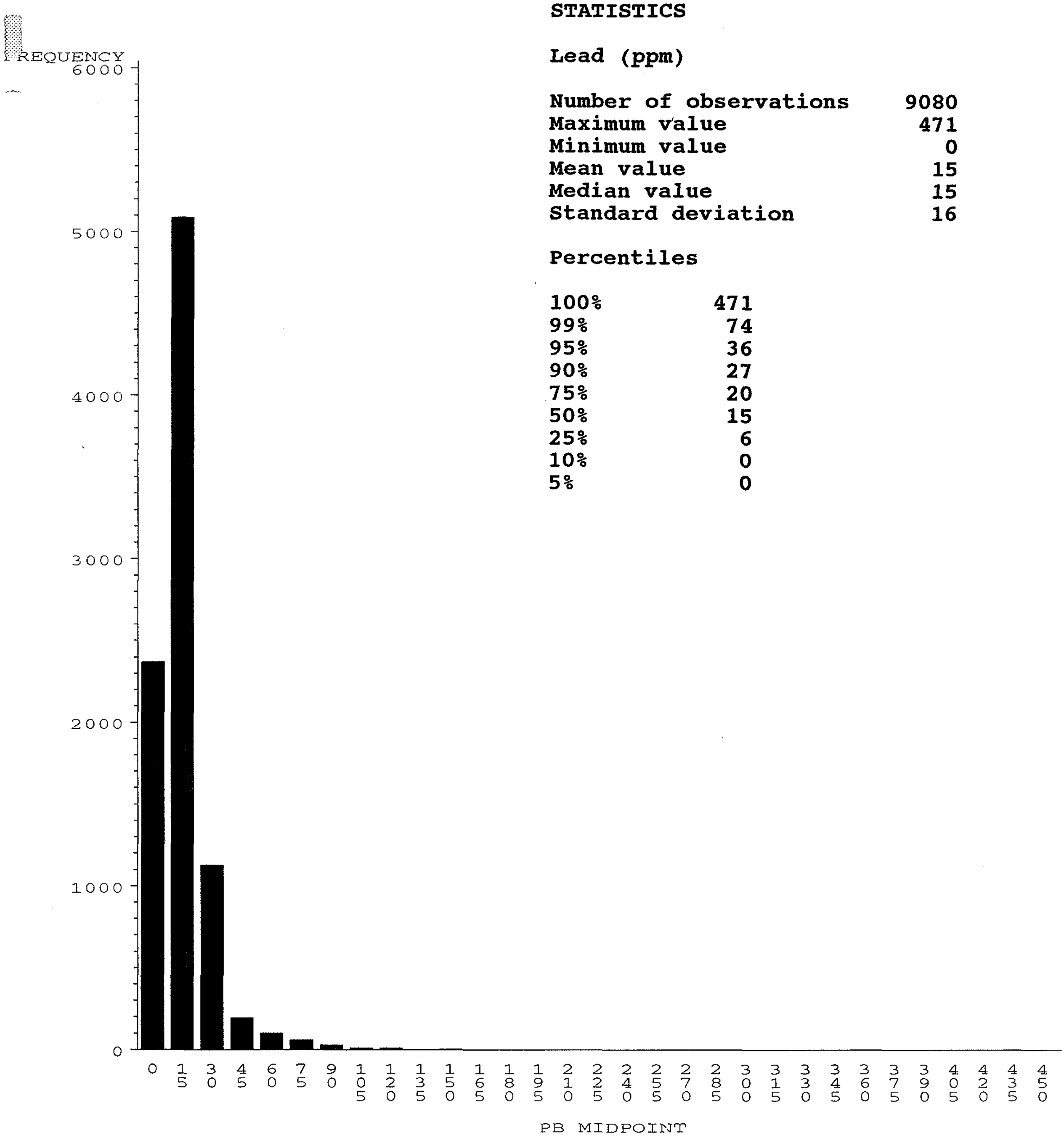
LEAD NORMALISED TO CHROMIUM



LEAD NORMALISED TO POTASSIUM



LEAD



STATISTICS

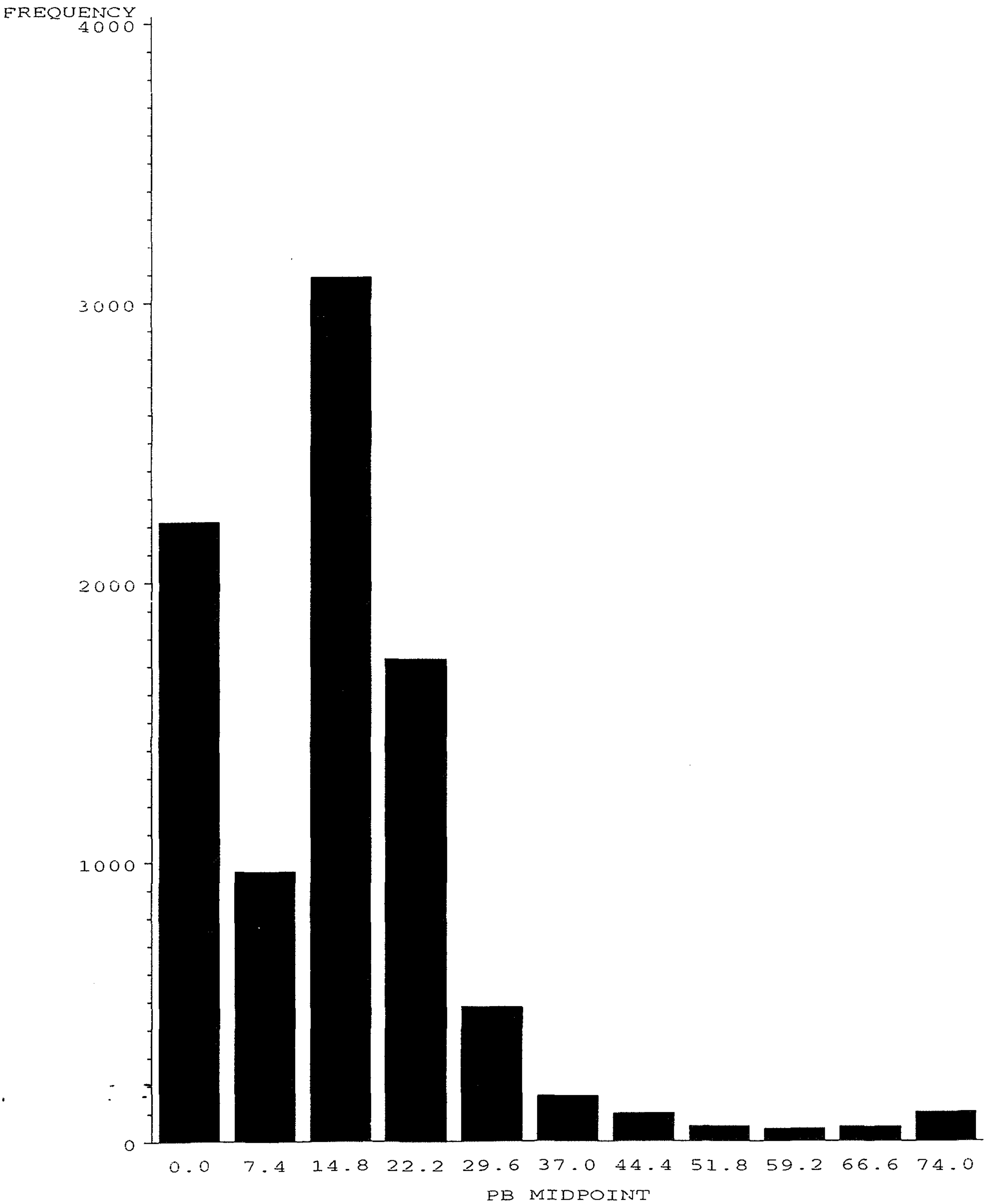
Lead (ppm)

Number of observations	**9080**
Maximum value	**471**
Minimum value	**0**
Mean value	**15**
Median value	**15**
Standard deviation	**16**

Percentiles

100%	**471**
99%	**74**
95%	**36**
90%	**27**
75%	**20**
50%	**15**
25%	**6**
10%	**0**
5%	**0**

LEAD



FREQUENCY
4000
3000
2000
1000
0
0.0
7.4
14.8
22.2
29.6
37.0
44.4
51.8
59.2
66.6
74.0
PB MIDPOINT

Lithium

Lithium

Southern North Sea

Li values are low throughout most of the region with the exception of areas of fine-grained sediment. However, sandy sediments have higher Li concentrations than those farther north (average 9.8ppm compared with 6.7ppm in the central North Sea) suggesting that sands here contain a higher proportion of clay minerals or organic matter. High Li values occur in muddy sediments in the Outer Thames Estuary (average 30.5ppm); off the East Anglian coast (average 34.8ppm); offshore of Skegness (average 20.9ppm); and in the Markham's Hole/Outer Silver Pit area (average 16.2ppm). The high Li concentrations in fine-grained sediments near the coast of the central and southern North Sea reflects the input of sediment from coastal erosion and rivers. Nicholson et al. (1985) reported a strong correlation between Li and elements which concentrate in clay minerals. However, they considered a weaker correlation with Mg to indicate a probable lower incidence of montmorillonite (which would favour the retention of Mg) relative to illite and kaolinite in sea-bed sediments of the North Sea.

Central North Sea

A group of high Li values occur in muddy sediments along the coast between Flamborough Head and St Abb's Head (average 30.1ppm between Flamborough Head and the Tees estuary; 44.4 ppm offshore of the Tyne-Tees estuaries). High Li values extend farther offshore into the Farn Deeps (average 28.8ppm) but muddy sediments west of this area, such as in the Gorsethorn Deep (average 15.9ppm), have only slightly higher Li concentrations than the surrounding sands. Li concentrations are high in the muddy sediments of the Firth of Forth (average 51.7ppm) and in an elongated band of muddy sands north of the Tay Estuary, which originate from the River Tay. The high Li values in sediments off the estuaries of industrialised river catchments, in contrast to those in unpolluted areas such as the Outer Moray Firth, may reflect high organic content due to sewage outfalls or, in areas such as around the Bell Rock and Outer Forth Estuary, to sewage dumping.

Northern North Sea

The muds of the Fladen Ground Basin are delineated by a group of high Li values (average 30.9ppm) with a sharp decrease northwards in the muddy sands of the Witch Ground Basin (average 13.8ppm). High concentrations of organic matter have been observed in the muds of the Fladen Ground (Eisma,1981), which would affirm the importance of organic matter in controlling the distribution of Li throughout the study area. The association of Li with high B values also indicates the occurrence of illite as the predominant clay mineral component in the muds of this area. Li concentrations are significantly lower in muddy sediments nearshore, such as in the Moray Firth (average 11ppm), compared to those off the estuaries of industrialised river catchments farther south.

Hebrides and West Shetland shelves

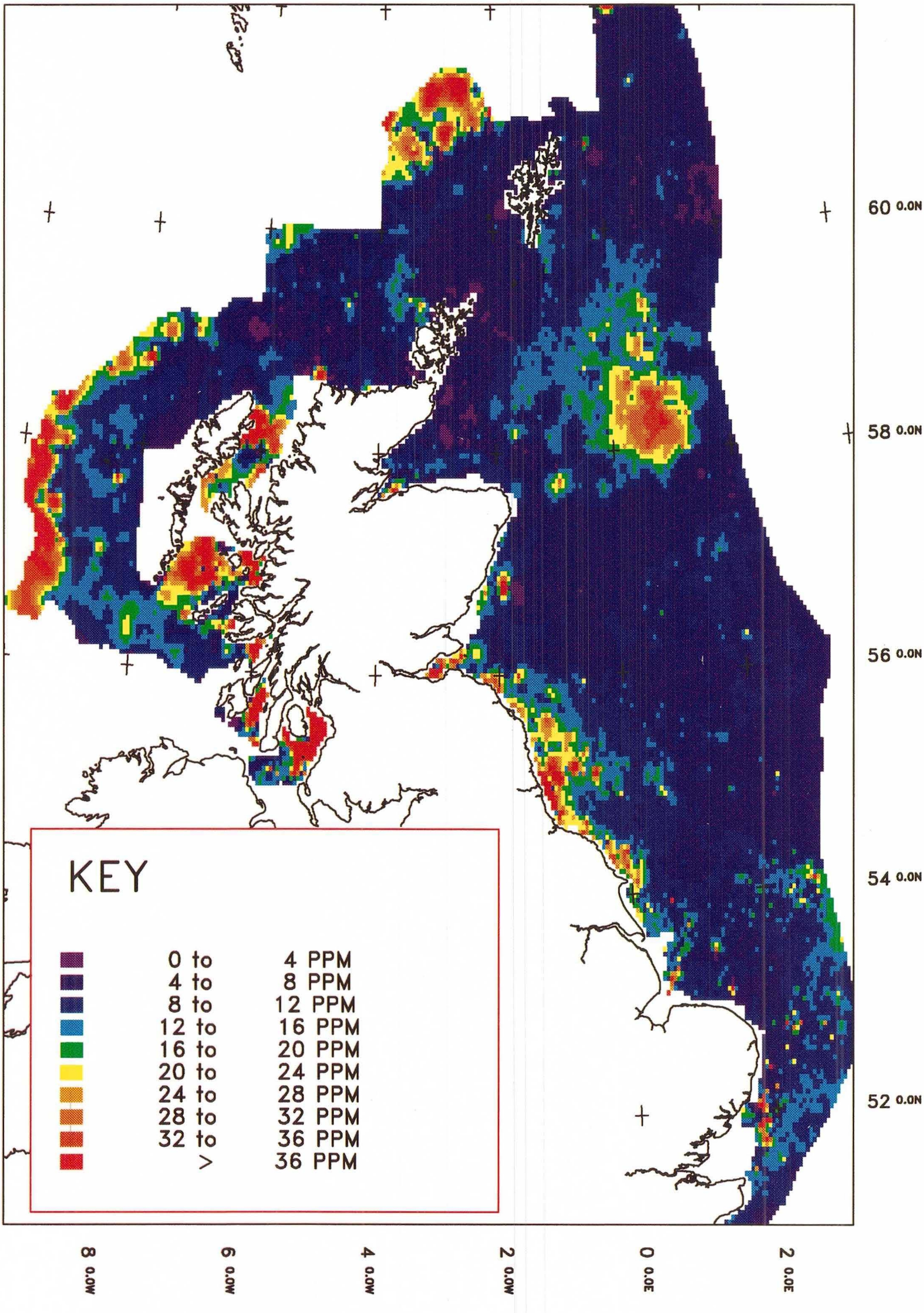
The sandy and gravelly sediments of the area are characterised by low Li concentrations (average 6.9ppm in gravels on the Orkney-Shetland Platform; 6.8ppm in sand and 8.3ppm in gravelly sand on the West Shetland Shelf). Fine-grained sediments at the shelfbreak have intermediate to high Li values (average 17.9ppm north-west of Shetland; 34.4ppm west of the Outer Hebrides).

Malin-Hebrides

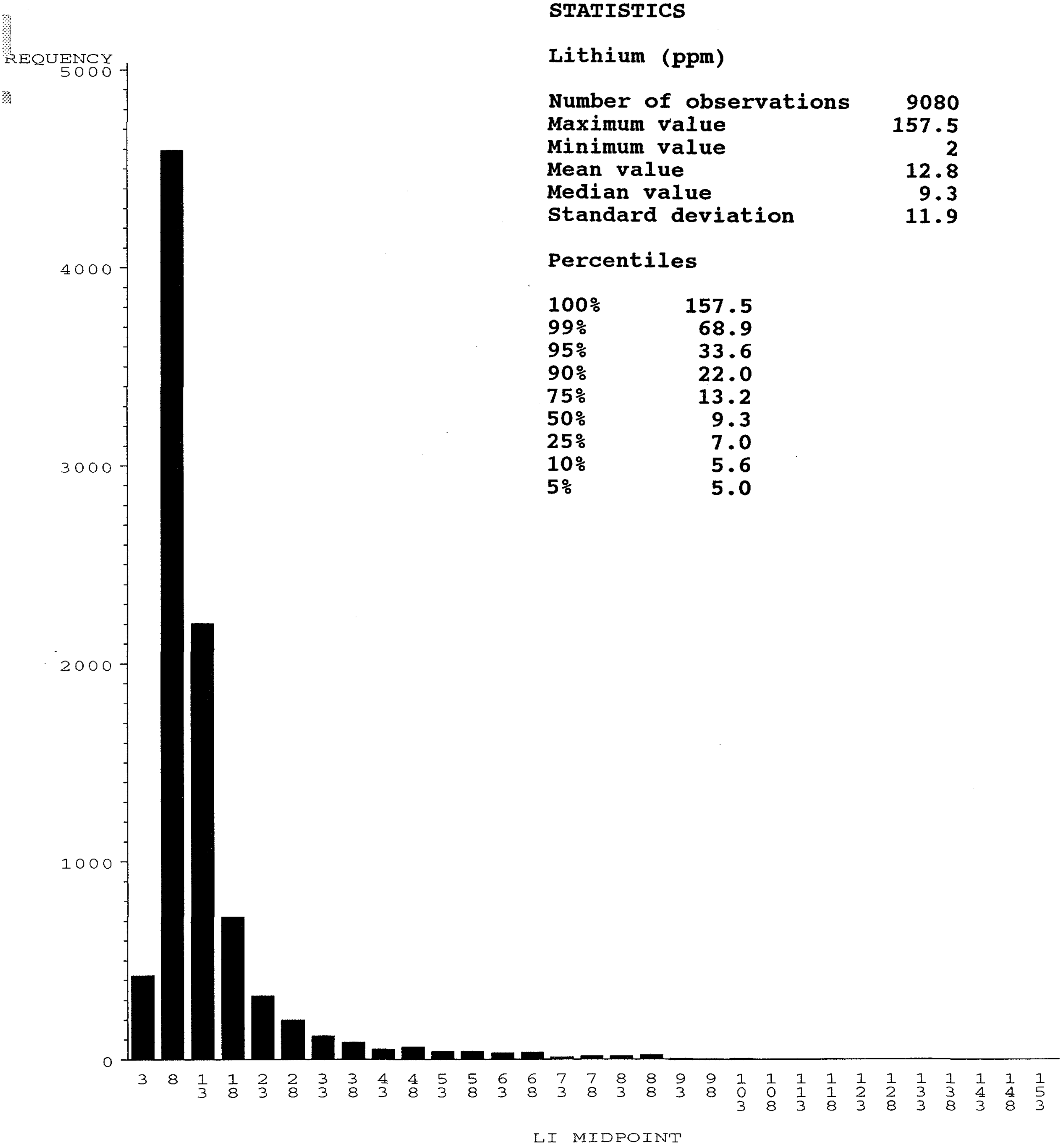
High Li values occur in all fine-grained sediments within the region. The highest average concentration occurs in muddy sediments of the Sound of Jura (average 79.6ppm), which is significantly higher than in fine-grained sediments in The Minch and Sea of the Hebrides (average 30.7ppm). As organic content is unlikely to be a significant factor in these areas, the high Li levels near Jura probably reflect derivation from Li-enriched Dalradian rocks, whereas the fine-grained sediments farther north contain a high proportion of clay minerals and lithic fragments derived from Pleistocene sediments eroded from the Precambrian, Mesozoic and Tertiary rocks of the region. Schist and slate formations of the Dalradian in Argyllshire have high Li concentrations whereas the metamorphic and igneous rocks farther north have mainly low to intermediate Li levels (British Geological Survey, 1990).

High Li values in the Firth of Clyde (average 60.4ppm) may also be attributable to the underlying Pleistocene deposits being derived from Dalradian and Carboniferous lithologies, however sewage disposal in the estuary has contributed to the high organic content of these sediments (see Chromium section).

LITHIUM IN SEA-BED SEDIMENT



LITHIUM



STATISTICS

Lithium (ppm)

Number of observations	9080
Maximum value	157.5
Minimum value	2
Mean value	12.8
Median value	9.3
Standard deviation	11.9

Percentiles

100%	157.5
99%	68.9
95%	33.6
90%	22.0
75%	13.2
50%	9.3
25%	7.0
10%	5.6
5%	5.0

Magnesium

Magnesium

Southern North Sea

Intermediate to high MgO values occur in gravels in the Dover Strait, and fine-grained sediment off the coast of East Anglia (average 1.28%). The largest group of MgO values within or above background range, occur near the coast between The Wash and Flamborough Head where the highest concentrations occur in gravelly sands (average 2.91%). High MgO values also occur farther offshore to the west of Spurn Head, are mainly associated with high levels of Fe_2O_3, MnO and to a lesser extent Zn, and occur predominantly in coarse-grained sediments. This association suggests that the sandy and gravelly sediments of the area contain a high proportion of resistate ferromagnesian silicates. MgO occurs in minerals such as glauconite and high levels could reflect the occurrence of this mineral in sediments derived from underlying Pleistocene or Tertiary deposits. Intermediate to high MgO values also occur in the fine-grained sediments of the Markham's Hole/Outer Silver Pit area (average 0.99%).

Central North Sea

In the central North Sea, high MgO values occur mainly near the coast in a wide range of sediments but northward extend offshore in areas of fine-grained sediments such as the Farn Deeps. Average values range from 1.03% in sands (compared to 0.39% in sands farther offshore) to 2.43% in gravelly sediments. Nicholson et al. (1985) observed that MgO shows affinity for both gravel and fine-grained sediments along the UK coastal margins. They interpreted high MgO values near some estuaries to indicate input from river transport and noted that the Carboniferous Limestone of the Coal Measures along the north-east English coast , and the Cretaceous chalk on the northern coast of Yorkshire, were probably responsible for the high MgO levels found in these areas. High MgO values along the coast also support the view of Dearnley (1989) that a 'plume' of sediment derived from the basic igneous rocks of the Midland Valley of Scotland extends southward along the coast to Flamborough Head (see Conclusions). In coarse-grained deposits, as in the southern North Sea, high MgO may be due to the presence of resistate ferromagnesian minerals. Consistent with derivation from mainly Carboniferous sedimentary and basic igneous rocks, the fine-grained sediments in the Firth of Forth (average 1.79%), and north of the Tay Estuary, have high MgO concentrations.

Northern North Sea

The muddy sediments of the Fladen Ground and Witch Ground basins are delineated by intermediate to high MgO values (up to an average 2.08% in mud). Johnson and Elkins (1979) working mainly in the Fladen Ground area noted that K is a major constituent of illite while Fe and Mg are more abundant in smectite and chlorite. Consequently sediments enriched in illite and depleted in smectite should have high K/Al and low Fe/Al and Mg/Al ratios. They found that such a relationship existed for K and Al but when Mg/Al was plotted against both illite/smectite and illite/chlorite ratios there was too much scatter to show any useful correlation, suggesting that Mg content is influenced by factors other than clay mineralogy, such as carbonate content. The mainly shelly gravels of the Orkney-Shetland Platform have high MgO values (average 1.68%). Organisms secreting calcite are known to contain up to 8 per cent by weight Mg in their crystal lattices (Wedepohl, 1978). Normalised MgO/Li data depict areas of high carbonate production in coarse-grained sediments in the northern North Sea and the shelf area north and west of Scotland.

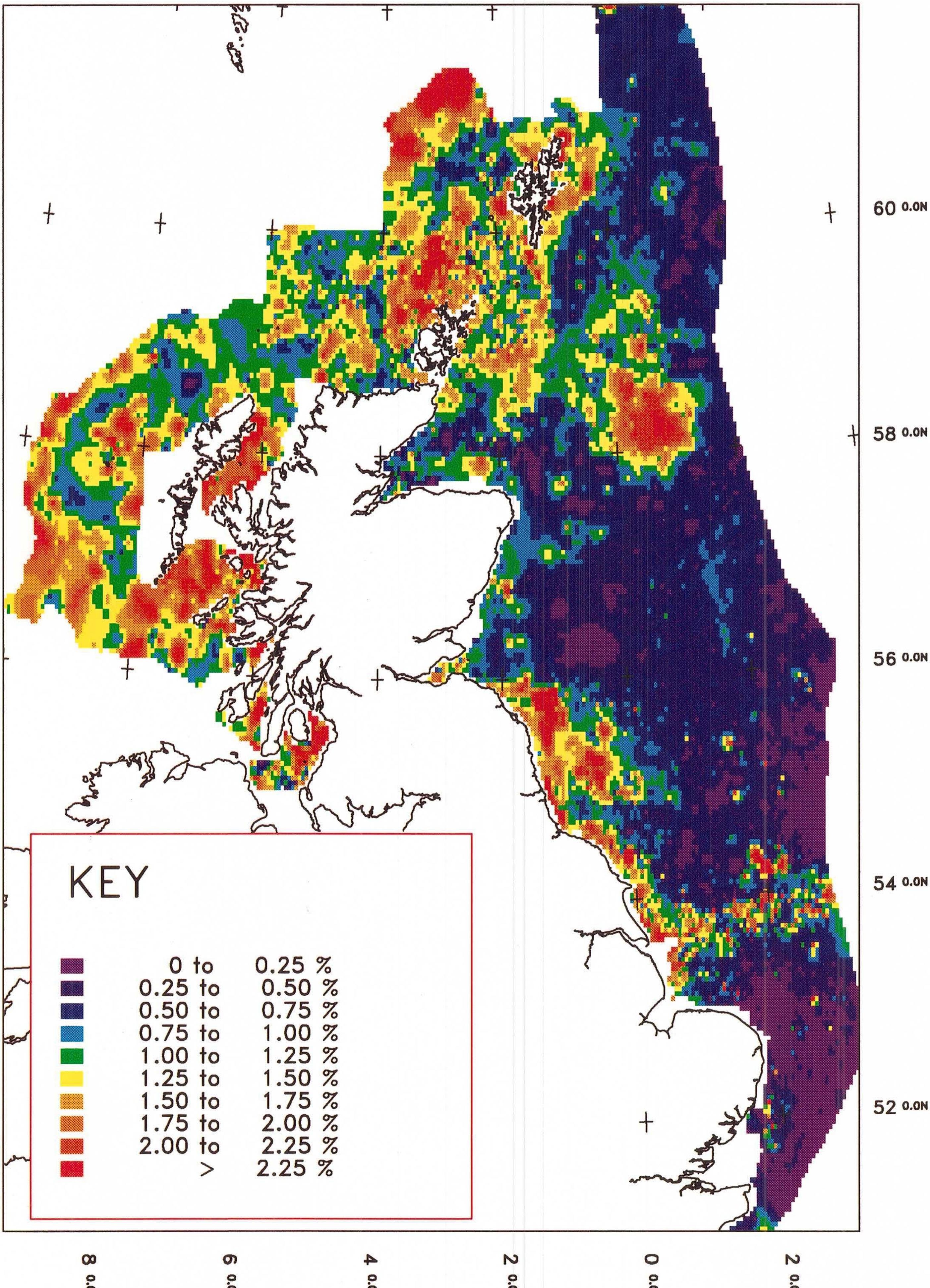
Hebrides and West Shetland shelves

MgO values in this region are generally high, mainly reflecting the concentration of Mg in shelly material, as indicated by the distribution of CaO and normalised MgO/Li data, but also partly by the influence of high MgO in sediments derived from basic igneous rocks. Concentrations in fine-grained sediments such as those at the shelfbreak (average 1.8% west of the Outer Hebrides), are comparable or only slightly higher than in coarse-grained sediments (average 1.49% in gravels on the Hebrides Shelf)

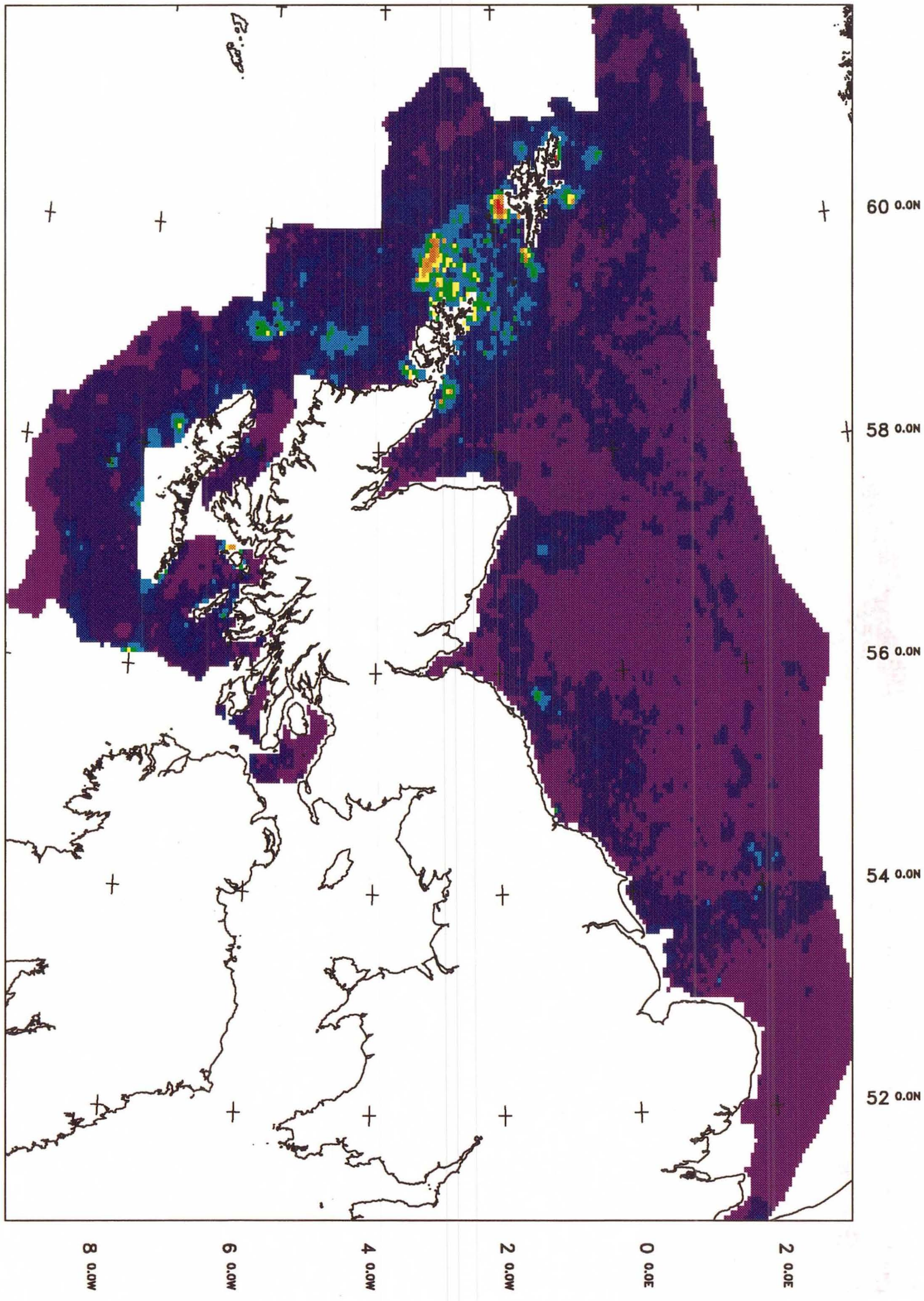
Malin-Hebrides

The influence of the Tertiary igneous rocks of the area dominates the distribution of MgO and it is uniformly high in all sediment types including coarse-grained shelly sediments. The highest MgO concentrations reflect the greater affinity of Mg for argillaceous sediments, with the muddy sediments of The Minch/ Sea of the Hebrides (average 2.01%), Sound of Jura (average 2.28%) and the Firth of Clyde (average 2.38%) displaying some of the highest MgO values in the study area.

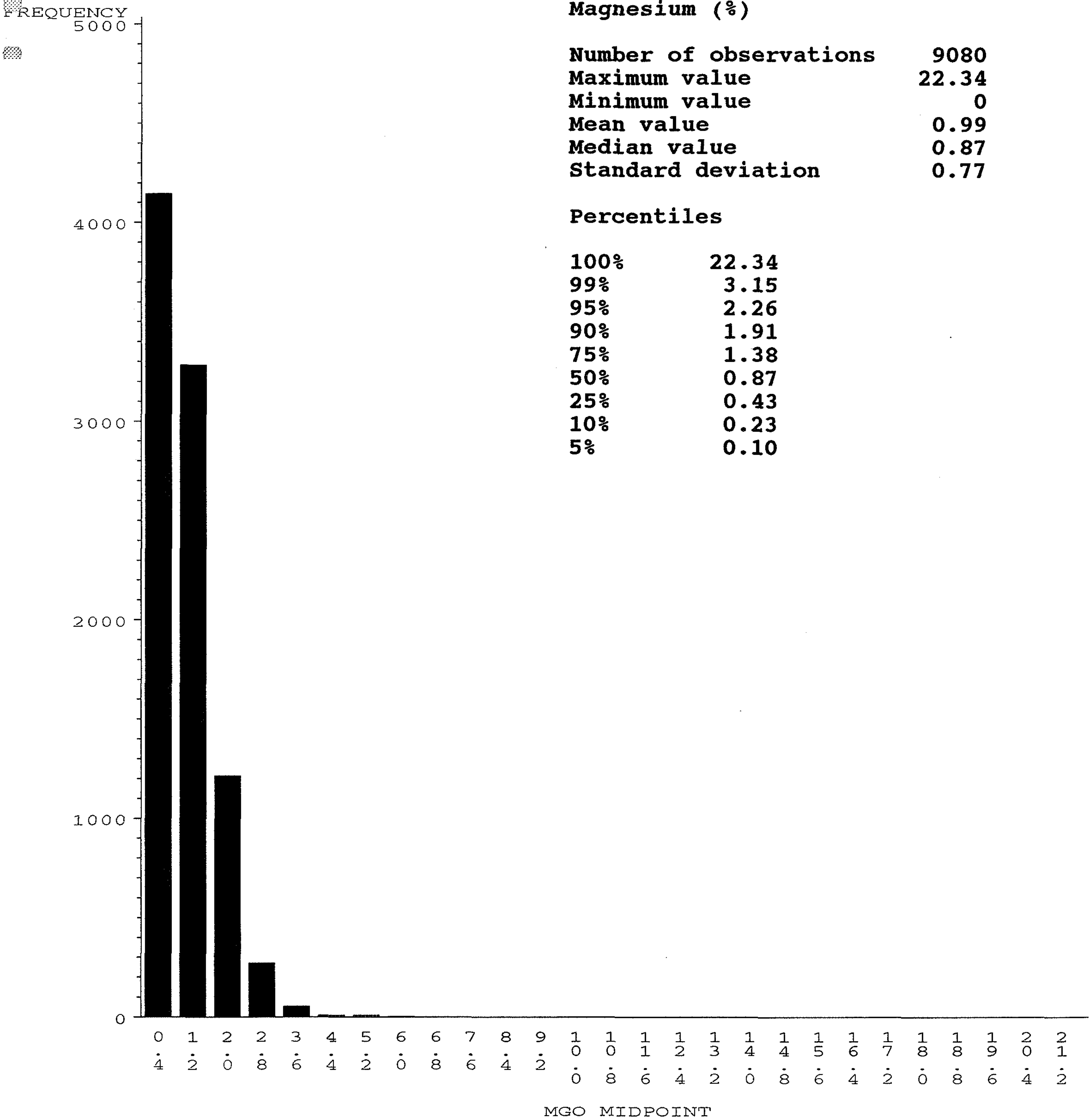
MAGNESIUM IN SEA-BED SEDIMENT



MAGNESIUM NORMALISED TO LITHIUM



MAGNESIUM



STATISTICS

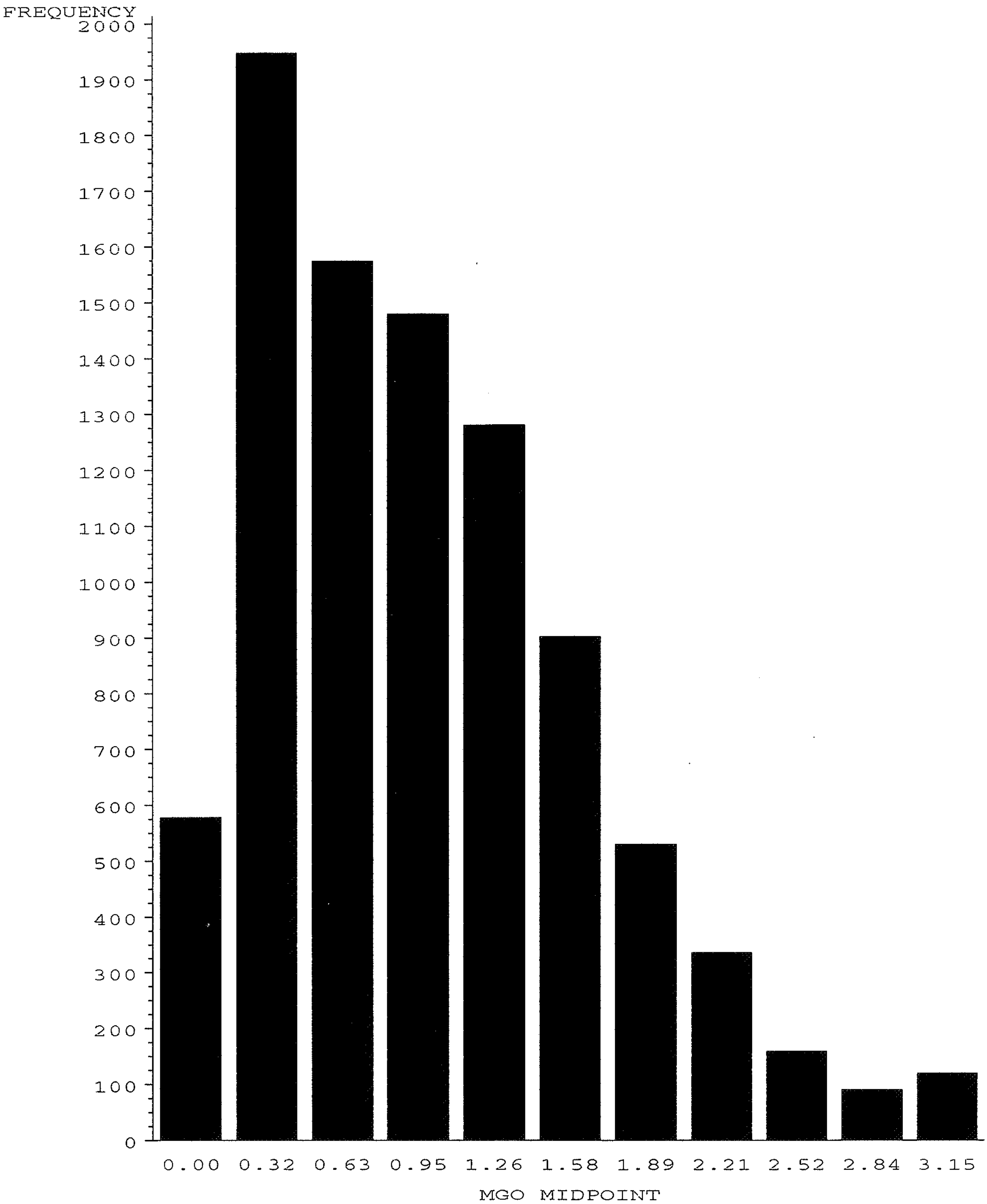
Magnesium (%)

Number of observations	**9080**
Maximum value	**22.34**
Minimum value	**0**
Mean value	**0.99**
Median value	**0.87**
Standard deviation	**0.77**

Percentiles

100%	**22.34**
99%	**3.15**
95%	**2.26**
90%	**1.91**
75%	**1.38**
50%	**0.87**
25%	**0.43**
10%	**0.23**
5%	**0.10**

MAGNESIUM



FREQUENCY
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
0.00 0.32 0.63 0.95 1.26 1.58 1.89 2.21 2.52 2.84 3.15
MGO MIDPOINT

Manganese

Manganese

Southern North Sea

MnO values are generally low throughout the region. High concentrations in coarse-grained sediments in the Dover Strait (average 0.06%) are associated with high Fe_2O_3 levels and are therefore due to precipitation of Fe and Mn hydroxides. The largest group of high MnO values occurs in the nearshore zone between Skegness and Flamborough Head (average 0.06% in both muddy and gravelly sediments) although high values also occur farther offshore, mainly on banks overlain by coarse-grained sediments.

The general distribution pattern of MnO shows that intermediate to high concentrations are mostly associated with shallow banks and high Fe_2O_3 concentrations in sea-bed samples. This suggests therefore that mixing of the water column produces oxygenation of the sea floor and the precipitation of hydrous Fe-Mn oxides as coatings on lithic or shell fragments in coarse-grained sediments. The map of normalised MnO/Li provides a good indication of areas where MnO distribution is influenced by hydroxide precipitation or detrital minerals, relative to concentration in clay minerals. Nicholson et al. (1985) noted the similarity of the distribution of MnO to that of Fe_2O_3 and MgO and a strong correlation between these three elements. MnO also showed strong correlations with Y, Ni, carbonate content and the gravel fraction which can be accounted for by incorporation into oxide coatings on pebbles and shell material. Comparison of the MnO/Fe_2O_3 map in this section with Fe_2O_3/MnO normalised data (see Iron section), indicates that MnO is concentrated relative to Fe_2O_3 in coarse-grained sediments whereas high Fe_2O_3/MnO ratios occur mainly in fine-grained sediments.

Central North Sea

A similar process to that which occurs on shallow banks in the southern North Sea may account for an area of high MnO values on the Dogger Bank (average 0.05% in gravelly sands). However, MnO concentrations may also be enhanced by the occurrence of heavy minerals such as magnetite and ilmenite. High MnO values occur nearshore in a wide range of sediments. For example, muddy sediments between Flamborough Head and the Tees Estuary have an average MnO concentration of 0.12%, and in gravelly sands between the River Tyne and Spurn Head MnO concentrations average 0.13%. Nicholson et al. (1985) reported high MnO values along the coast, with the highest values between the estuaries of the Tyne and Tees, which they attributed to derivation from Permian Magnesian Limestone that forms the coastal cliffs of this area. High MnO levels were also found to the south where Jurassic Oolite Series rocks reach the coast. The map of normalised MnO/CaO suggests that calcium carbonate in the rocks from which the nearshore sediments are derived is one of the principal influences on MnO distribution.

Offshore of the Scottish coast, in contrast to the areas to the south, MnO values are generally low in coarse-grained sediments, particularly with distance from the coast. The highest values occur on the Aberdeen and Marr Banks (average 0.06 and 0.04% respectively) which have been shown to have similar geochemistry to the Dogger Bank sediments (see Chromium section). As well as a possible provenance relationship, the banks in this part of the North Sea have similar physiographic features to those farther south. Some degree of water column mixing is therefore suggested in this area. The Marr and Aberdeen Banks are also areas of high carbonate production and Cronan (1970) reported a strong correlation between MnO and calcium carbonate in sea-bed sediments in the north-eastern Irish Sea. Mn is known to substitute for Ca in the lattices of carbonate minerals (Wildeman, 1970) however this process is considered secondary to the precipitation of Fe-Mn oxides on shell debris.

Northern North Sea

Intermediate MnO values occur in the fine-grained sediments of the Fladen Ground Basin (average 0.039% in muds) indicating Mn adsorption on clay minerals.

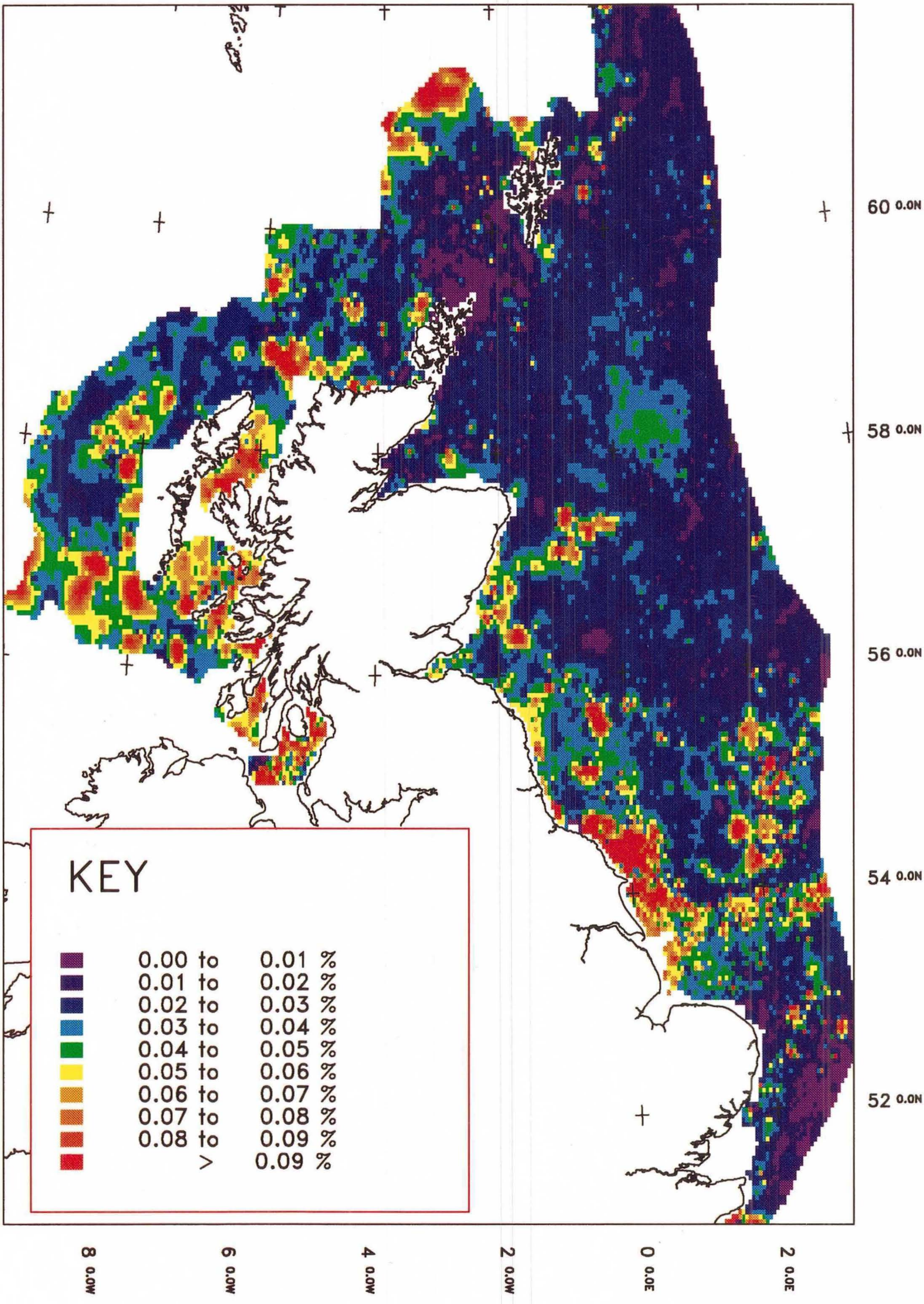
Hebrides and West Shetland shelves

High MnO concentrations occur in fine-grained sediments near the shelfbreak (average 0.049% north-west of Shetland; 0.045 west of the Outer Hebrides) and in areas of coarse-grained sediments north-west of Cape Wrath, and to the west of the Outer Hebrides (average 0.04% in sand and gravelly sand; 0.05% in gravel). Where they occur in coarse-grained sediments, high MnO values are generally related to precipitation of Fe-Mn hydroxides on shallow banks such as Stanton Banks. The high MnO/Li and MnO/Fe_2O_3 ratios relative to MnO/CaO, suggest that Mn-hydroxide precipitation on shell material is the main influence on MnO distribution throughout most of this region. High values in the St Kilda area are thought to reflect a high proportion of Fe-Ti heavy minerals such as magnetite and ilmenite.

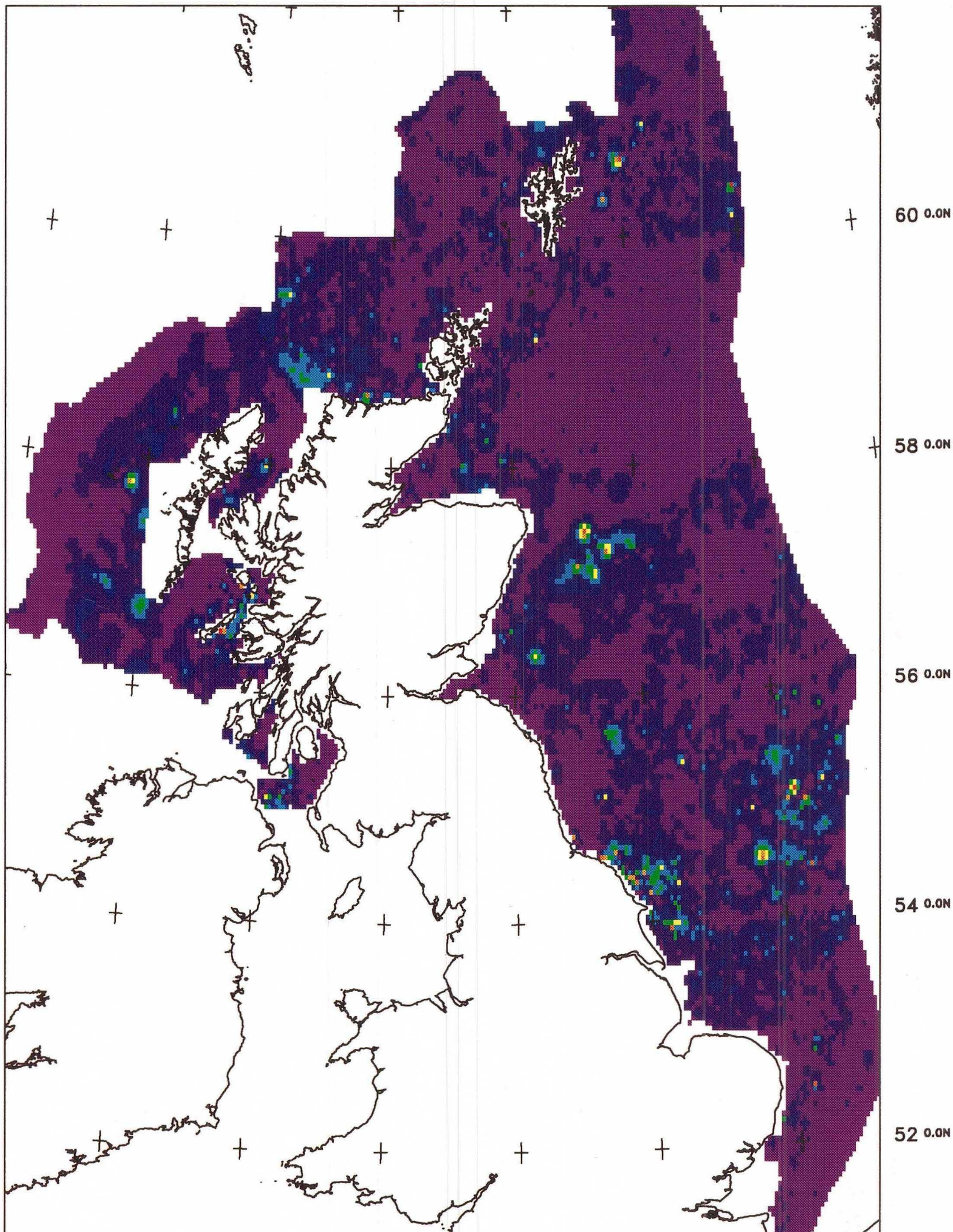
Malin-Hebrides

Mn values are generally high in The Minch, off the coast of Argyllshire and in the Firth of Clyde. Within these areas high MnO concentrations are related to a number of processes, such as adsorption on clay minerals in fine-grained sediments; concentration in heavy minerals or ferromagnesian silicates derived from the basic igneous rocks of Mull and Skye; or precipitation as Fe-Mn hydroxides in areas of coarse-grained sediment with high current activity such as the North Channel. The region contains areas of various sediment facies with the highest MnO concentrations of any in the study area. For example, the highest average MnO concentrations in gravelly sediments occur in the Minch/Sea of the Hebrides (average 0.09%) and the highest in fine-grained sediments occur in the Sound of Jura (average 0.07%) and Firth of Clyde (average 0.09%). Gravels south of the Kintyre Peninsula have high concentrations for this sediment type (average 0.05%) and reflect precipitation of Mn hydroxide in an area of strong currents and water mixing.

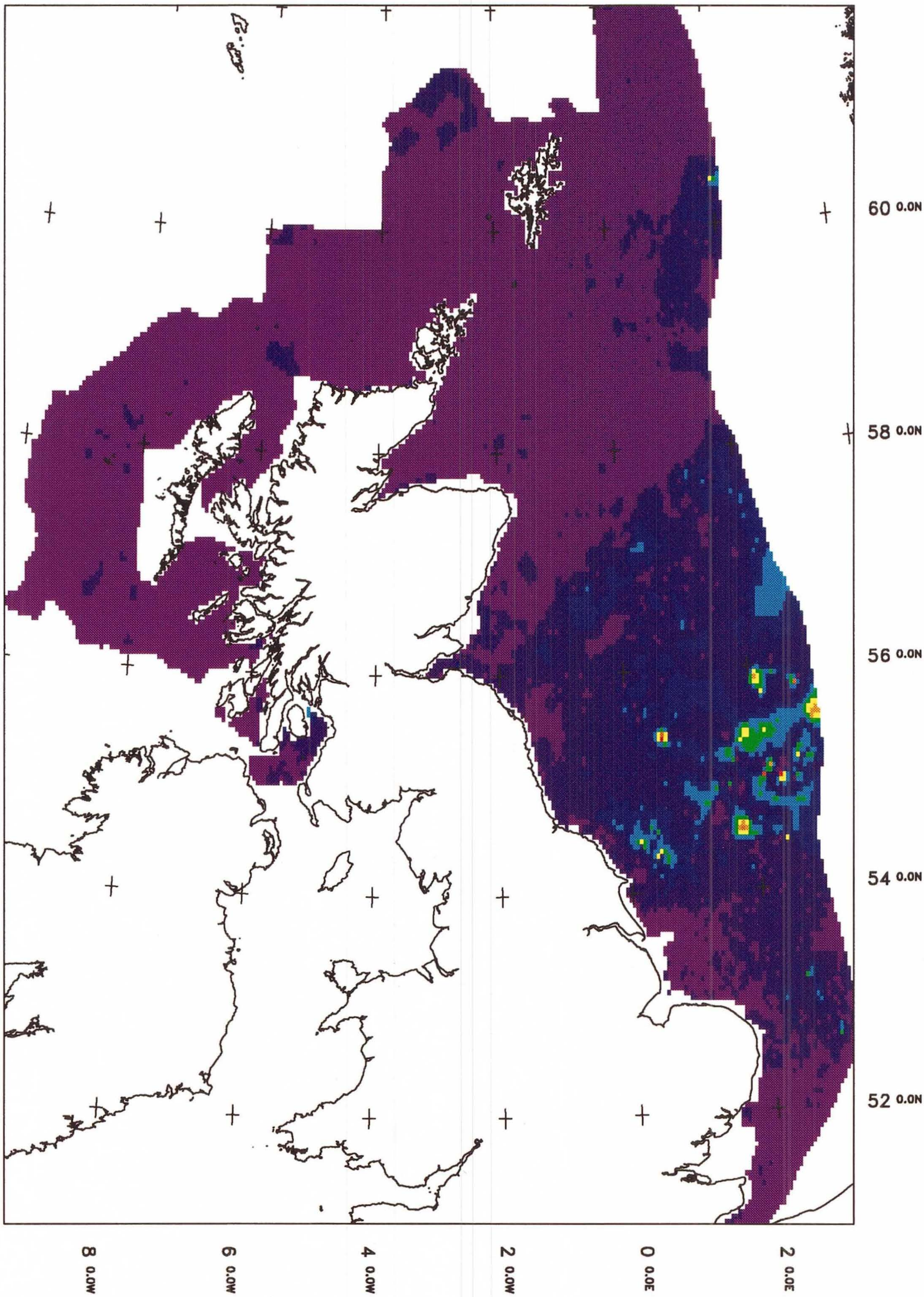
MANGANESE IN SEA-BED SEDIMENT



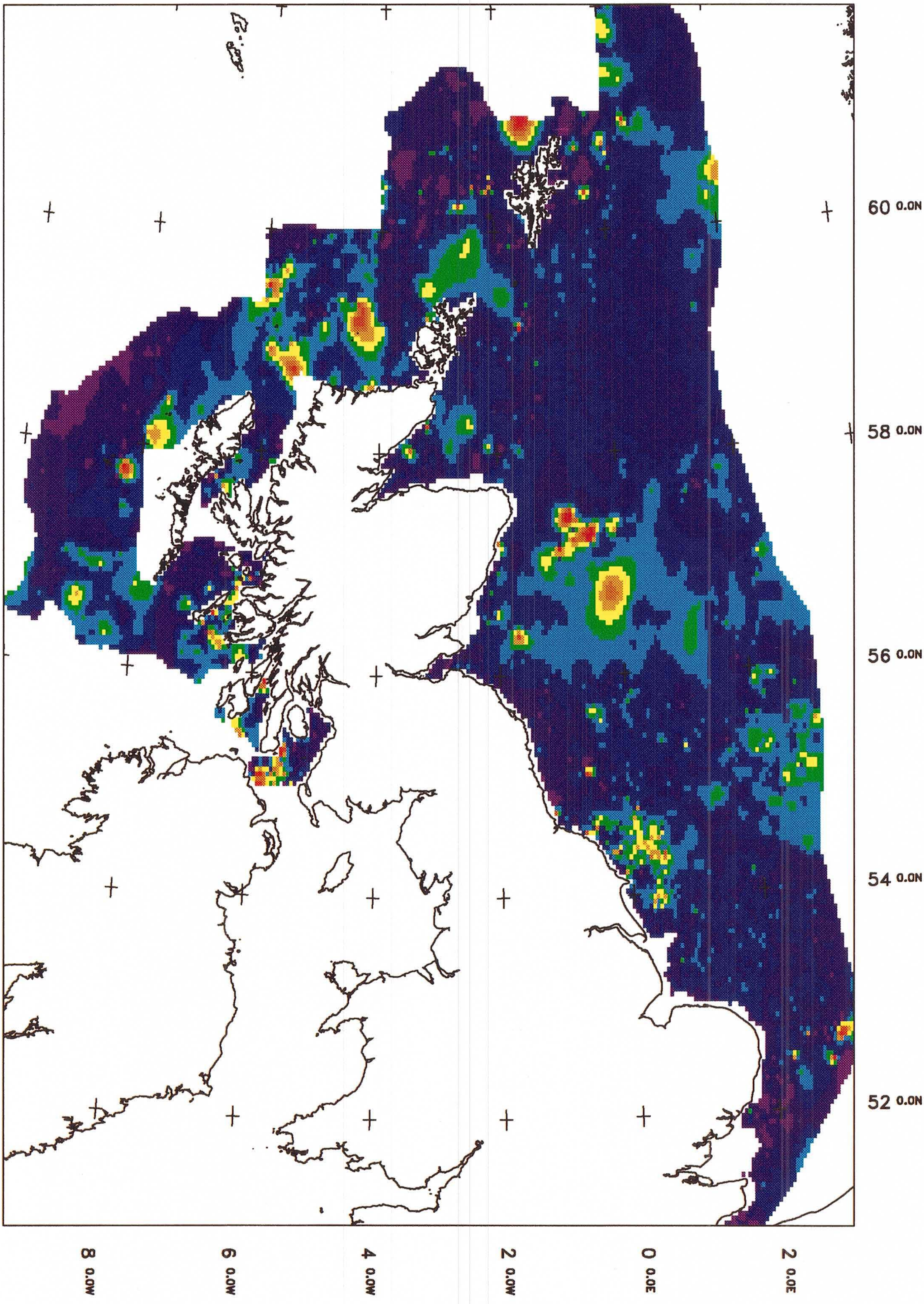
MANGANESE NORMALISED TO LITHIUM



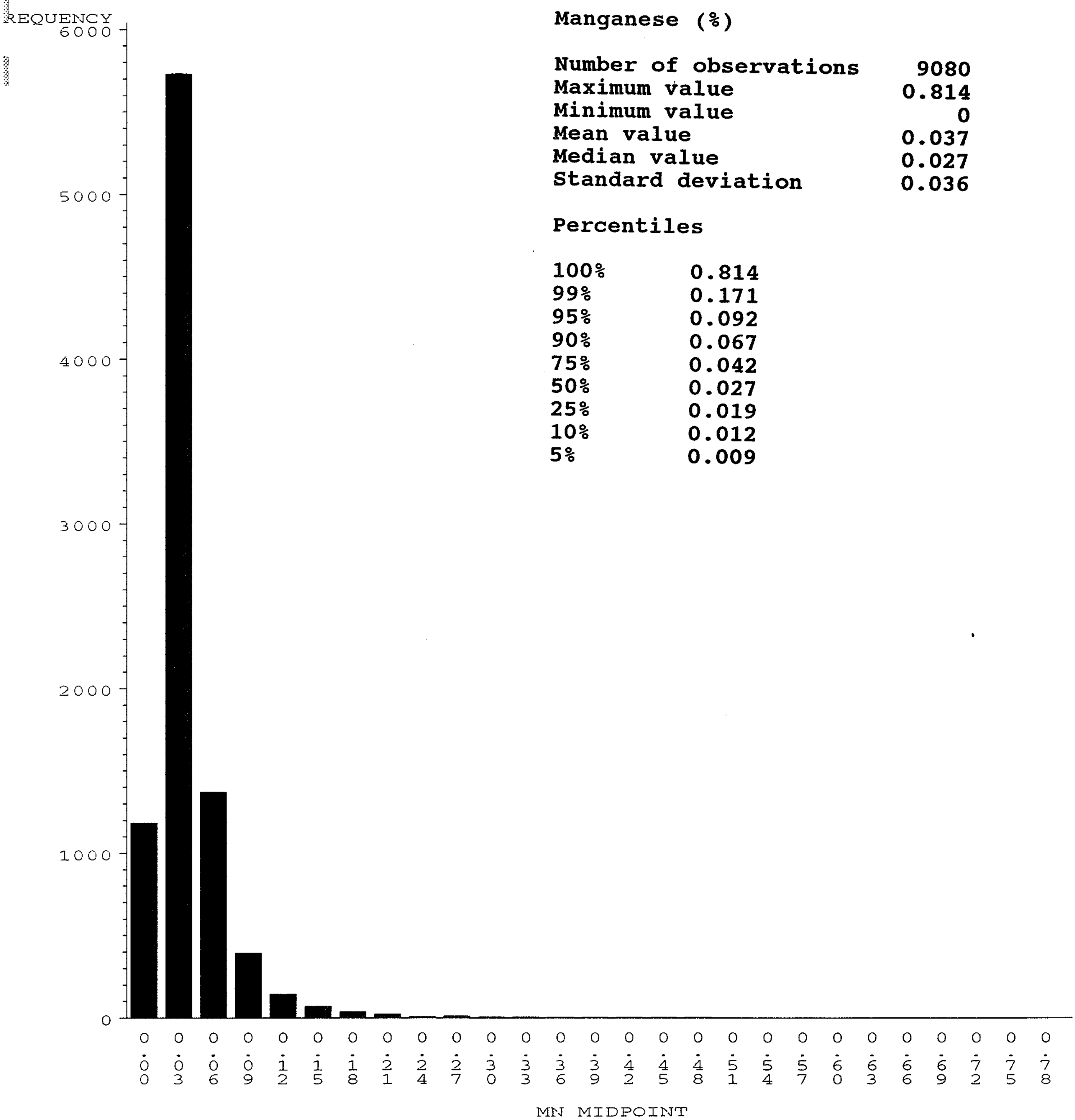
MANGANESE NORMALISED TO CALCIUM



MANGANESE NORMALISED TO IRON



MANGANESE



STATISTICS

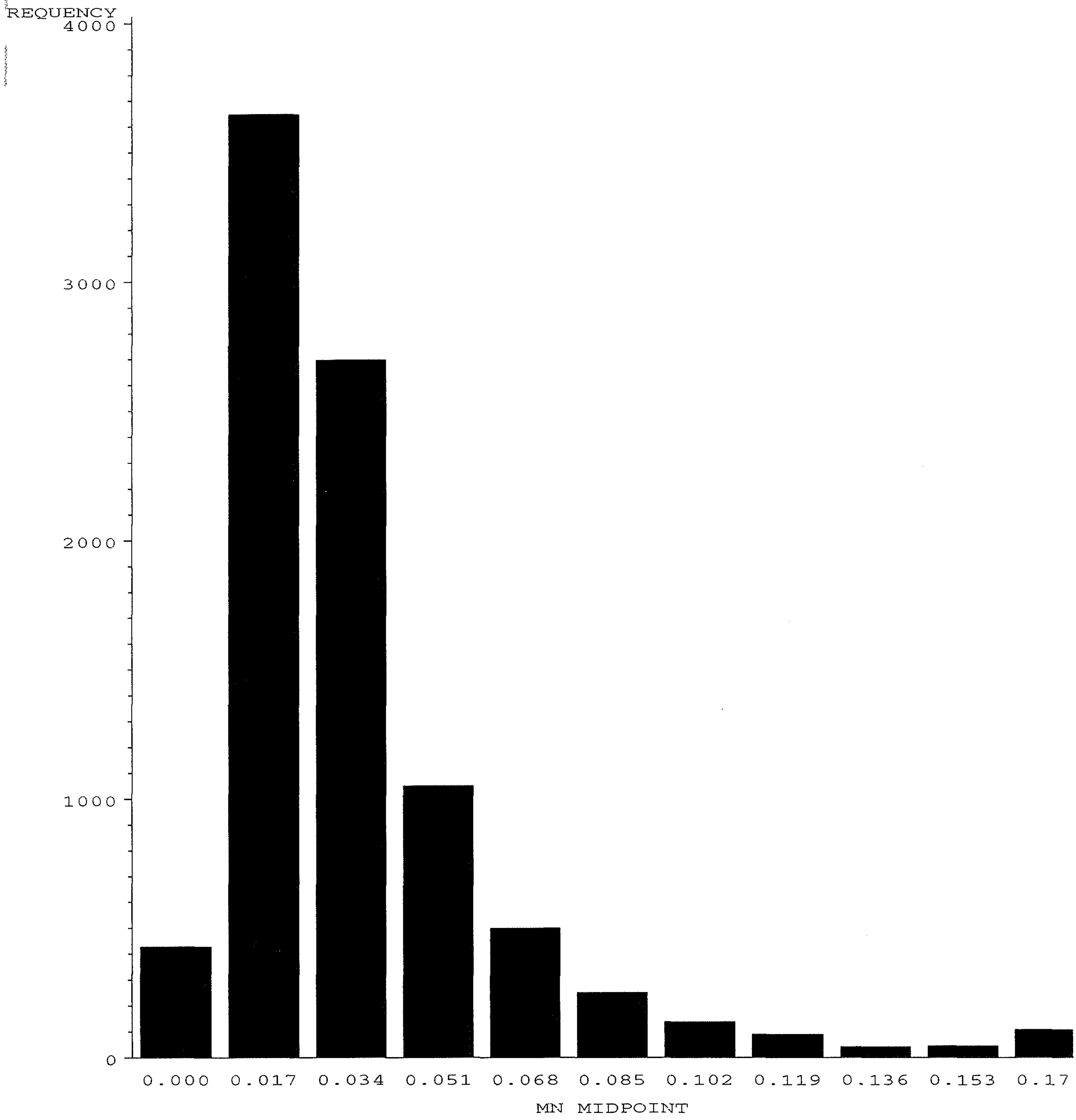
Manganese (%)

Number of observations	9080
Maximum value	0.814
Minimum value	0
Mean value	0.037
Median value	0.027
Standard deviation	0.036

Percentiles

100%	0.814
99%	0.171
95%	0.092
90%	0.067
75%	0.042
50%	0.027
25%	0.019
10%	0.012
5%	0.009

MANGANESE



REQUENCY
4000
3000
2000
1000
0
0.000
0.017
0.034
0.051
0.068
0.085
0.102
0.119
0.136
0.153
0.17
MN MIDPOINT

Mercury

Mercury

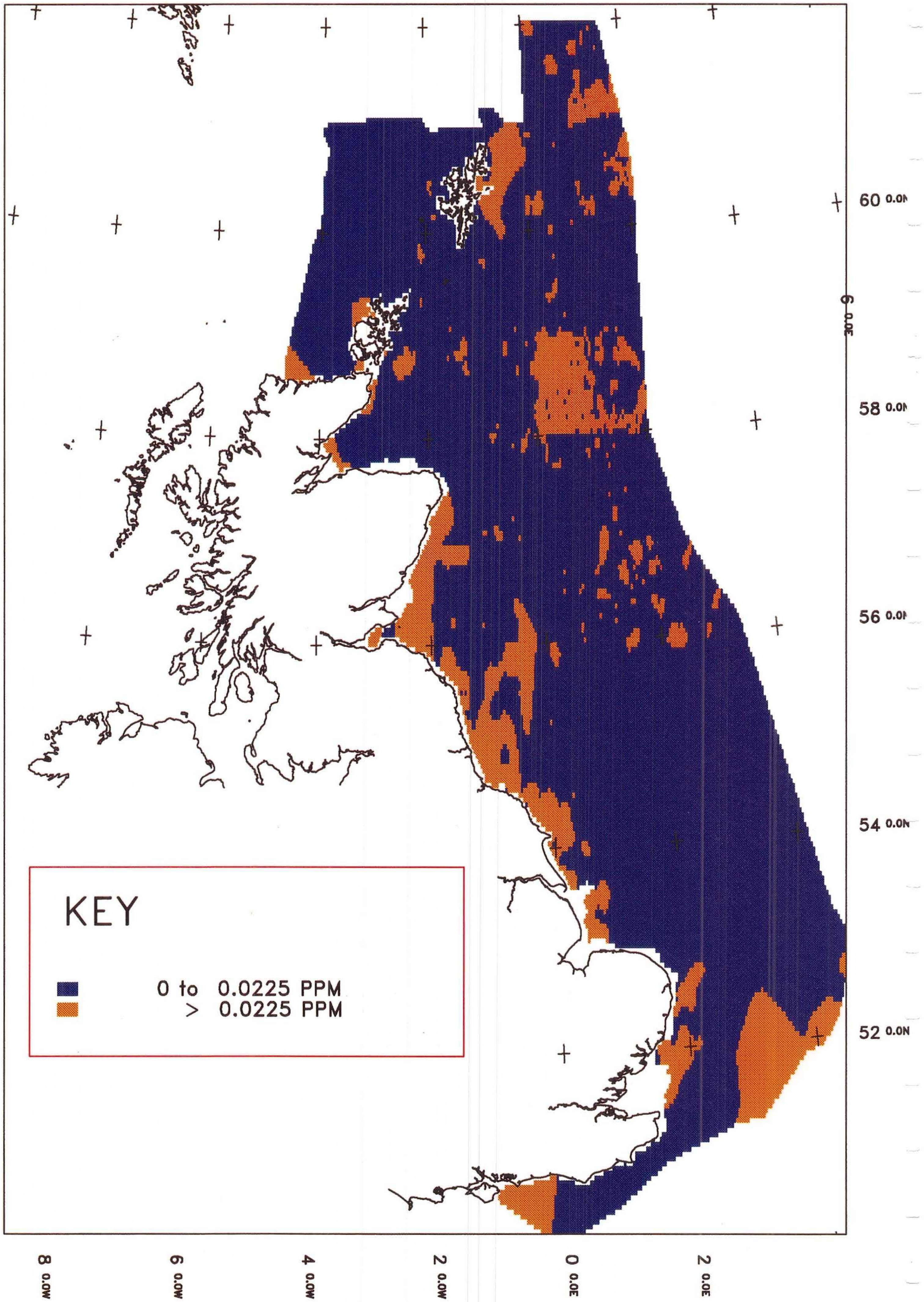
The distribution of Hg data shown on the map opposite is based on a compilation of data from the Offshore Marine Survey and analysis first published by Nicholson and Moore (1981). The data extends farther south than that of other elements in the report, but does not include samples from west of Scotland. It should be noted also that due to the low sample density (4012 Hg analyses compared to 9080 for other elements) the resolution of the contoured map is more generalised. Some of the areally extensive groups of Hg values are therefore due to extrapolation between widely spaced individual sample locations.

The Hg data is displayed in two class intervals, 0.02ppm being the detection limit for the analytical technique. The majority of values above the detection limit occur in fine-grained sediments. Nicholson and Moore (1981) commented on this association noting that even relatively small patches of muddy sand can be identified by their slightly higher Hg contents compared with surrounding coarser sediments.

North Sea Task Force (1993) reported that, of 600 samples analysed for Hg, 75 per cent had concentrations lower than 0.025ppm and only 19 had values above 0.5ppm. The higher values in the North Sea were found at a number of local point sources along the east coast of England, in the estuaries of the rivers Tyne and Thames, and in the Dogger Bank area. With the exception of the latter, they took this to imply that Hg discharged into the North Sea is trapped in estuaries and near-coastal areas.

As Hg is absent or in trace quantities only in the common rock-forming minerals, all of the values detected in the BGS offshore samples are most probably due to contaminants.

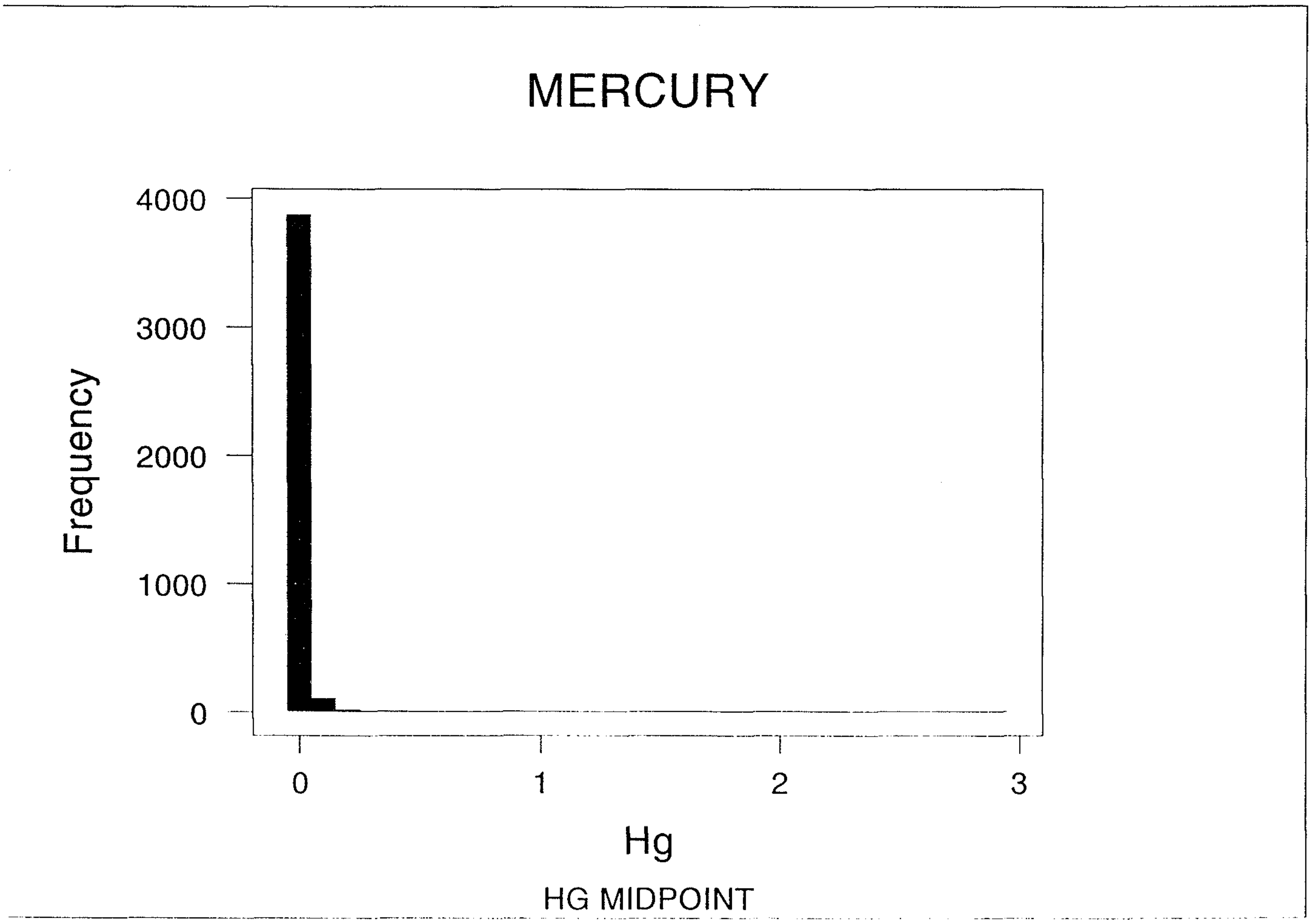
MERCURY IN SEA-BED SEDIMENT



STATISTICS

Mercury (ppm)

Number of observations	4012
Maximum value	2.9
Minimum value	0
Mean value	0.019
Median value	0.01
Standard deviation	0.062



Molybdenum

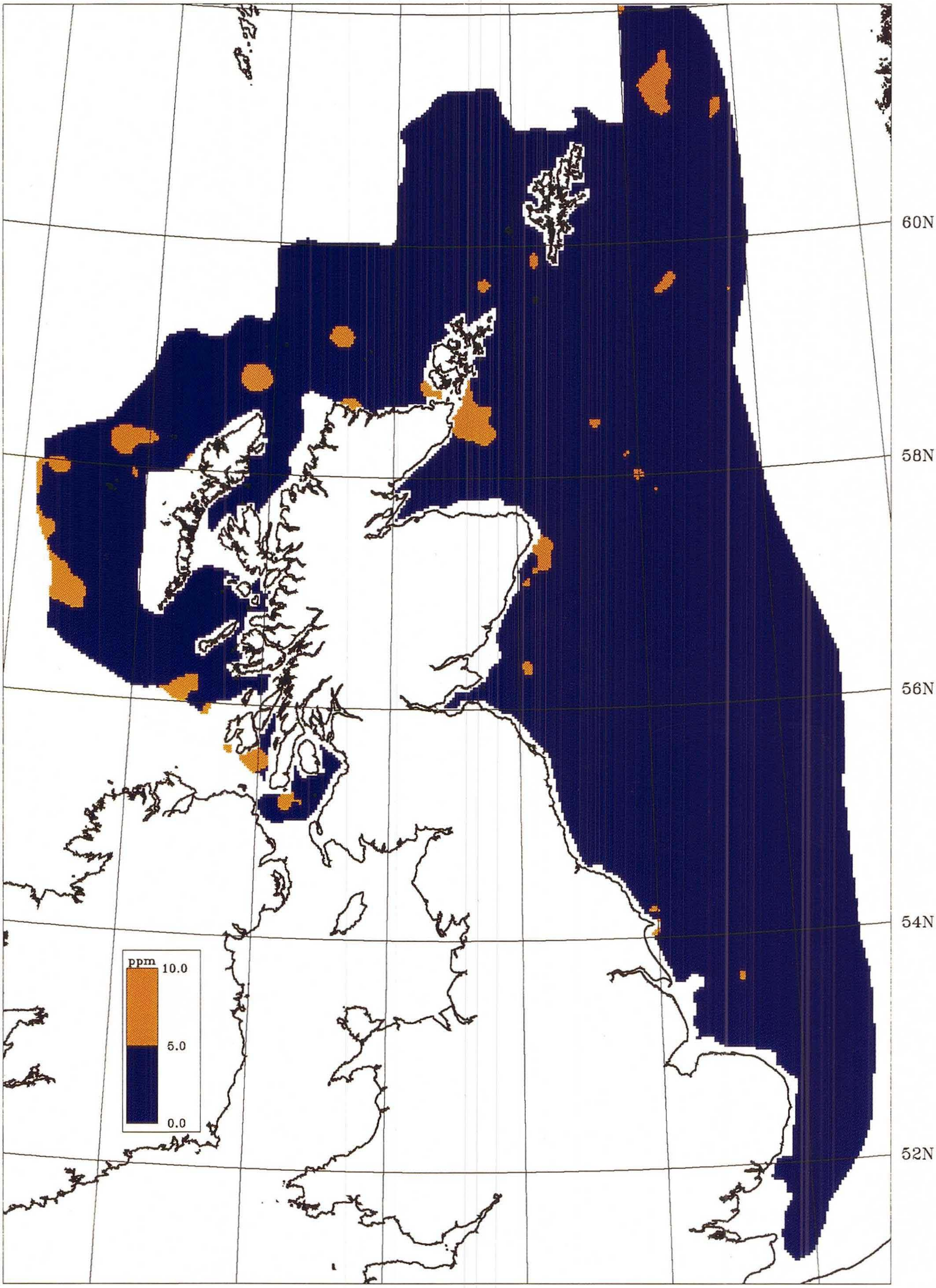
Molybdenum

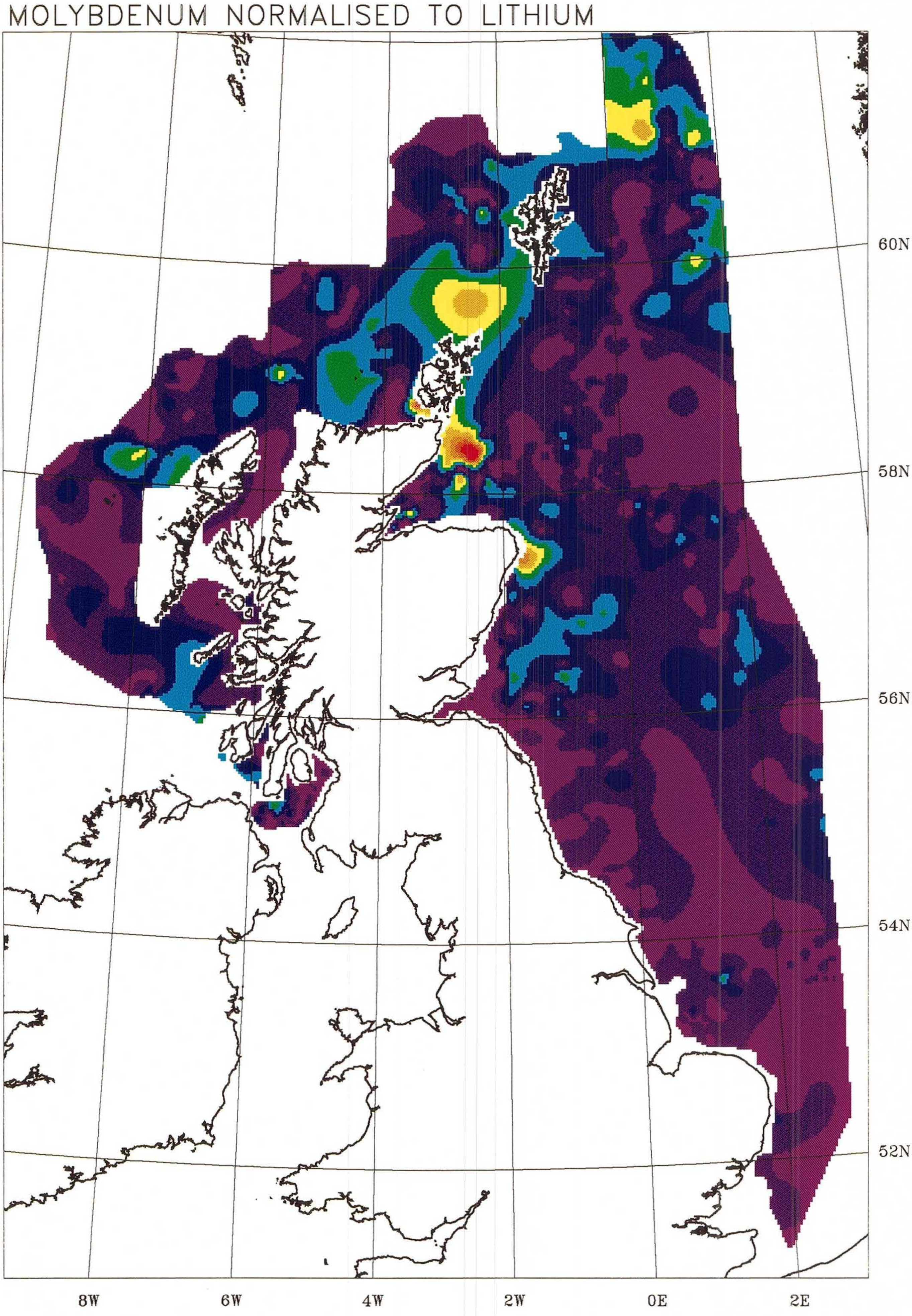
The majority of Mo values are below detection limit (5ppm) or are affected by the correction for high calcium values (see Table 3).

Published mean concentrations of Mo in sedimentary rocks are generally low except in sediments deposited under oxidising conditions characterised by the precipitation of manganese oxides or in highly reducing conditions accompanied by accumulation of organic matter and precipitation of iron sulphide. Average values range from 0.3ppm in carbonates to 2ppm in shales from non-anoxic environments (Manheim and Landergren, 1978). Similarly average Mo values in stream sediments from the UK land area are generally less than the analytical detection limit (5-8 ppm; British Geological Survey, 1991;1993)

Most of the values between the detection limit and the maximum concentration recorded during this survey (9.9ppm), occur in areas of high carbonate near the east coast of England, around Orkney or to the west of Scotland. The majority of these values are thought to be due to calcium interference at levels just below the 10 per cent correction limit.

MOLYBDENUM IN SEA-BED SEDIMENT

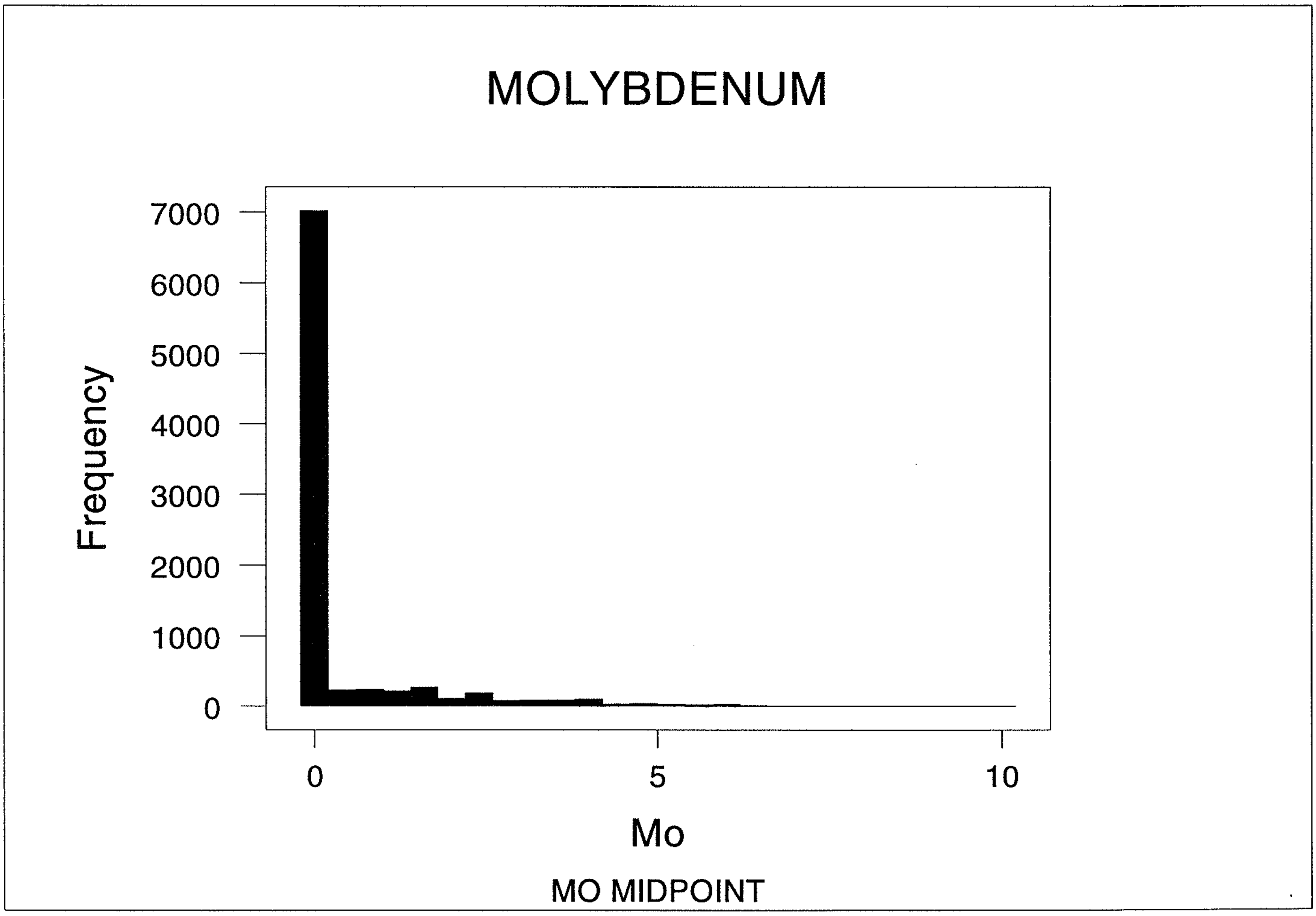



MOLYBDENUM NORMALISED TO LITHIUM
60N
58N
56N
54N
52N
8W
6W
4W
2W
0E
2E

STATISTICS

Molybdenum (ppm)

Number of observations	8782
Maximum value	9.9
Minimum value	0
Mean value	0.41
Median value	0.0
Standard deviation	1.054



Nickel

Nickel

Southern North Sea

Ni values are low in the sandy and gravelly sediments of the region with the exception of two areas of intermediate values in the Dover Strait (average 13ppm) and offshore of Skegness (average 14ppm). The highest concentrations occur in fine-grained sediments in the Outer Thames Estuary (average 24ppm) and off the coast of East Anglia (average 29ppm). Intermediate values occur in the Outer Silver Pit/Markham's Hole area in both coarse- and fine-grained sediments indicating both clay mineral and heavy detrital mineral accumulation. Nicholson et al. (1985) noted a strong correlation between Ni and various groups of elements. They considered high Ni values near the coast to reflect derivation from oolitic ironstones which form coastal cliffs south of the Humber Estuary.

Central North Sea

Intermediate to high Ni concentrations occur in muddy deposits along the eastern coast of England between Flamborough Head and the River Tees (average 25ppm), offshore of the Tyne-Tees estuaries (average 27ppm) and in the Devil's Hole area (average 14ppm). The highest Ni values in the region occur in muddy sediments in the Firth of Forth (average 53ppm), reflecting derivation from the basic igneous rocks of the Midland Valley of Scotland. The significantly higher concentrations in the Firth of Forth also suggests enhancement of Ni values due to adsorption on organic matter or by contamination. North Sea Task Force (1993) found high levels of Ni associated with enhanced concentrations of organic carbon in the Skaggerak area off Norway. High Ni values (greater than 20ppm) were found in samples between the Firth of Forth and Flamborough Head by Dearnley (1991). Ni concentrations decrease farther offshore of the Scottish coast in coarse-grained sediments, although isolated high values are probably due to contamination.

Northern North Sea

Intermediate to high Ni values occur in fine-grained sediments in the Fladen and Witch Ground basins where muds (average 31ppm) have higher concentrations than the surrounding muddy sands and sandy muds. High Ni values in the vicinity of Shetland, which are also evident on the normalised Ni/Li map, suggest localised accumulation of heavy minerals derived from ultrabasic rocks on the islands of Unst and Fetlar (Beg 1990).

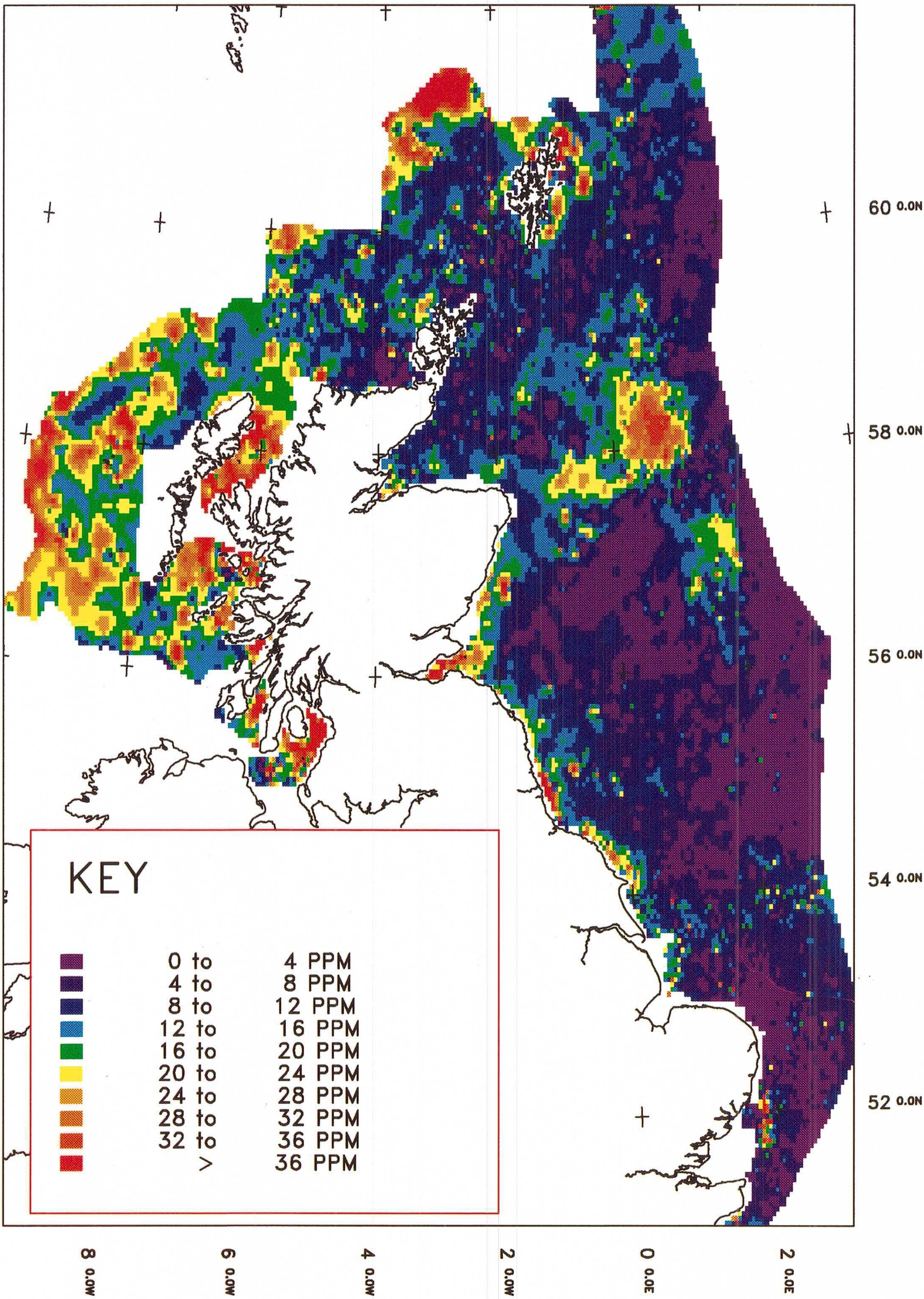
Hebrides and West Shetland shelves

Ni concentrations in sands (average 12ppm on the West Shetland Shelf; 18ppm on the Hebrides Shelf) and gravelly sands (average 13ppm on the West Shetland Shelf; 19ppm on the Hebrides Shelf) are higher than those of the North Sea, reflecting the influence of Tertiary basic igneous rocks in the region. Dearnley (1991) reported seventeen samples of sand from this area which have an average Ni concentration of 18ppm. Dearnley also recorded Ni values greater than 20ppm in association with high concentrations of Cr, Co, V, Y, Zn and Cu in the sands of the region and related the distribution of these samples to a contour line of 15 per cent basic igneous rock lithic fragment content. Groups of high Ni values around St Kilda, in association with high Cr and TiO_2 concentrations, indicate detrital minerals derived from the basic igneous rocks which crop out on the St Kilda Platform. The highest values occur in muddy sediments at the shelfbreak (e.g. 32ppm west of the Outer Hebrides)

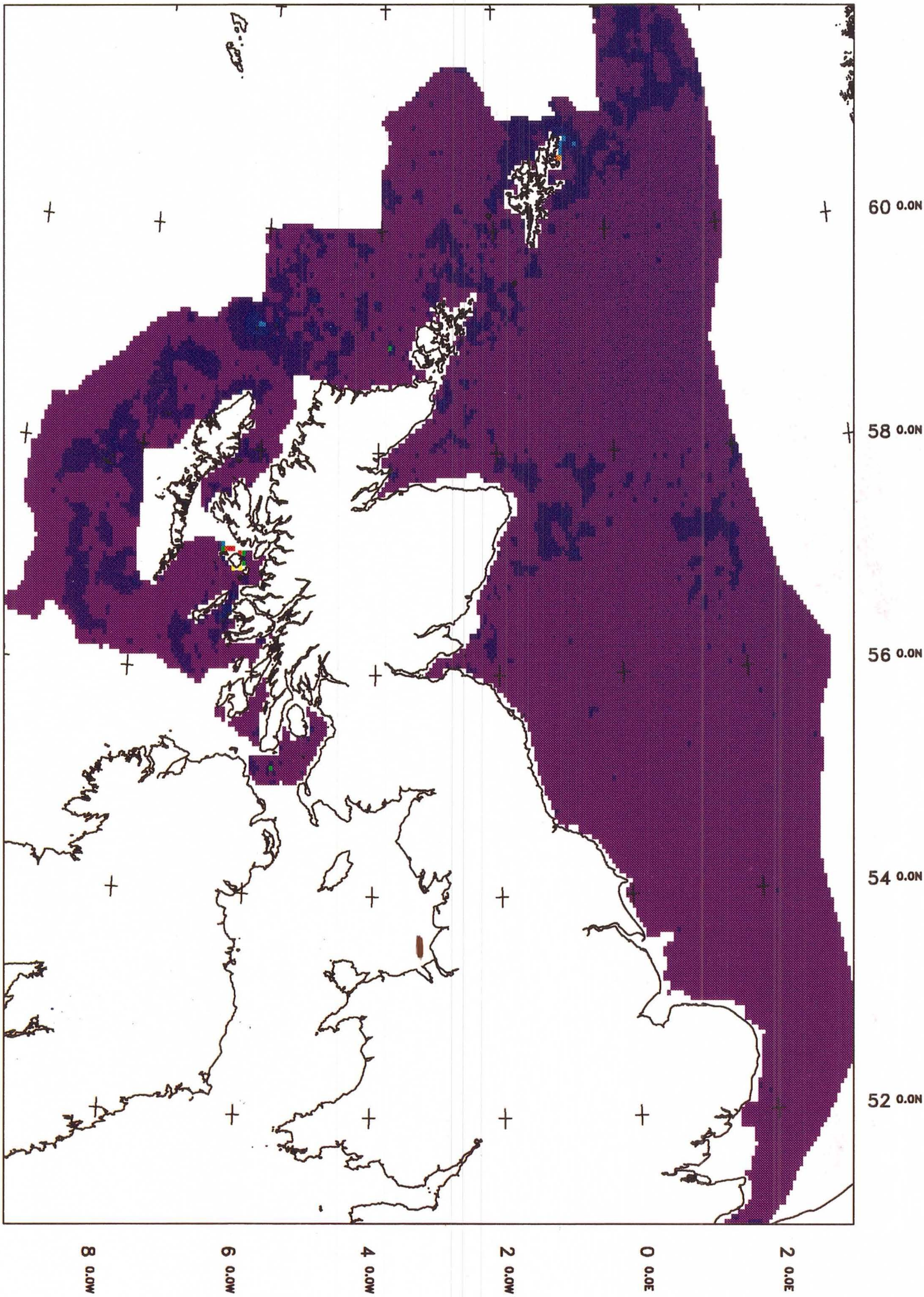
Malin-Hebrides

As on the outer shelf, Ni values are uniformly enriched in both fine-grained and coarse-grained sediments of The Minch and Sea of the Hebrides due to derivation of the underlying Quaternary deposits from Tertiary basic and ultrabasic igneous rocks. In Dearnley (1991), the highest Ni value (49ppm) occurred in sands to the north of Skye. Normalised Ni/Li data show high values around Rum where high concentrations of minerals such as chromite were reported by Gallagher (1989) (see Cr section). High values also typify the muddy sediments of the Sound of Jura (average 42ppm) and the Firth of Clyde (average 50ppm) although in the latter area Ni values may be enhanced due to adsorption on organic matter or by metallic contamination.

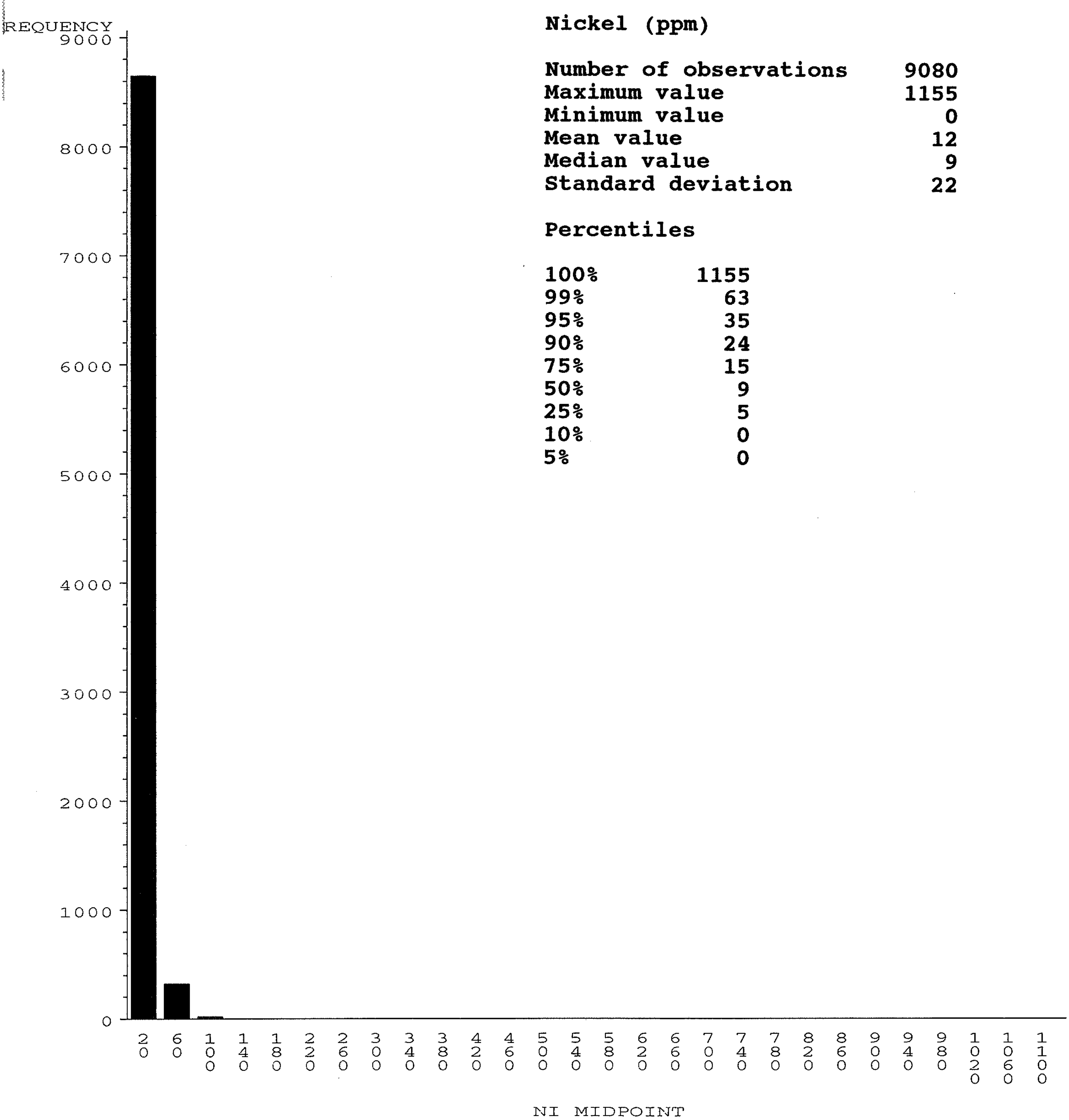
NICKEL IN SEA-BED SEDIMENT



NICKEL NORMALISED TO LITHIUM



NICKEL



STATISTICS

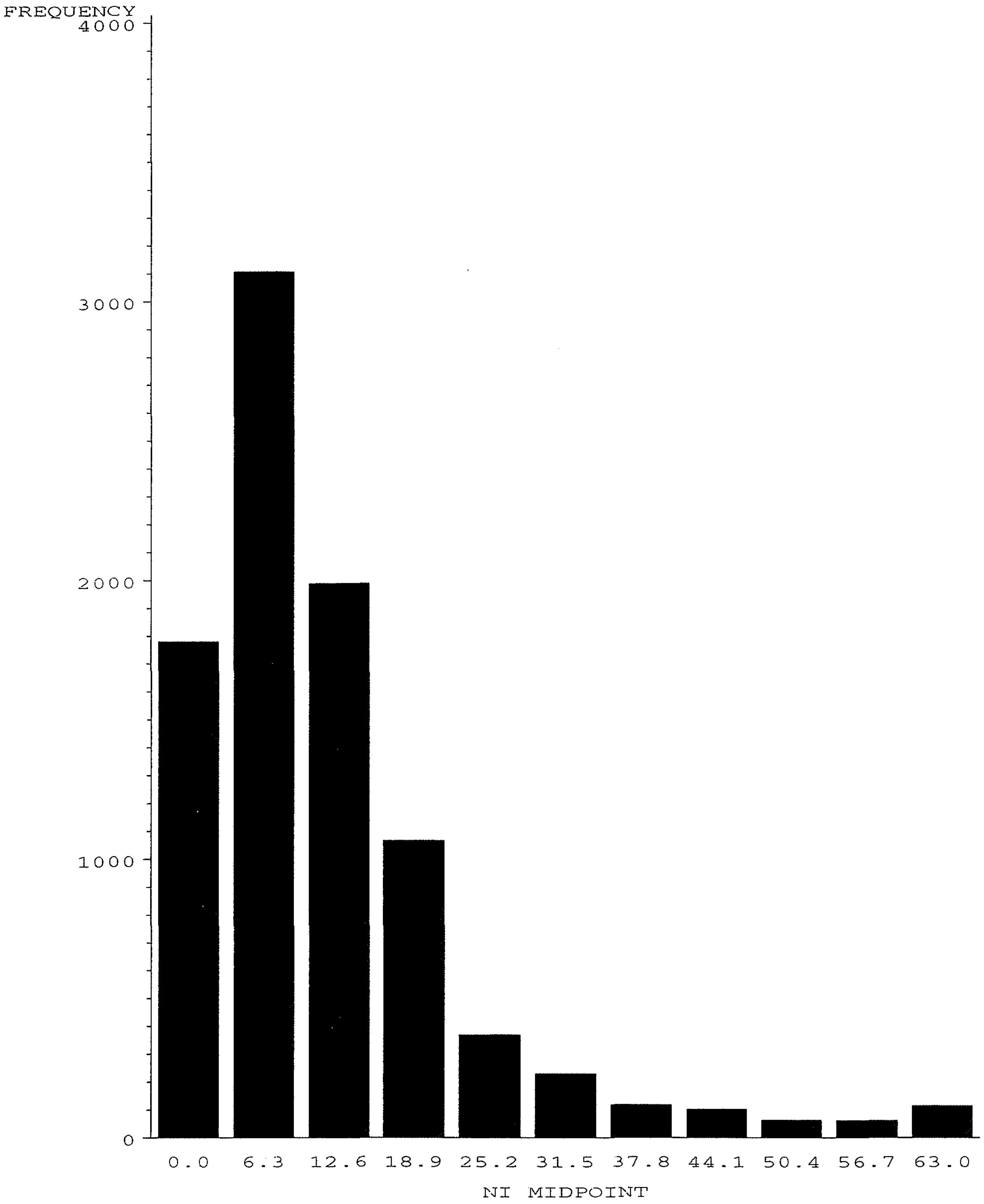
Nickel (ppm)

Number of observations	9080
Maximum value	1155
Minimum value	0
Mean value	12
Median value	9
Standard deviation	22

Percentiles

100%	1155
99%	63
95%	35
90%	24
75%	15
50%	9
25%	5
10%	0
5%	0

NICKEL



FREQUENCY
4000
3000
2000
1000
0
0.0
6.3
12.6
18.9
25.2
31.5
37.8
44.1
50.4
56.7
63.0
NI MIDPOINT

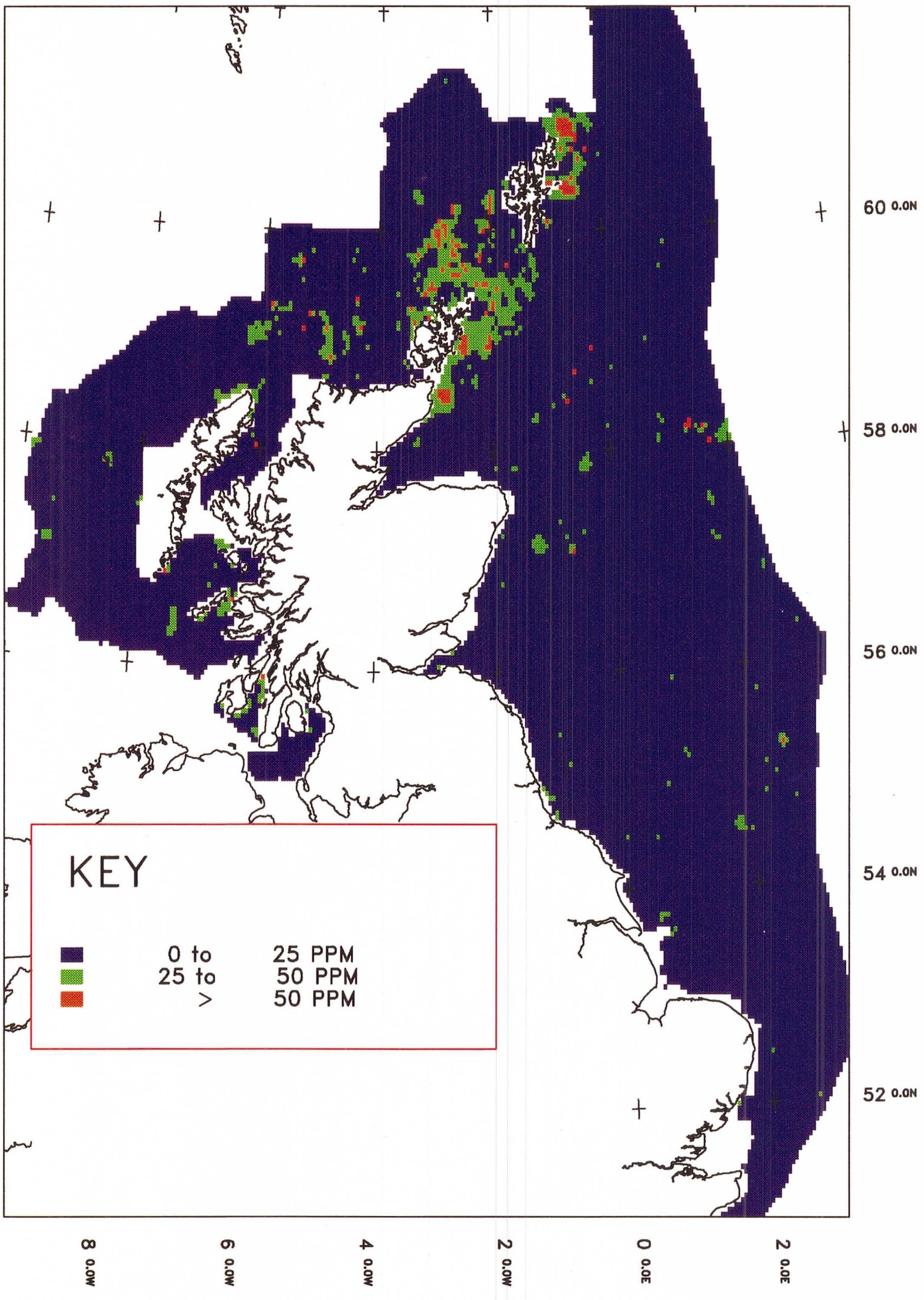
Niobium

Niobium

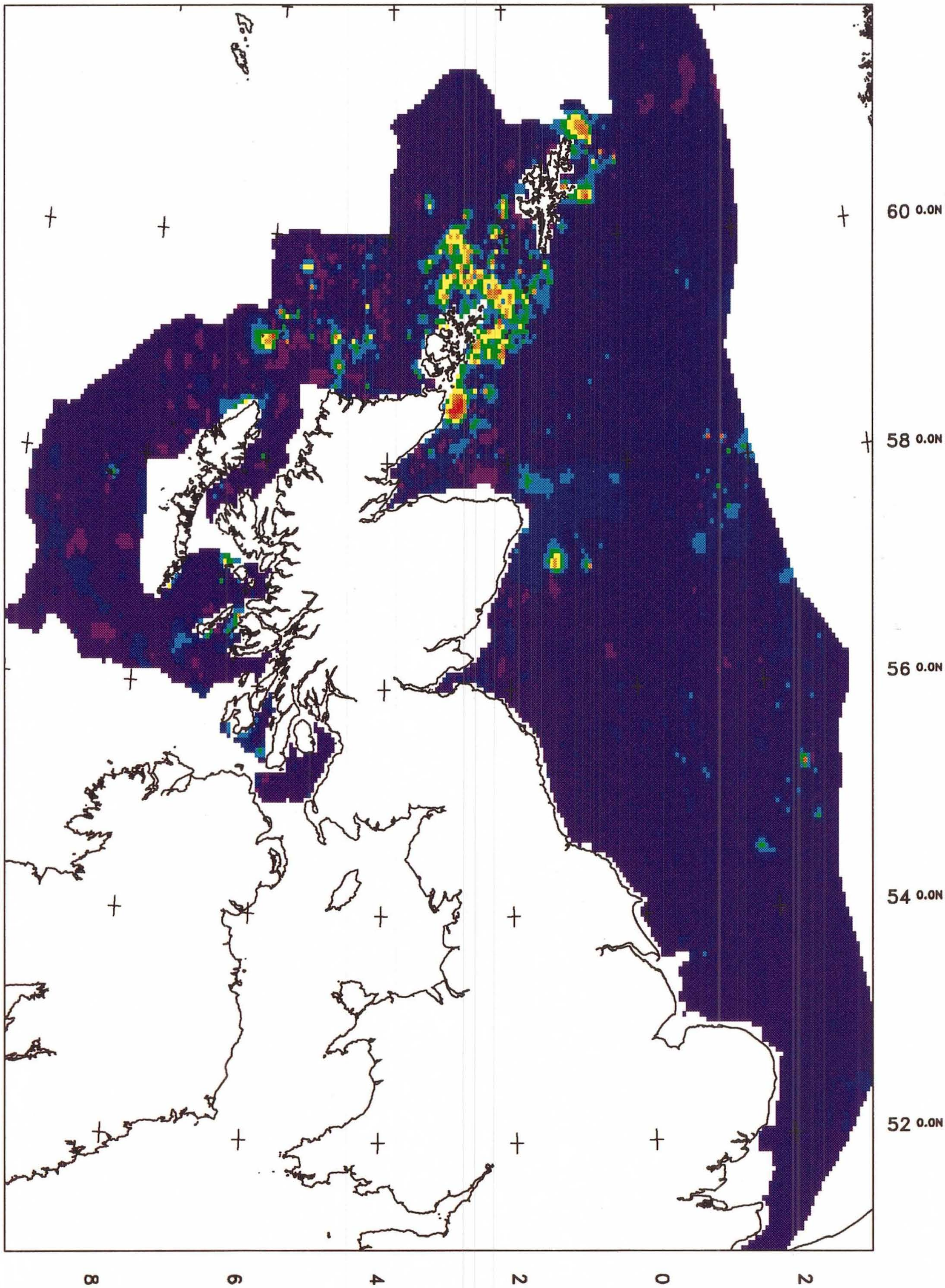
Nb values are generally low (below detection limit) over most of the North Sea. Appendix 1 shows that most of the muddy sediments of the study area have intermediate concentrations, with the highest values occurring in the estuaries of the rivers Forth (average 19ppm) and Clyde (average 13 ppm), and in the Sound of Jura (average 15ppm).

The distribution pattern of Nb generally reflects the affinity of the element for Ca in areas of high carbonate production. In the southern North Sea, sandy and gravelly sediments in the Deep-Water Channel and off the Humber Estuary (average 12ppm) have the highest Nb values. Farther north, Nb values are generally high off the coast of Buchan (average 18ppm in sands near the coast at Peterhead; 12 ppm in gravelly sands on Aberdeen Bank); in gravelly sediments on the Orkney-Shetland Platform (average 27ppm) and on the West Shetland Shelf. Gravels in The Minch and Sea of the Hebrides (average 17ppm) have higher concentrations than fine-grained (average 4ppm) and sandy sediments (average 8ppm).

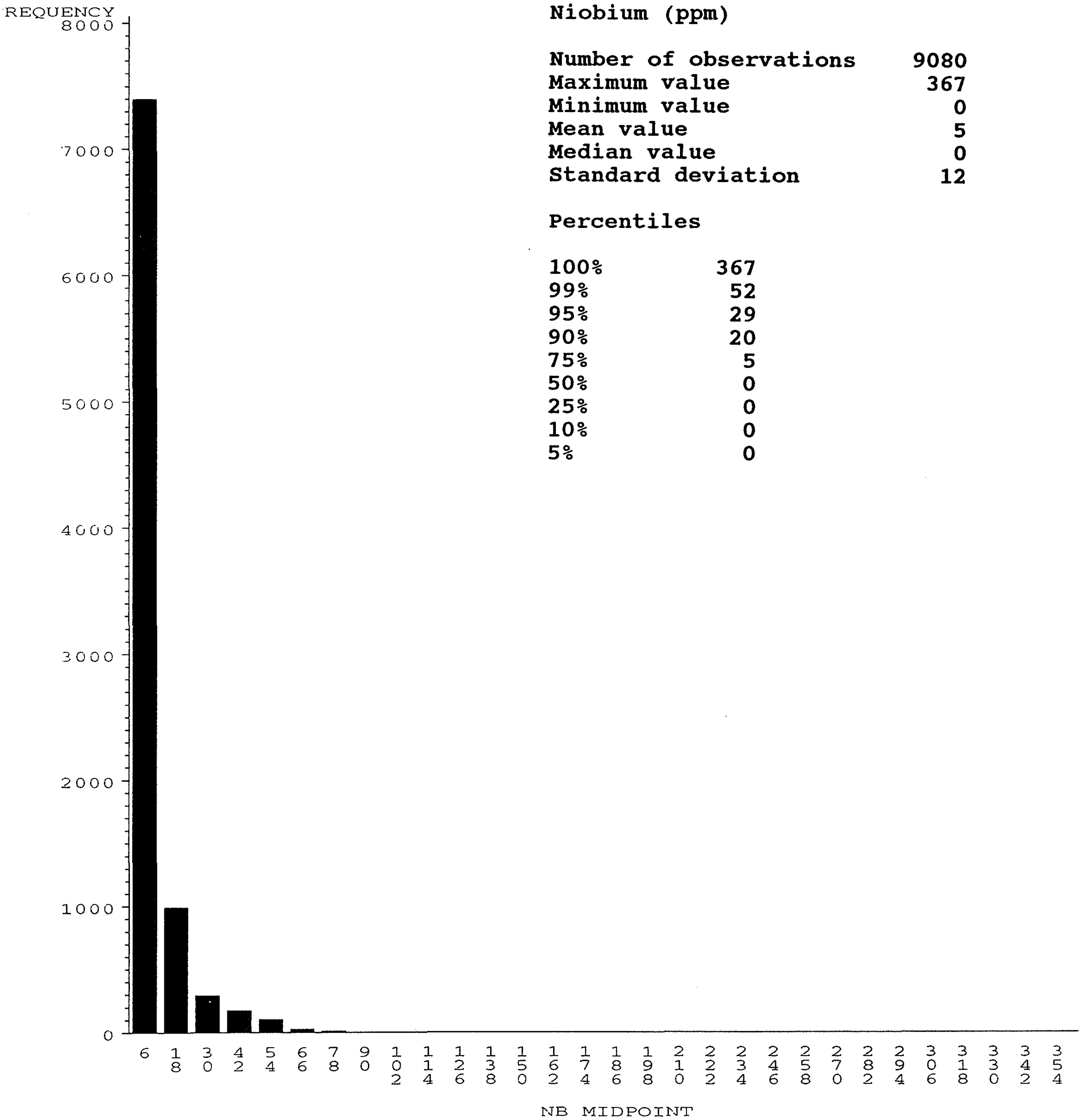
NIOBIUM IN SEA-BED SEDIMENT



NIOBIUM NORMALISED TO LITHIUM



NIOBIUM



STATISTICS

Niobium (ppm)

Number of observations	9080
Maximum value	367
Minimum value	0
Mean value	5
Median value	0
Standard deviation	12

Percentiles

100%	367
99%	52
95%	29
90%	20
75%	5
50%	0
25%	0
10%	0
5%	0

Phosphorus

Phosphorus

Southern North Sea

P concentrations occur over a wide range in most sediment types within the area, although sandy sediments generally have the lowest P concentrations here and elsewhere in the study area. The highest P concentrations occur in both muddy and gravelly sediments near the coast of East Anglia (average 0.21% in gravelly sediments; 0.17% in muddy sediments), and in the Markham's Hole/Outer Silver Pit area (average 0.27% in gravelly sediments ; 0.11% in muddy sediments). In the area off the coast of East Anglia, gravels have been shown to contain rounded phosphorite pebbles reworked from Pliocene lag deposits (Balson, 1989) and Pliocene deposits also occur extensively to the east of the Outer Silver Pit (Cameron et al. 1992). In the Markham's Hole/Outer Silver Pit area, high P may also reflect concentrations of heavy minerals such as apatite, the most important and abundant phosphate mineral, or monazite, especially where associated with high concentrations of Rare Earth Elements such as Y and La.

Although carbonate production is generally low in the southern and central North Sea (Figure 12), erosion of older shell-rich sediments has supplied carbonate to the surface sediments. The distribution of P in nearshore areas in particular is therefore controlled by it's incorporation in carbonate by replacement of Ca. Adsorption of P on clay minerals and the accumulation of detrital organic matter are also important factors in the general distribution of P in this area.

Central North Sea

As in the southern North Sea, P concentrations are generally low in sands but increase in muddy and gravelly sediments nearshore (average 0.16% in muddy sediments off the Tyne and Tees estuaries; 0.12% in gravelly sediments from the same area). The high concentrations nearshore between Flamborough Head and the Firth of Forth in both coarse and fine-grained sediments reflect the same processes which control P distribution farther south, in particular derivation from older carbonate-rich sediments such as those of the Carboniferous sedimentary rocks of north-east England and central Scotland. Farther offshore in predominantly sandy sediments the variable distribution of low and high P values is probably due to the absence or occurrence of heavy minerals. Dangerfield and Tulloch (1989) recorded the variability in concentrations of 'minor acid igneous' minerals, including apatite and monazite, in the very fine and fine-grained sand fractions of samples from the central and northern North Sea but reported the highest concentrations of these minerals in the Devil's Hole area.

Northern North Sea

P values are generally low to intermediate throughout this area with the highest values associated with the shelly gravels of the Orkney-Shetland Platform.

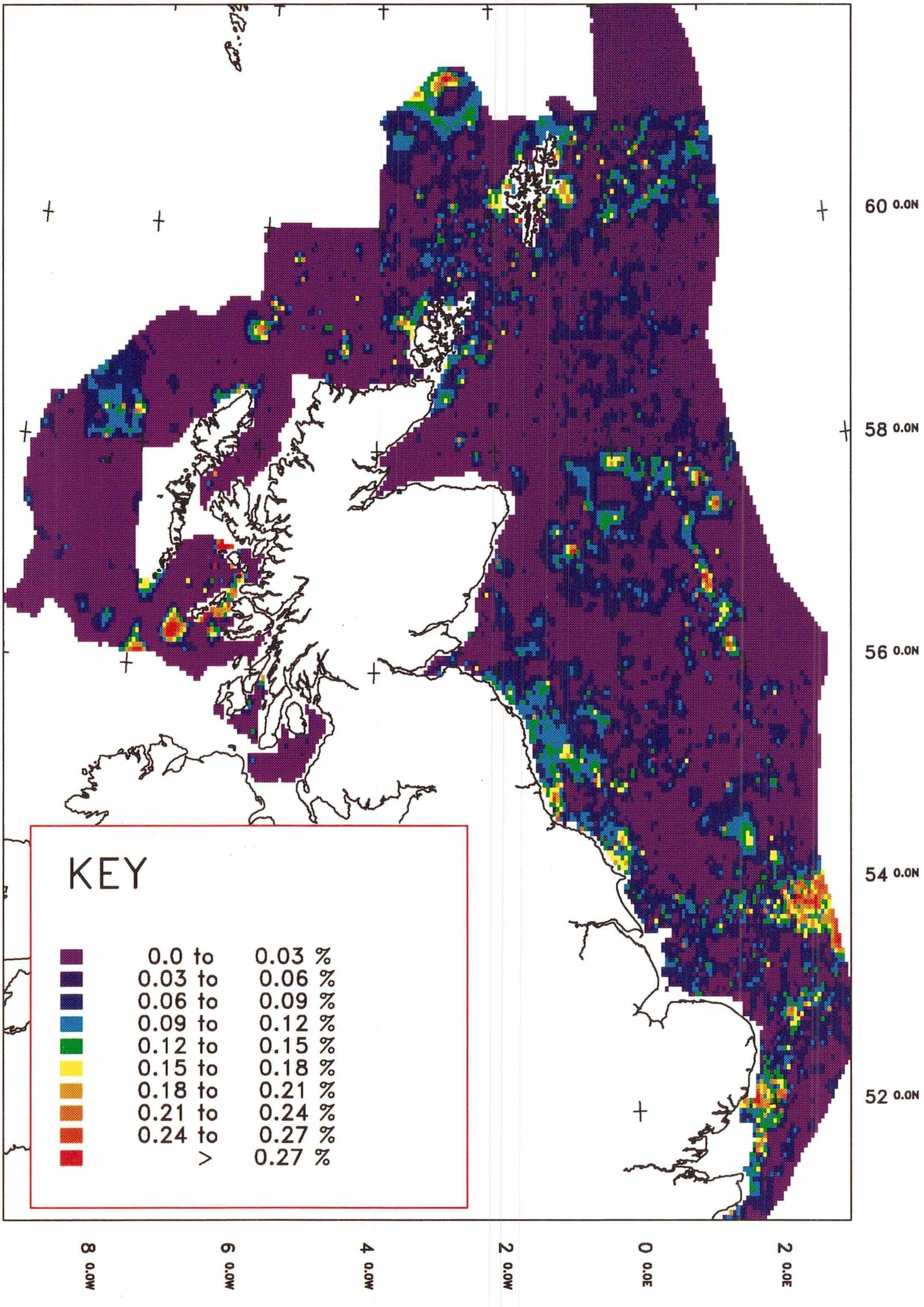
Hebrides and West Shetland shelves

As in the area to the east high P values occur in shell-rich sediments between Orkney and Shetland and also in gravelly sediments towards the shelfbreak, however fine-grained sediments on the slope have low P concentrations (average 0.01%). A group of intermediate to high P values on the Hebrides Shelf north of St Kilda occur in an area of distinctive geochemistry associated with high concentrations of element such as Cr, Fe_2O_3, TiO_2 and Zr suggesting that heavy minerals have accumulated on this part of the shelf.

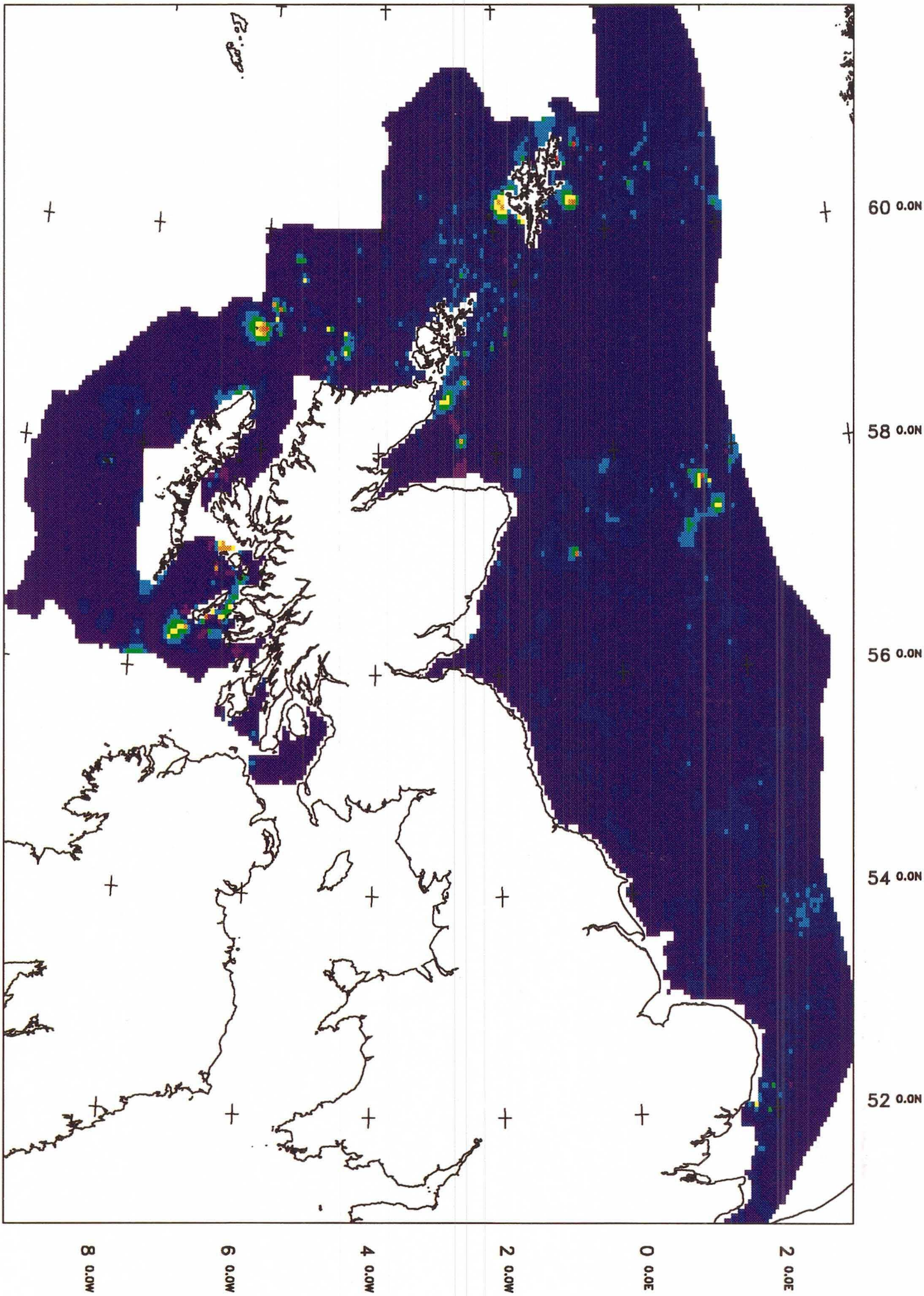
Malin-Hebrides

P values are generally low in this region, however gravelly sediments in the Sea of the Hebrides to the south of Skye have high P concentrations (average 0.16%), the highest average outside of the southern North Sea and north-east coast of England. In this area P is weakly positively correlated with Ca and Sr and is therefore due to the high shell content of these sediments (Figure 12).

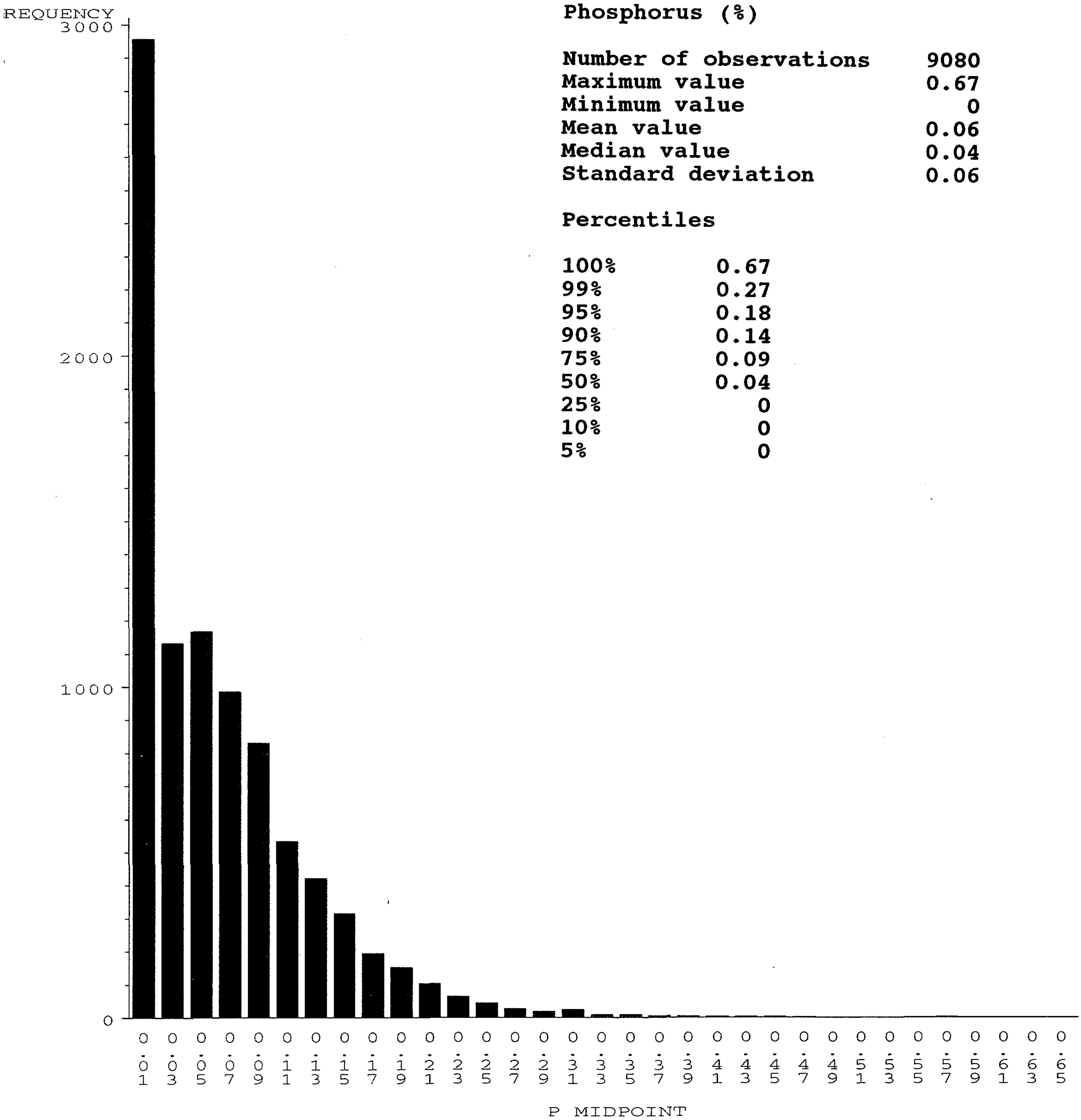
PHOSPHORUS IN SEA-BED SEDIMENT



PHOSPHORUS NORMALISED TO LITHIUM



PHOSPHORUS



STATISTICS

Phosphorus (%)

Number of observations	9080
Maximum value	0.67
Minimum value	0
Mean value	0.06
Median value	0.04
Standard deviation	0.06

Percentiles

100%	0.67
99%	0.27
95%	0.18
90%	0.14
75%	0.09
50%	0.04
25%	0
10%	0
5%	0

Potassium

Potassium

Southern North Sea

K_2O values are generally low in the sandy sediments of the region (average 0.96%) with higher values in areas of fine-grained sediment. The largest group of intermediate to high K_2O concentrations occur in the Markham's Hole area (average 1.55%) where K is strongly correlated with other elements of clay mineral association such as Li and Rb. Intermediate K_2O values (average 1.82%) also occur in muddy sediments offshore of East Anglia to the south of Lowestoft, but here they correlate with a much wider range of elements. The importance of K in the sedimentary cycle and the weathering of potassic minerals followed by incorporation of K ions in clay mineral lattices was commented upon by Nicholson et al. (1985).

Central North Sea

Intermediate to high K_2O concentrations occur in fine-grained sediments in the nearshore area between Flamborough Head and the Tees Estuary (average 1.52%); offshore of the Tyne-Tees estuaries (average 2.33%); the Firth of Forth (average 2.07%); and the Farn Deeps (average 2.11%), Gorsethorn Deep (average 2.09%), Devil's Hole (average 1.6%) and Silver Pit areas farther offshore. A notable feature of the distribution of K_2O is the general increase in concentration north of a line between Dogger Bank and the Firth of Forth, particularly evident on the normalised K/Li map. This line corresponds to a limit between areas with sediment containing lithic fragments derived from basic to acid igneous rocks to the south, and those with sparse or no basic igneous lithic fragments to the north (Dearnley 1991). Dangerfield and Tulloch (1989) and Dearnley (1991) both distinguished these two areas on the basis of analysis of heavy minerals such as garnet, amphibole and other minerals derived from metamorphic and acid igneous rocks, and common rock-forming minerals such as quartz, potassium and sodic feldspar; these minerals forming the main component of sediments in the northern area. This is reflected in the general increase in K concentrations from the southern North Sea (average 0.74%) to the central and northern North Sea (average 1.09%). A map of K_2O/Al_2O_3 is presented to show the association between these two elements in aluminosilicate minerals in the central and southern North Sea.

Northern North Sea

Intermediate to high K_2O values occur in the Fladen Ground and Witch Ground basins where the highest values (average 2.64% in mud) may be due to incorporation of K in illite. High K_2O values, associated with high Ba and Rb, in sands near the east coast of Scotland (e.g offshore of Peterhead - average 1.68%) reflect a high proportion of alkali feldspar probably derived from Dalradian (Southern Highland Group) sediments. These Dalradian rocks are enriched in elements associated with acid igneous rocks and have been attributed to an immature granitic or acid-volcanic provenance. A similar association of elements in coarse-grained sediments in the Moray Firth can also be attributed to potassium feldspar concentrations, but in this area they may be derived from the Devonian rocks of Caithness.

Normalised K_2O/Li data show several groups of high values in areas of sandy sediment in the Moray Firth and in the area surrounding the Fladen Ground and Witch Ground basins. Other elements which demonstrate a similar distribution when normalised to Li are Al and Rb. This association would suggest that these sediments contain high concentrations of K-bearing aluminosilicates such as K-feldspar and mica. Although K-feldspar has been recorded in sands throughout the central and northern North Sea, the distinctive geochemical signature of the northern area may signify a difference in provenance for the underlying Quaternary deposits. Enrichment of K, Al, Ba and Rb relative to Li suggests K minerals may have undergone less degradation during transport and weathering.

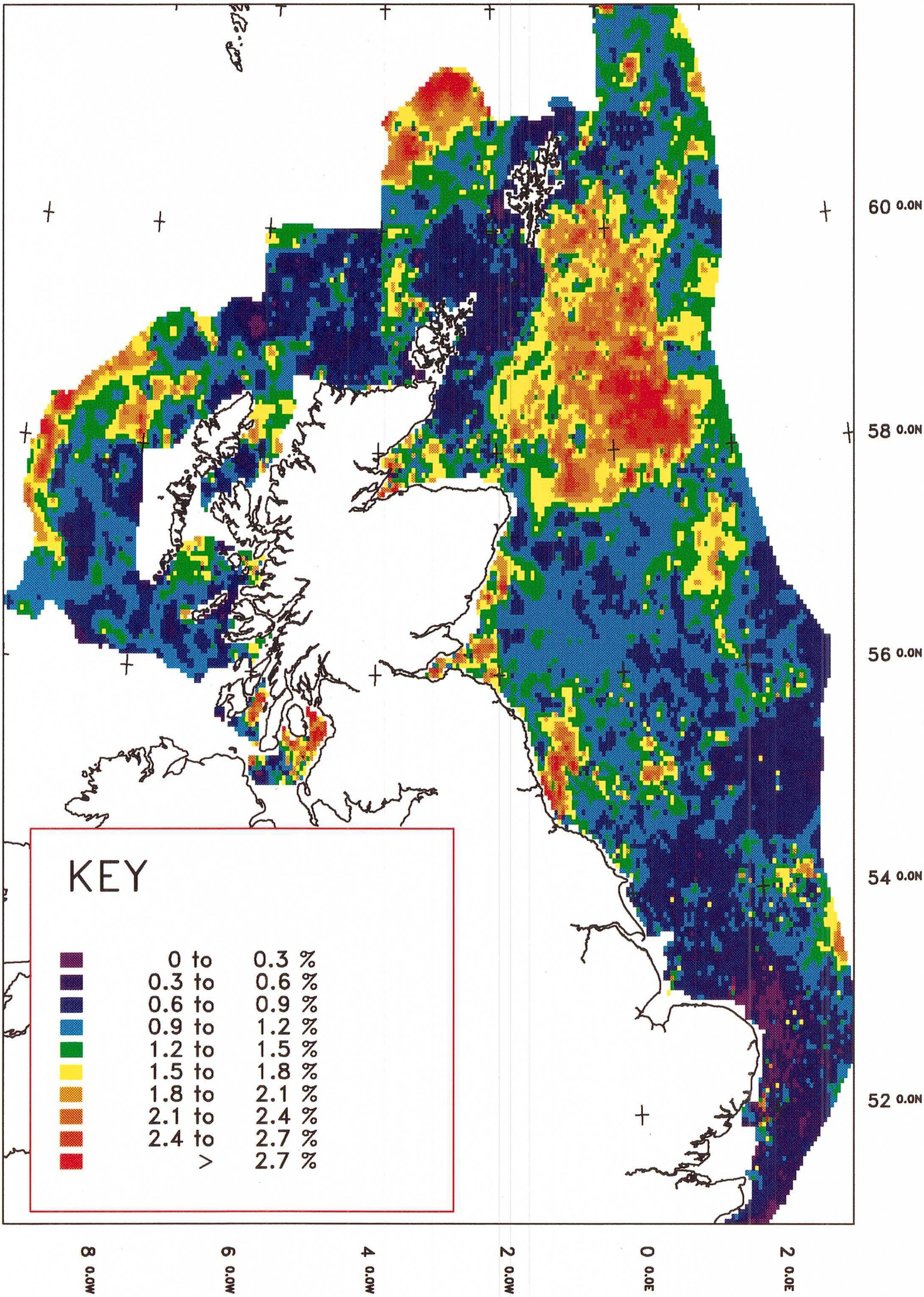
Hebrides and West Shetland shelves

K_2O levels are generally low throughout the region (average 0.77% in gravels on the Orkney-Shetland Platform; 0.8% in sand and 0.77% in gravelly sand on the West Shetland Shelf). Intermediate to high K_2O values occur in fine-grained sediments to the north-west of Orkney (average 1.52%) and at the shelfbreak (average 1.26% north-west of Shetland; 1.94% west of the Outer Hebrides). High K_2O values in areas of coarse-grained deposits, normally associated with Rb, reflect alkali feldspar or possibly micaceous rock fragments. A group of high K_2O/Li values west of the Outer Hebrides has similar characteristics to those of the sandy sediments of the northern North Sea (associated with high Al_2O_3/Li and Rb/Li) suggesting comparable composition and possible provenance for the underlying Quaternary deposits.

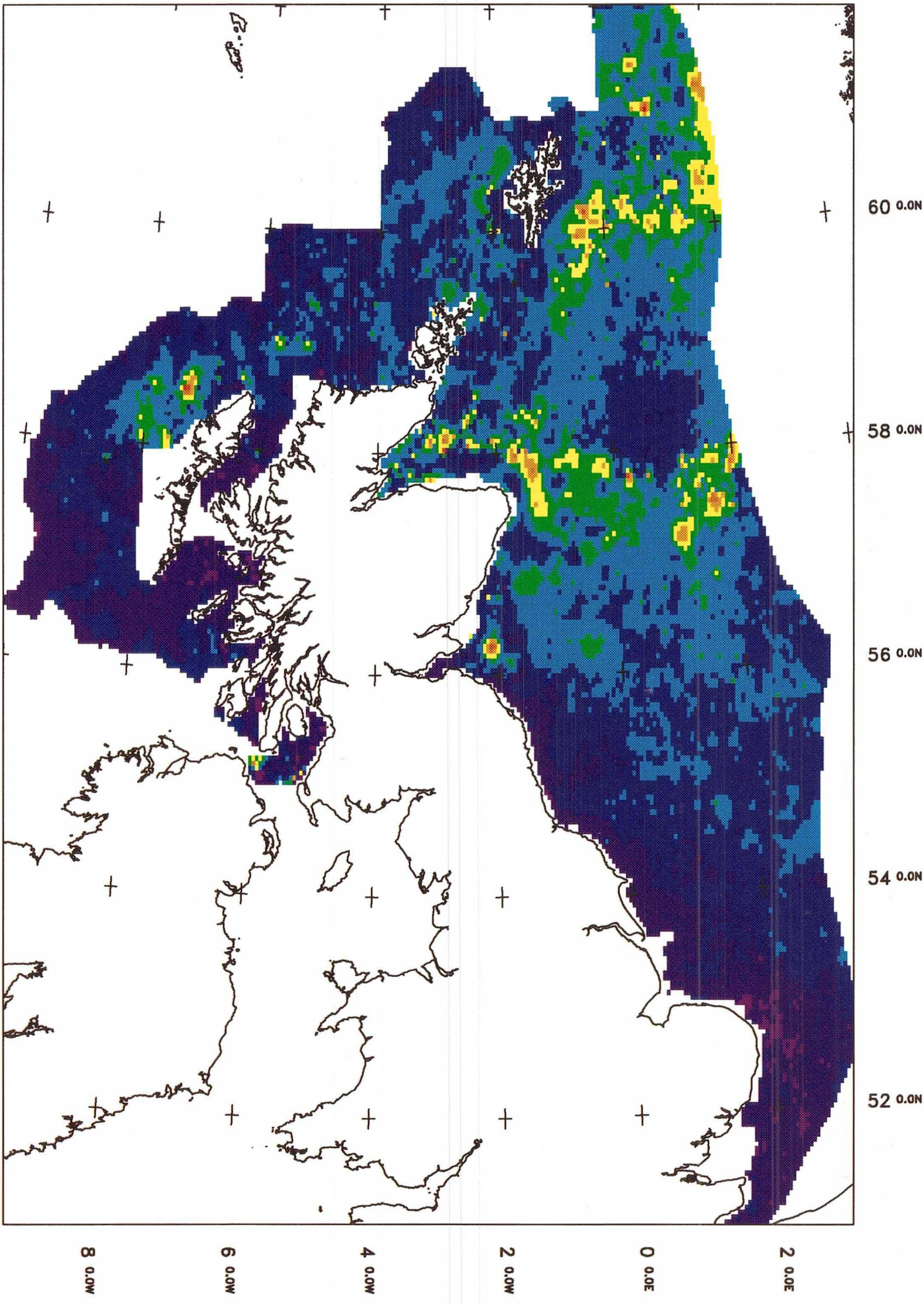
Malin-Hebrides

Intermediate K_2O values occur in fine-grained sediments in The Minch and Sea of the Hebrides (average 1.25%). High values occur in fine-grained sediments in the Sound of Jura (average 2.36%) and the Firth of Clyde (average 2.22%).

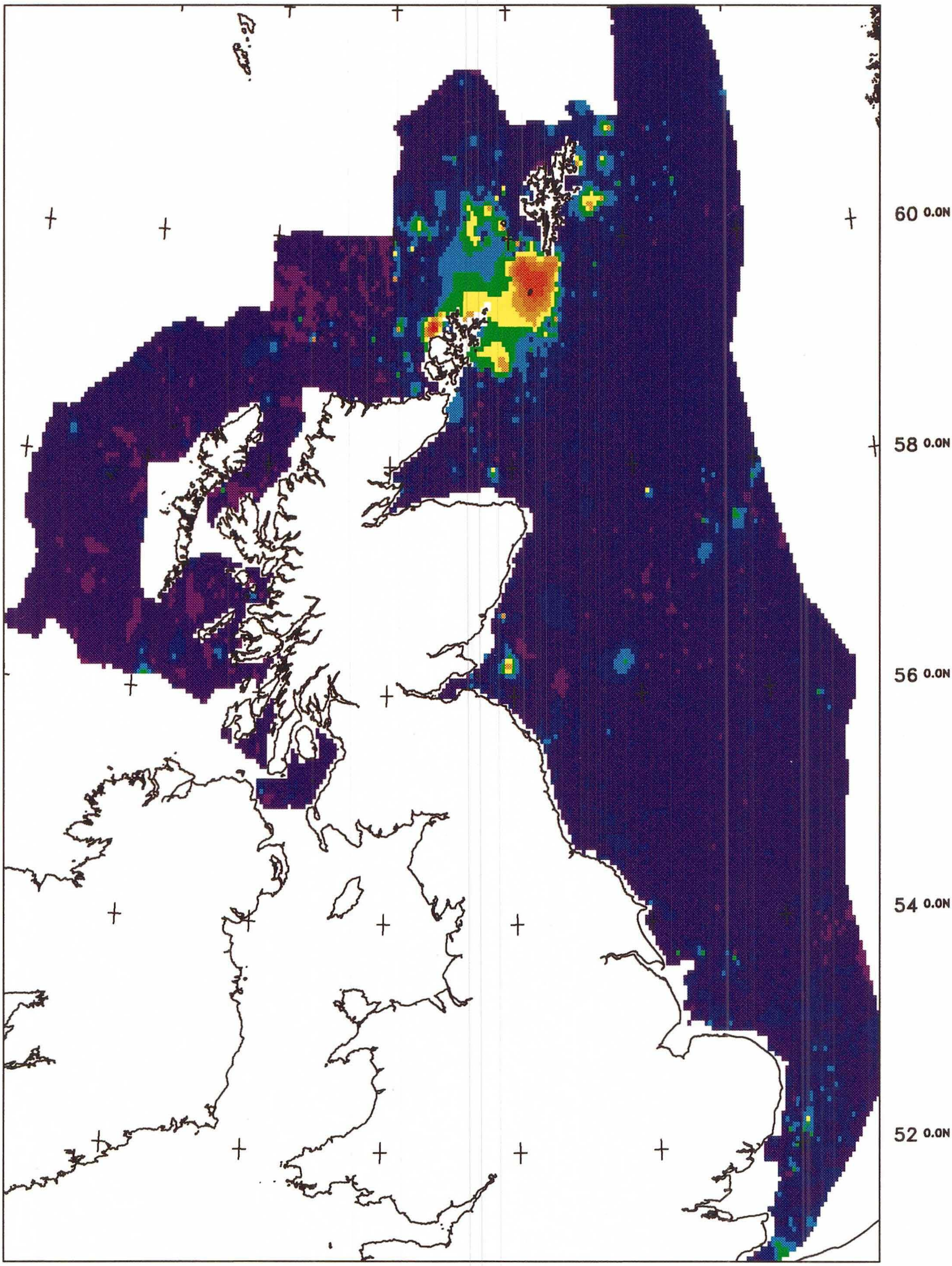
POTASSIUM IN SEA-BED SEDIMENT



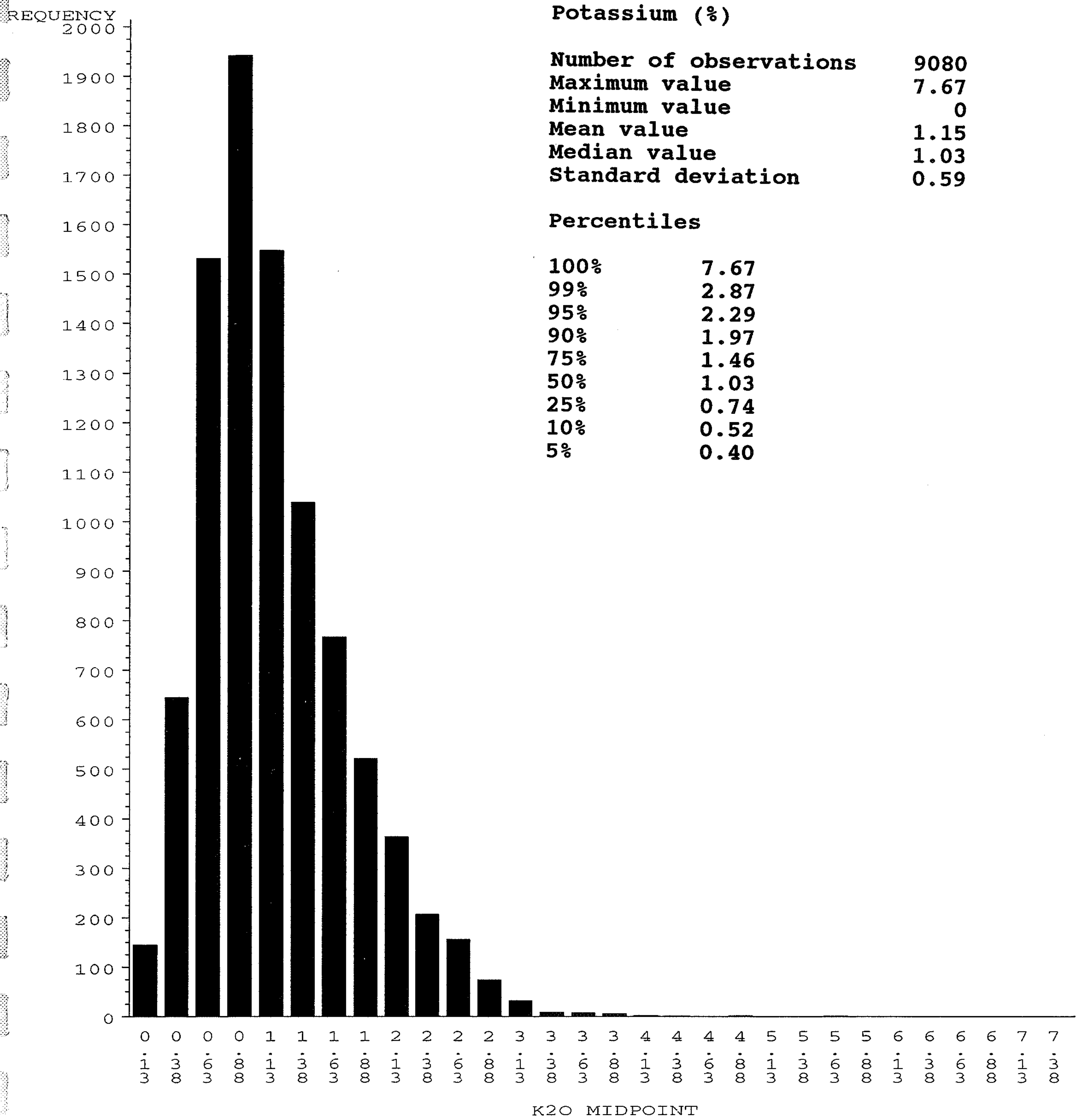
POTASSIUM NORMALISED TO LITHIUM



POTASSIUM NORMALISED TO ALUMINIUM



POTASSIUM



STATISTICS

Potassium (%)

Number of observations	9080
Maximum value	7.67
Minimum value	0
Mean value	1.15
Median value	1.03
Standard deviation	0.59

Percentiles

100%	7.67
99%	2.87
95%	2.29
90%	1.97
75%	1.46
50%	1.03
25%	0.74
10%	0.52
5%	0.40

Rubidium

Rubidium

The geochemistry of Rb is closely related to that of K because of the similarity in their ionic radii allowing Rb to replace K in mineral lattices. Comparison of the Rb geochemical map and normalised Rb/Li with those of K and K/Li, confirm that their distribution patterns are similar. To avoid repetition, the following description summarises Rb levels in each region, however reference should be made to the K section for interpretation of the distribution pattern.

Southern North Sea

Rb values are low except in areas of fine-grained sediment where they occur with high levels of elements which concentrate in clay minerals. The highest values occur in the fine-grained sediments of the Outer Thames Estuary (average 48ppm), off the coast of East Anglia (average 57ppm) and in the Markham's Hole area (average 43ppm). The map of normalised Rb/K_2O shows that the highest values are in areas where both elements occur in low concentration. the concentration of Rb relative to K_2O is probably due to the proportion of mica and potassium feldspar present in the sediment. Butler (1957) stated that Rb concentration was related to K only when illite formed from weathered micas and feldspars and Goldschmidt (1954) found that Rb was held in adsorption sites more firmly than K during weathering processes. The high Rb/K_2O ratios in the southern North Sea may therefore reflect a contrast in sediment composition and weathering history of these sediments to those farther north.

Central North Sea

High Rb values characterise the fine-grained sediments offshore of the Tyne-Tees estuaries (average 65ppm); the Firth of Forth (average 74ppm); the Farn Deeps (average 54ppm), the Gorsethorn Deep (average 50ppm) and the Devil's Hole area (average 43ppm).

Northern North Sea

Like other elements which concentrate in clay minerals, particularly those associated with illite (such as B) which act as adsorption sites for Rb, intermediate to high Rb values define all areas of fine-grained sediment in the northern North Sea. These include the Fladen Ground and Witch Ground basins (up to average 75ppm in muds) and the Moray Firth (average 46ppm).

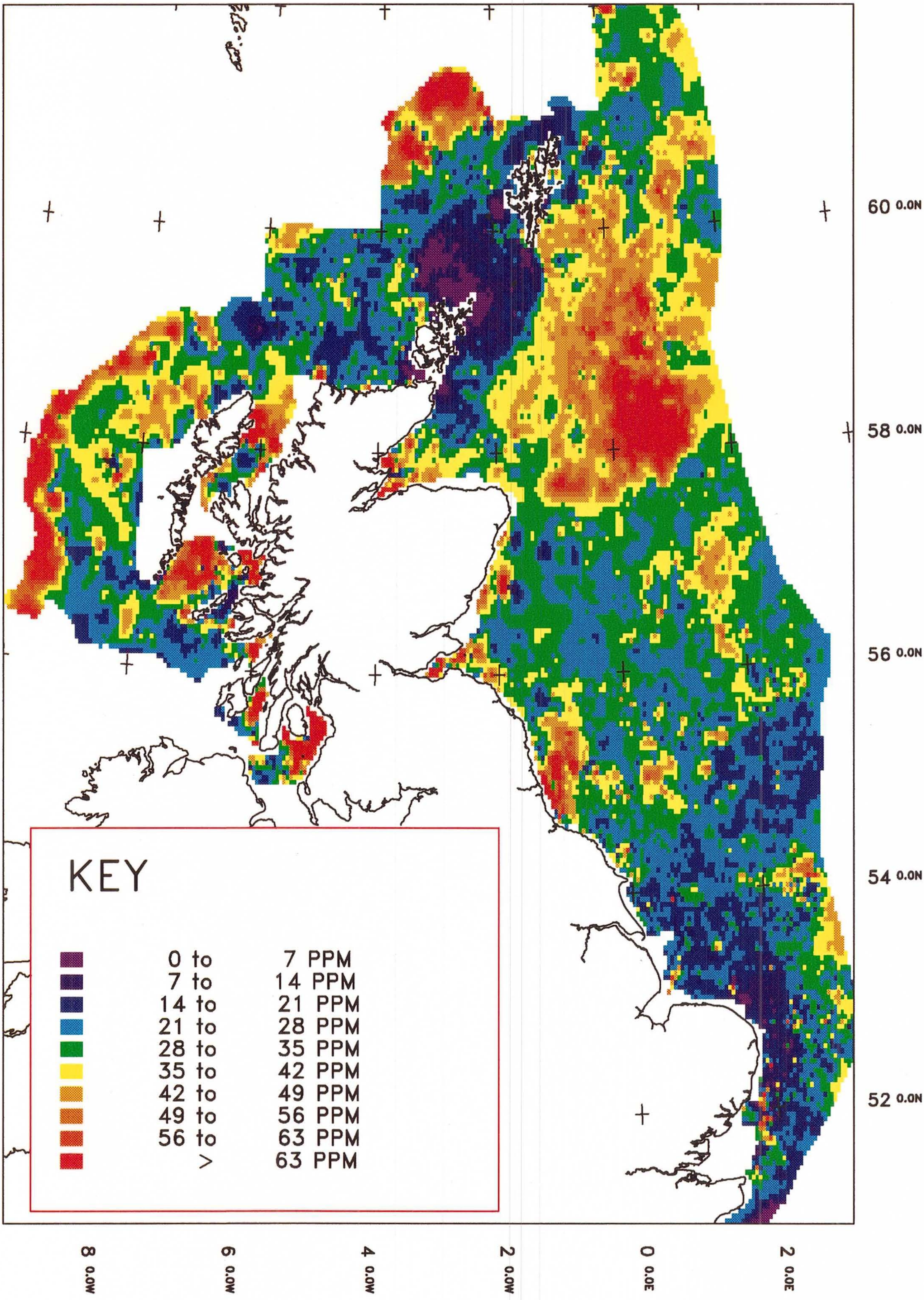
Hebrides and West Shetland shelves

Rb values are mainly low over the region with the highest values occurring in muddy sediments at the shelfbreak (average 42ppm north-west of Shetland; 68ppm west of the Outer Hebrides). Groups of intermediate to high Rb values in the coarse-grained sediments around St Kilda indicate the occurrence of feldspar or mica in rock fragments in sandy and gravelly sediments. As in the southern North Sea, the distribution of areas of high Rb/K_2O and Rb/Li ratios may indicate variations in clay mineral composition and weathering history.

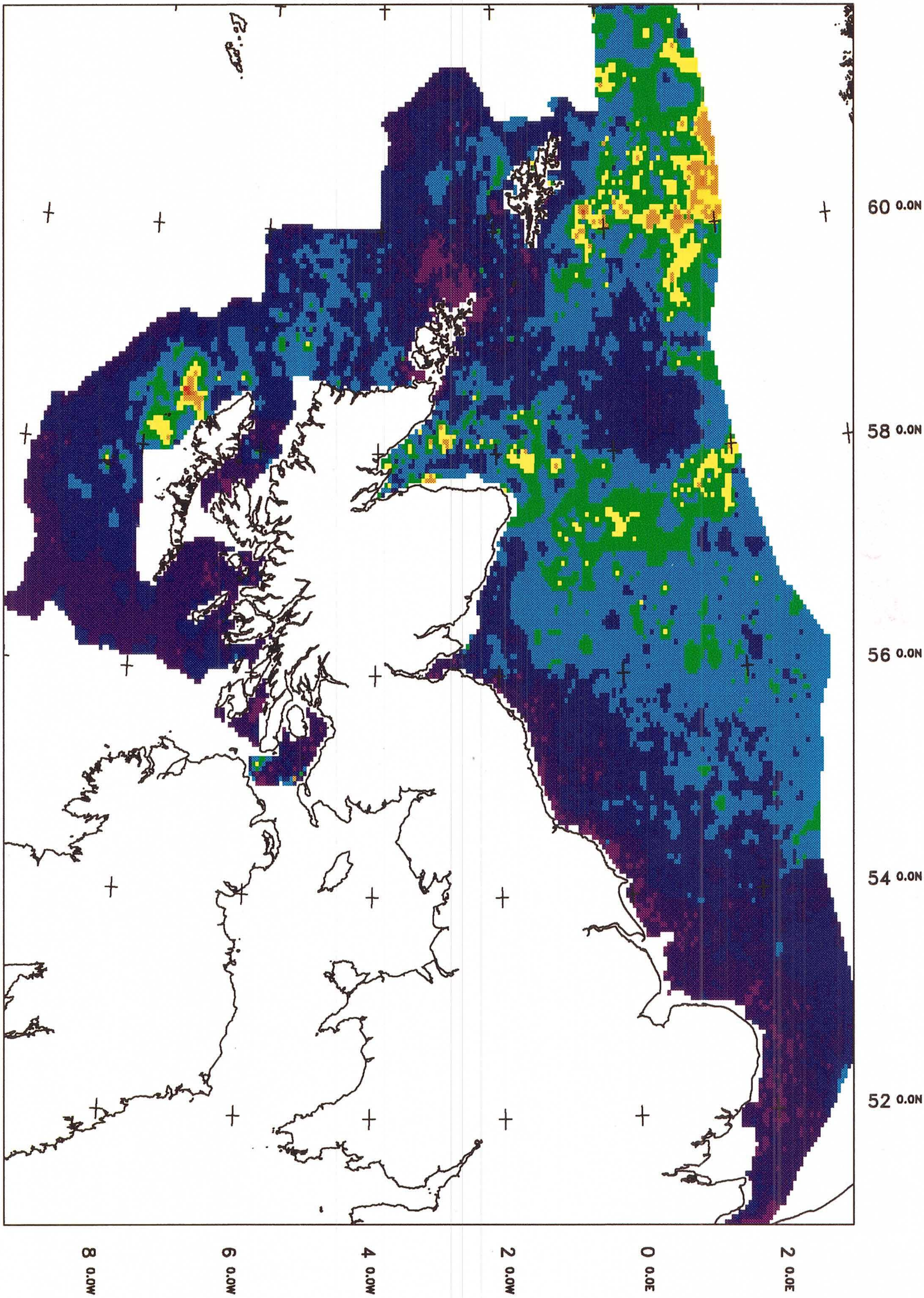
Malin-Hebrides

High Rb concentrations occur in all fine-grained sediments in the area, with the highest values found in muddy sediments of the Sound of Jura (average 89ppm) and the Firth of Clyde (average 94ppm).

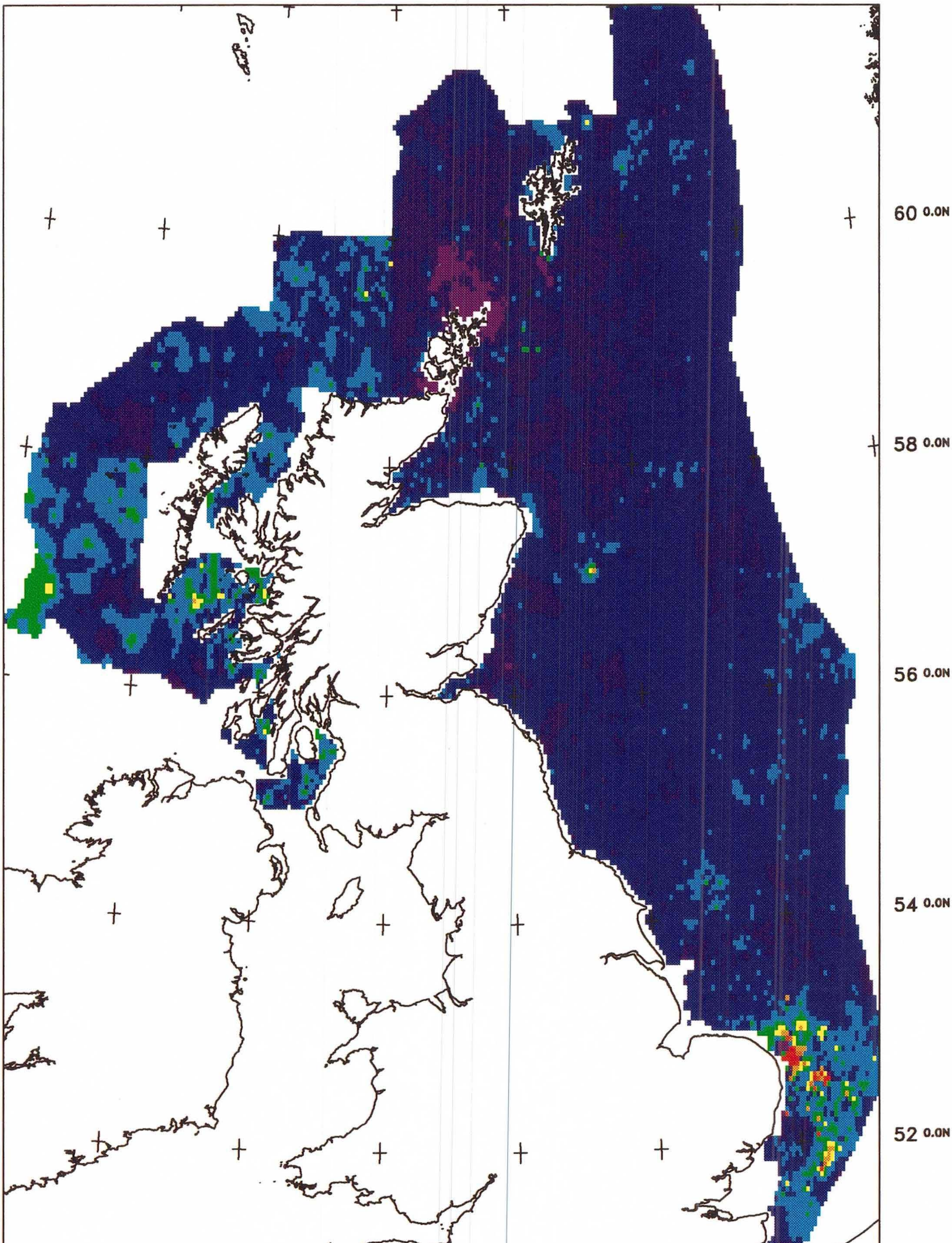
RUBIDIUM IN SEA-BED SEDIMENT



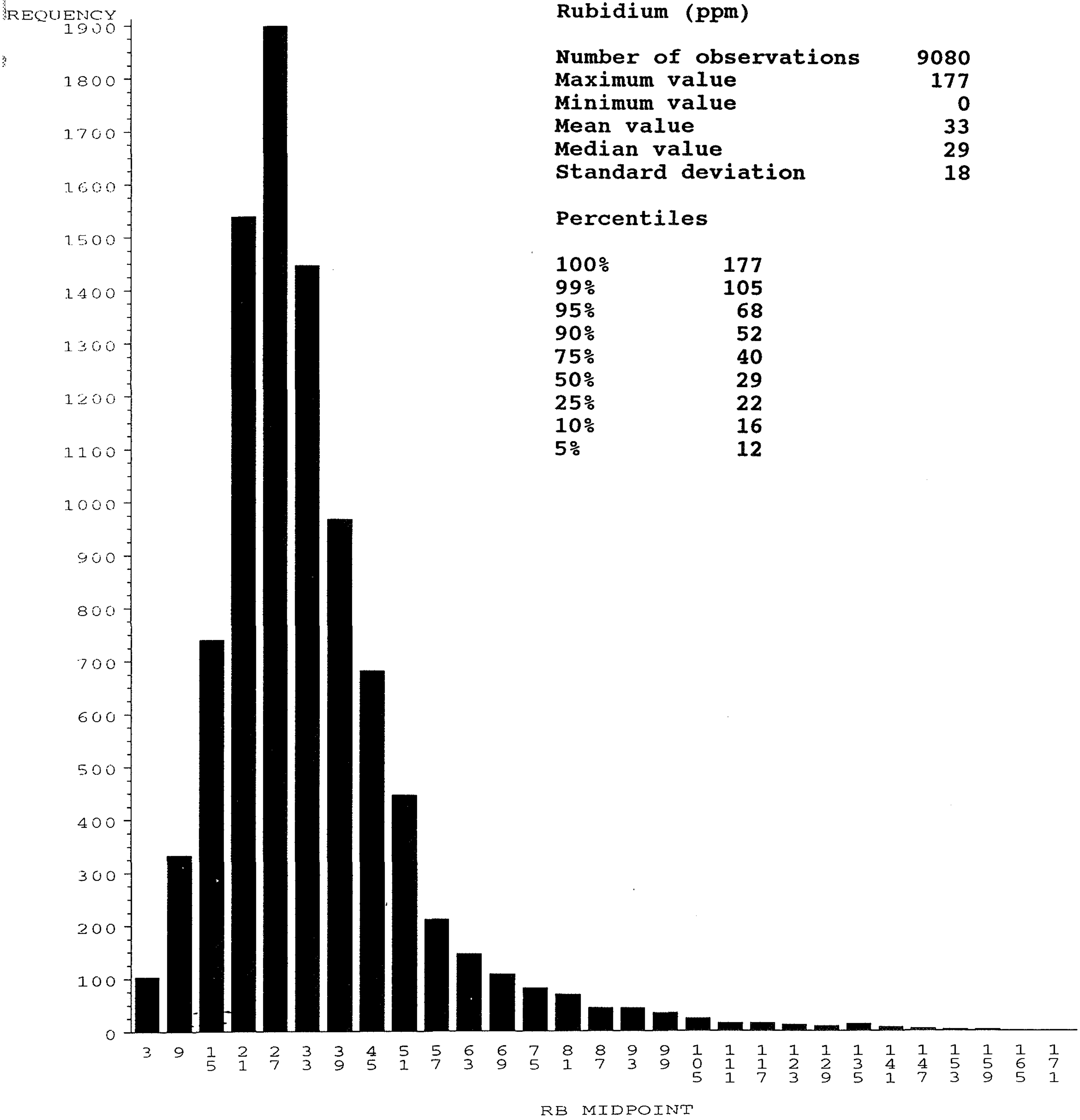
RUBIDIUM NORMALISED TO LITHIUM



RUBIDIUM NORMALISED TO POTASSIUM



RUBIDIUM



STATISTICS

Rubidium (ppm)

Number of observations	9080
Maximum value	177
Minimum value	0
Mean value	33
Median value	29
Standard deviation	18

Percentiles

100%	177
99%	105
95%	68
90%	52
75%	40
50%	29
25%	22
10%	16
5%	12

Strontium

Strontium

The distribution of Sr in the marine environment around the UK is governed by its substitution in the Ca and Ba lattice sites of carbonates. Several workers have noted an enrichment of Sr in carbonate minerals (Cronan, 1970). Sr occurs in aragonite, a metastable form of calcium carbonate, which forms stratified layers in molluscan shells (Nicholson et al., 1985). The co-ordination state of the metal atom in the aragonite lattice allows greater ease of incorporation in strontium carbonate. Although some Sr may be held in detrital feldspars in the lithic fraction, Sr distribution throughout the study area closely follows that of Ca and mainly reflects the presence of shell material in sea-bed sediments.

Nicholson et al. (1985) reported a strong correlation between Sr and loss on ignition at 1050°C (a measure of calcium carbonate) and a moderate correlation with the gravel fraction which probably contains most of the shell debris, and also with Cd. Nicholson and Moore (1981) also found an association between Cd and shell material. The correlation matrices presented in this report all indicate a very strong correlation between Sr and Ca and a negative correlation with almost all other elements. The main anomalies in each region are summarised below however, to avoid repetition, they are considered to reflect shell-rich sediments unless otherwise stated. A map of normalised Sr/Li shows the area of carbonate-rich sands and gravels on the Orkney-Shetland Platform. To distinguish between Sr in shell debris and that held in silicates a map of Sr normalised to Ca is also presented.

Southern North Sea

The highest Sr values in the area occur in the Dover Strait where they indicate the presence of chalk fragments in gravelly sediments derived from the underlying Tertiary strata. Other areas of intermediate Sr concentrations off the coast of East Anglia, and off the Humber Estuary, are also thought to reflect sediments originating from coastal erosion or river input which contain lithic fragments derived from Cretaceous or Tertiary sedimentary rocks.

Central North Sea

Sr values are low over most of the area, with the exception of slightly higher values in the coastal zone between Flamborough Head and the Tees Estuary. Erosion of cliffs of Jurassic sedimentary rocks which consist mainly of calcareous mudstone, sandstone and oolitic limestone probably account for increased Sr levels. Intermediate to high Sr values occur farther offshore on Marr Bank (average 339ppm) and Aberdeen Bank (average 822ppm) and Sr is strongly correlated with Ca reflecting high carbonate production. Sr is concentrated relative to CaO in most of the sandy sediments of the region (see Sr/CaO normalised data). The substitution of Sr for K or Ba in detrital feldspars, or it's occurrence in heavy minerals such as, for example, minerals of the apatite series, may also be an important control on Sr distribution.

Northern North Sea

Like most of the North Sea, this region is characterised by low Sr concentrations. Slight increases occur in gravelly sediments extending from the north-east of Scotland towards the Fladen Ground Basin, which may indicate Ca-feldspar in rock fragments. The most extensive groups of intermediate to high Sr values are all related to areas of high carbonate production such as the Orkney-Shetland Platform (average 2616ppm).

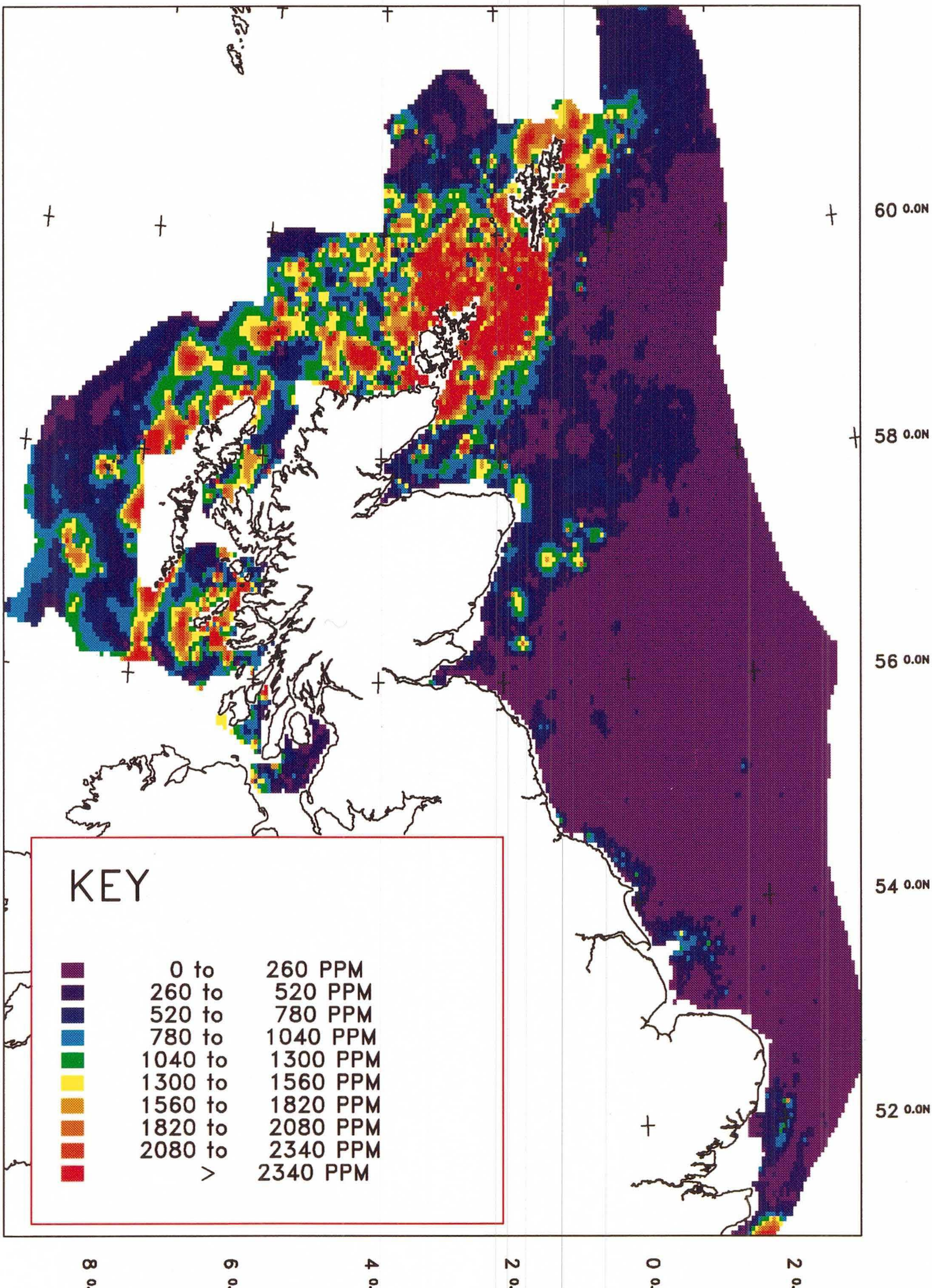
Hebrides and West Shetland shelves

High Sr values occur throughout the West Shetland Shelf reflecting the shell-rich nature of these sediments. Average values range from 1050ppm in sandy sediments to 1311 ppm in gravels. Although muddy sediments are sparse on this part of the shelf, a small area north-west of Orkney also has high Sr values (average 1856ppm) indicating that they are mainly derived from comminuted shell material. Muddy sediments at the shelfbreak have low Sr concentrations (average 394ppm). Farther south on the Hebrides Shelf, high Sr concentrations occur mainly on the inner shelf near the coast of the Outer Hebrides.

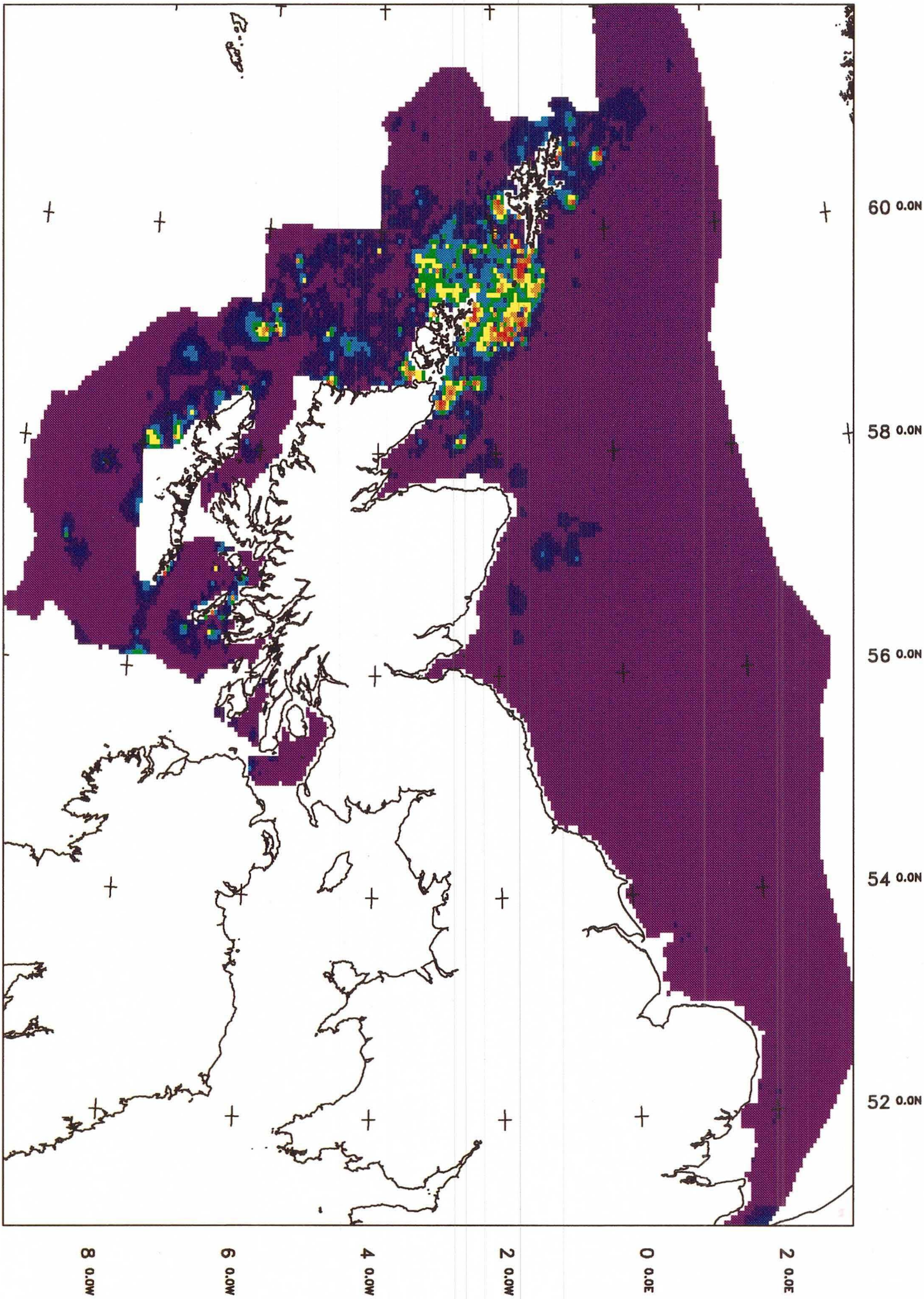
Malin-Hebrides

As in other parts of the shelf west of Scotland, high Sr concentrations occur in shelly sands and gravels in The Minch and around the islands of Coll and Tiree (average 1524ppm in sands; 2082ppm in gravel). Although Sr values in muddy sediments from this area are lower (average 1052ppm), they are significantly higher than in fine-grained deposits in areas where carbonate production is low (Appendix 1).

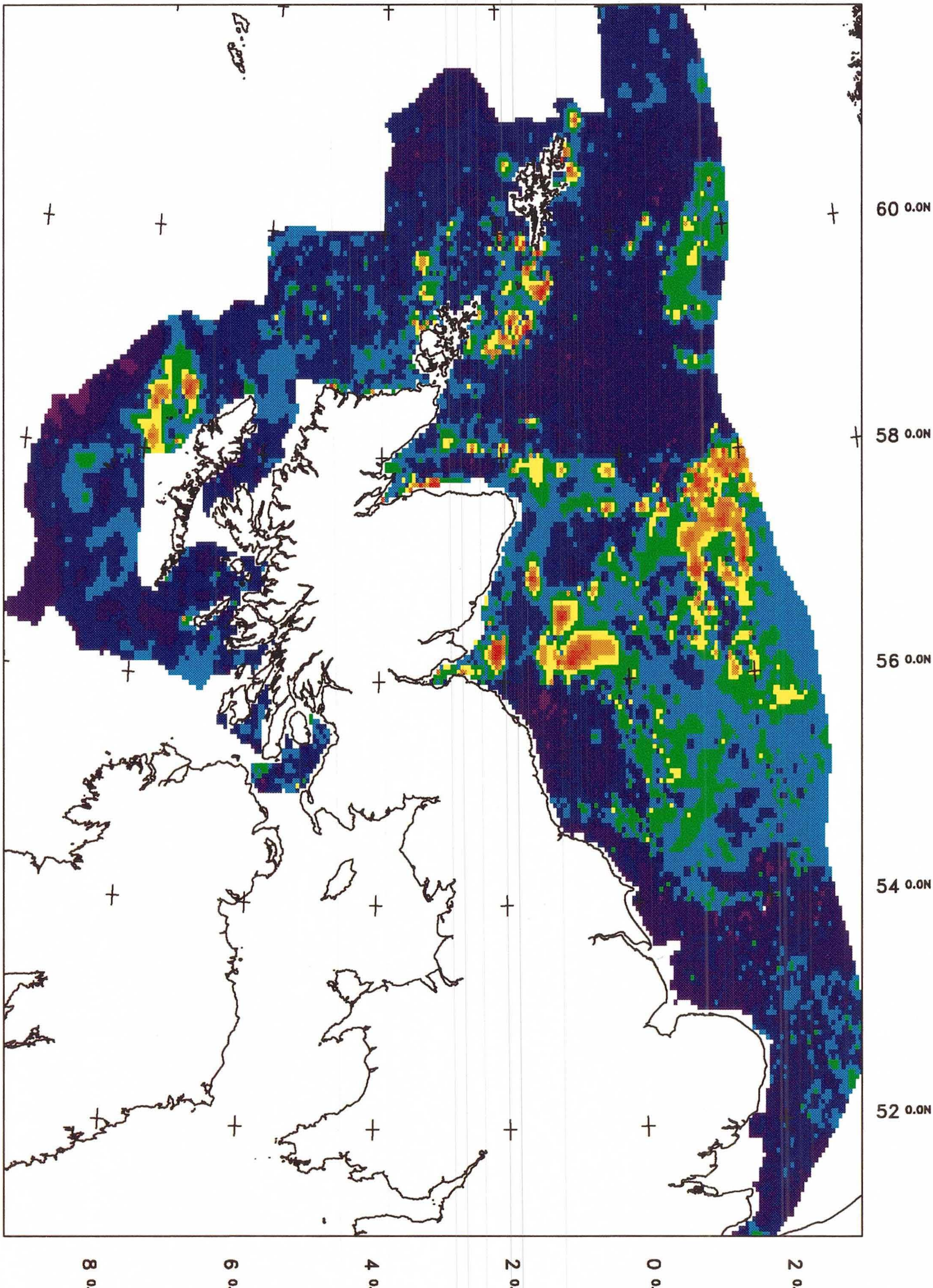
STRONTIUM IN SEA-BED SEDIMENT



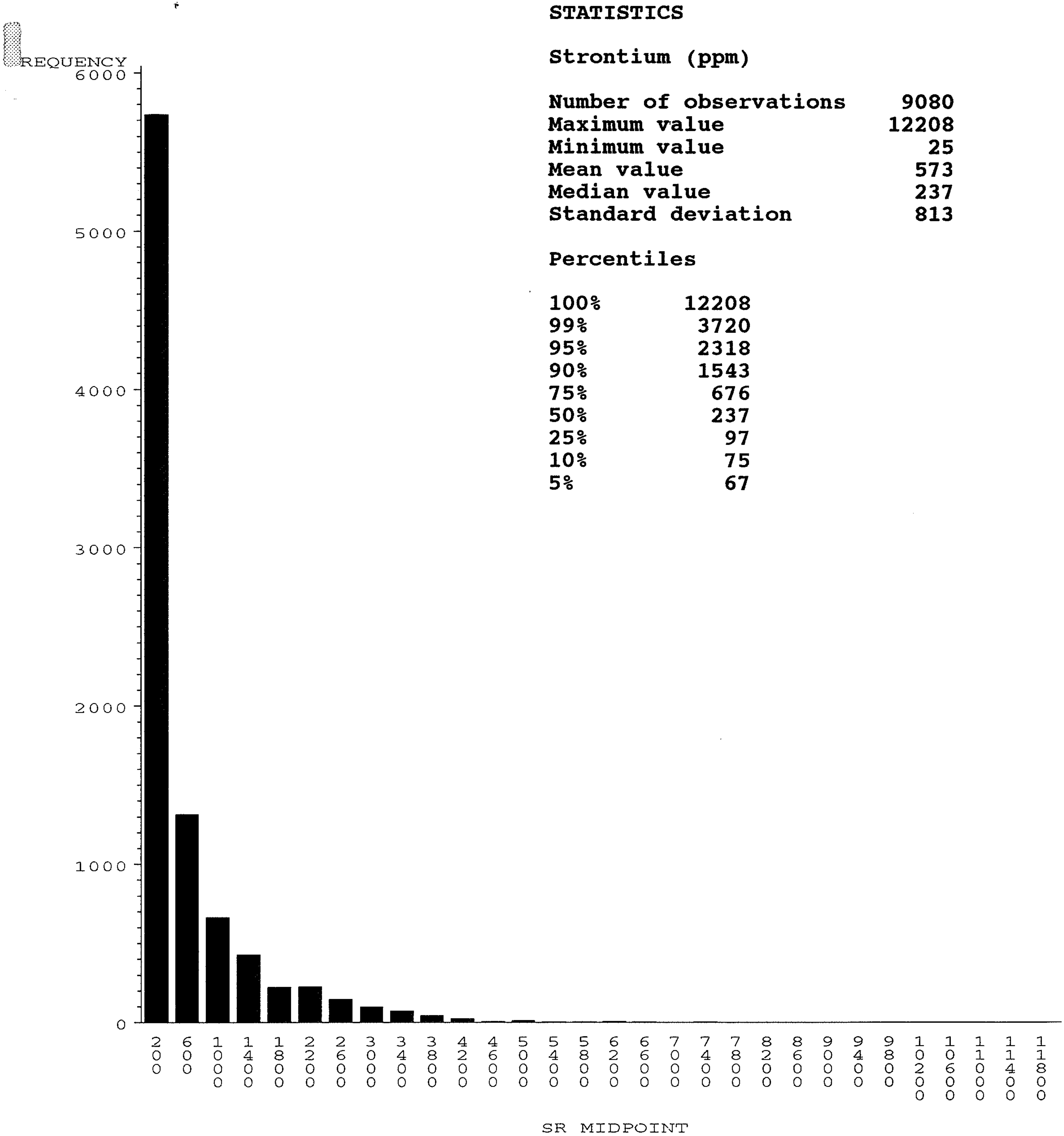
STRONTIUM NORMALISED TO LITHIUM



STRONTIUM NORMALISED TO CALCIUM



STRONTIUM



STATISTICS

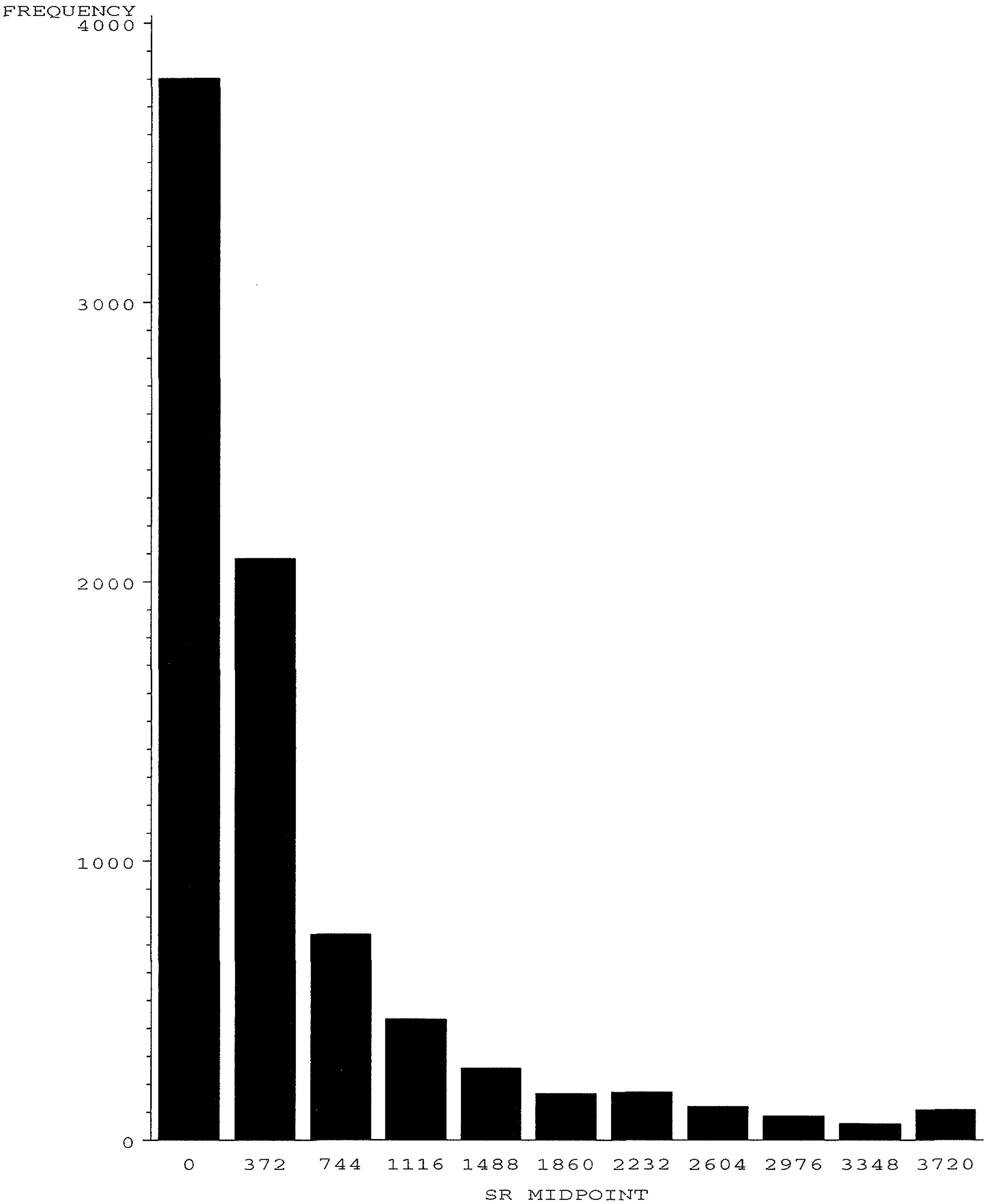
Strontium (ppm)

Number of observations	**9080**
Maximum value	**12208**
Minimum value	**25**
Mean value	**573**
Median value	**237**
Standard deviation	**813**

Percentiles

100%	**12208**
99%	**3720**
95%	**2318**
90%	**1543**
75%	**676**
50%	**237**
25%	**97**
10%	**75**
5%	**67**

STRONTIUM



FREQUENCY
4000
3000
2000
1000
0
0
372
744
1116
1488
1860
2232
2604
2976
3348
3720
SR MIDPOINT

Titanium

Titanium

Southern North Sea

Sands and gravelly sediments in the region have uniformly low TiO_2 concentrations (average 0.11% and 0.24% respectively), although slightly higher values in gravel suggest these sediments contain detrital minerals or rock fragments derived from basic igneous rocks. Like most elements of basic igneous rock association, TiO_2 values are enhanced in sediments between Spurn Head and The Wash extending offshore towards the Markham's Hole/Outer Silver Pit. Muddy sediments in the latter area have similar average concentrations (0.27%) to the surrounding coarse-grained sediments.

Central North Sea

Intermediate levels of TiO_2 occur in muddy sediments along the coast between Flamborough Head and the Tees Estuary (average 0.33%), offshore of the Tyne-Tees estuaries (average 0.37%) and in the Devil's Hole area (average 0.35%). Nicholson et al. (1985) reported high TiO_2 values either in, or offshore of, the estuaries of the rivers Humber, Tyne, Tees and Wear. They noted that high TiO_2 values were associated with high concentrations of organic matter, heavy metals, Zr and Ba. Similar concentrations occur farther offshore in fine-grained sediments such as those of the Gorsethorn Deep (average 0.31%).

The highest average TiO_2 concentrations in the area occur in muddy sediments in the Firth of Forth (average 0.97%). TiO_2 values here are considerably higher than in the muddy sediments along the coast to the south and suggest that the fine-grained fraction consists not only of clay minerals but detrital minerals derived from local basic igneous rocks in the Midland Valley. High TiO_2 values in sediments to the north of the Tay Estuary support their derivation from basic igneous rocks in the catchment areas of the Forth and Tay rivers.

The most significant TiO_2 anomaly in the region is identified by the map of normalised TiO_2/Li, where intermediate to high values (average 0.36%) occur in the predominantly gravelly sands of Dogger Bank. TiO_2 is strongly correlated with Cr and Zr in this area and this suggests that the sediments on the bank mainly comprise resistate detrital minerals, probably concentrated by proglacial processes (see Chromium section). Dearnley (1991) and Dangerfield and Tulloch (1989) reported ilmenite and other Ti minerals such as rutile in the sediments of the central North Sea. Nicholson et al. (1985) also observed high TiO_2 values offshore which they related to coarse particulate matter and/or shell debris and suggested that Ti occurred in concentrations of heavy minerals such as rutile or ilmenite along with zircon and tourmaline.

Northern North Sea

Intermediate to high TiO_2 values in sands offshore of Buchan (average 0.44%) may reflect underlying glacial deposits containing lithic fragments derived from the basic and ultrabasic igneous rocks of the East Grampians. Farther offshore, TiO_2 concentrations are intermediate to high in muddy sediments in the Fladen Ground and Witch Ground basins (up to an average of 0.53% in mud). TiO_2 may be present in clay-sized Ti bearing minerals or structurally bound in the lattices of clay minerals.

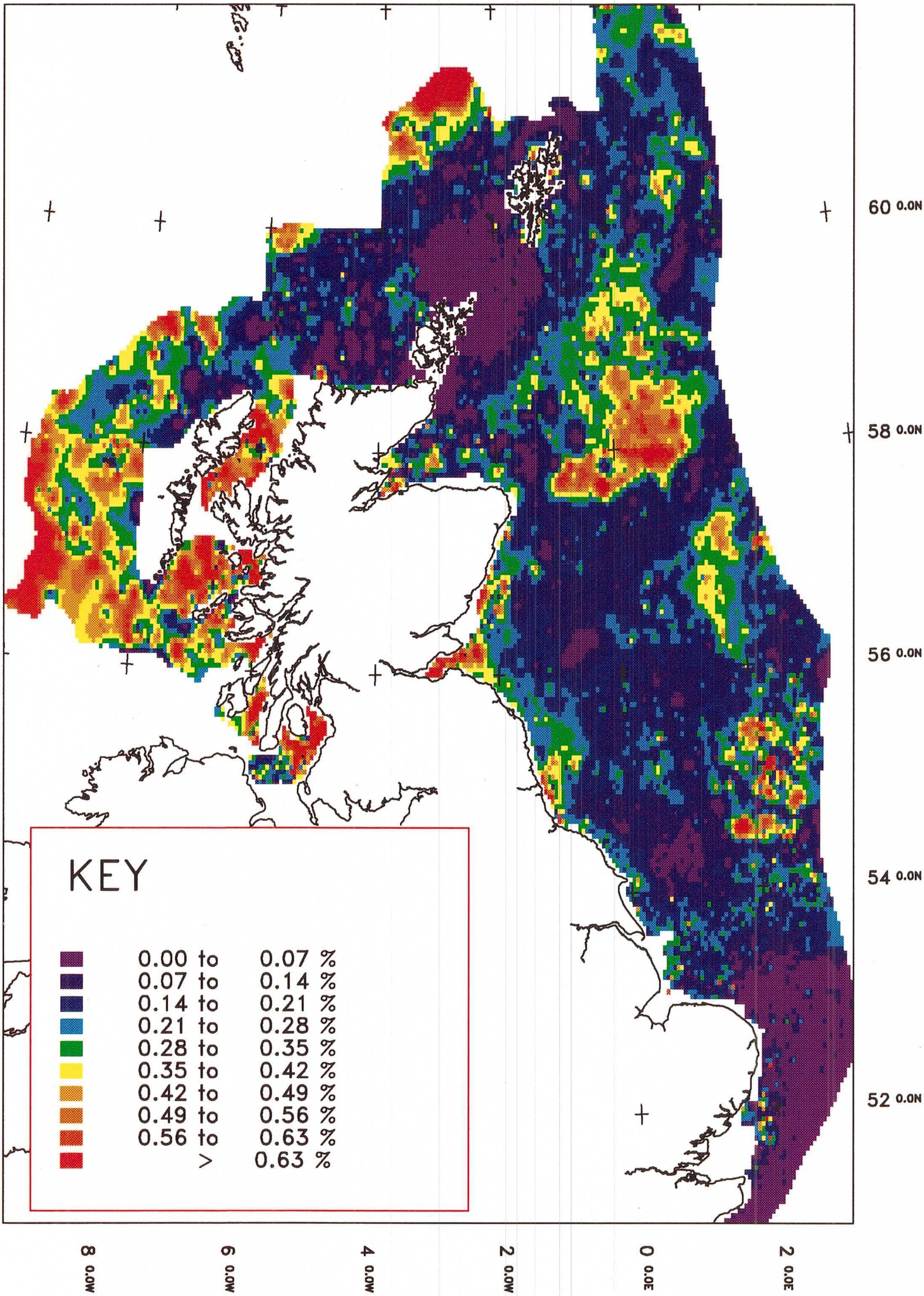
Hebrides and West Shetland shelves

TiO_2 values are uniformly low in the gravelly sediments of the Orkney-Shetland Platform (average 0.05%) however there is a gradual increase across the West Shetland Shelf towards the shelfbreak where the highest concentrations in the area occur in fine-grained sediment (average 0.52%). Farther south on the Hebrides Shelf, TiO_2 levels in sands (average 0.33%), gravels (average 0.33%) and gravelly sands (average 0.29%) are higher than in those of the West Shetland Shelf (Appendix 1) reflecting the influence of basic igneous rocks in this area. The continuous pattern of high TiO_2 values from The Minch to the outer shelf possibly reflects the direction of ice-sheet movement during the late Devensian glaciation (Figure 57 in Fyfe et al., 1993). High TiO_2 values around St Kilda indicate local accumulation of heavy minerals derived from the basic igneous rocks of the island.

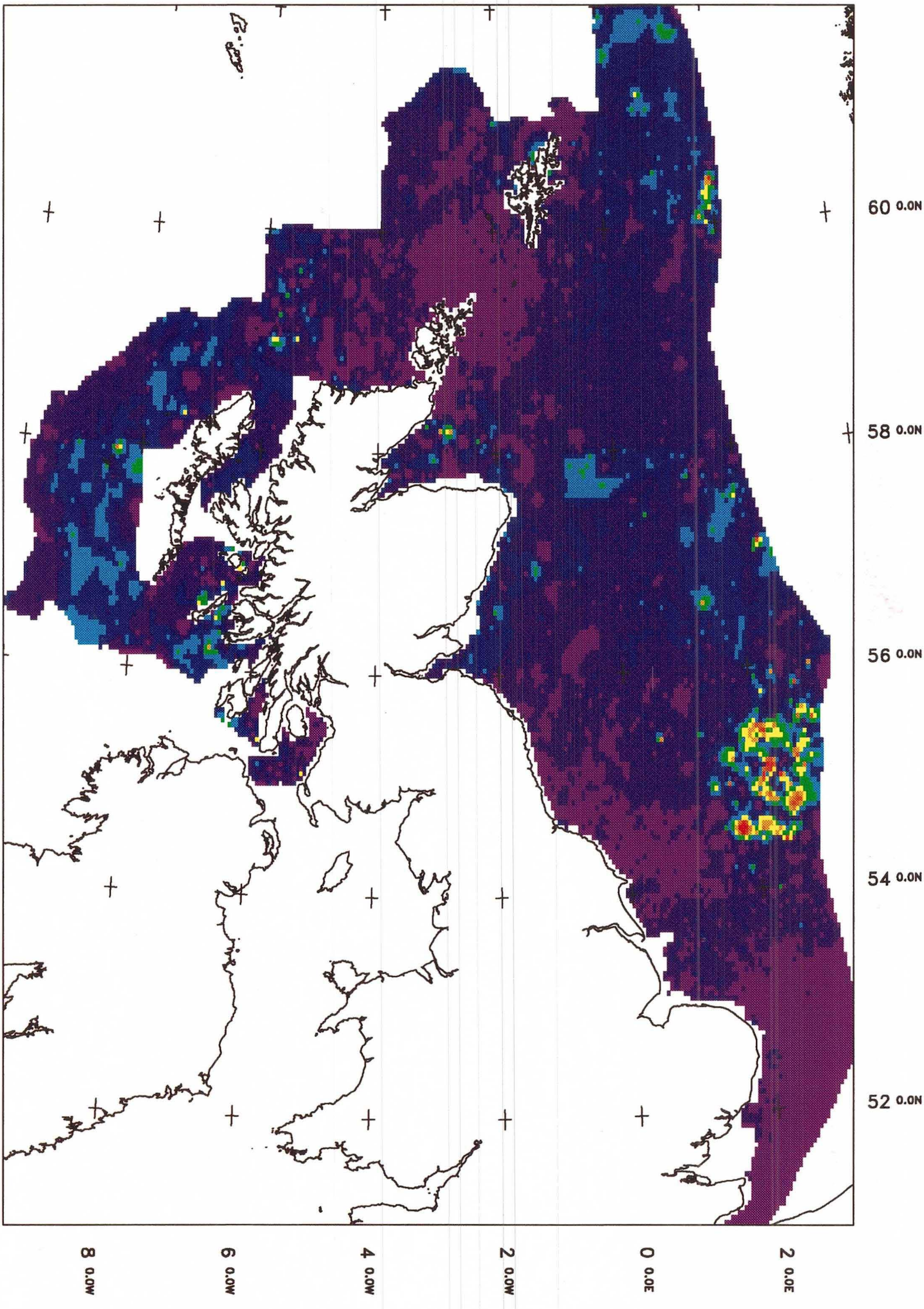
Malin-Hebrides

Intermediate to high TiO_2 values in both fine-grained (average 0.61%) and coarse-grained sediments in The Minch and Sea of the Hebrides are related to derivation of the underlying Quaternary deposits from the Tertiary basic igneous rocks of the region. High TiO_2/Li ratios around Rum indicate heavy minerals such as ilmenite in sands to the south-west of the island (Gallagher et al., 1989). Near Coll and Tiree, and south-west of Mull, where rock platforms of Lewisian basement occur, high TiO_2/Li ratios in gravels derived from basement rocks contain high concentrations of Ti minerals. The highest TiO_2 values in the area occur in fine-grained sediments in the Sound of Jura (average 0.74%) and the Firth of Clyde (average 0.0.73%). These are related to the high clay mineral content in the former area and, in addition to clay content, high organic matter and possibly contaminants in the Clyde Estuary.

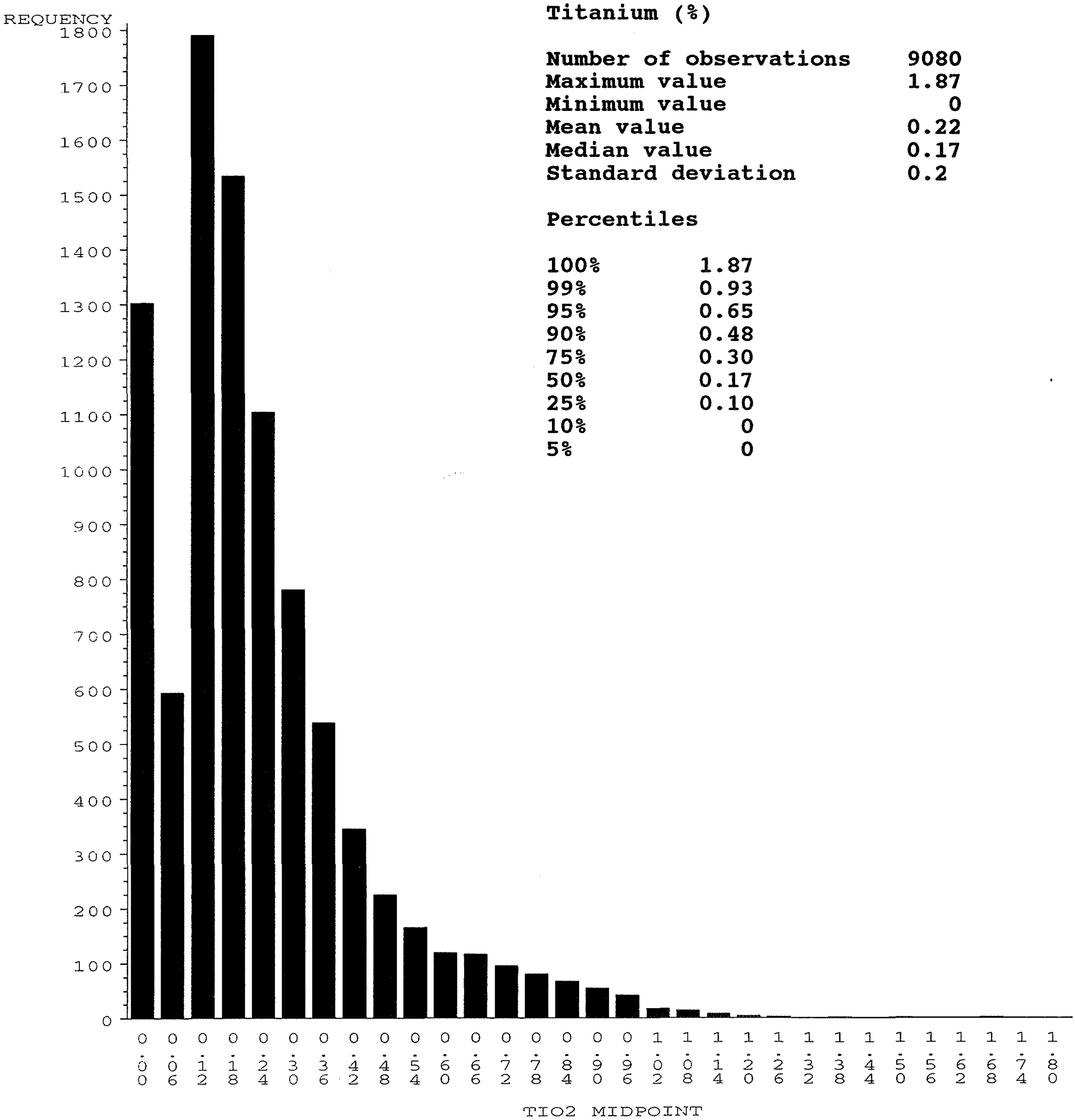
TITANIUM IN SEA-BED SEDIMENT



TITANIUM NORMALISED TO LITHIUM



TITANIUM



STATISTICS

Titanium (%)

Number of observations	**9080**
Maximum value	**1.87**
Minimum value	**0**
Mean value	**0.22**
Median value	**0.17**
Standard deviation	**0.2**

Percentiles

100%	**1.87**
99%	**0.93**
95%	**0.65**
90%	**0.48**
75%	**0.30**
50%	**0.17**
25%	**0.10**
10%	**0**
5%	**0**

Uranium

Uranium

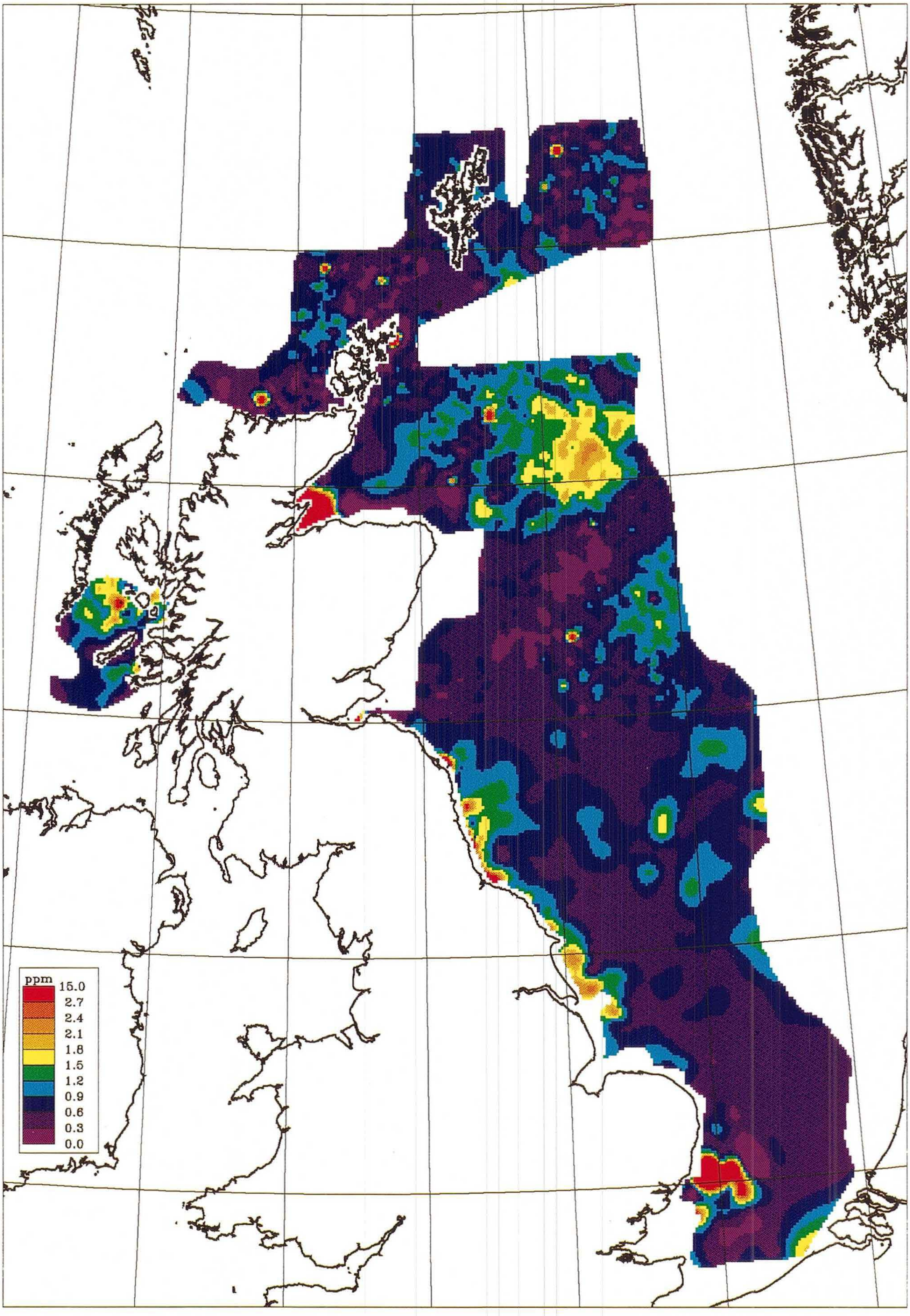
Nicholson et al. (1985) and Nicholson and Stuart (1986), interpreted the distribution of U in the central and southern North Sea in relation to either organic-rich, fine-grained sediments and/or carbonate-rich, coarse-grained sediments. In the former instance, U is generally confined to estuarine sediments with high U values associated with high concentrations of heavy metals, detrital elements and organic matter. In coarse-grained sediments there is a definite link with carbonate and associated elements such as La and Sr. The highest U value recorded off the coast of east Anglia was associated with a P concentration of 10 per cent, indicating the occurrence of rock phosphate. Phosphatic nodules are known to occur in the crags of East Anglia and it seems likely that weathering and subsequent transport of these strata are responsible for the high U concentrations.

In the northern North Sea and on the shelf west of Scotland, U shows a similar distribution to that of the southern North Sea. Sandy sediments have mainly low to intermediate U concentrations with the highest values occurring in fine-grained and coarse, shell-rich sediments. Three main groups of intermediate to high values occur in muddy sediments in the Sea of the Hebrides, Fladen and Witch Ground basins and the Devil's Hole area. The muds in the Fladen and Witch Ground basins are known to be organic rich and it is probable that this also applies to the other two areas.

Elsewhere, high values occur in individual samples of coarse-grained sediments, generally in association with high concentrations of Ca, Sr, Y and La, supporting the link between U and carbonate observed by Nicholson et al. (1985). High U values are also found in samples with high Zr concentrations which, in addition to the association with Y and La, may indicate concentration in heavy detrital minerals such as zircon.

The highest U value in the area (11.9ppm) occurs in gravelly sand off the east coast of Orkney in association with high Ca and Sr concentrations. High U values have also been recorded in water samples from streams draining the Devonian sedimentary rocks of these islands, and U mineralisation has been recorded in the lacustrine facies of Middle Old Red Sandstone rocks in south-west Mainland where they are associated with organic-rich and phosphatic horizons (Institute of Geological Sciences, 1978).

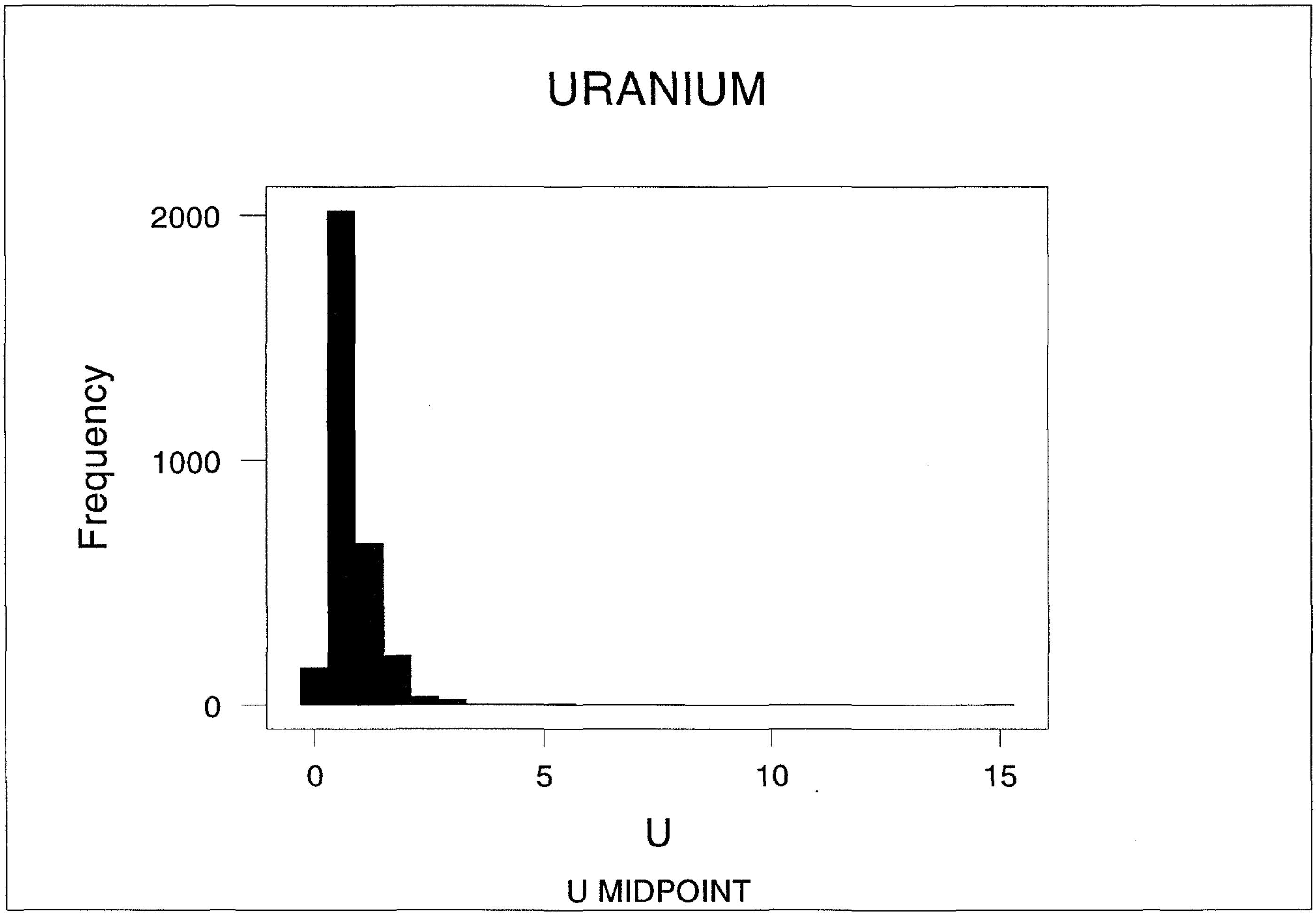
URANIUM IN SEA-BED SEDIMENT



STATISTICS

Uranium (ppm)

Number of observations	3123
Maximum value	14.9
Minimum value	0
Mean value	0.84
Median value	0.70
Standard deviation	0.77



Vanadium

Vanadium

Southern North Sea

V concentrations are generally low in gravelly and sandy sediments south of a line extending due east from Lowestoft (average 8ppm in gravelly sands off the Kent coast; 14ppm in the Ostend 1:250 000 sheet area). The highest V values in this area occur in fine-grained sediments off the East Anglia coast (average 78ppm), and in gravelly sands in the Dover Strait (average 63ppm). In the latter area V is correlated with Be, B, MnO, Fe_2O_3, Co, Ni, Cu and Pb and probably represents co-precipitation with Fe and Mn hydroxides. Farther north, offshore of The Wash, V concentrations are intermediate to high in gravels (average 32ppm) but lower in muddy sediments (average 18ppm) and sandy muds (average 7ppm), suggesting that V occurs in detrital minerals rather than clays. All sediments in the Markham's Hole/Outer Silver Pit area have intermediate to high concentrations of V (average 49ppm in muddy sediments; 44ppm in gravelly sands), indicating regional enrichment in both detrital and clay minerals.

Central North Sea

The highest V values in the area occur near the coast in fine-grained sediments (average 45ppm) between Flamborough Head and the Tees Estuary (66ppm offshore of the Tyne-Tees estuaries). Muddy sediments farther offshore have similar V concentrations (average 50ppm in the Farn Deeps; 38ppm in Gorsethorn Deep), however the high levels in the Tyne-Tees area and in the industrialised rivers farther north (see below), suggest that V values are enhanced by adsorption on organic matter or by contamination. The continuous zone of V values along the eastern UK coast between Aberdeen and Flamborough Head would also support the view of Dearnley (1991) that a plume of sediment derived from basic igneous rocks in the Midland Valley of Scotland was transported along the coast (see Conclusion).

The pattern of higher V values nearshore continues into the northern North Sea where intermediate to high values occur in both fine-grained and gravelly sediments (average 39ppm) between the River Tyne and St Abb's Head. High values occur in the muddy sediments of the Firth of Forth (average 87ppm) where sediment input may be derived from fine-grained detrital minerals, clay minerals, organic matter and contamination; the sediments north of the Tay Estuary have similar V concentrations. Farther offshore, most of the sandy sediments of the region have intermediate V concentrations (average 30ppm) with higher values in fine-grained sediments in the Devil's Hole area(average 38ppm).

Northern North Sea

High V concentrations occur in the fine-grained sediments in the Fladen Ground and Witch Ground basins (average 25ppm in muddy sands). V distribution over parts of the Fladen Ground and Orkney-Shetland Platform is obscured by Ca interference correction.

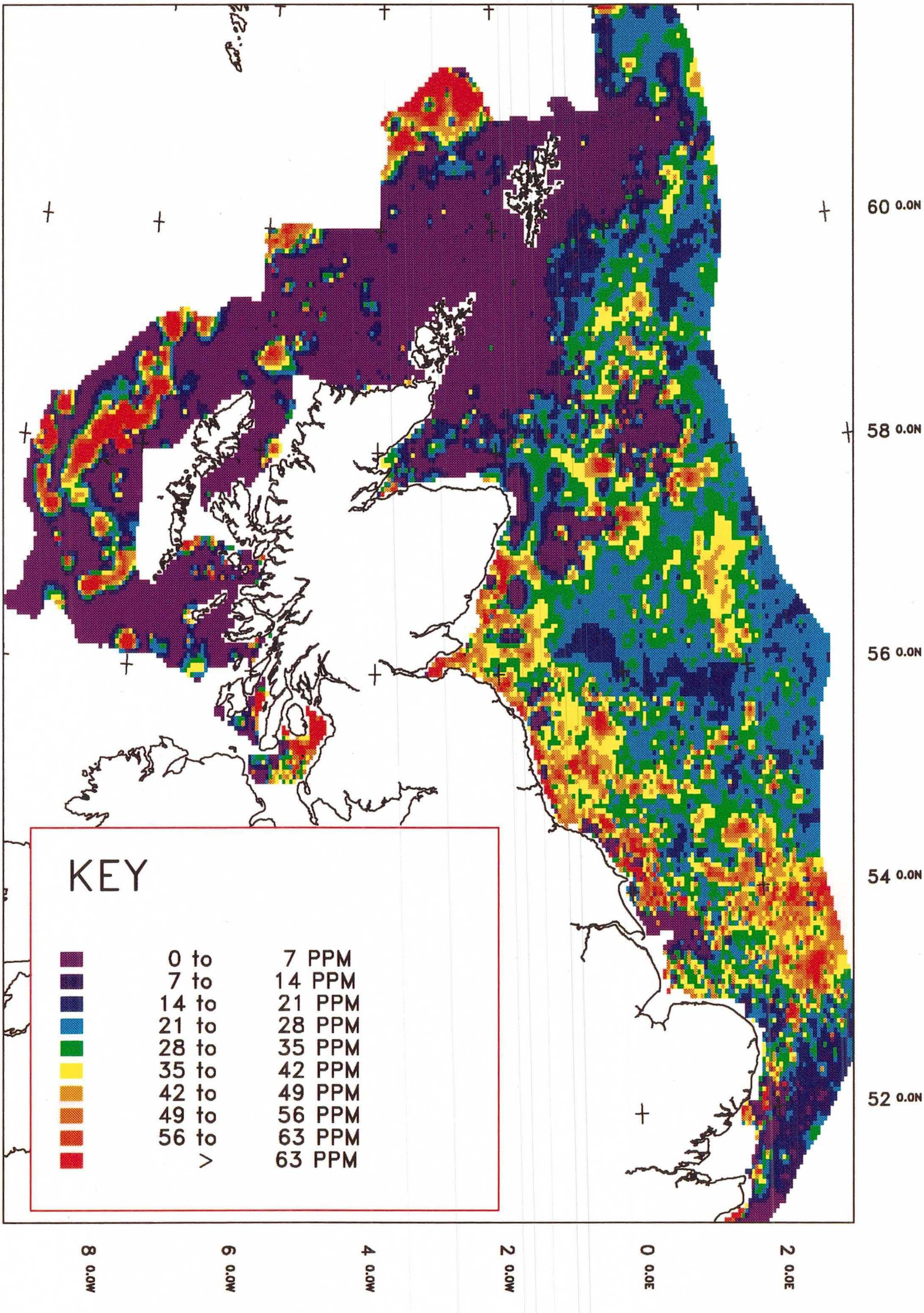
Hebrides and West Shetland shelves

Due to the widespread occurrence of high Ca values in this area, V distribution is almost entirely masked by the Ca interference correction applied to the data. In areas of low Ca, V concentrations are high on the Hebrides Shelf, particularly in fine-grained sediments at the shelfbreak (average 54ppm). Dearnley (1991) reported V concentrations greater than 40ppm in the sand fraction of sediments from this region, associated with high Cr, Ni, Co, Zn, Y and Cu values.

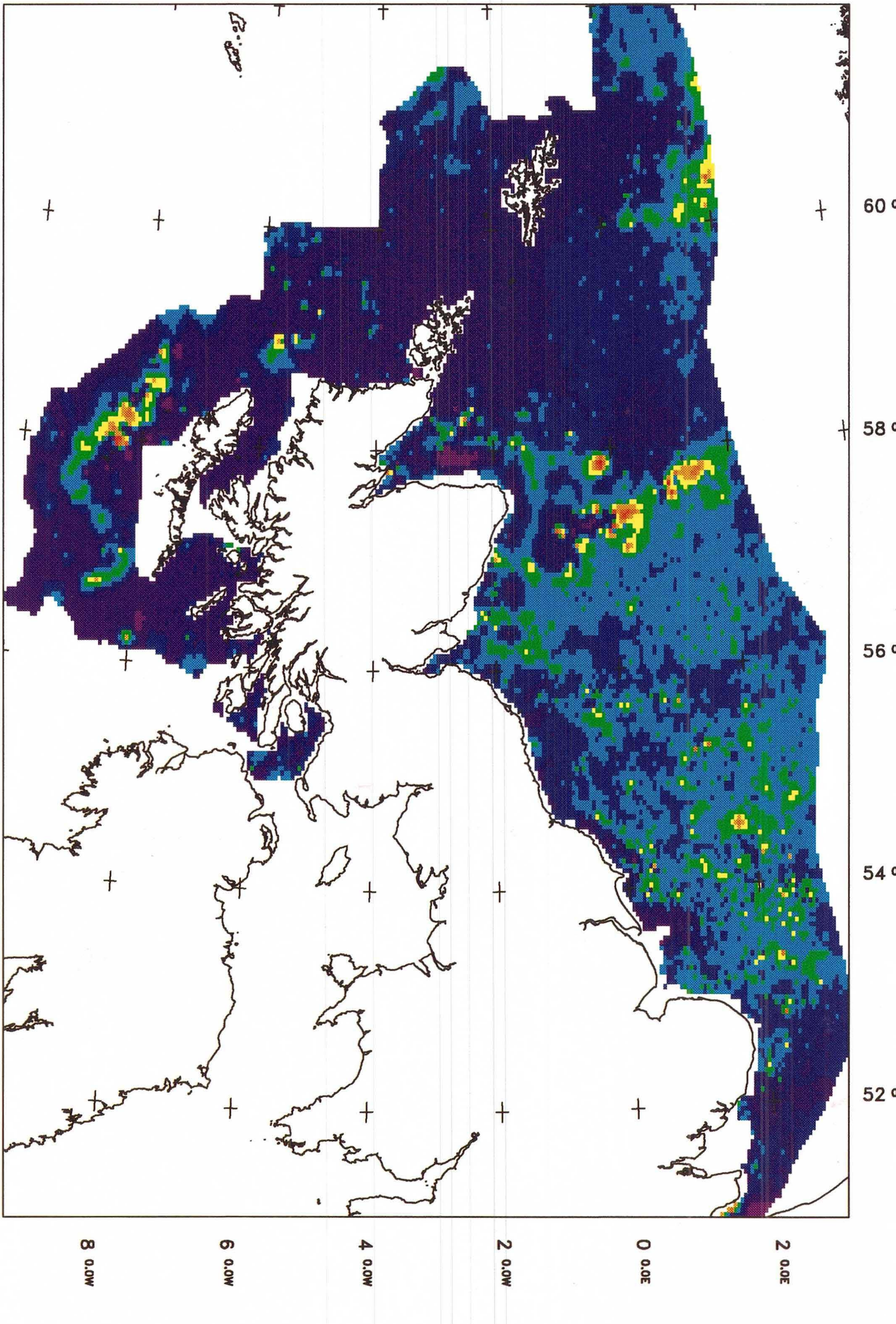
Malin-Hebrides

The distribution of V in this region may be predicted by comparing maps of other elements which concentrate in basic igneous rocks, but which are unaffected by Ca interference. Combined with the available information for V concentrations it is expected that V levels in The Minch and Sea of the Hebrides are highest in muddy sediments. Farther south, high V concentrations occur in fine-grained sediments in the Sound of Jura and the Firth of Clyde (average 75ppm in each area).

VANADIUM IN SEA-BED SEDIMENT



VANADIUM NORMALISED TO LITHIUM



VANADIUM

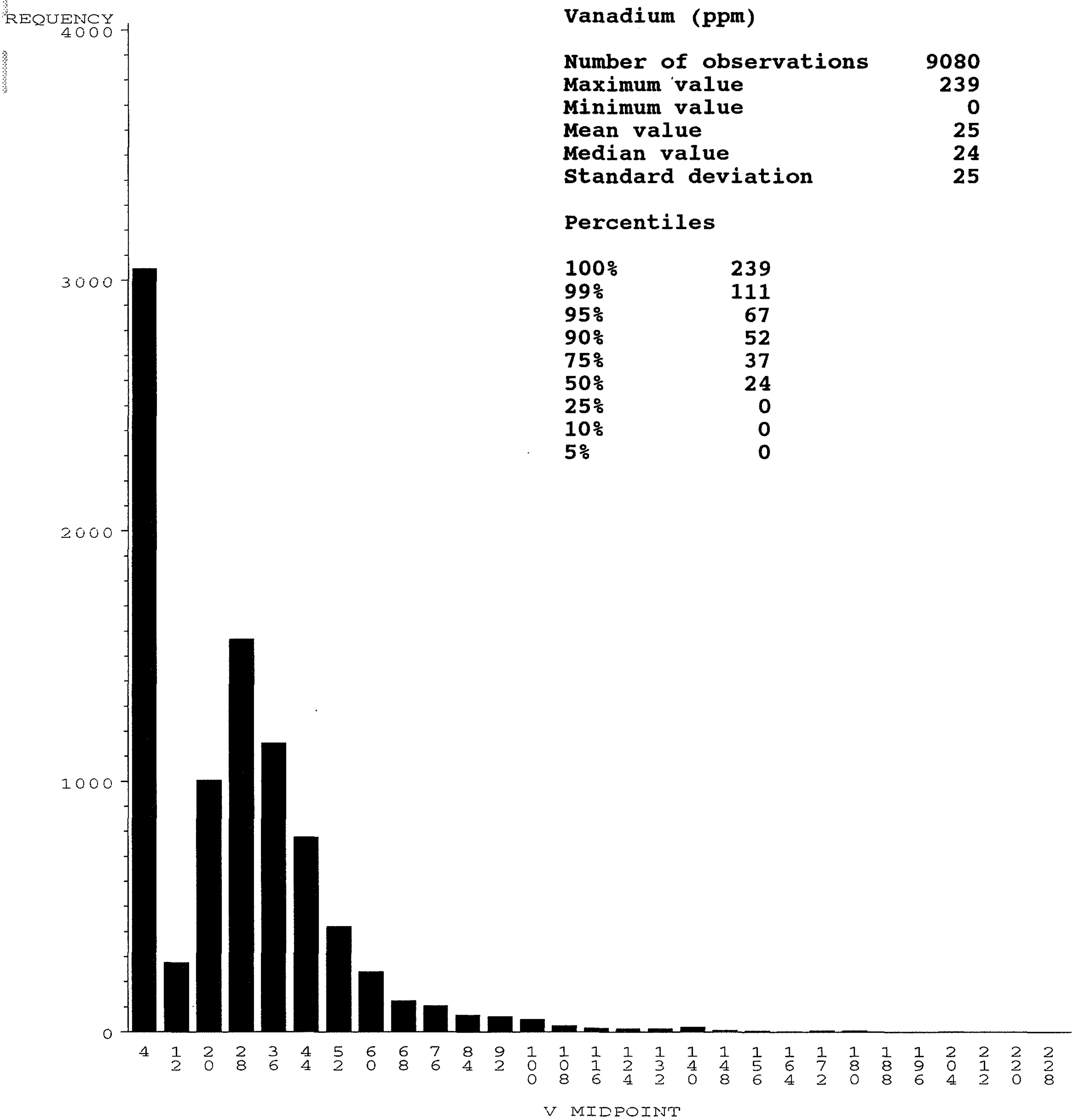
STATISTICS

Vanadium (ppm)

Number of observations	9080
Maximum value	239
Minimum value	0
Mean value	25
Median value	24
Standard deviation	25

Percentiles

100%	239
99%	111
95%	67
90%	52
75%	37
50%	24
25%	0
10%	0
5%	0



Yttrium

Yttrium

Southern North Sea

The sandy sediments of the North Sea are typified by low Y concentrations (Appendix 1), however those of the southern North Sea have the lowest values (average 6ppm). Intermediate to high Y concentrations occur in fine-grained sediments in the Outer Thames Estuary and off the coast of East Anglia (average 16 and 19ppm respectively) where Y is adsorbed on clay minerals. In the coastal zone between The Wash and Flamborough Head high Y values occur in both fine-grained (average 18ppm) and coarse-grained sediments (average 15ppm). The high Y in sandy and gravelly deposits suggests accumulation of heavy minerals such as zircon, in which Y tends to concentrate. This is supported by normalised Y/Li data which indicate Y distribution is not associated with clays. The map also shows that gravels off East Anglia (average 12ppm) may also contain Y-bearing detrital minerals. Moderately high Y values (average 12ppm) occur in the fine-grained sediments of the Markham's Hole area. Nicholson et al. (1985) noted that the highest concentrations of Y are generally distributed in a similar pattern to those of Mn, Fe and Ni and that high values occur in both fine- and coarse-grained sediments. They also noted a small group of high Y values associated with La, Sr, U and P off the coast of Suffolk which they attributed to incorporation into phosphatic nodules.

Central North Sea

Most high Y values occur near the coast in fine-grained sediments (average 22ppm between Flamborough Head and the Tees Estuary; 20ppm offshore of the Tyne-Tees estuaries; 17ppm in the Farn Deeps). Farther offshore, in sands and gravelly sands on the Dogger Bank, intermediate Y values (average 9 and 11ppm respectively) support the suggestion that this is an area with high concentrations of detrital minerals, including zircon (see Chromium section). Normalised Y/Li data depict the Dogger Bank area being enriched in Y and several other elements related to resistate minerals. The distribution pattern of high Y values in nearshore muddy and sandy sediments continues northward along the east coast of Scotland into the Moray Firth. The highest values along the coastal zone occur in fine-grained sediments in the estuaries of the rivers Tyne and Tees (average 20ppm) and the Firth of Forth (average 27ppm). Muddy sediments farther offshore have intermediate levels of Y although they are significantly higher than in the surrounding sands (e.g. fine-grained deposits in Devil's Hole have an average Y concentration of 12ppm compared to 4ppm in sands).

Northern North Sea

The highest Y values in the region occur in the Fladen Ground and Witch Ground basins (average 25ppm in muddy sediments). Gravelly sands on the Marr and Aberdeen banks (average 11 and 10ppm respectively), have a similar geochemical signature to those of Dogger Bank (see Chromium, Titanium and Zirconium sections).

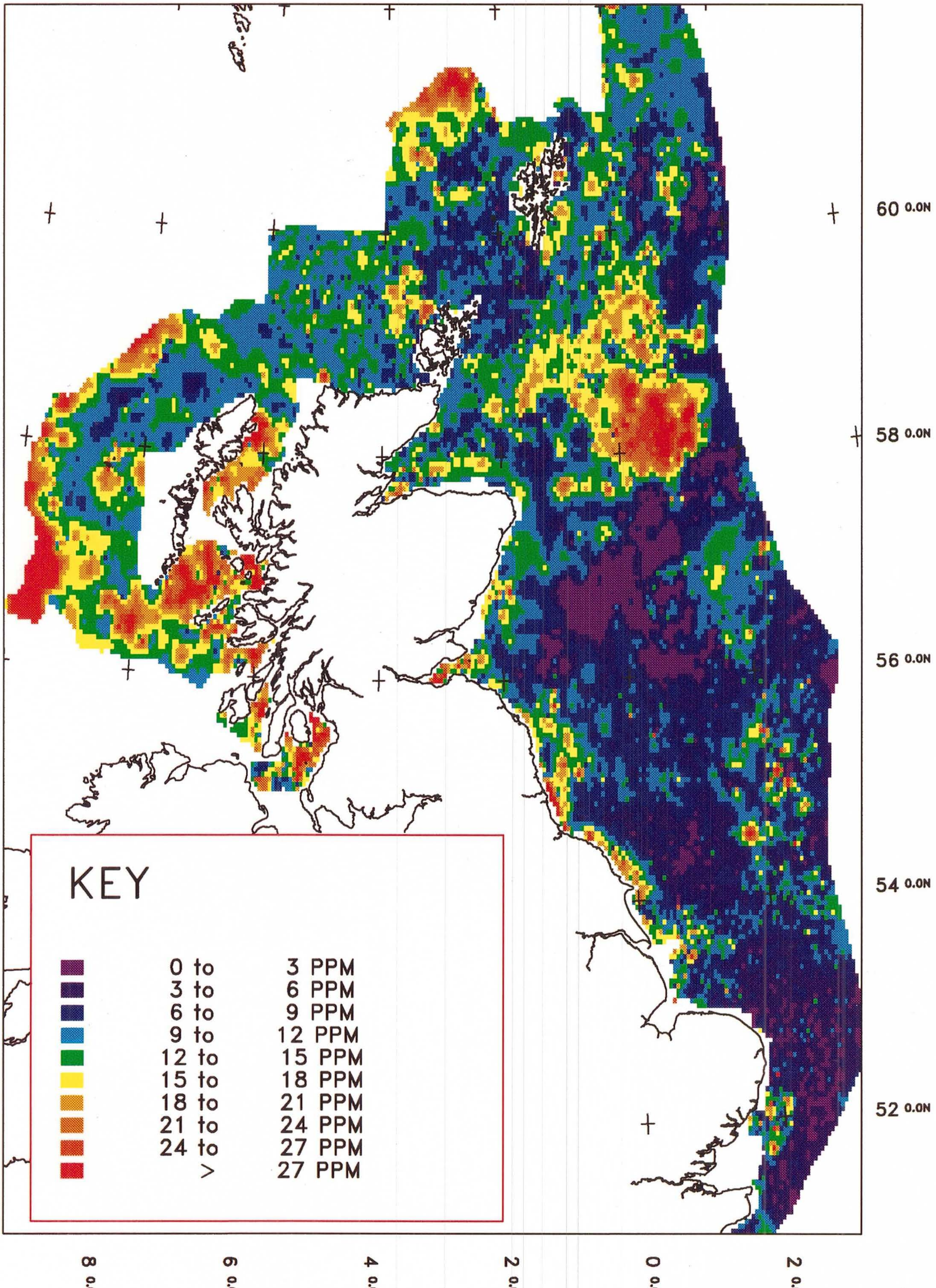
Hebrides and west Shetland shelves

With the exception of a group of high values associated with muddy sediments in the area to the north-west of Orkney (average 18ppm), and at the shelfbreak (average 13ppm north-west of Shetland; 23ppm west of the Outer Hebrides), Y values are generally low to intermediate over this area of the shelf. High Y values in coarse-grained sediments around St Kilda and the Stanton Banks are associated with high Ti, Ni and Cu and reflect the occurrence of heavy minerals.

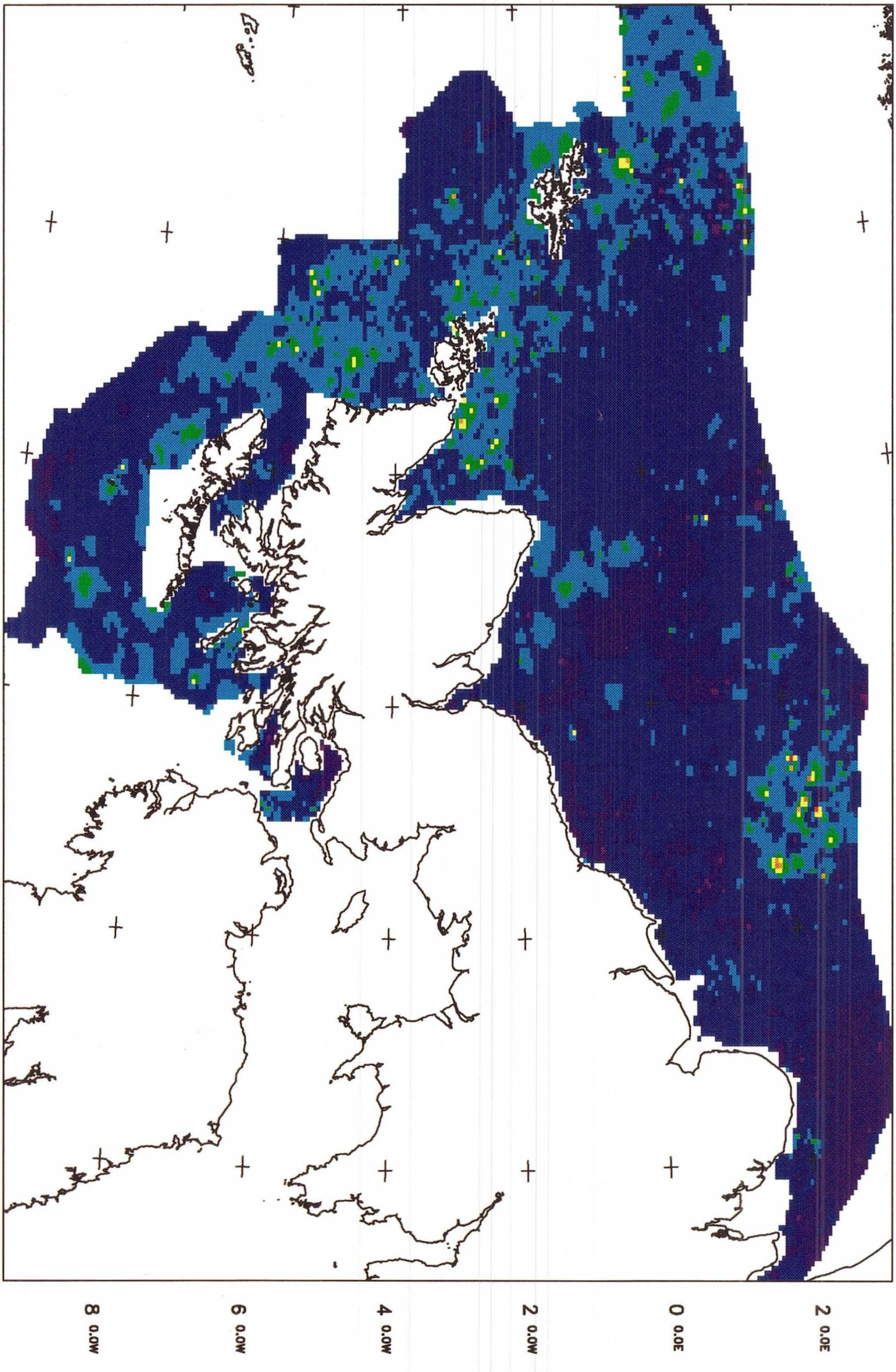
Malin-Hebrides

Both fine-grained and coarse-grained sediments have intermediate to high Y concentrations in The Minch and Sea of the Hebrides (average 24ppm in muddy sediments; 16 ppm in sands and 17ppm in gravels). In muddy sediments, Y is adsorbed on clay minerals and in the sandy and gravelly deposits probably indicate accumulation of Y-bearing minerals such as garnet, amphibole or zircon. In contrast to the offshore sediments, the Torridonian and Moine metasedimentary rocks of the North-west Highlands generally have much higher Y concentrations (British Geological Survey, 1987). Low Y levels offshore therefore may reflect a higher proportion of Lewisian metamorphic or Tertiary basaltic lithic fragments in the sea-bed sediments, both of which have low Y concentrations (British Geological Survey, 1987; 1990). Farther south, intermediate to high levels occur in the fine-grained sediments of the Sound of Jura (average 24ppm) and Firth of Clyde (average 25ppm).

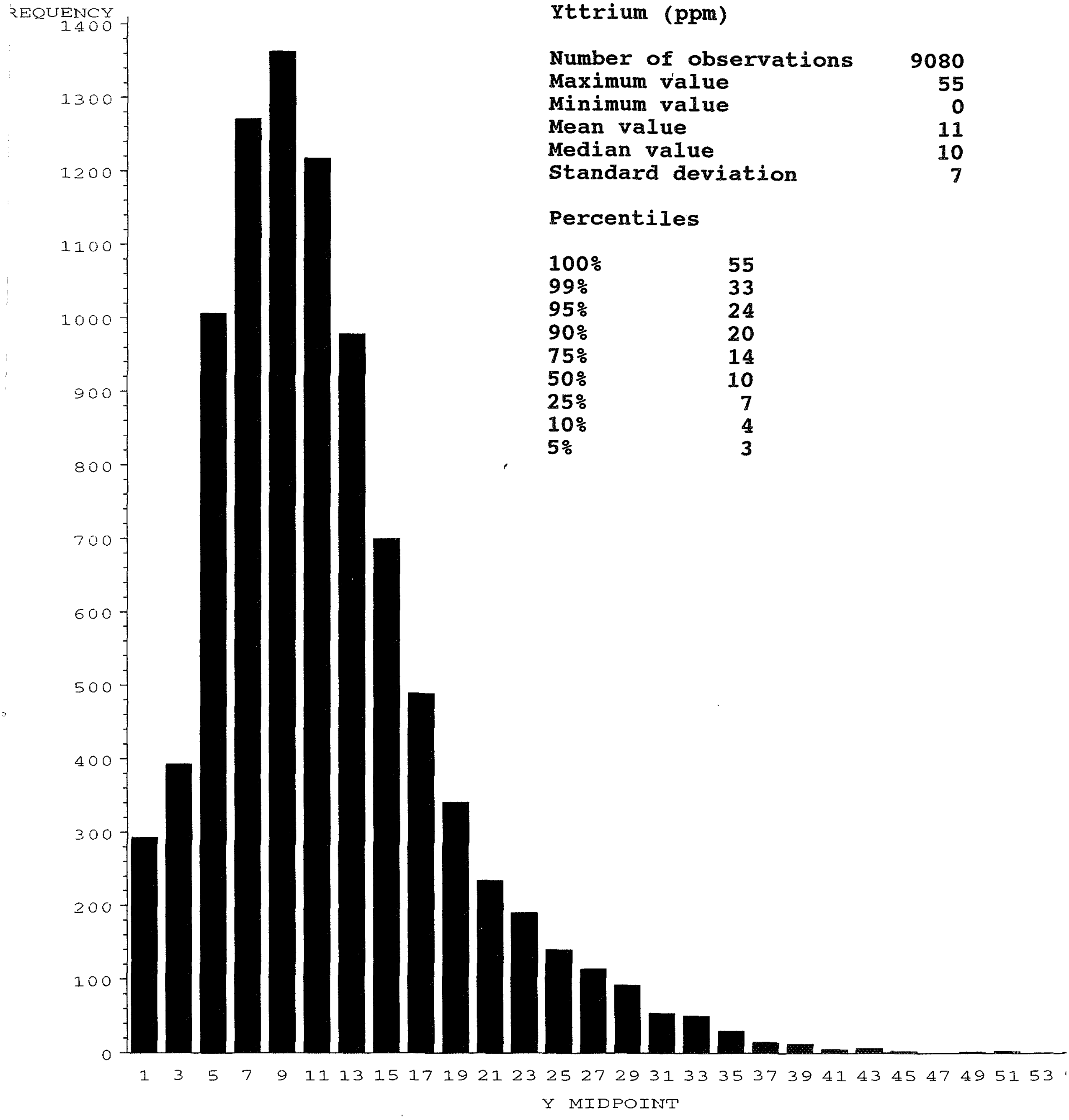
YTTRIUM IN SEA-BED SEDIMENT



YTTRIUM NORMALISED TO LITHIUM



YTTRIUM



STATISTICS

Yttrium (ppm)

Number of observations	9080
Maximum value	55
Minimum value	0
Mean value	11
Median value	10
Standard deviation	7

Percentiles

100%	55
99%	33
95%	24
90%	20
75%	14
50%	10
25%	7
10%	4
5%	3

Zinc

Zinc

Southern North Sea

Both fine- and coarse-grained deposits of the southern North Sea are characterised by high levels of Zn, although sandy sediments generally have the lowest concentrations (e.g. average 92ppm in gravelly sediments ; average 42ppm in sands). The absence of uniformly high values of other possible contaminants, such as Pb or Cu, suggest that this is not related to pollution. Nevertheless, individual high values on the map of normalised Zn/Li, here and throughout the study area, are probably due to contamination. Burt et al. (1992) noted widespread Zn contamination in estuarine sediments around the UK coast. In areas of high Fe and/or Mn, increased Zn values reflect precipitation of hydroxides. Because of the affinity of Zn for organics it is possible that sediments from this part of the southern North Sea have a high organic content. Duinker (1981) noted the correlation between zinc and organic carbon in suspended particulate matter in the southern North Sea. Intermediate to high values occur in nearshore muddy sediments (average 86ppm in the Outer Thames Estuary; 115ppm off the coast of East Anglia), and in the Markham's Hole/Outer Silver Pit area. The gravelly sands and gravel in the Dover Strait have high Zn concentrations (average 85ppm)

Central North Sea

The highest Zn concentrations in the report area occur along the coast in muddy sediments between Flamborough Head and the Tees Estuary (average 236ppm) and offshore of the Tyne and Tees estuaries (average 130ppm). High Zn levels were also found in sediments off the coast of the Tyne, Tees and Humber estuaries by the North Sea Task Force (1993). High Zn values occur farther offshore in the fine-grained sediments of the Farn Deeps (average 89ppm) and the Gorsethorn Deep (average 67ppm).

Intermediate to high values near the east coast of Scotland north of the Tay Estuary may reflect Zn in biotite, which occurs in high concentrations in the sediments of this area (Dangerfield and Tulloch, 1989). Zn values are generally lower than in the southern North Sea (average 20ppm in sands). Intermediate Zn levels occur along the Scottish coast between St Abb's Head and Dunbar, however the highest concentrations in the region are found in muddy sediments in the Firth of Forth (average 167ppm). Normalised Zn/Li data indicate Zn enrichment in parts of the firth which are not related to grain size. These samples, and an isolated high Zn value of 483ppm directly east of the Forth Estuary, with no associated elements, are due to contamination.

Northern North Sea

The fine-grained sediments in the Fladen Ground and Witch Ground basins have intermediate to high Zn concentrations (up to an average 59ppm in muds). High Zn values in the Inner Moray Firth, associated with Cu and Pb anomalies, probably reflect sediment contamination.

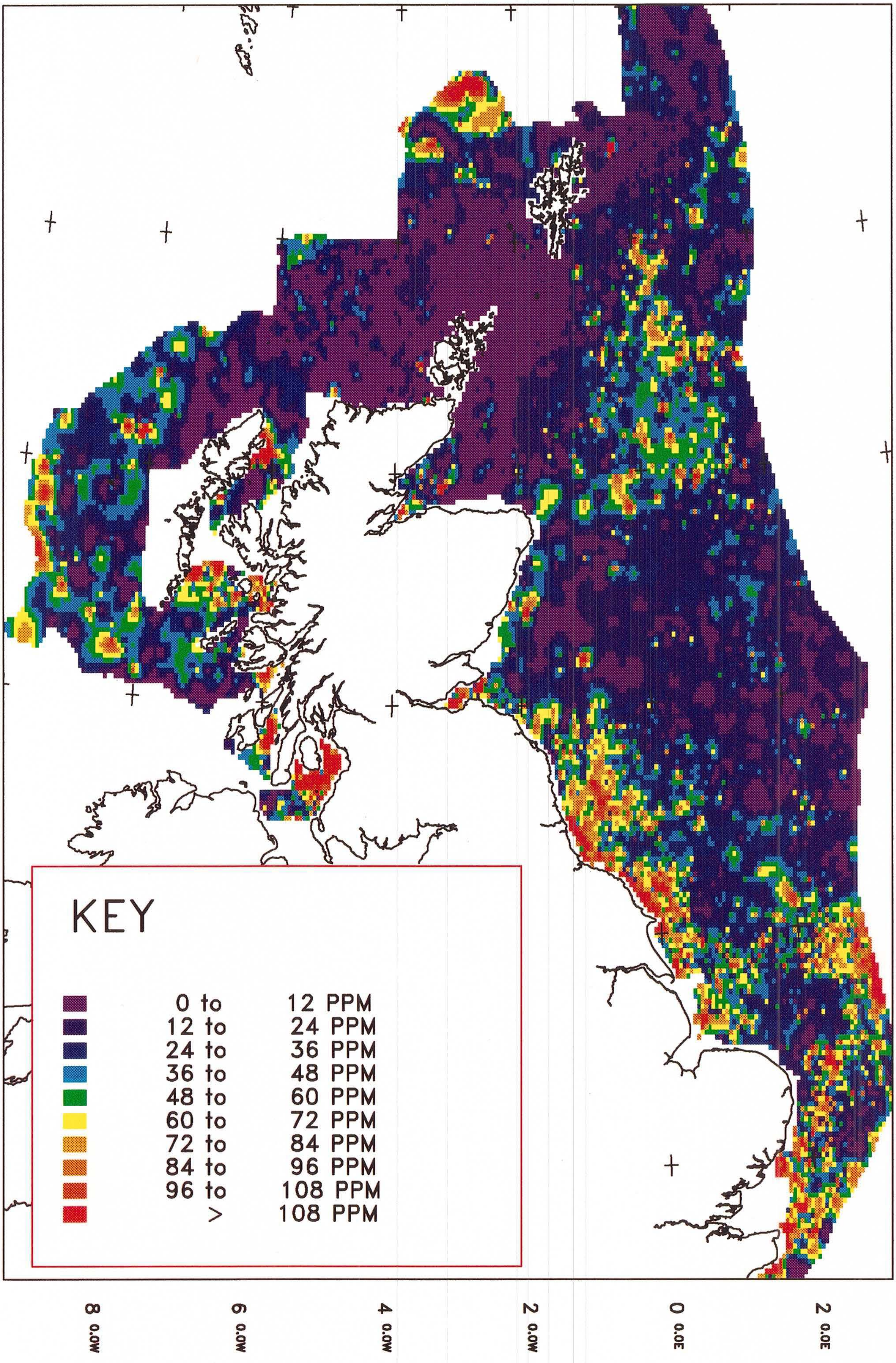
Hebrides and West shetland shelves

Zn values are generally low on the shelf north of Scotland. Dearnley (1989) reported Zn concentrations greater than 40ppm in the sand fraction of samples from this area. However, because of the high carbonate content (30-96 per cent), the lithic fraction was concentrated prior to analysis and so are not directly comparable with the geochemical results presented here. Dearnley's work provides a useful indicator of element values in the non-carbonate fraction of these sediments, as data for most of this region is dominated by high CaO concentrations arising from the shell-rich nature of the sediments. Fine-grained sediments at the shelfbreak north-west of Shetland have intermediate to high concentrations of Zn (average 51ppm), as do those farther south (average 58ppm). A group of intermediate to high Zn values near St Kilda, associated with MgO, Cr, Ni and TiO_2, probably reflect heavy mineral accumulation in coarse-grained sediments derived from the basic igneous rocks which crop out on the island.

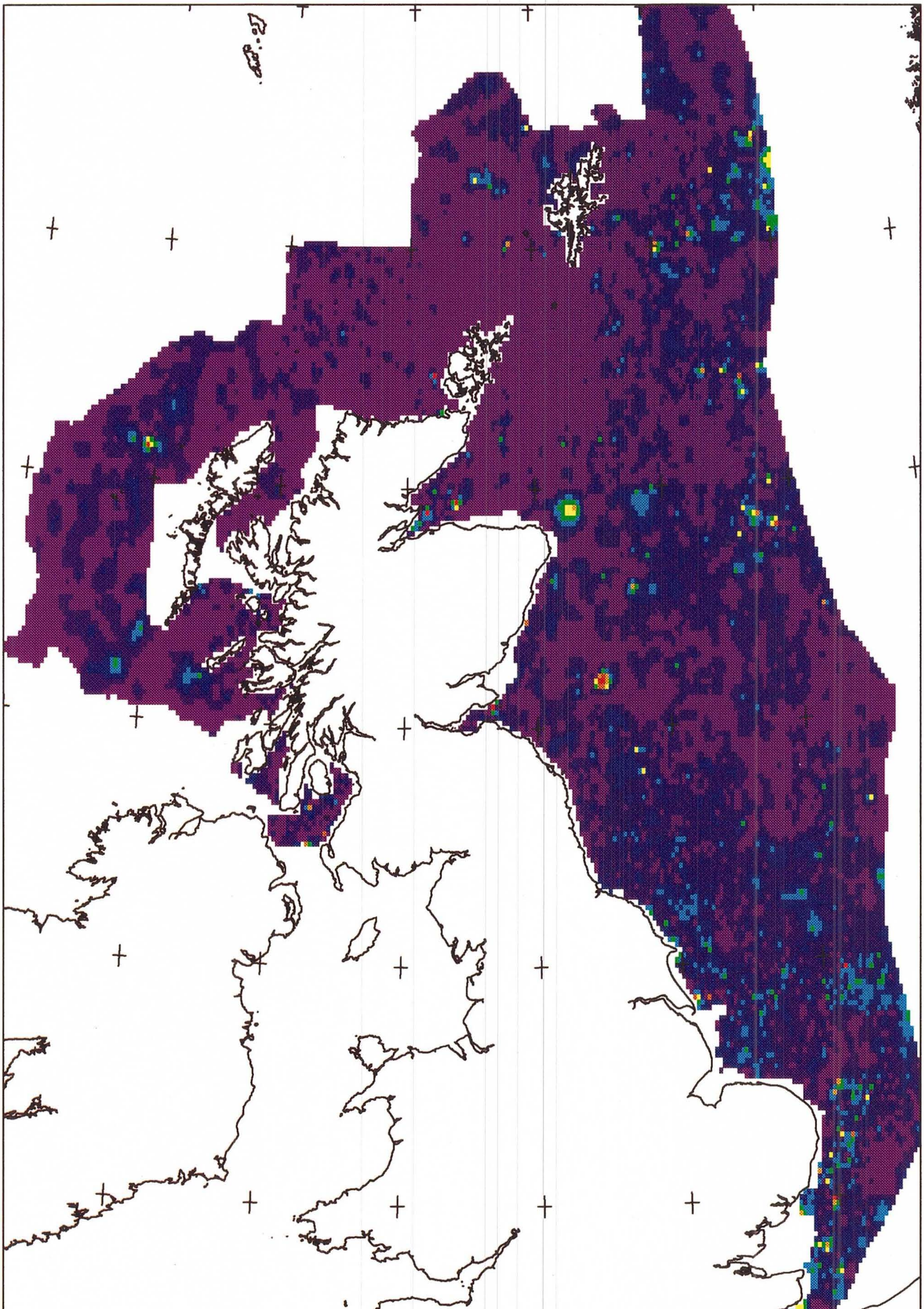
Malin-Hebrides

Zn values are generally high in the muddy sediments in The Minch and Sea of the Hebrides (average 66ppm) due to adsorption on clay minerals derived from the Tertiary igneous rocks of the region. The coarser-grained sediments have generally lower Zn concentrations (average 21ppm in sand; 25ppm in gravel) although local increases may indicate accumulation of detrital ferromagnesian silicates or magnetite, which are the main carriers of Zn in basic rocks. High Zn concentrations occur in the fine-grained sediments in the Sound of Jura (average 125ppm) and the Firth of Clyde (161ppm). In the latter area, Zn is concentrated in clay minerals, organic material and, particularly where correlated with Cu and Pb, in contaminants.

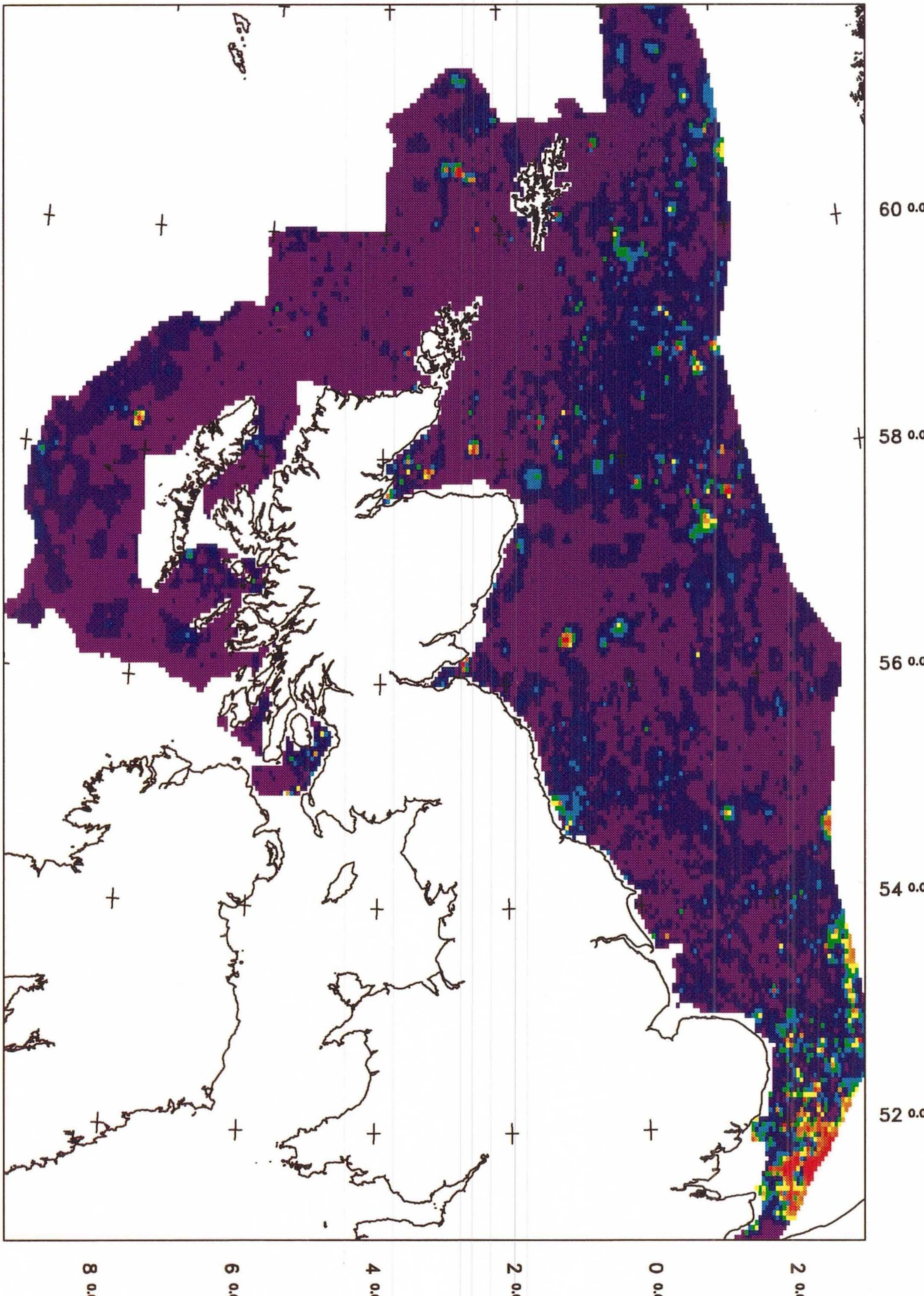
ZINC IN SEA-BED SEDIMENT



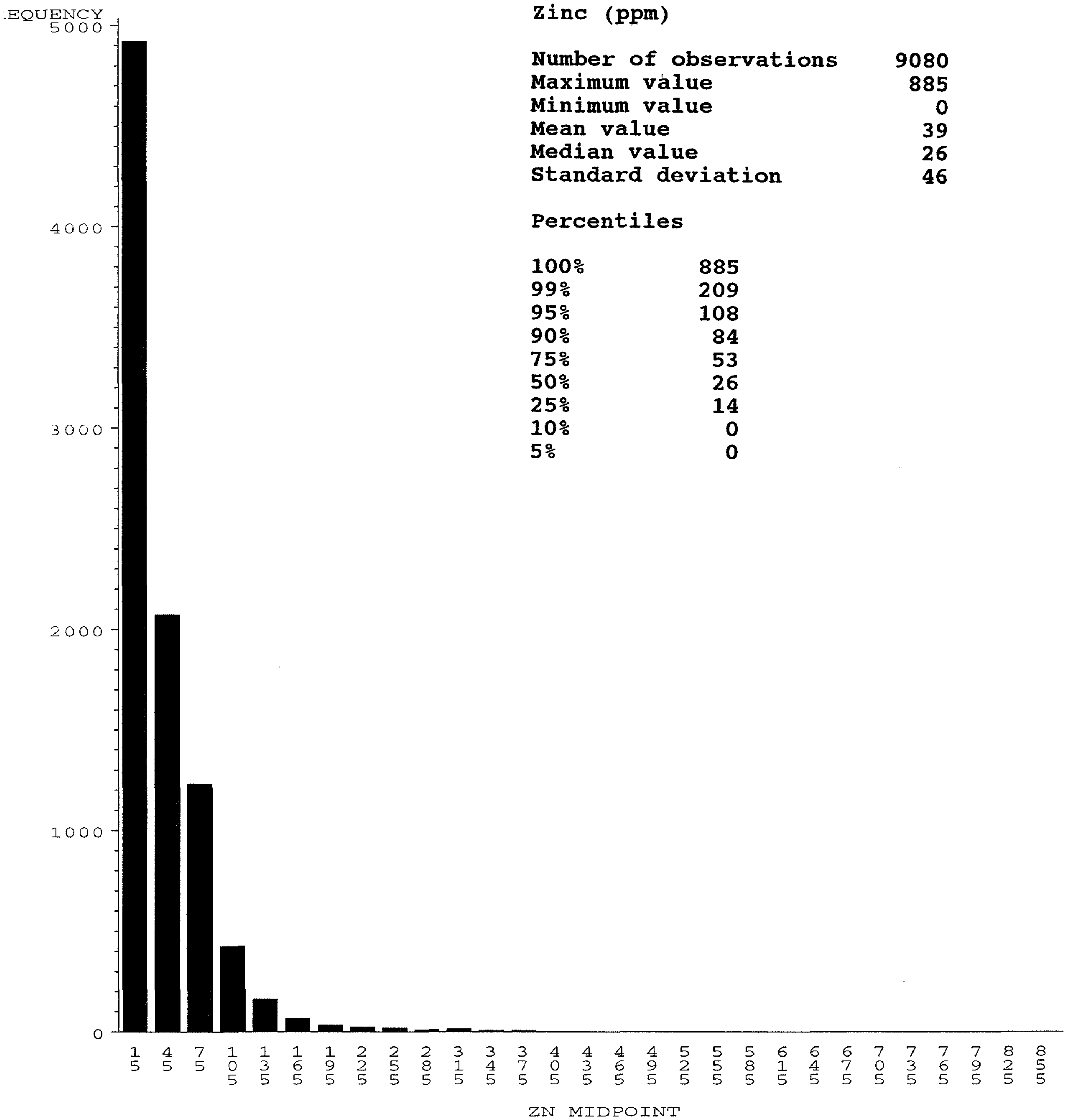
ZINC NORMALISED TO LITHIUM



ZINC NORMALISED TO MANGANESE



ZINC



STATISTICS

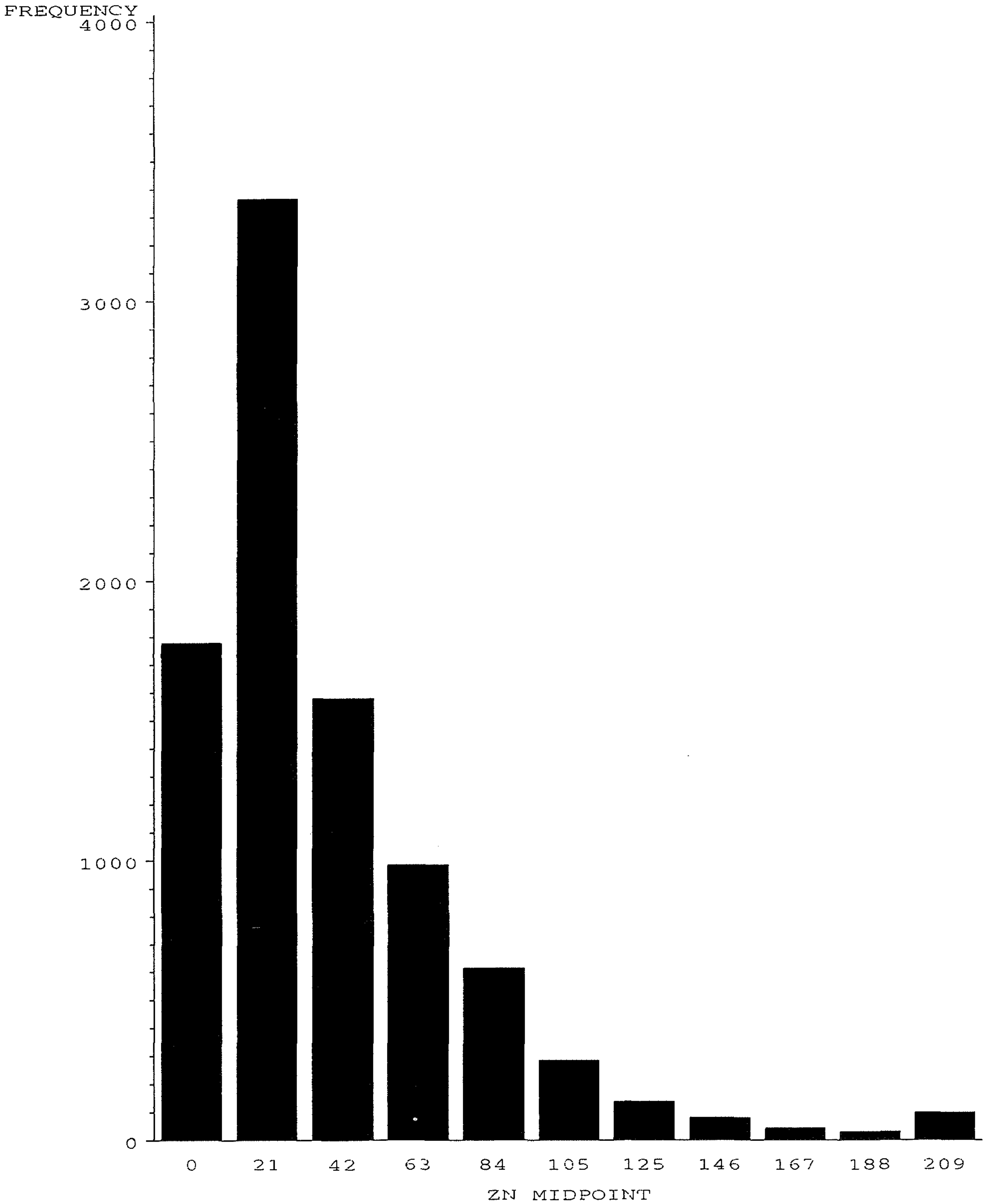
Zinc (ppm)

Number of observations	9080
Maximum value	885
Minimum value	0
Mean value	39
Median value	26
Standard deviation	46

Percentiles

100%	885
99%	209
95%	108
90%	84
75%	53
50%	26
25%	14
10%	0
5%	0

ZINC



FREQUENCY
4000
3000
2000
1000
0
0
21
42
63
84
105
125
146
167
188
209
ZN MIDPOINT

Zirconium

Zirconium

Southern North Sea

The abundance of Zr in coarse-grained sediments is almost entirely related to the presence of heavy minerals such as zircon and sphene. Zr values are generally low over the sands of the region (average 140ppm) compared to the central North sea (see below). High Zr values occur mainly near the coast in gravelly sediments indicating the occurrence of detrital minerals (average 310ppm in sandy gravels offshore of The Wash). Intermediate to high concentrations in the fine-grained sediments of the Outer Thames Estuary (average 408ppm); off the East Anglian coast (average 562ppm) and in the Markham's Hole area (average 442ppm), demonstrate that quantities of authigenic zircon may also occur as adsorbed coatings on clays (Nicholls and Loring, 1962).

Central North Sea

High Zr values occur in fine-grained sediments between the Tyne-Tees estuaries (average 573ppm) and farther offshore in the Farn Deeps (average 483ppm). The most extensive group of high Zr values anywhere on the UK Continental Shelf , occur on the Dogger Bank (average 847ppm in gravelly sand and 564 ppm in sand) and sandy sediments to the north (average 546ppm). High values also occur in the muddy sands of the Devil's Hole area (average 414ppm). These are mainly associated with high values of Cr, Ti, and Fe, and therefore reflect accumulation of heavy minerals. Nicholson et al (1985) noted a similar correlation in the North Sea. Dangerfield and Tulloch (1989) reported zircon concentrations up to 23.6 per cent in the very fine sand fraction of samples from this region, the highest recorded in the North Sea. Normalised Zr/Li data indicate the Dogger Bank to be an area of heavy mineral enrichment, as do normalised maps of Cr/Li and Ti/Li. Higher Zr concentrations occur in muddy sands in the Outer Forth Estuary (average 545ppm) than in the fine-grained sediments in the firth (average 349ppm).

Northern North Sea

High values occur in the fine-grained sediments of the Fladen Ground and Witch Ground basins and parts of the surrounding sandy sediments , indicating adsorption of Zr onto clay minerals or the presence of detrital minerals such as zircon and sphene in the sand fraction. Higher average Zr concentrations in the muddy sand facies (average 435ppm in Witch Ground/Fladen Ground) compared to the mud facies in Fladen Ground (average 298ppm) suggest that the main influence on Zr distribution is detrital mineral content in the fine-grained sand fraction rather than clay minerals. A similar distribution of Zr between the mud and sand fraction was found in the north-eastern Irish Sea by Cronan (1970).

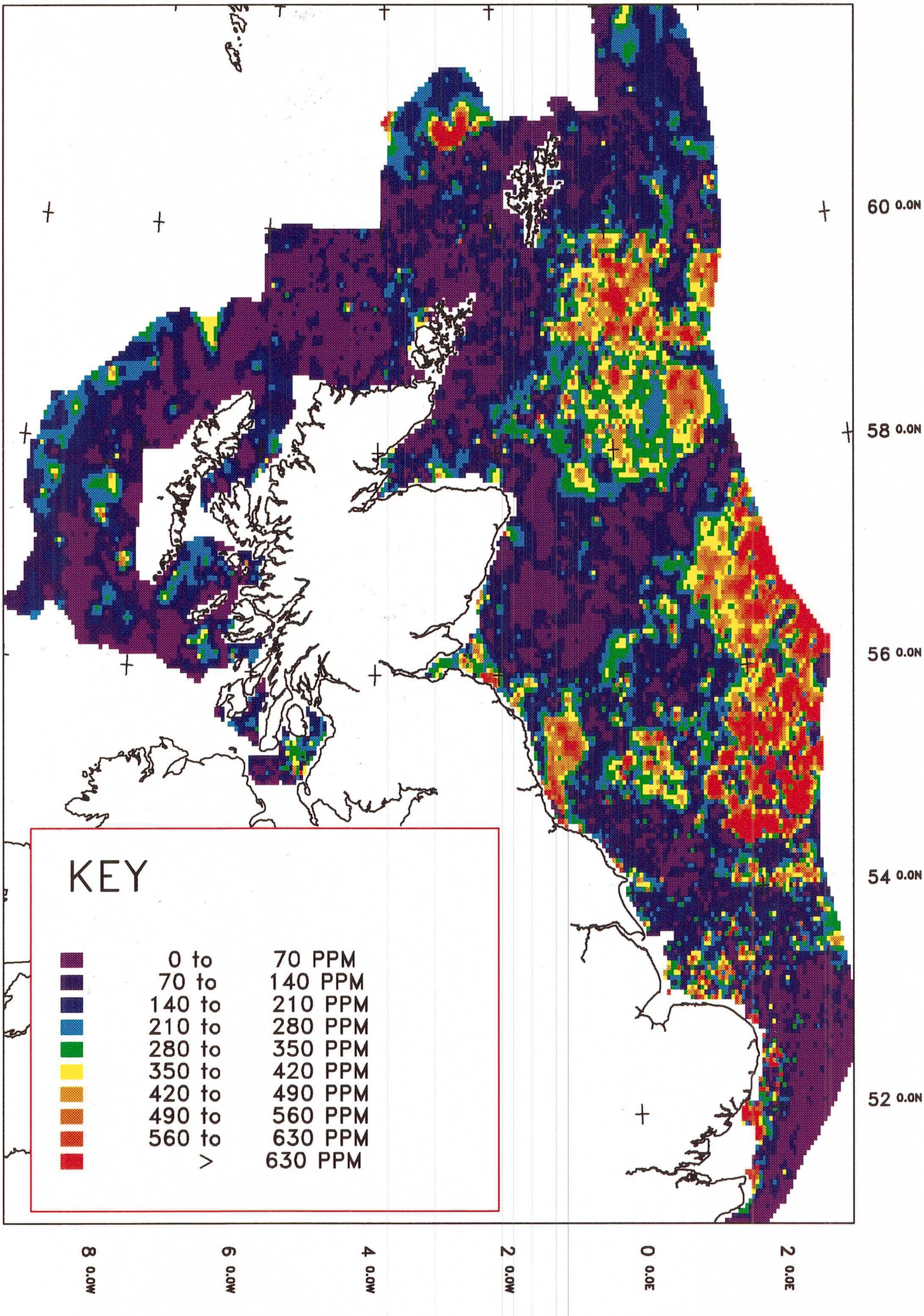
Hebrides and West Shetland shelves

Zr values are uniformly low in all sediments in this area with the exception of muddy sediments at the shelfbreak north-west of Shetland. Intermediate Zr levels occur in the fine-grained sediments at the shelfbreak (average 210ppm west of the Outer Hebrides) and in coarse-grained sediments around St Kilda. The overall depletion of Zr in the area does not reflect the relatively high concentrations in the Lewisian, Moine and Dalradian rocks British Geological Survey, 1987;1990) from which the Pleistocene deposits underlying the sea-bed sediments are derived. This suggests that fragments of basic igneous rocks, which have low Zr concentrations, are the dominant lithic component in the sediments in this region.

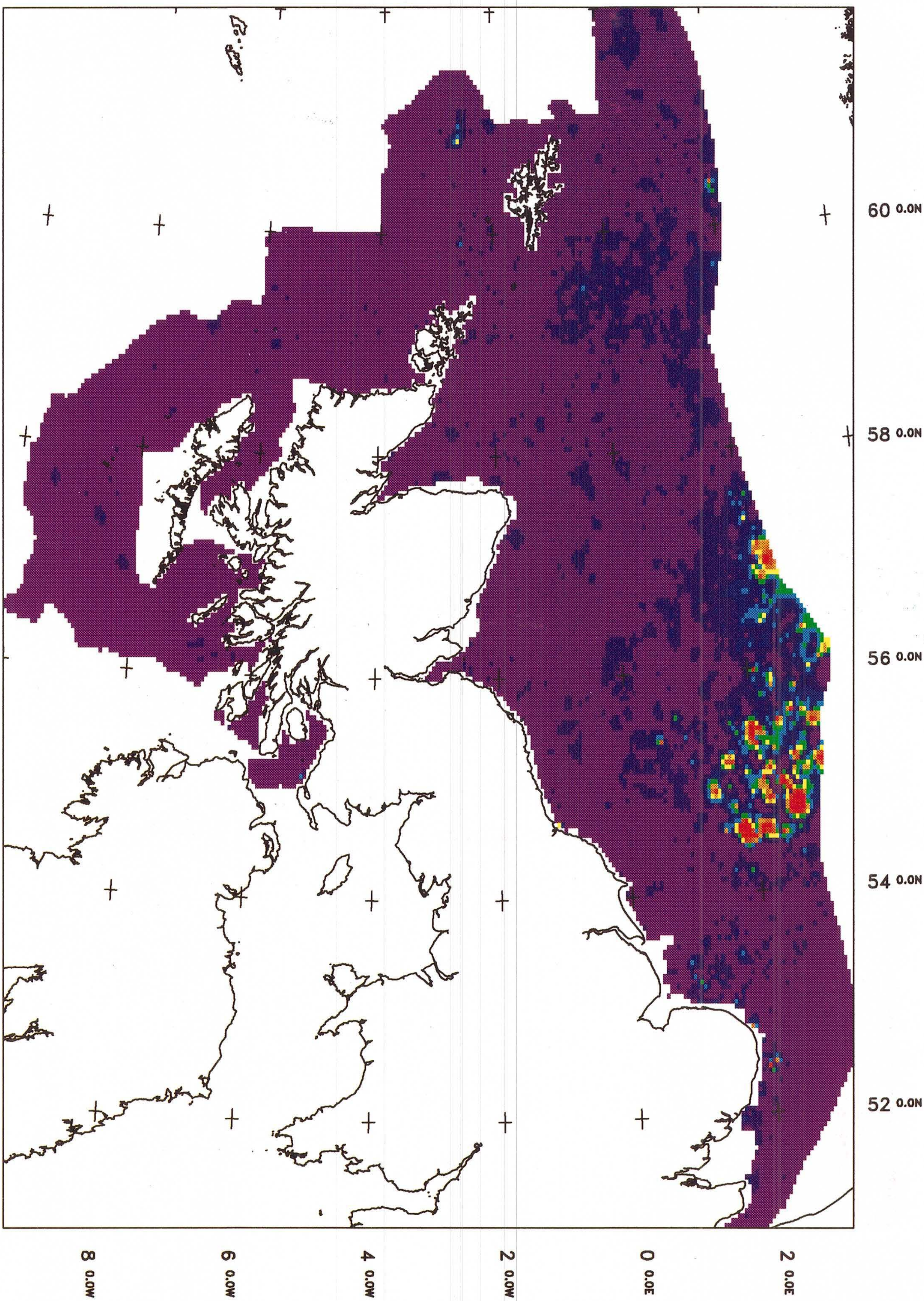
Malin-Hebrides

Comparable with the outer shelf, low Zr values also occur in all sea-bed sediments in this area. This is mainly due to the high proportion of lithic fragments and heavy minerals derived from Tertiary basic and ultrabasic rocks in the Pleistocene and Holocene sediments of the area. Intermediate to high values occur in fine-grained sediments in The Minch/Sea of the Hebrides (average 167ppm); the Sound of Jura (average 233ppm) and the Firth of Clyde (average 238ppm).

ZIRCONIUM IN SEA-BED SEDIMENT



ZIRCONIUM NORMALISED TO LITHIUM



ZIRCONIUM

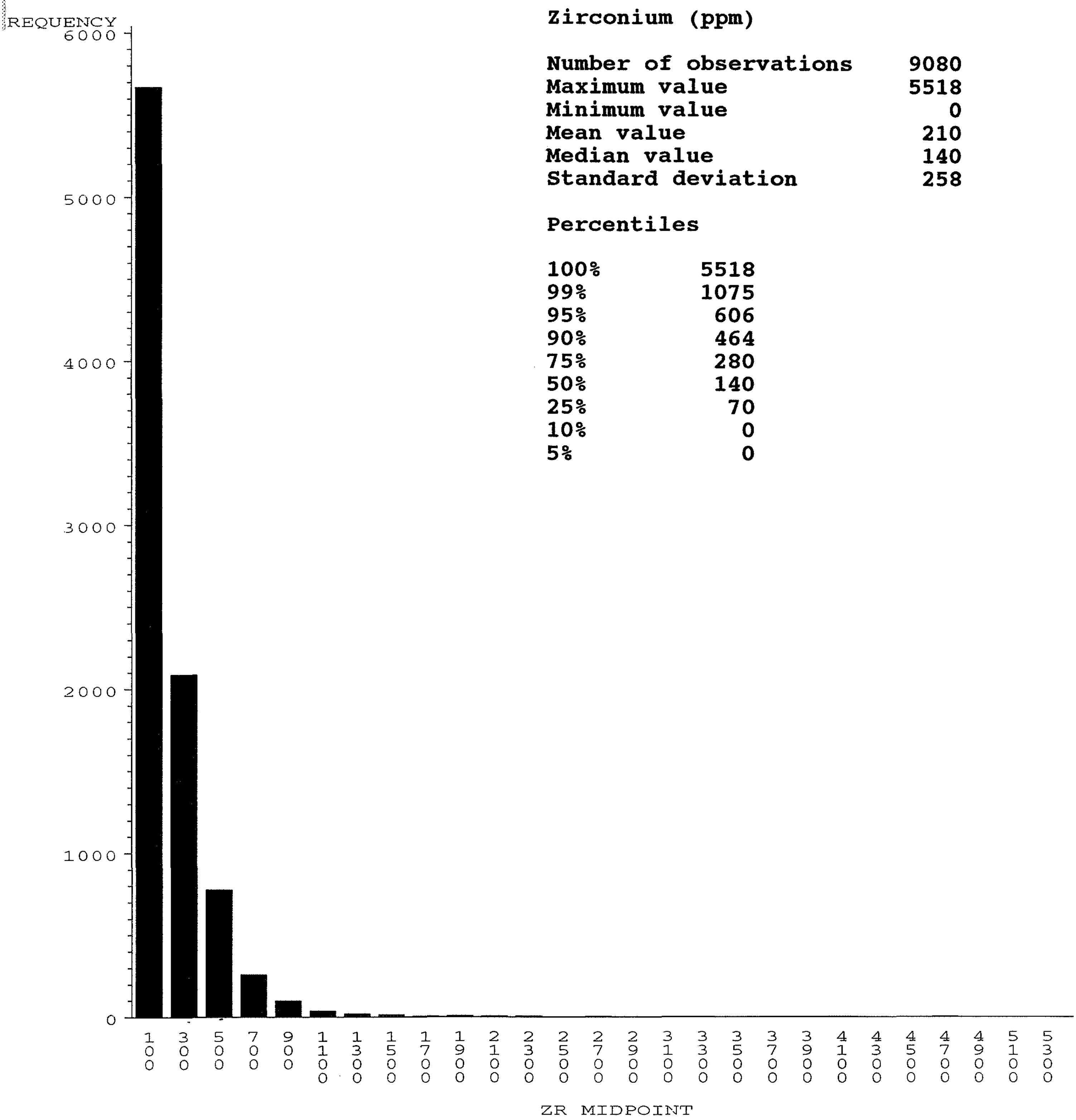
STATISTICS

Zirconium (ppm)

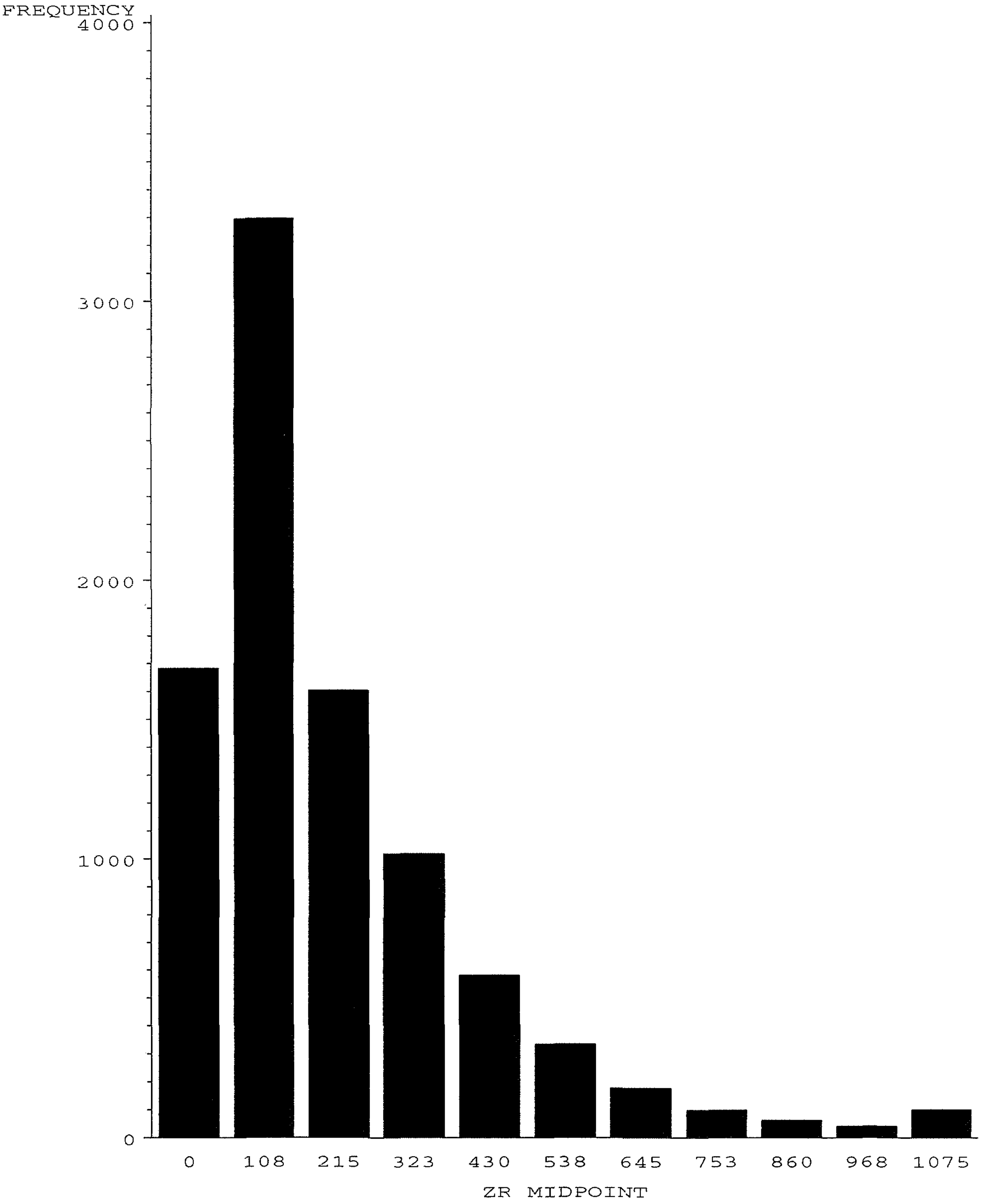
Number of observations	9080
Maximum value	5518
Minimum value	0
Mean value	210
Median value	140
Standard deviation	258

Percentiles

100%	5518
99%	1075
95%	606
90%	464
75%	280
50%	140
25%	70
10%	0
5%	0



ZIRCONIUM



FREQUENCY
4000
3000
2000
1000
0
0
108
215
323
430
538
645
753
860
968
1075
ZR MIDPOINT

12 CONCLUSIONS

The distribution of chemical elements in sea-bed sediments on the UK Continental Shelf is principally controlled by the variation in grain size of the sediments. Within areas of similarly classified sediments, however, a wide range of element concentrations can occur. These may be related to differences in the mineral composition of source areas from which the sediments are derived, such as the strong influence of basic igneous rocks on the chemistry of sea-bed sediments west of Scotland. The sea-bed sediments around the UK are, however, mainly the product of underlying Quaternary deposits, with recent deposition taking place only nearshore or in enclosed areas of deep water farther offshore.

Investigation of geochemical patterns in relation to the distribution of Quaternary sequences may prove a useful method of determining their provenance and therefore an indication of ice movement during periods of glacial deposition. In particular, the element variations across a boundary extending from the Firth of Forth to Dogger Bank may be an important factor in explaining the depositional history of Quaternary deposits. From this conclusion, it is thought that the movement of sediment 'plumes' proposed by Dearnley (1989) to explain the distribution of lithic fragments derived from the Tertiary volcanic province of western Scotland and Northern Ireland, or from the Midland Valley to Flamborough Head, is secondary to erosion and transportation by glacial processes during Pleistocene times.

Wave-induced, wind-driven and tidal currents, particularly in shallow waters nearshore, locally affect the redistribution of sea-bed sediments, and larger scale movements of water masses and oceanic currents have a broader effect on sea-bed conditions. The formation of fronts between the main water masses which separate areas of well-mixed and stratified water appears to have an important influence on sediments and their geochemistry. This is confirmed by the concordance between the location of fronts shown on Figure 8, and distinct geochemical boundaries shown on many of the geochemical distribution maps. The distribution of areas of mixed water may also be a significant feature in assessing the importance of coprecipitation of metals by Fe and Mn hydroxides which coat the surface of sediment particles under oxidising conditions.

In addition to sea-bed sediments derived from older deposits exposed at the sea-floor, recent input from rivers, cliff erosion, the atmosphere and growth of calcium carbonate secreting organisms, all have a major effect on the geochemistry of the marine environment. In the case of cliff erosion and carbonate production, inputs are entirely natural, whereas those from rivers or the atmosphere may be both natural and derived from human activities. With the exception of atmospheric, these inputs are mostly localised; for example, sediments carried by rivers are mainly deposited in the nearshore zone, and even fine-grained material in suspension is returned shoreward as it settles through the water column due to the transport direction of higher density sea water.

Contaminants entering the sea are therefore largely confined to the coastal zone by hydrodynamic processes, and the geochemical maps presented in this report show that sea-bed sediments near the major river estuaries of the UK have much higher metal concentrations than those farther offshore. The introduction of organic material by rivers is also considered to be important as organic particles have very high sorption capacities and are able to remove metals dissolved in sea water. As would be expected, this process has most influence on geochemical patterns near river estuaries, but more generally, high concentrations of elements such as Zn in the southern North Sea may be related to accumulation of organic matter, derived not only from the rivers of the UK but to those of Continental Europe, such as the Rhine. The wide distribution of high Zn concentrations in both fine and coarse-grained sediments suggests that the organic matter occurs not only in association with clay particles, but also in the pore spaces of coarser-grained sediments.

With distance from the coast, sites of metal contamination are more isolated and limited in extent. These are mainly related to activities such as sewage dumping or shipping operations. The samples analysed in this report were mostly collected before the main phase of hydrocarbon production in the North Sea, however in areas where production had already commenced, such as around the gasfields of the southern North Sea or some of the larger oilfields in the northern North Sea, isolated high values of elements such as Cu and Zn may reflect these activities.

The wide range of possible explanations for the distribution of geochemical elements in the North Sea can be assessed by the use of normalisation techniques. These methods can be selected not only to minimise the effect of grain size, but also to eliminate the influence of a particular factor which mainly controls the distribution of a particular element. For example the close association of Sr with Ca in shell debris can be reduced by normalisation of Sr/Ca to allow features of Sr distribution related to mineral composition to be identified.

To assess the levels of element concentrations in sea-bed sediments around the UK in a broader context, Table 5 shows average element values in a number of different sediment and rock types. An interesting comparison is that of the values calculated in this report with those of stream sediments collected by the BGS Geochemical Survey Programme. The stream sediment value is based on an average of approximately 45 000 samples from the Scottish Highlands and islands to the River Tyne. As such, they reflect a cross-section of the major stratigraphic units of the UK with the exception of Jurassic to Paleogene sedimentary rocks for which data has not yet been published. Of the 26 elements which are common to both surveys, only two, Ca and Sr, have higher average values in the marine environment due to the influence of calcium carbonate in shell material. Of more significance is that of the 26 elements, the average stream sediment value occurs above the 90th percentile value of the marine data for all but Ca, Sr and B. The reason for Ca and Sr is explained above, and B is known to be enriched in marine sediments relative to lacustrine and fluvial deposits.

Allowing for the difference in grain size of the samples, whereby stream sediments are sieved to material finer than 150μm (consisting of very fine sand, silt and clay) prior to analysis, average element values in the marine environment are a significant factor lower than in streams and rivers. Data in Table 5 also shows that even the fine-grained marine sediments, which are predominantly less than 63μm in grain size, have lower average element concentrations than stream sediments. The processes of transfer of sediment from land to the sea must therefore significantly reduce the metal concentrations. The reasons for this must lie in the grain size of the sediment reaching the sea and the processes which take place in river estuaries. Coarse-grained material is deposited in or close to the estuaries whereas fine-grained sediment is transported in suspension. Under the hydrodynamic conditions prevailing in the seas around the UK, the fine-grained material may be retained in suspension and ultimately removed from the shelf area by oceanic currents, or as described earlier, be returned to the coastal zone by sea water as it settles through the water column.

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