



**Hydraulics Research**  
Wallingford

**SLUDGE DISPOSAL IN LIVERPOOL BAY**

**Fourteenth bed monitoring survey**

**November 1986**

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## ABSTRACT

This report describes the fourteenth HR survey carried out in November 1986, continuing the long-term monitoring of the bed sediments of Liverpool Bay. The objective is to determine whether any changes are occurring in the abundance of heavy metals and of organic matter in the finer fraction of the bed sediment as a consequence of sewage sludge disposal. The differences in measured concentration arising from the selection of  $90\mu\text{m}$  instead of the more traditional  $63\mu\text{m}$  as the upper limit of the finer fraction is germane to the future conduct of the monitoring programme by the North West Water Authority. The findings of the first half of a two-year study into the expected consequences of making this choice are described.





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## 1 INTRODUCTION

Surveys of the organic carbon and heavy metals abundance in the sediments of Liverpool Bay have been conducted by Hydraulics Research (HR) on a roughly annual basis since 1973. The objective of this sediment surveillance is to detect whether any long-term trends are taking place in terms of organic and metal enrichment of the surface sediments as a consequence of the discharge of sewage sludge to the Bay. This report presents the results of the last survey, the fourteenth of the series, which was undertaken in November 1986.

Standard procedure in the past has been to determine the concentration of organic carbon and heavy metals in the so-called mud fraction of the surface 25mm of the bed obtained by grab sampling or by shallow coring. Throughout the survey series HR has adopted the traditional size split at  $63\mu\text{m}$  as the upper limit of the mud fraction. One further survey by HR is planned for autumn 1987 but thereafter North West Water Authority (NWWA) will assume full responsibility for the monitoring programme following a two-year overlap. Although NWWA have continued the same sampling pattern that has evolved from the HR programme, they have decided to make the mud size split at  $90\mu\text{m}$  instead of  $63\mu\text{m}$  in order to conform to present practice at the Fisheries Laboratory, Burnham-on-Crouch (MAFF). This change may pose problems in relating the results of future surveys to the long time series collected by HR. Therefore, it has been decided to take advantage of the two-year overlap by attempting to evaluate the effect of changing the size limit. Both for the presently reported survey and for the forthcoming 1987 survey HR are doubling their customary analysis by examining the "less than  $63\mu\text{m}$ " fraction and the "less than  $90\mu\text{m}$ " fraction. Furthermore sub-sets of the total sediment from each sampling location are being made available to MAFF and NWWA to permit comprehensive inter-laboratory calibration.

Grab samples were taken from the M.V. Branding on 11-13 December at 67 sites (Fig 1). The sampling grid included twenty-three of the group of twenty-four standard sites visited regularly since 1973. The remaining one, T6, the closest to the Dee estuary was omitted as it was on the previous survey. Because of the requirement to divide the sample into three parts (one for MAFF and one for NWWA as well as one for HR), duplicate grab samples were taken at some sites to ensure sufficient mud was available for analysis. The top 25mm was separated on board the survey vessel and the duplicates bulked prior to their return to the laboratory.

Core samples up to 1.5m long were also taken at seven sites at the eastern end of the Bay in a continuing attempt to reach the basal unpolluted sediments below the surface muds. These have not yet been analysed and will be the subject of a later report.

### 3 LABORATORY TREATMENT

In the laboratory, each station sample was tipped out on to a plastic tray well mixed and divided into three equal parts. These were then placed in polythene bags and deposited in a deep-freeze until required. The HR sample was further divided into two, one half being split into mud and sand fractions by wet sieving at  $63\ \mu\text{m}$  as usual and the other half being split at  $90\ \mu\text{m}$  in order to examine how sensitive the metal concentrations are to the sieve size chosen for the separation. Wet separation was accompanied by hand brushing of the sediment on the chosen sieve. In spite of extra grab samples being taken, the quantity of fine material available for analysis was not always sufficient for organic matter determinations to be made at sites where the mud content was much below 1%. However, heavy metal determinations were made at all sites on both the 0 -  $63\ \mu\text{m}$  and 0 -  $90\ \mu\text{m}$  fractions. As on the last survey, the mud fraction was oven dried at  $50^\circ\text{C}$  prior to grinding and mixing before the sub-samples for organic matter and heavy metals were withdrawn.

Organic carbon determinations were made by the standard wet oxidation method used previously (the organic carbon is reported as organic matter, a factor of 2.5 being used as in the past to convert carbon to the equivalent of dried organic residues).

Standard (NBS 1645) and HR's own reference samples were included with the samples submitted to the commercial analytical laboratory for heavy metal determinations by atomic absorption spectrophotometry as in the previous four surveys. Correction factors were derived and applied to ensure that the results of the current survey are as comparable as possible with those of the previous five surveys for which the data is included in this report.

The factors used on this occasion were:

Hg	1.085	Pb	0.980
Cu	0.969	Ni	0.949
Zn	1.013	Cr	0.971

They are typical of those used in the past and in most cases the individual check samples were within the  $\pm 10\%$  claimed accuracy for this method of analysis.

The previous five surveys from which the data is included in this report were made on substantially the same grid covering between 60 and 67 sites so comparisons are more realistic than with some of the earlier surveys with their lower sampling density. Nevertheless, the ability to return to a particular site the following year is limited by navigational accuracy so that local non-uniformity of bed composition rather than temporal change can account for substantial differences from year to year (cf mud, position R14, 85% last year 0.7% this year).

#### 4 MUD CONTENT

The mud content of each of the 67 sampling positions is shown in Fig 2. The mud distribution is similar to that found in past surveys although the peak at R14, found for the first time last year, is no longer evident. The value of 0.7% is similar to that of the 2.9, 0.2 and 0.7% found on surveys 10 - 12.

There appears to be less mud overall in the surface layer this year: a mean of 8% compared with the more customary 11% found on the previous four surveys. The mean difference owes much to the reduction in mud at a few particularly mud-rich sites such as YY1, 3 and 4 where values of 65, 62 and 81% compare with values of 98, 91 and 89% recorded last year.

## 5 ORGANIC CONTENT

The distribution of organic matter in the "less than 63  $\mu\text{m}$ " mud fraction is shown in Fig 3. Due to the need to effectively duplicate the analysis (<63 and <90  $\mu\text{m}$ ) and the lower overall mud contents, 27 organic analysis had to be omitted. This unfortunatley makes comparisons based on overall means less valid as from past experience the muds from areas low in mud are normally richer in organic matter. Nevertheless, at positions at which comparisons are possible, there appears to be a slight reduction in organic matter on the eastern side of the Bay. The one high value at R9 was due to the presence of coal in the sediment, noticed before in this area (Ref 1).

The "total" organic matter content (Fig 10) is calculated from the product of the mud and organic matter percentages, and a factor for the average dry bulk density of the top 25mm of bed sediment is similar to that of the previous five years.



In this section, only the metals in the  $< 63\mu\text{ m}$  fraction will be considered and the comparisons made will be with past surveys.

The heavy metal concentrations have been illustrated as in previous reports. Figs 4 - 9 show the concentration of metals in the mud fraction of the sediment expressed in micrograms metal per gram of mud. Figs 11 - 16 shown the "total" metals expressed as the product of the metal concentration, the mud percentage, and a factor based on the mean dry bulk density of a number of cores. This "total" metal concentration is expressed as kilograms (mercury only) or tonnes of metal in the top 25mm per square kilometre of bed. If it is assumed that the metal content of the fine sediment ( $< 63\mu\text{ m}$ ) is mainly derived from adsorption of metals from solution, then this "total" metal figure represents the input to the area from man-made sources together with any natural sources that produce soluble metals.

Mercury concentrations are again slightly down with only one peak value exceeding 4 mg/g (Fig 4). There has been a gradual decline in the mercury values over the past 5 years and the current mean of over 60 sites is less than half the figure of the 1982 survey (Ref 2).

To the west, the concentrations have not changed appreciably and there is no evidence of sediment accretion.

Zinc (Fig 5) also has shown a reduction in concentration this year although there is no evidence of a long term decline, more an annual fluctuation around a mean value of about 400 mg/g.

Lead (Fig 6) is showing another consistant decline after a particularly high year in 1983. The current year's results are similar to those of last year with the number of sites exceeding 300 mg/g dropping from five to two.

Nickel and copper (Figs 7 & 8) show little change over the years with spatially averaged concentrations of  $60 \pm 10$  mg/g and  $90 \pm 10$  mg/g (except for 1983) respectively.

Chromium (Fig 9) has an unusual distribution this year although not dissimilar to that of 1984. High values are concentrated in the eastern area of the Bay with outliers in the vicinity of the disposal ground. The prominent north-south division between the high and low concentrations near the Mersey outfall is not allied to changes in mud or organic matter concentrations and does not follow the normal distribution around the Mersey plume. Reasons for this distribution are so far unknown.

The mean values ( $M_{\mu}$  g/g) and the relative standard deviation (RSD %) for the last five surveys are as follows:

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Survey No.	10		11		12		13		14	
	M	RSD	M	RSD	M	RSD	M	RSD	M	RSD
Hg	3.8	135	2.0	97	2.8	249	1.9	39	1.7	52
Zn	388	45	497	47	386	43	465	25	346	22
Pb	349	158	459	120	266	93	172	56	146	45
Ni	51	37	56	51	66	20	55	17	51	31
Cu	86	65	165	116	99	50	90	43	97	46
Cr	43	24	73	50	85	43	69	25	50	51

---

"Total" metals are again closely correlated with the mud content. The four main areas of high concentrations are to the north and south of the Mersey outfall, to the far north around Q12, and lastly the northern sector of the sludge dumping ground. The abundance of mud in areas between the Mersey outfall and Newcome Knoll apparently results in the region being the major sink of heavy metals. North of the Mersey outflow there is the other zone of metal accumulation that has been consistently present since our measurements began.

The main difference between this and last years total metals is due to the absence of the high mud area around R14. To some extent this has been transferred westward to Q12 and Q13 making the general distribution similar to those of 1982, 1983 and 1984 (Figs 11-16).

The total organic matter (Fig 10) is much the same as before. The absence of organic content data from 27 sites does not affect the general outline because of the low mud contents at these sites and hence the low total organics.

## MUD FRACTION COMPARISONS

Separation of the total sediment at  $63\mu\text{m}$  and  $90\mu\text{m}$  to give 0 -  $63\mu\text{m}$  and 0 -  $90\mu\text{m}$  fractions yields two sets of results for mud, organic matter and heavy metals (Table 1). The  $63\mu\text{m}$  split has been the standard used at HR and is commonly used elsewhere. Other size limits have been chosen by workers in the same field ranging from  $20\mu\text{m}$  (Ref 3) to no split at all, in other words using the entire sediment (Ref 4). Other workers have assumed the total metal content is confined to the  $16\mu\text{m}$  fraction (Ref 5). MAFF currently split at  $90\mu\text{m}$ , claiming that sediment aggregates are not fully broken down by wet sieving so that more of the metals adsorbed on the clay particles are included in the less than  $90\mu\text{m}$  fraction than in the less than  $63\mu\text{m}$ . Earlier studies (Ref 2, 6) have demonstrated that even when aggregates are fully broken down certain metals such as copper, chromium and iron are present at higher concentrations in the 50 to  $100\mu\text{m}$  fraction. However, in these cases it is normally assumed that elevations in the non-aggregated 63 to  $90\mu\text{m}$  fraction are not in the form of adsorbed metals. They are more likely to be of natural origin than the consequence of contamination from sludge disposal or effluent from the Mersey estuary.

From a large number of size gradings made in the period 1973 to 1981 the maximum percentage sediment found in the 63 -  $90\mu\text{m}$  range was less than 10%. The current comparisons (Table 1) show that on average about one per cent of the sample is in the 63 -  $90\mu\text{m}$  fraction. Sub-sampling errors particularly when dividing the coarser samples resulted in some 63 -  $90\mu\text{m}$  fractions being apparently negative e.g. K9, K11, L12, M12, P11, S12, T9. However, comparison of the means for the 67 sample pairs indicate that sieving at the  $90\mu\text{m}$  divide yields 14% more sediment than sieving at  $63\mu\text{m}$ .

The principal question to be resolved for the continuation of the time series by NWWA is whether sieving at  $90\mu\text{m}$  brings about a significant difference in the metal and organic concentrations derived from the "less than  $63\mu\text{m}$ " fraction. For the limiting case where no metal is present in the "63 -  $90\mu\text{m}$ " fraction then the metal concentration obtained on the "less than  $63\mu\text{m}$ " will be diluted on average to  $100/114 = 0.88$ . It should not be possible to fall below the  $0.88 \times$  concentration of "less than  $63\mu\text{m}$ ". However, many individual sample

pairs display a greater dilution and in the case of mercury the mean concentration obtained from the "less than 90  $\mu$  m" set is 0.82 of that obtained on the "less than 63  $\mu$  m" set. Inadequate sample mixing leading to unrepresentative sub-sampling in the first place taken together with minor differences in sieving, grinding, secondary sub-sampling and analysis are responsible for such anomalies. A relative concentration factor of unity means that concentrations derived for a 90  $\mu$  m split will faithfully represent the concentration derived from a 63  $\mu$  m split. A value greater than unity implies that the 63 - 90  $\mu$  m fraction contains a disproportionate excess of that metal. The same argument applies to the relative organic content given by the two sample sets. Examination of the mean pairs of Table 1 give the following relative concentration factors. The outcome of tests for the null hypothesis to check the order of significance of differences between the means is also given below:

Relative concentration factor		
Mercury	0.82	highly significant
Copper	0.88	significant
Zinc	0.94	probably significant
Lead	0.93	not significant
Nickel	0.94	not significant
Chromium	1.32	probably significant
Organic matter	0.94	not significant

The absence of mercury in the 63 - 90  $\mu$  m fraction is in accord with earlier HR findings (Ref 2) that mercury is concentrated on the finer fractions with only negligible amounts on the coarser particles. The other inference to be drawn from the relative values of mercury in the two sample sets is that wet sieving as practised by HR ie. sieving accompanied by hand brushing, provides adequate reduction of any sediment aggregates.

It seems likely that copper is also only weakly represented in the 63 to 90  $\mu$  m fraction. Statistical uncertainty is too great to quantify the relative significance of the 63 - 90  $\mu$  m fraction as far as the zinc, lead, nickel and

organic matter content are concerned. However, the inclusion of the coarser fraction appears to enhance the chromium concentration. The findings with regard to mercury suggest that this chromium cannot be attached to fines that have escaped the sieving separation by being included in aggregates. Instead it must be present either on or within discrete particles of grain size 63 to 90  $\mu$ . It is a moot point whether chromium or any other metals found in sediments of this narrow size band are of natural or anthropogenic origin.

Although the sampling network differed little from that used over the last four years, mud content when averaged over the area as a whole is found to be appreciably lower. Lead, zinc and mercury concentrations in the mud fraction also display reduced levels compared with the recent past, while nickel, copper and organic matter are little changed. For reasons given earlier the organic matter content is averaged over considerably fewer sampling locations than is normal. No very high metal peaks in concentration were found on the present survey. The declared intention (Ref 7) to investigate the grain size dependence of such peaks is therefore postponed until the opportunity arises from future sampling, possibly on the next and final HR survey.

The distributions of "total" metals and organic matter generally conforms with past results: the two areas to the north and south of the Mersey outflow being the main repositories for metals and organic material.

This first year's comparison between splitting the mud fraction at  $90\mu\text{m}$  instead of  $63\mu\text{m}$  suggests that the change to  $90\mu\text{m}$  will only lead to significant differences in the concentration values for mercury, copper and chromium. Both mercury and copper contents appear to be diluted by the inclusion of the  $63$  to  $90\mu\text{m}$  fraction. The additional fraction contains little or no mercury or copper. On the other hand, the  $63 - 90\mu\text{m}$  fraction is probably disproportionately rich in chromium and will lead to higher values being reported for the mud fraction based on a  $90\mu\text{m}$  upper limit. It seems doubtful, however, whether this additional chromium has its source in the disposal of sludge. The results for mercury and copper clearly indicate that the inclusion of fine particles within unbroken aggregates of  $63 - 90\mu\text{m}$  is not a significant factor, at least for the mud separation procedures practised at HR. We should point out that the findings do not necessarily apply if much gentler size separation techniques are in use. The results of MAFF's analyses on a companion set of bed samples should be revealing in this respect.

The opportunity to repeat the size-split comparison on bed samples recovered for the fifteenth survey planned for 1987 may improve the statistical significance of the results enough to decide whether any systematic differences apply to zinc, lead, nickel and organic matter.

## **9      ACKNOWLEDGEMENTS**

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## **Table**



TABLE 1 SIZE RANGE COMPARISONS

	MUD		ORG		Hg		Cu		Zn		Pb		Ni		Cr	
	< 63	< 90	< 63	< 90	< 63	< 90	< 63	< 90	< 63	< 90	< 63	< 90	< 63	< 90	< 63	< 90
G7	3.07	3.06	6.34	6.16	1.00	0.98	56	70	275	314	105	149	38	52	60	63
9	0.88	0.95	6.34	6.39	0.92	0.79	138	87	332	312	99	204	38	67	39	93
11	3.97	5.81	5.12	4.55	0.62	0.58	60	51	249	304	67	97	48	61	54	75
13	6.20	7.09	4.67	4.81	0.74	0.63	47	45	253	242	67	101	43	98	16	70
K9	2.65	2.20	5.84	6.14	1.63	1.59	96	94	355	358	119	310	42	98	25	57
10	9.04	11.11	6.13	4.78	1.29	1.19	71	68	290	265	110	158	47	49	63	64
11	10.07	8.88	5.24	4.59	1.04	0.97	80	59	297	274	96	91	62	28	38	31
L7	0.19	0.22	-	-	1.07	1.03	242	203	381	394	135	110	39	53	37	40
9	0.32	0.29	-	-	1.18	1.02	131	124	419	389	220	228	49	51	35	41
10	1.11	1.49	7.87	5.99	2.07	1.63	109	110	339	352	319	168	48	59	17	70
11	9.07	9.50	5.47	4.65	1.25	1.32	69	68	312	378	118	109	54	49	60	53
12	11.30	9.71	5.80	4.76	1.14	0.92	52	57	256	262	85	87	42	45	32	45
13	12.37	13.48	5.57	4.46	1.05	1.00	46	48	258	258	87	100	47	67	46	87
M8	0.14	0.16	-	-	7.18	6.00	234	202	349	359	153	154	47	53	35	45
9	0.63	0.74	7.85	-	2.07	1.67	130	123	318	342	184	186	57	55	93	82
10	0.54	0.58	-	-	3.49	2.06	120	118	349	374	198	223	46	59	55	126
11	7.29	10.03	5.94	4.73	1.67	1.05	58	62	274	255	113	104	38	43	36	34
12	5.84	4.87	5.61	7.27	1.13	0.91	63	65	277	365	93	103	37	40	35	32
N8	0.19	0.16	-	-	3.06	3.53	166	124	413	269	137	137	49	51	33	42
9	0.23	0.09	-	-	1.91	1.04	181	107	335	229	158	101	40	47	29	39
10	1.25	1.45	3.68	6.74	1.99	1.48	140	95	483	336	172	148	99	66	103	51
11	0.26	0.35	-	-	1.84	1.94	98	79	402	298	227	172	66	46	64	38
12	9.02	9.93	5.03	4.43	1.26	1.02	57	112	253	370	98	129	60	42	55	34
P8	0.33	0.28	-	-	1.04	0.81	77	90	301	334	139	172	39	40	62	25
9	0.09	0.08	-	-	1.46	0.95	134	112	521	438	230	227	60	37	34	18
10	0.09	0.01	-	-	1.94	1.00	190	93	598	294	205	120	61	34	26	8
11	1.71	1.08	7.22	-	3.26	1.26	97	109	388	381	153	151	46	58	38	55
12	0.87	1.13	5.69	5.77	1.31	1.37	59	69	264	286	113	156	38	53	20	44

TABLE 1 (con'd) SIZE RANGE COMPARISONS

	MUD		ORG		Hg		Cu		Zn		Pb		Ni		Cr	
	< 63	< 90	< 63	< 90	< 63	< 90	< 63	< 90	< 63	< 90	< 63	< 90	< 63	< 90	< 63	< 90
Q7	0.05	0.07	-	-	0.42	0.88	175	137	413	309	137	121	60	65	36	78
8	0.14	0.14	-	-	0.92	0.89	118	113	387	340	197	190	80	56	122	40
9	0.15	0.18	-	-	0.69	1.26	114	166	419	553	157	270	18	50	41	44
10	0.22	0.46	6.45	5.34	1.10	0.77	65	55	266	258	134	124	50	37	39	16
11	12.63	13.26	5.93	5.24	1.90	1.54	73	67	362	358	131	151	46	43	44	40
12	25.38	24.91	5.21	5.12	1.50	1.68	64	71	342	349	127	137	47	44	26	54
13	16.06	18.02	5.65	4.82	1.36	1.51	62	56	336	294	117	115	50	40	40	49
R8	0.14	0.26	-	-	1.32	1.01	102	96	357	300	150	121	45	35	63	44
9	1.96	2.62	12.58	7.33	1.70	1.45	93	92	409	397	124	158	36	30	41	58
10	0.36	0.54	-	3.64	1.25	1.00	81	56	328	250	125	72	31	42	47	73
11	7.59	15.20	5.03	6.27	2.14	0.77	70	75	373	397	148	147	55	70	29	50
12	0.43	0.51	6.42	6.28	1.99	1.54	96	81	329	330	181	181	54	36	17	31
13	1.00	1.04	5.50	4.50	1.99	1.68	70	58	322	321	135	135	66	40	18	35
14	0.70	0.98	-	-	1.78	1.51	77	64	365	323	170	133	46	29	16	29
S8	0.09	0.13	-	-	1.81	0.77	120	142	348	400	133	150	29	45	17	54
9	6.01	6.82	7.10	4.54	1.95	1.97	88	78	379	428	160	153	49	55	46	64
10	6.03	8.57	1.62	-	1.82	2.05	84	81	349	489	137	172	52	47	24	66
11	10.38	12.00	4.33	4.84	1.97	1.58	70	47	337	317	134	137	63	49	47	68
12	2.82	2.28	4.97	6.58	2.18	1.73	96	70	466	453	234	176	101	41	50	51
13	8.09	9.75	6.24	4.75	1.94	1.50	75	161	383	342	157	132	90	78	51	77
14	11.98	14.38	5.49	7.86	1.74	1.57	61	49	339	307	124	202	77	33	53	103
T8	0.20	0.21	-	-	1.96	1.19	94	81	377	323	165	125	62	28	52	58
9	11.50	10.24	6.68	-	2.55	2.21	73	63	408	436	169	176	32	40	41	71
10	0.06	0.09	-	-	1.87	1.74	53	52	182	186	77	68	60	17	38	23
11	0.34	0.40	-	-	1.46	1.31	112	125	314	397	137	118	68	39	37	50
12	22.14	32.10	4.79	6.39	1.77	1.03	68	52	313	282	142	127	64	32	75	88
13	45.71	50.53	6.26	6.34	2.23	2.00	72	76	413	424	154	131	31	31	47	27
14	11.63	15.33	4.35	3.91	1.92	1.62	76	54	377	341	136	103	46	36	53	69
15	0.13	0.02	-	-	0.49	1.57	47	23	153	70	123	25	33	12	68	49

TABLE 1 (con'd)      SIZE RANGE COMPARISONS

	MUD		ORG		Hg		Cu		Zn		Pb		Ni		Cr	
	< 63	< 90	< 63	< 90	< 63	< 90	< 63	< 90	< 63	< 90	< 63	< 90	< 63	< 90	< 63	< 90
U9	0.79	1.37	6.56	6.17	1.88	1.44	172	142	432	379	164	129	40	45	79	81
11	0.17	0.23	-	-	1.28	0.77	186	70	392	253	516	84	52	46	106	92
12	1.77	2.74	-	2.59	1.67	0.79	114	47	388	213	134	56	60	36	103	309
13	0.17	0.27	-	3.79	1.73	1.28	118	52	374	201	126	78	44	27	104	59
14	0.08	0.12	-	-	1.95	0.56	72	74	185	213	42	71	72	90	81	277
15	0.46	0.83	-	-	2.64	1.74	125	93	477	364	139	107	55	54	46	387
YY1	65.54	71.54	4.46	4.28	1.91	1.76	68	67	326	330	127	112	34	52	82	23
2	2.55	4.63	6.54	5.84	2.36	2.07	79	74	385	388	180	127	38	54	98	88
3	62.10	69.95	4.85	4.23	1.96	1.91	63	53	316	339	224	96	38	49	101	51
4	81.85	91.54	4.80	4.38	1.53	1.51	57	45	315	274	111	118	46	42	59	31



**Figures**





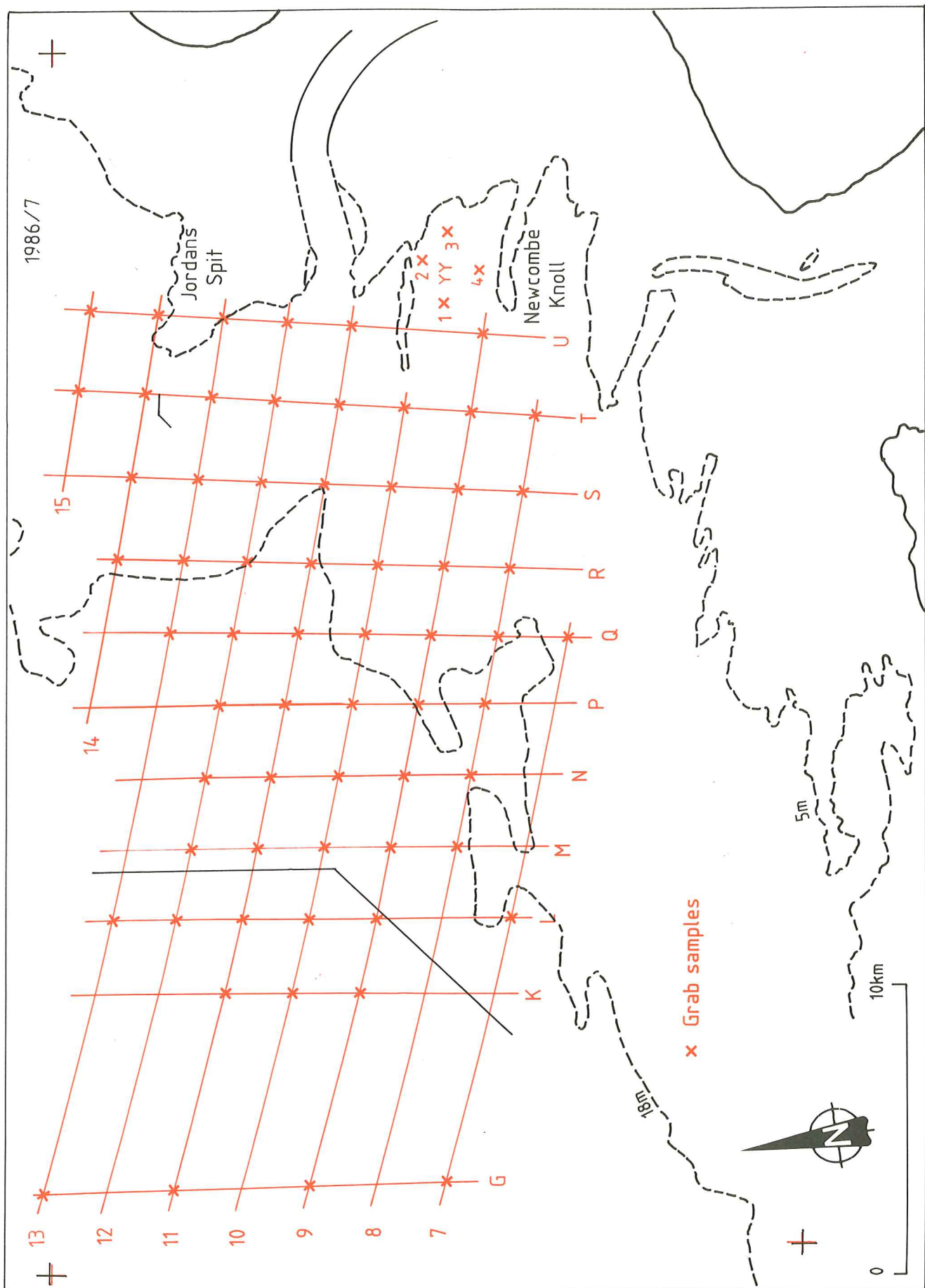


Fig 1 Monitoring positions

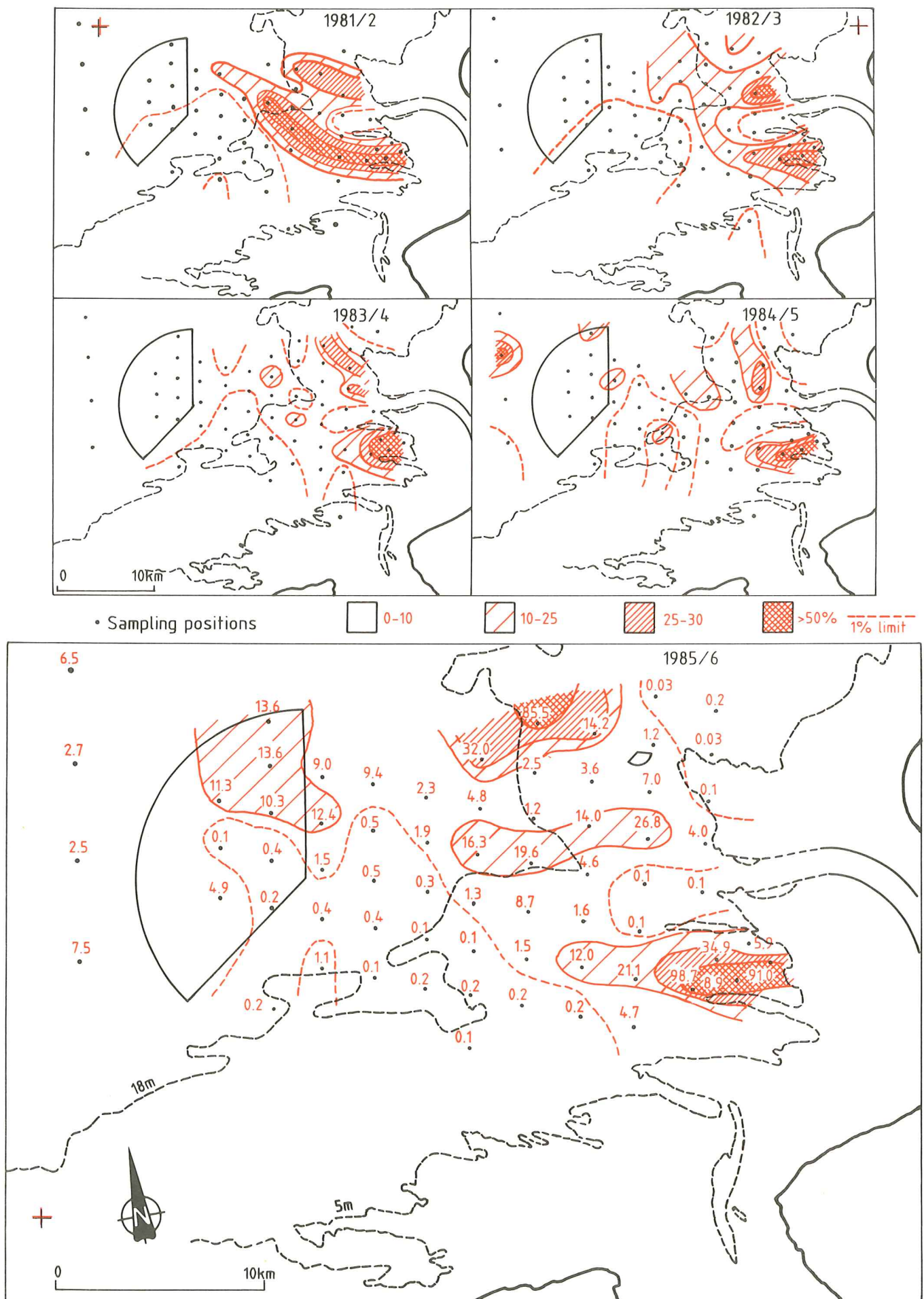


Fig 2 Mud content of the top 25mm of bed

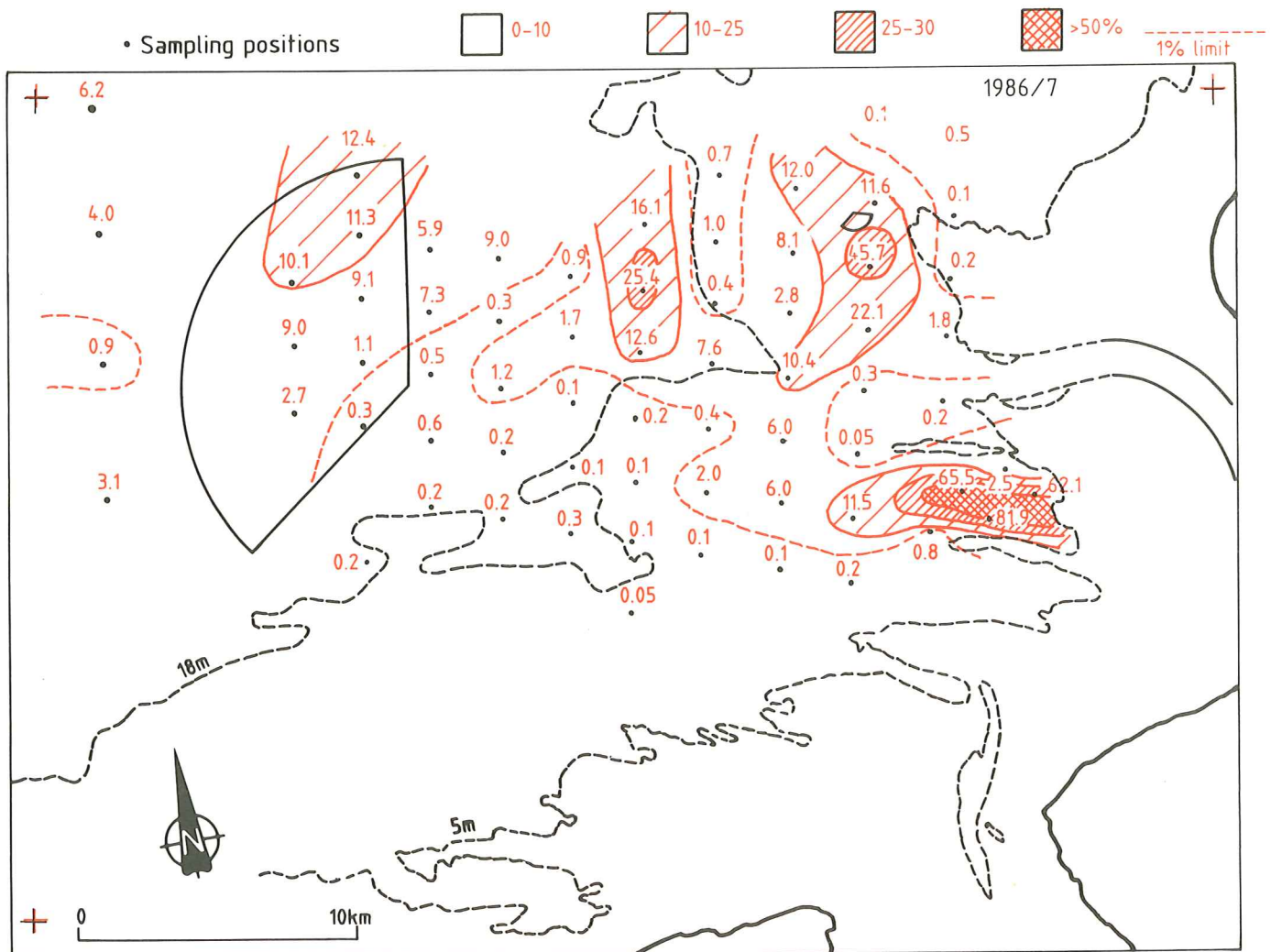


Fig 2 Mud content of the 25mm of bed



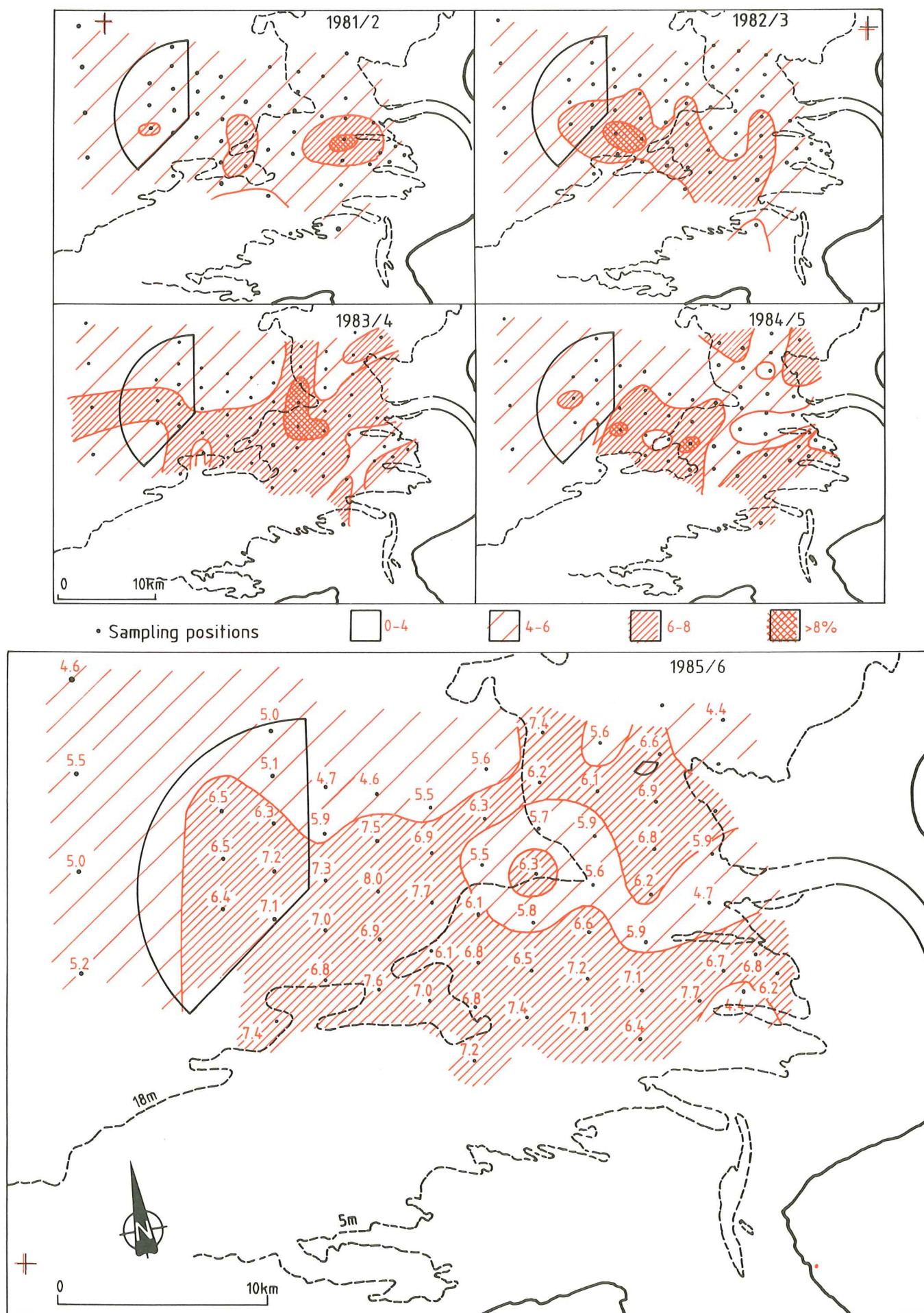


Fig 3 Organic content on the top 25mm of bed

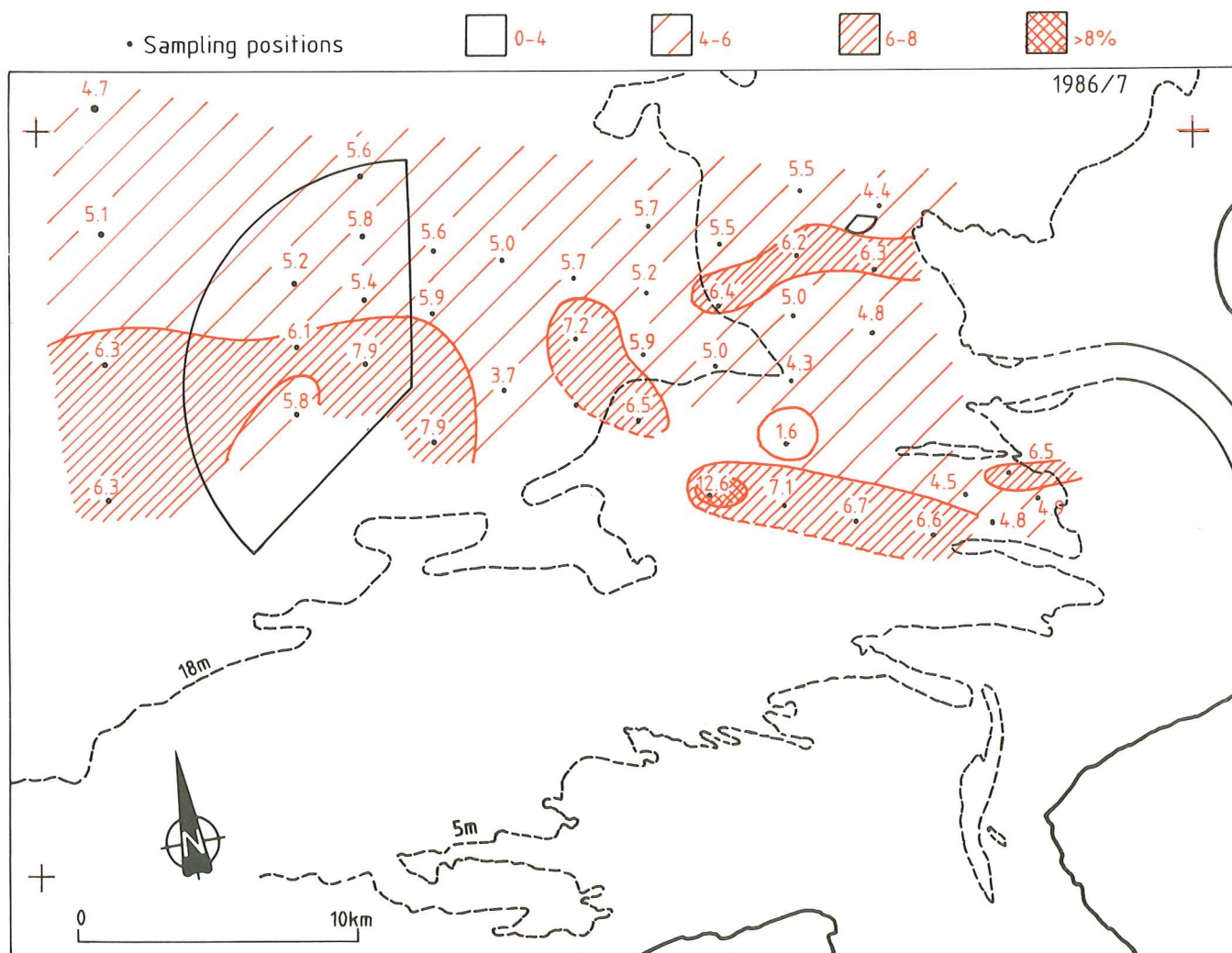
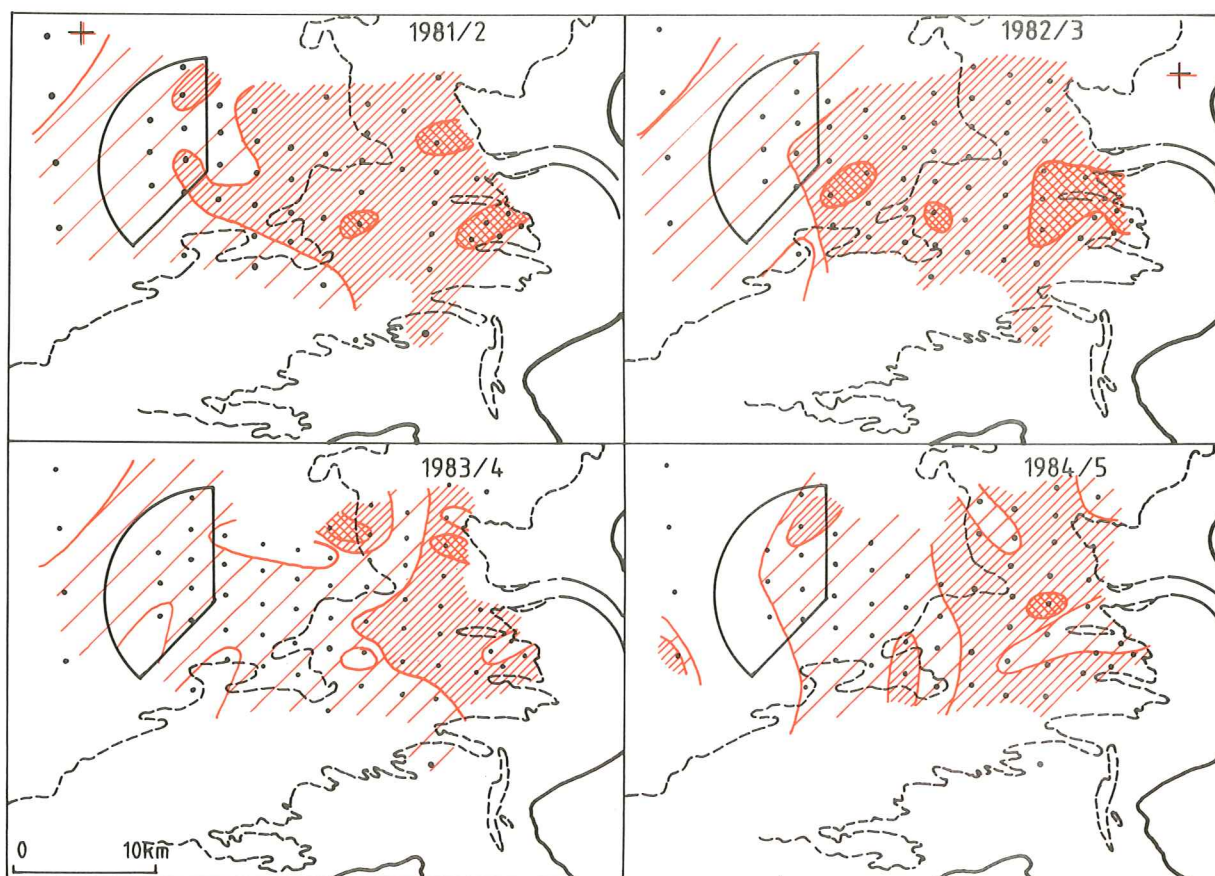


Fig 3 Organic content on the 25mm of bed





• Sampling positions

0-1

1-2

2-4

>4 µg/g

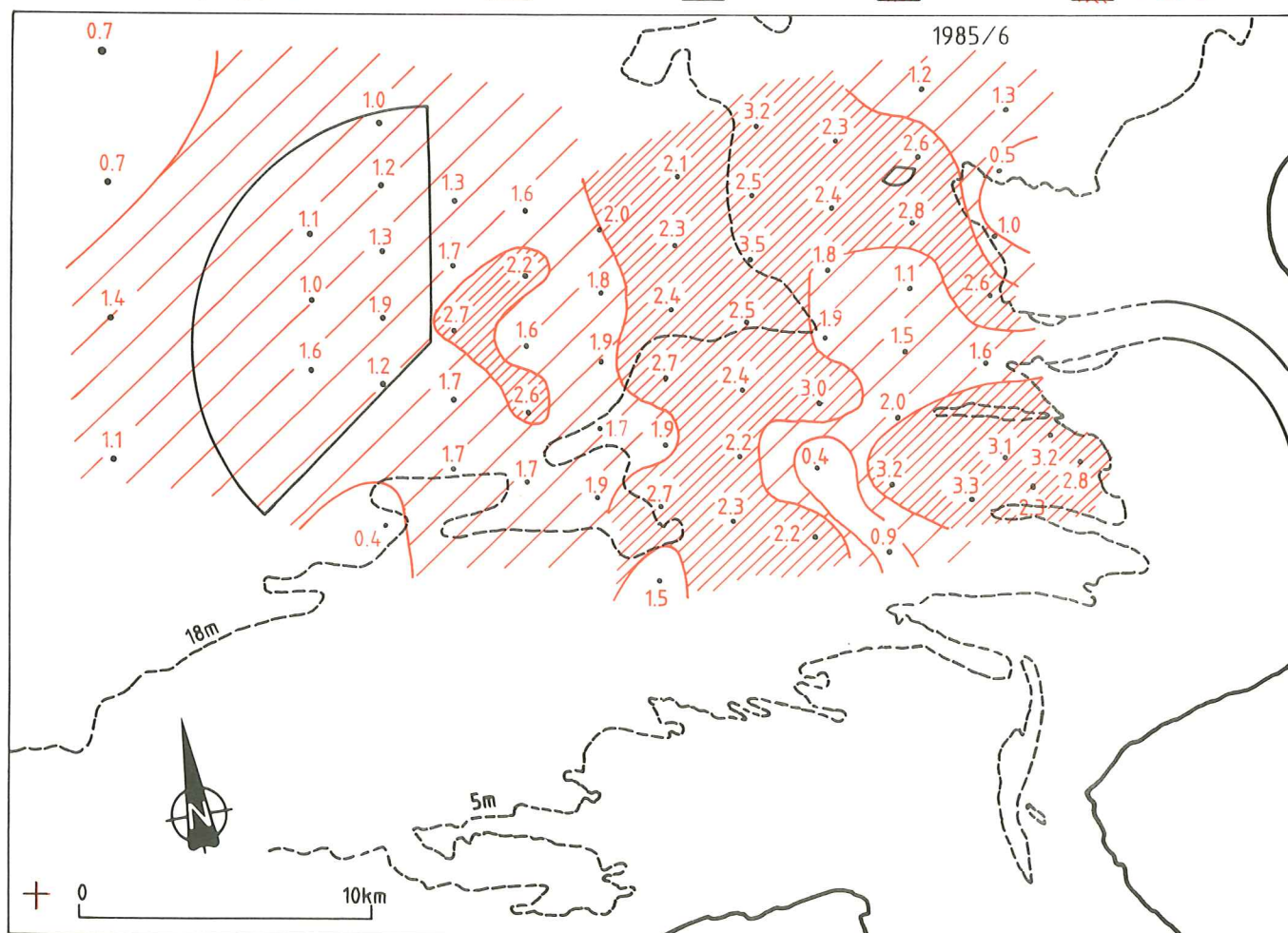


Fig 4 Mercury concentration in mud from the top 25mm of bed





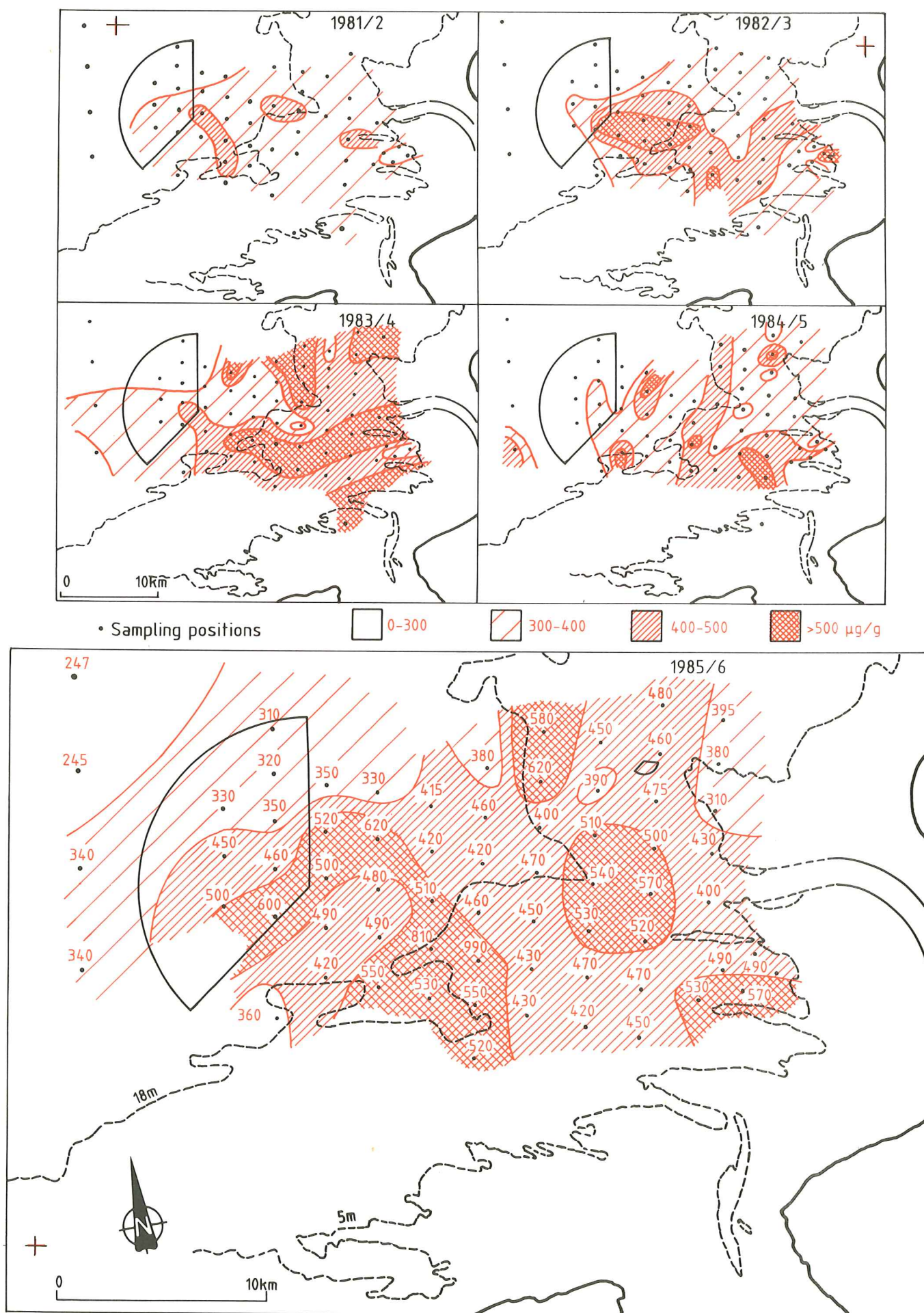


Fig 5 Zinc concentration in mud from the top 25mm of bed



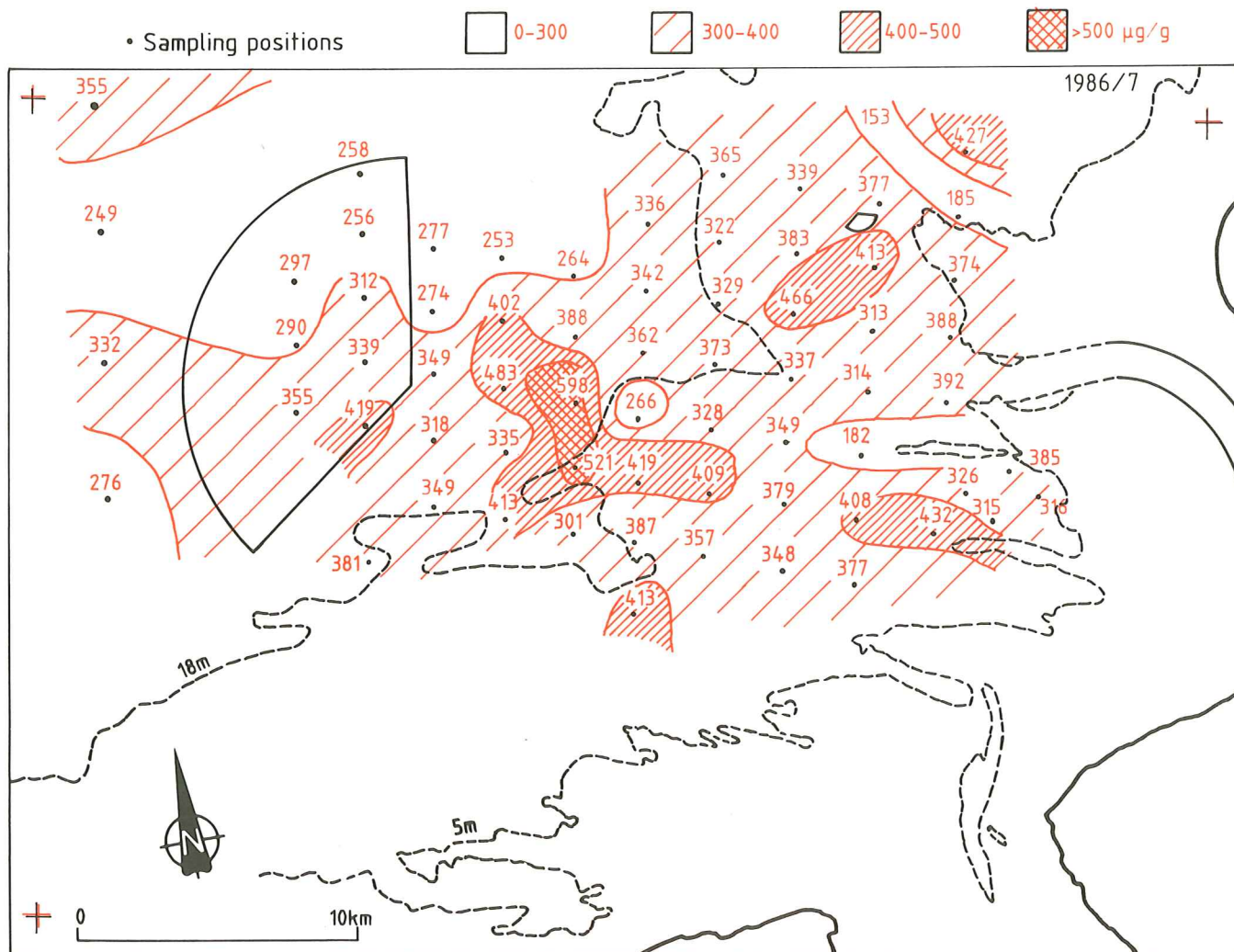


Fig 5 Zinc concentration in mud from the top 25mm of bed



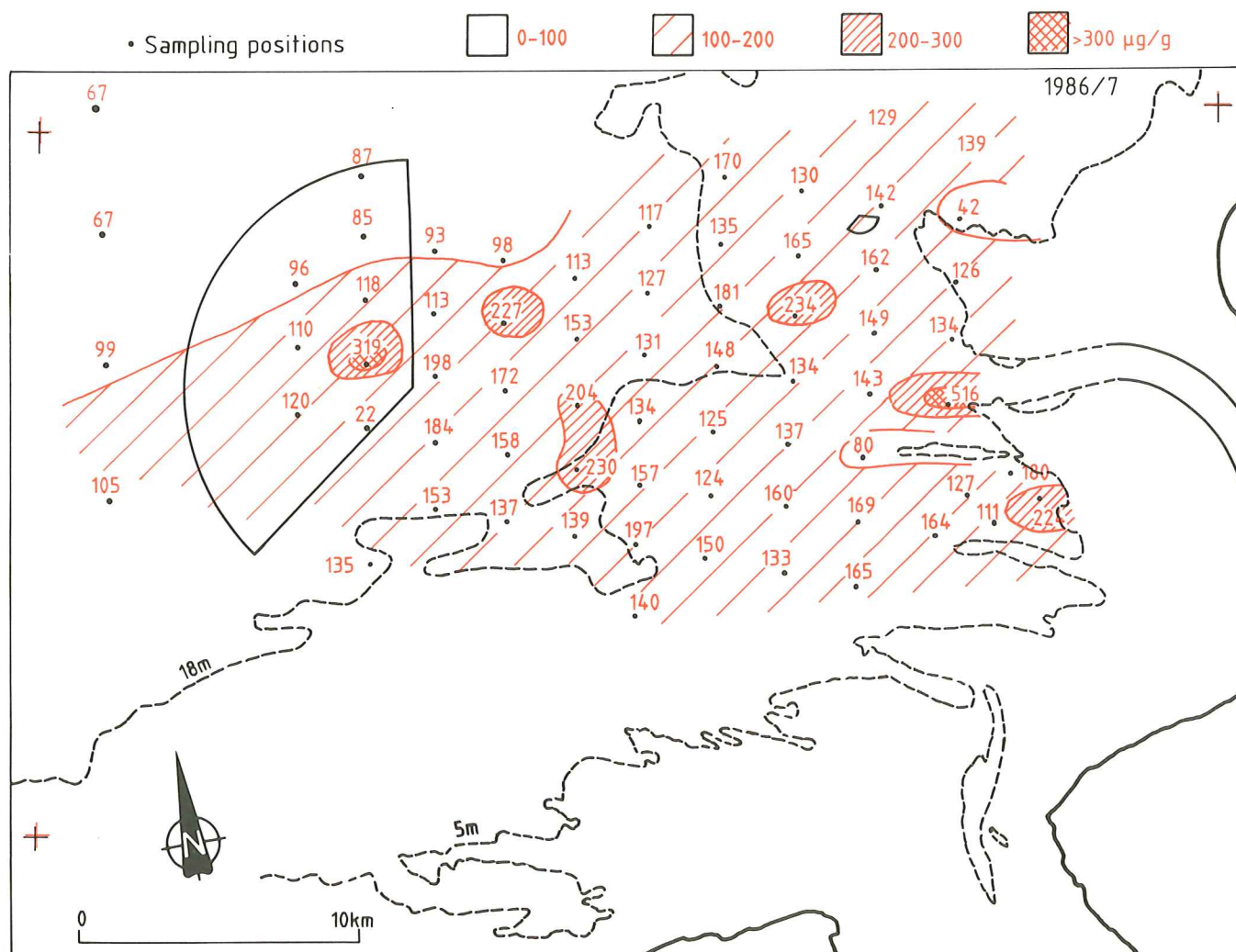


Fig 6 Lead concentration in mud from the top 25mm of bed



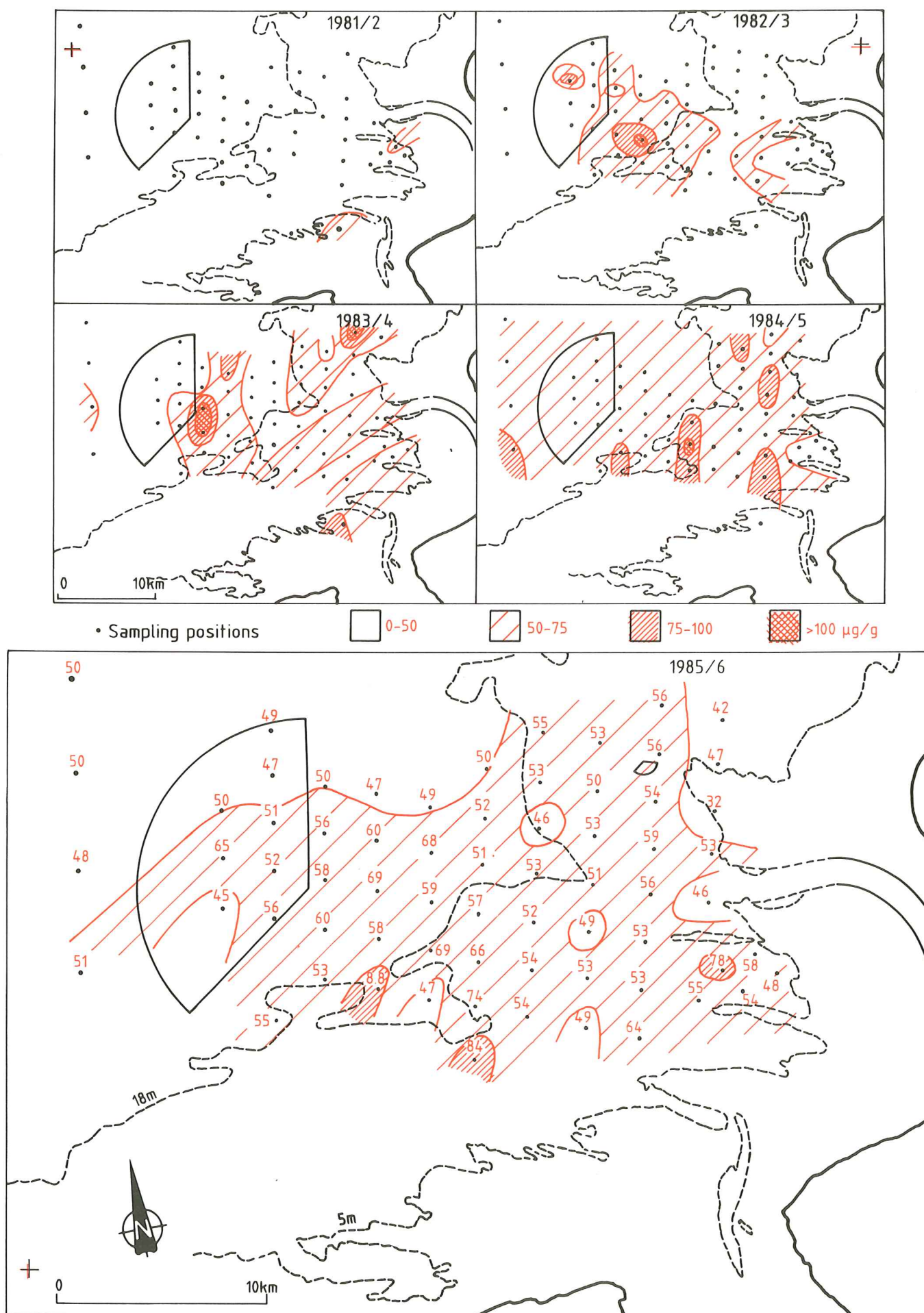


Fig 7 Nickel concentration in mud from the top 25mm of bed

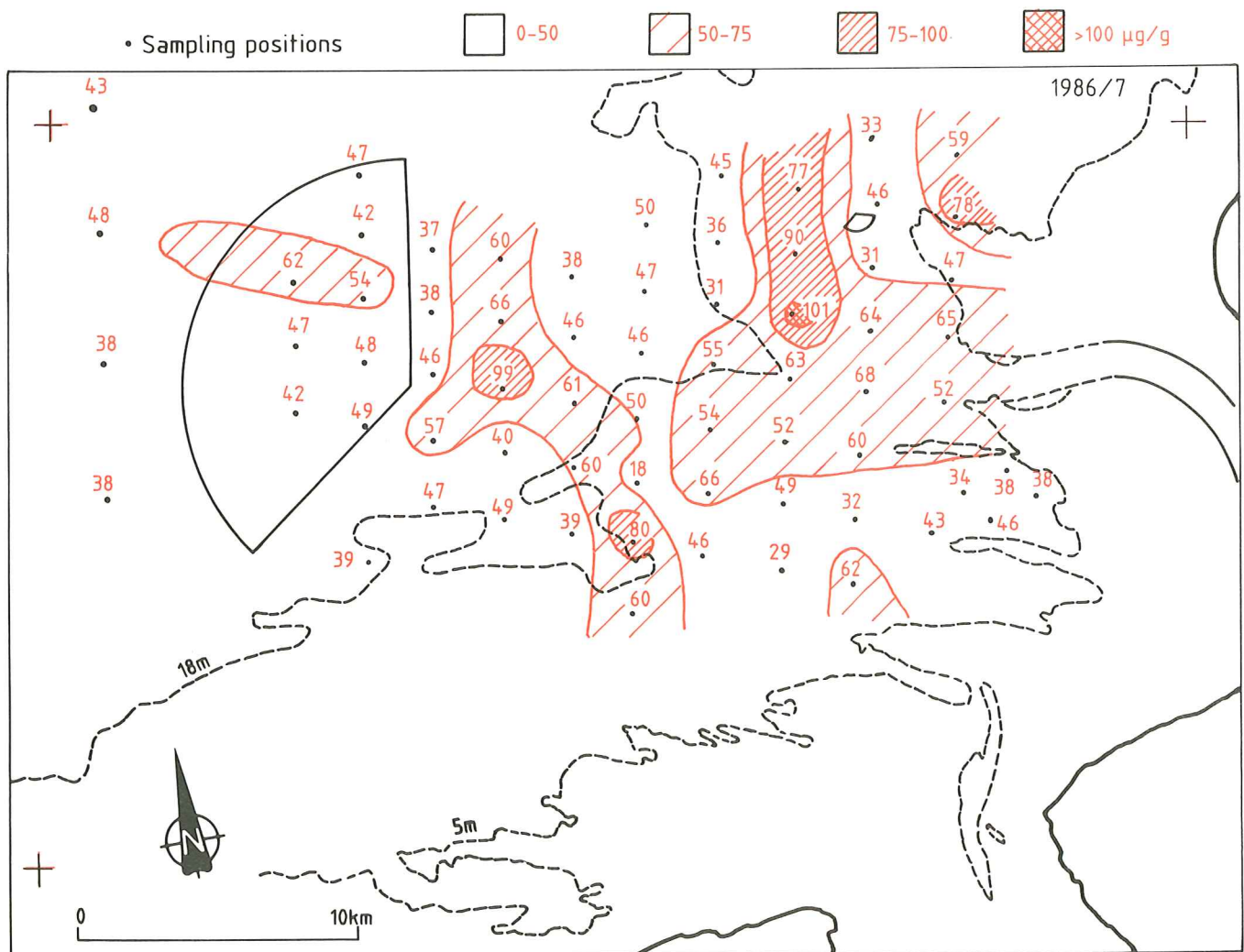


Fig 7 Nickel concentration in mud from the top 25mm of bed

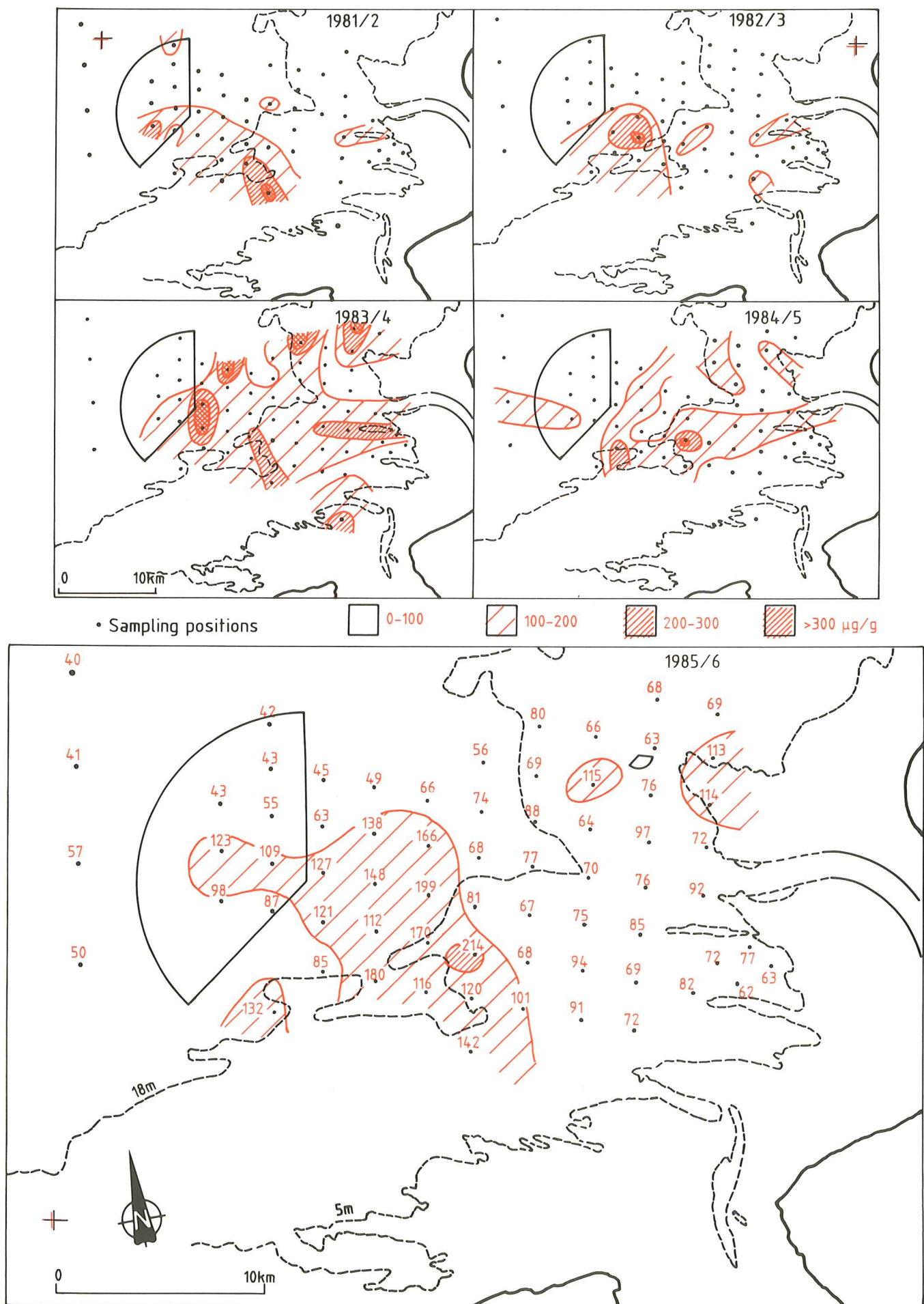


Fig 8 Copper concentration in mud from the top 25mm of bed



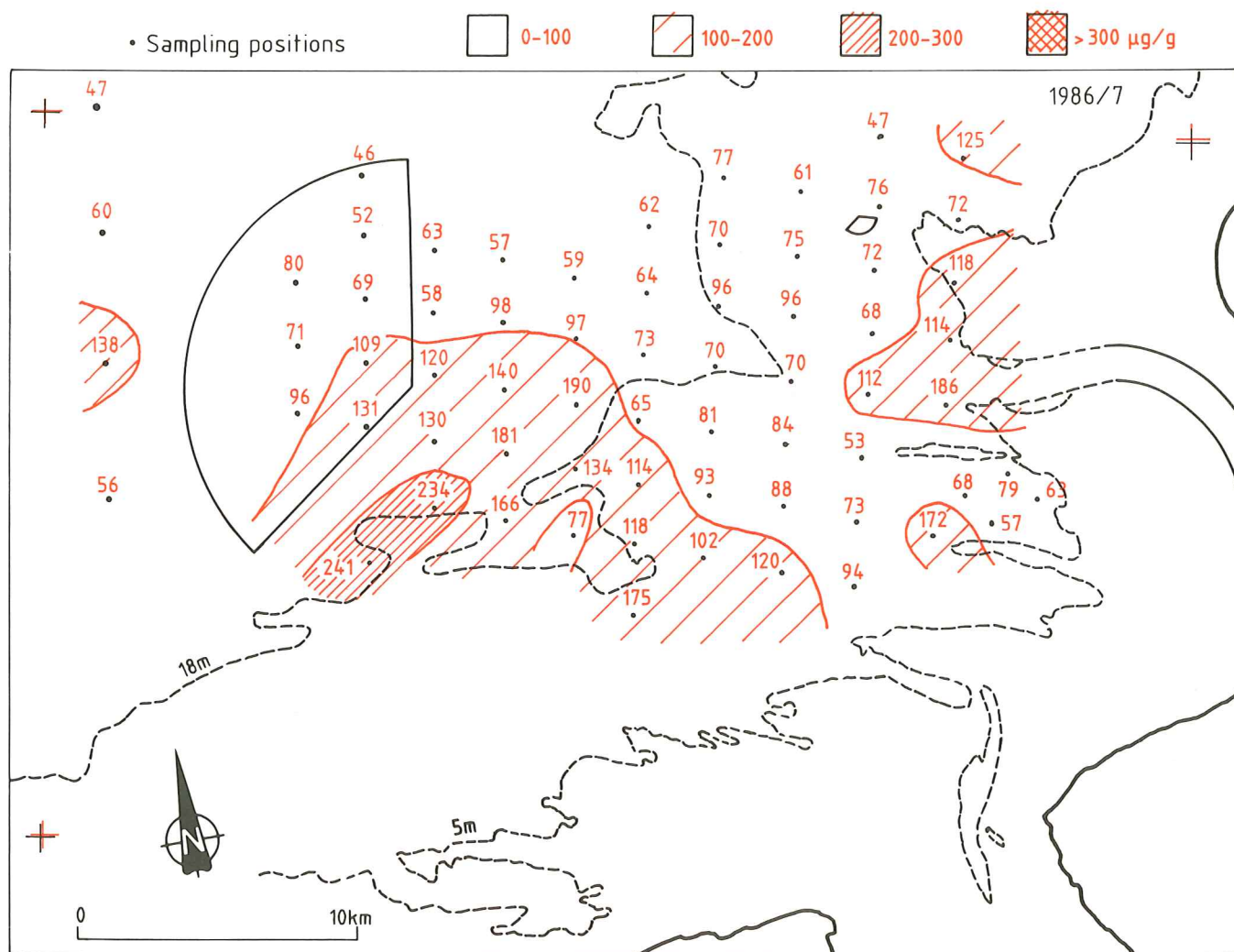


Fig 8 Copper concentration in mud from the top 25mm of bed





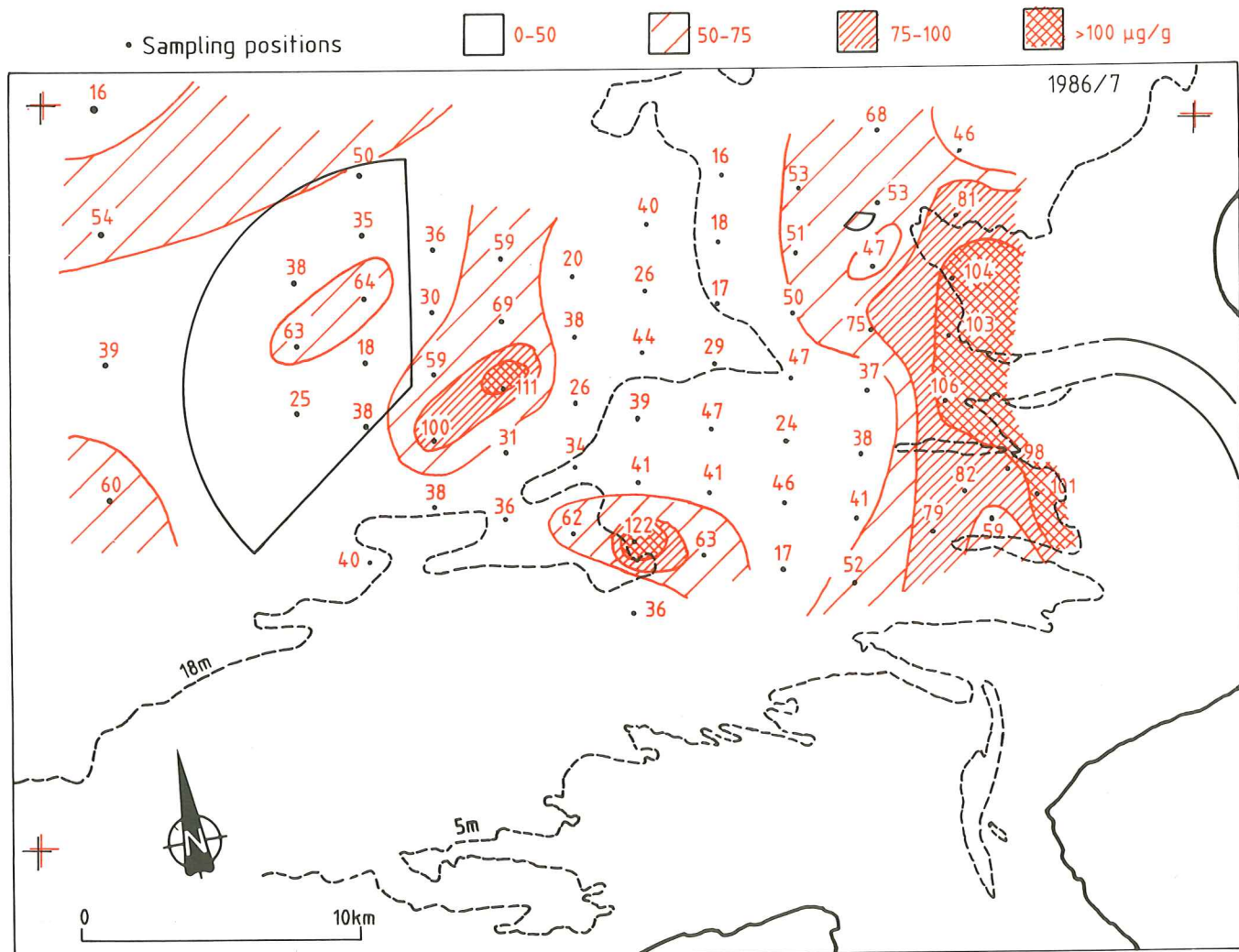


Fig 9 Chromium concentration in mud from the top 25mm of bed

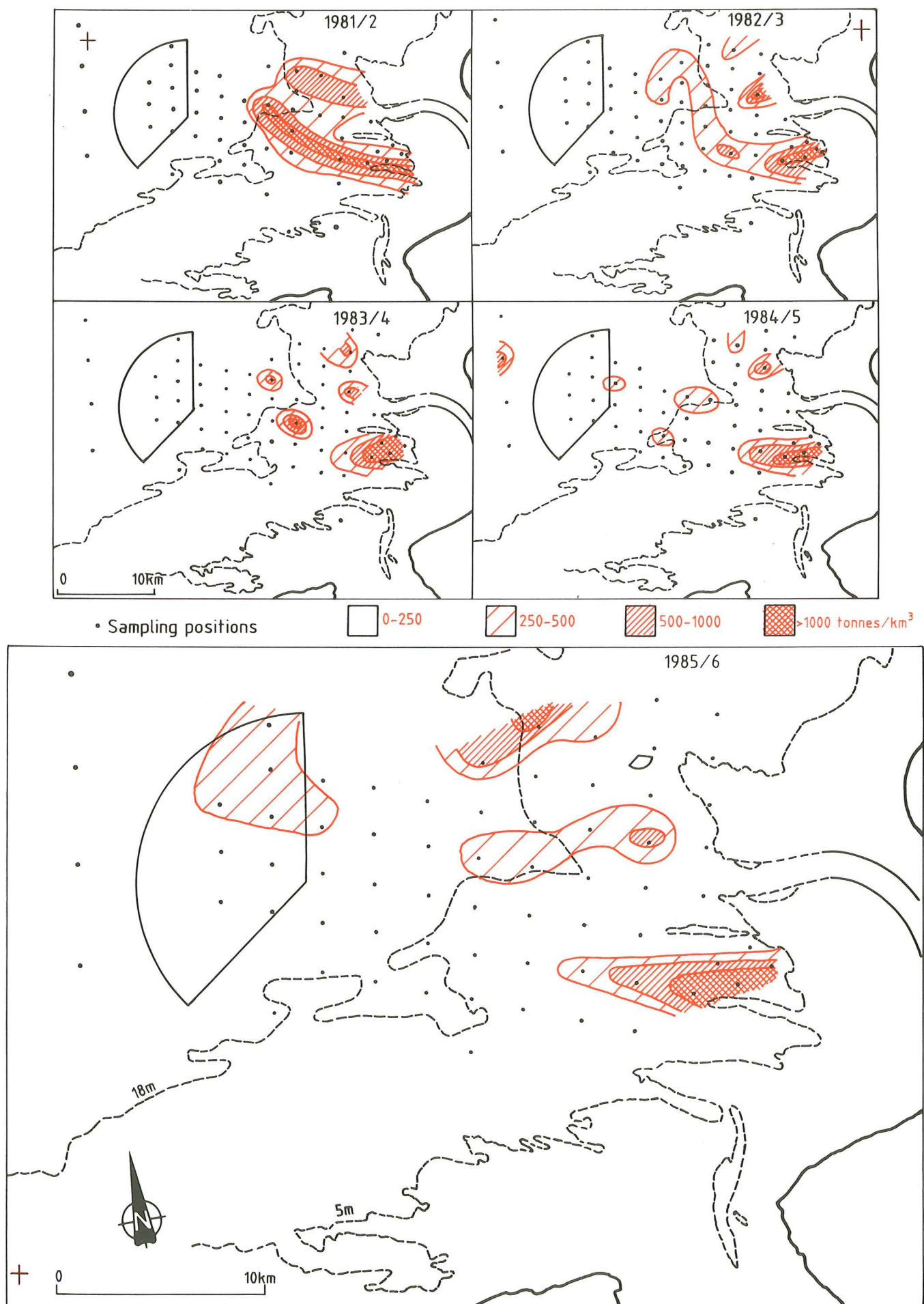


Fig 10 Total organics in mud from the top 25mm of bed

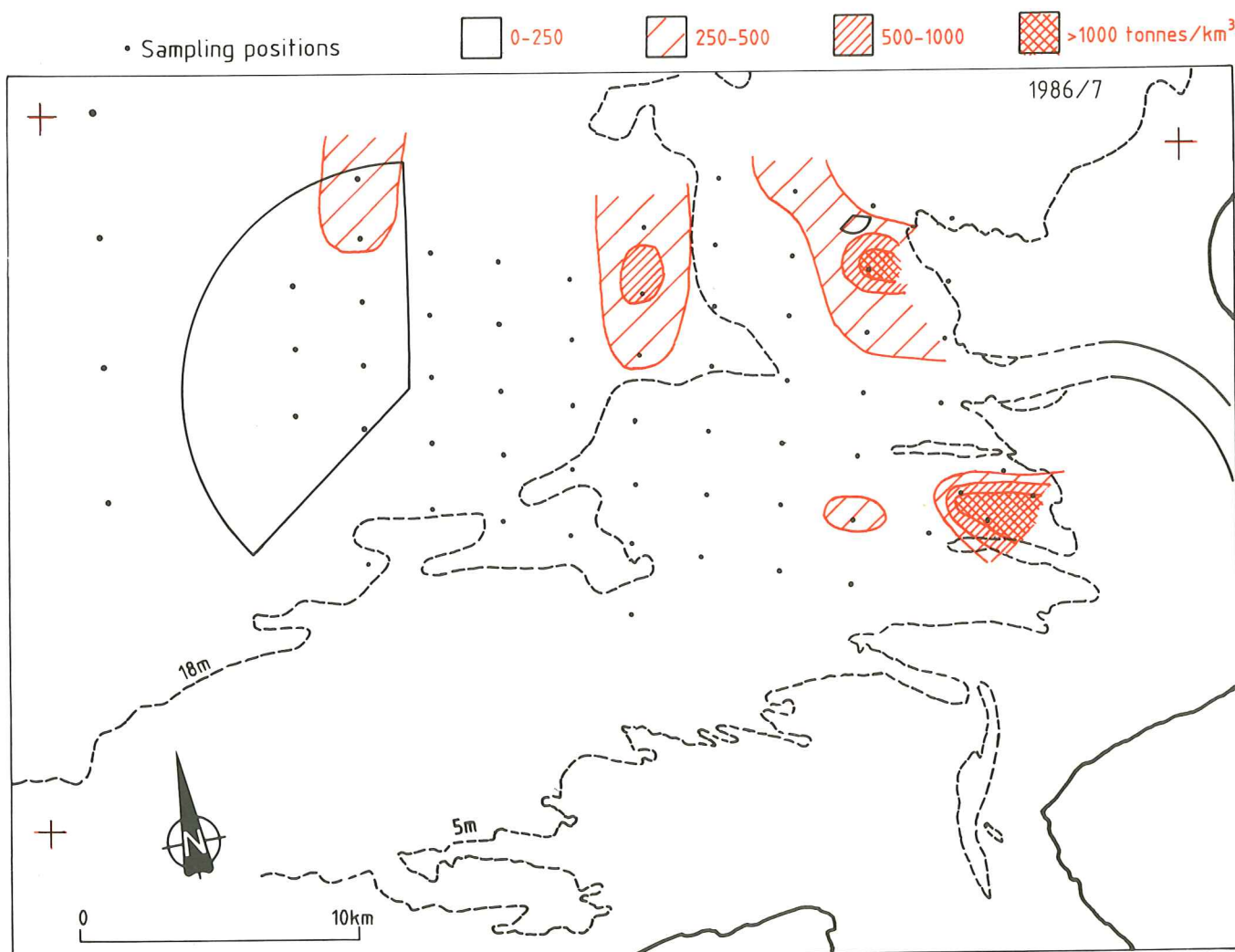
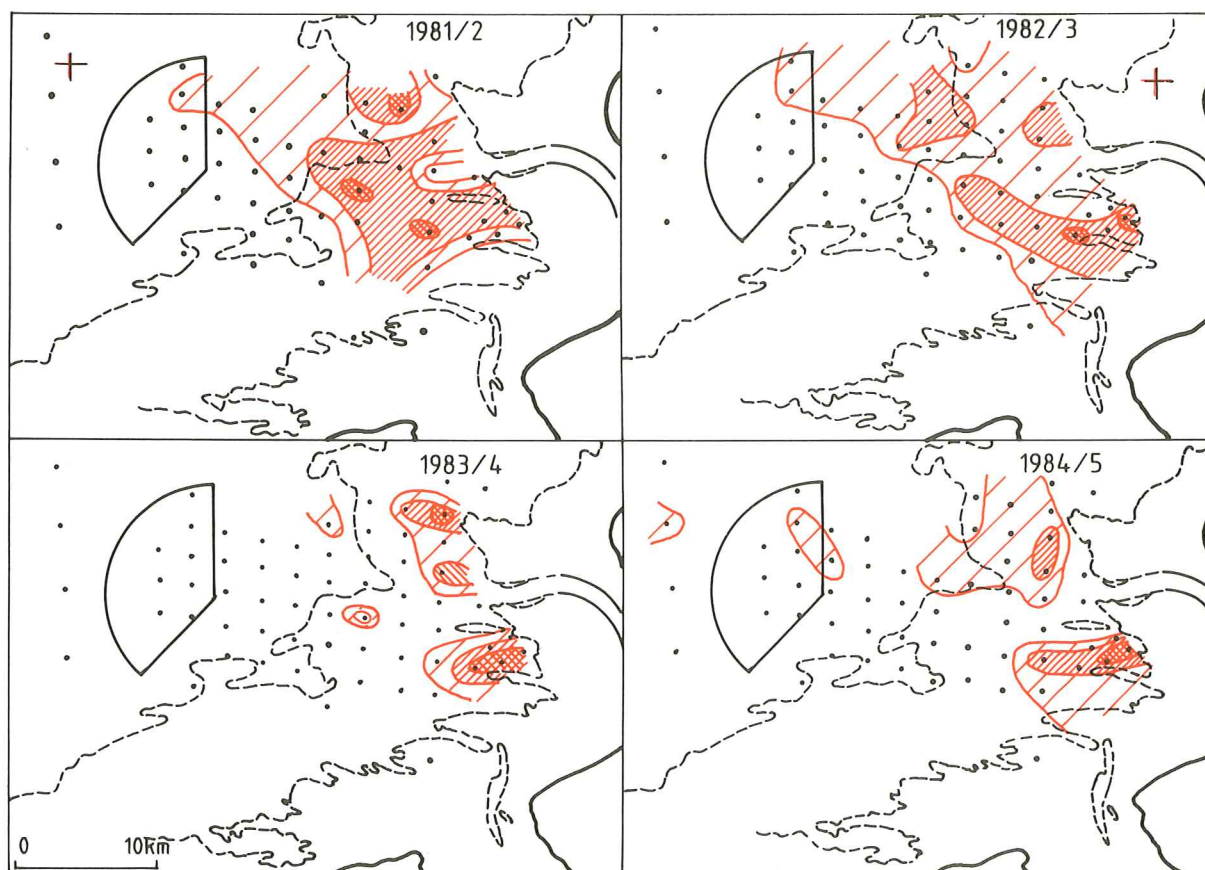


Fig 10 Total organics in mud from the top 25mm of bed



• Sampling positions

0-5

5-20

20-100

>100  $\mu\text{g/g}^2$

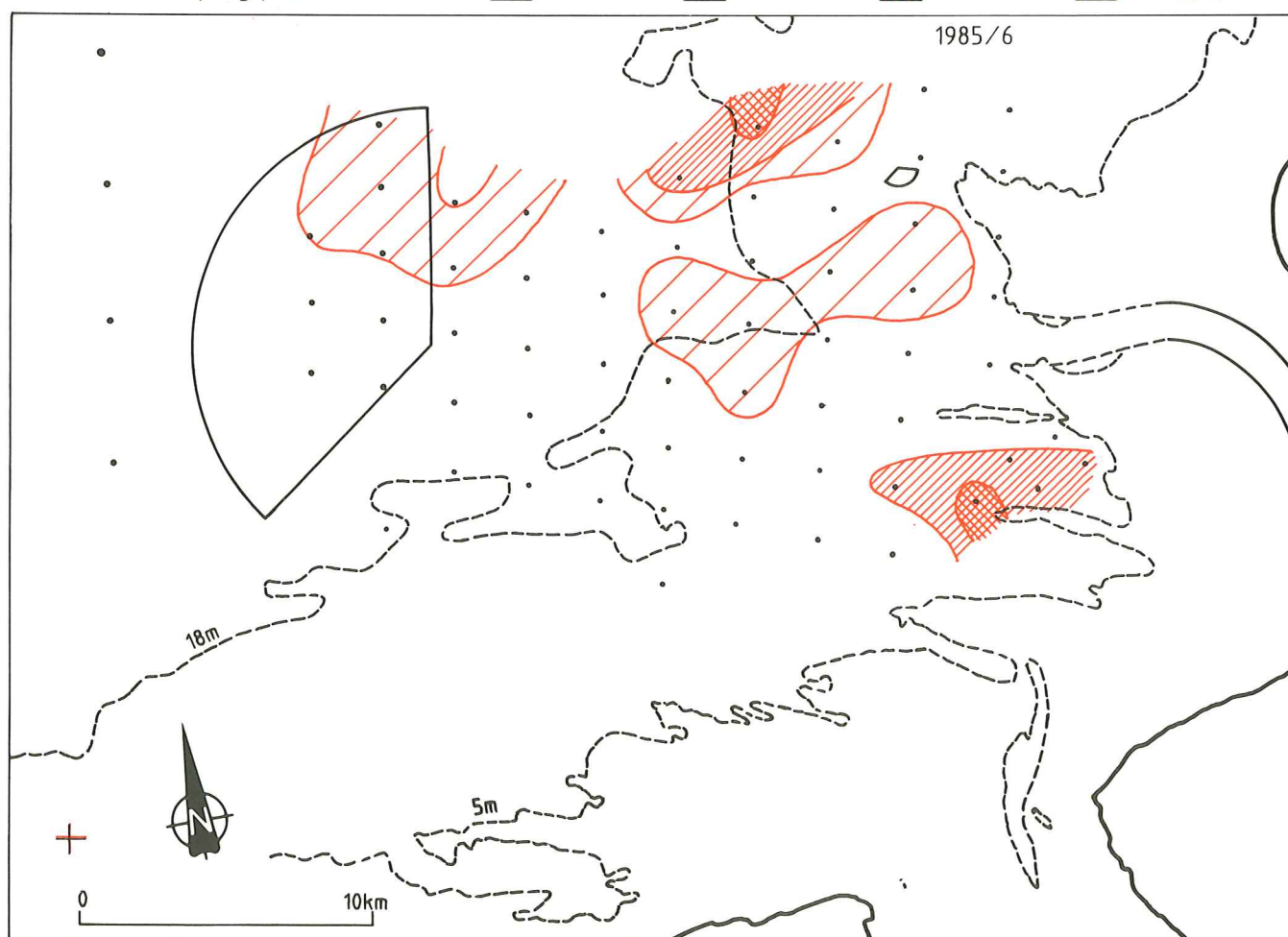


Fig 11 Total mercury in mud from the top 25mm of bed



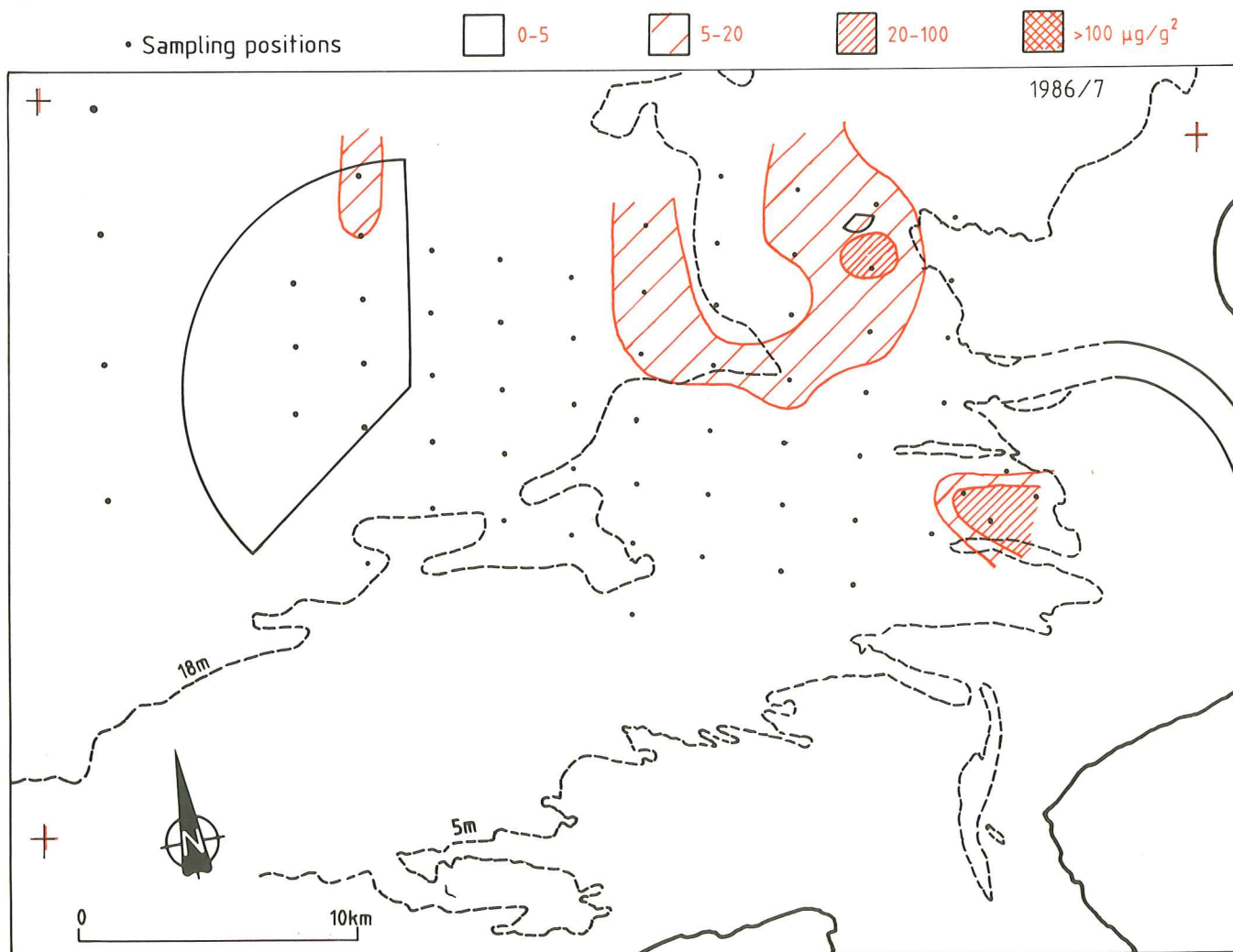


Fig 11 Total mercury in mud from the top 25mm of bed

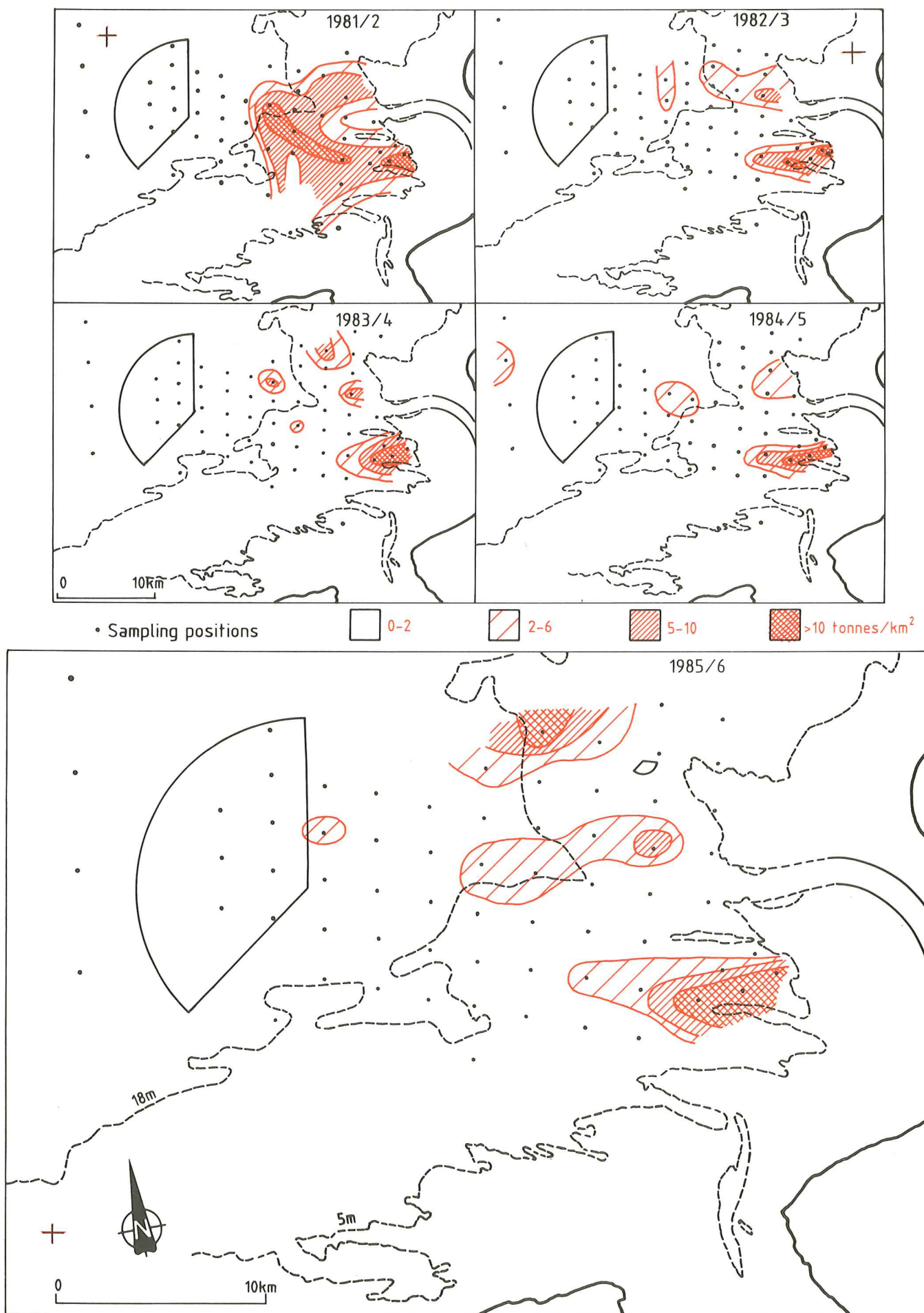


Fig 12 Total zinc in mud from the top 25mm of bed

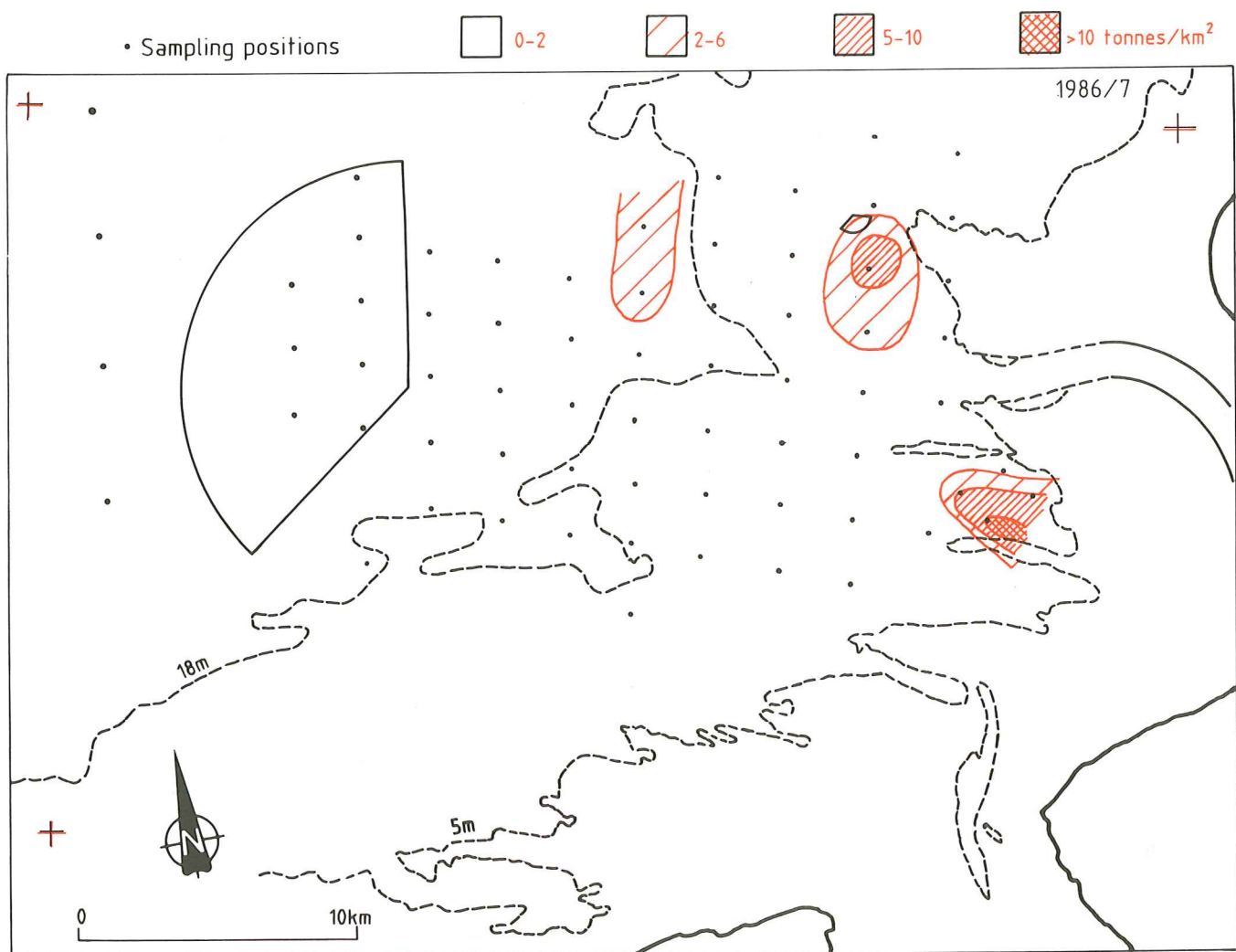


Fig 12 Total zinc in mud from the top 25mm of bed

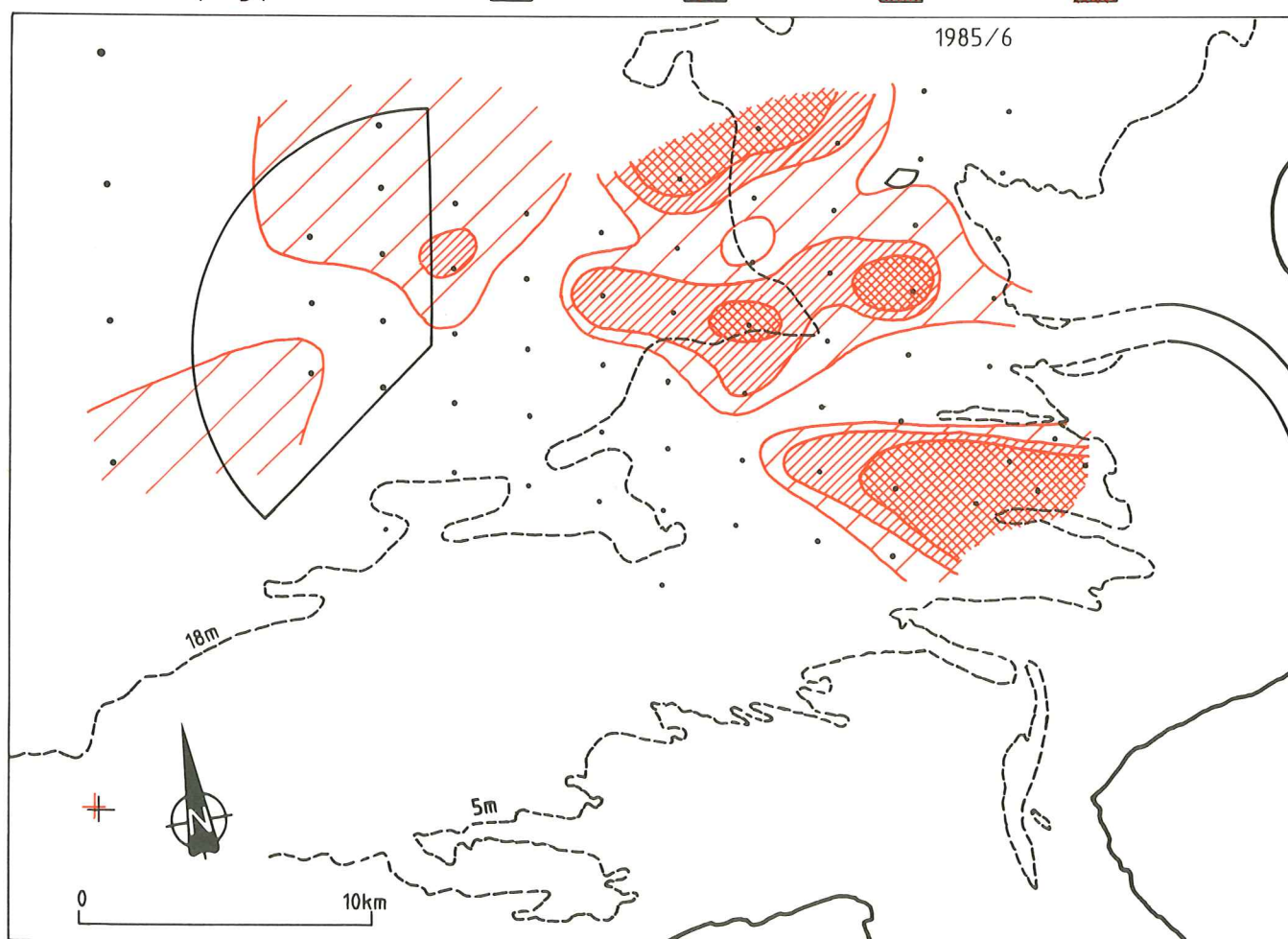
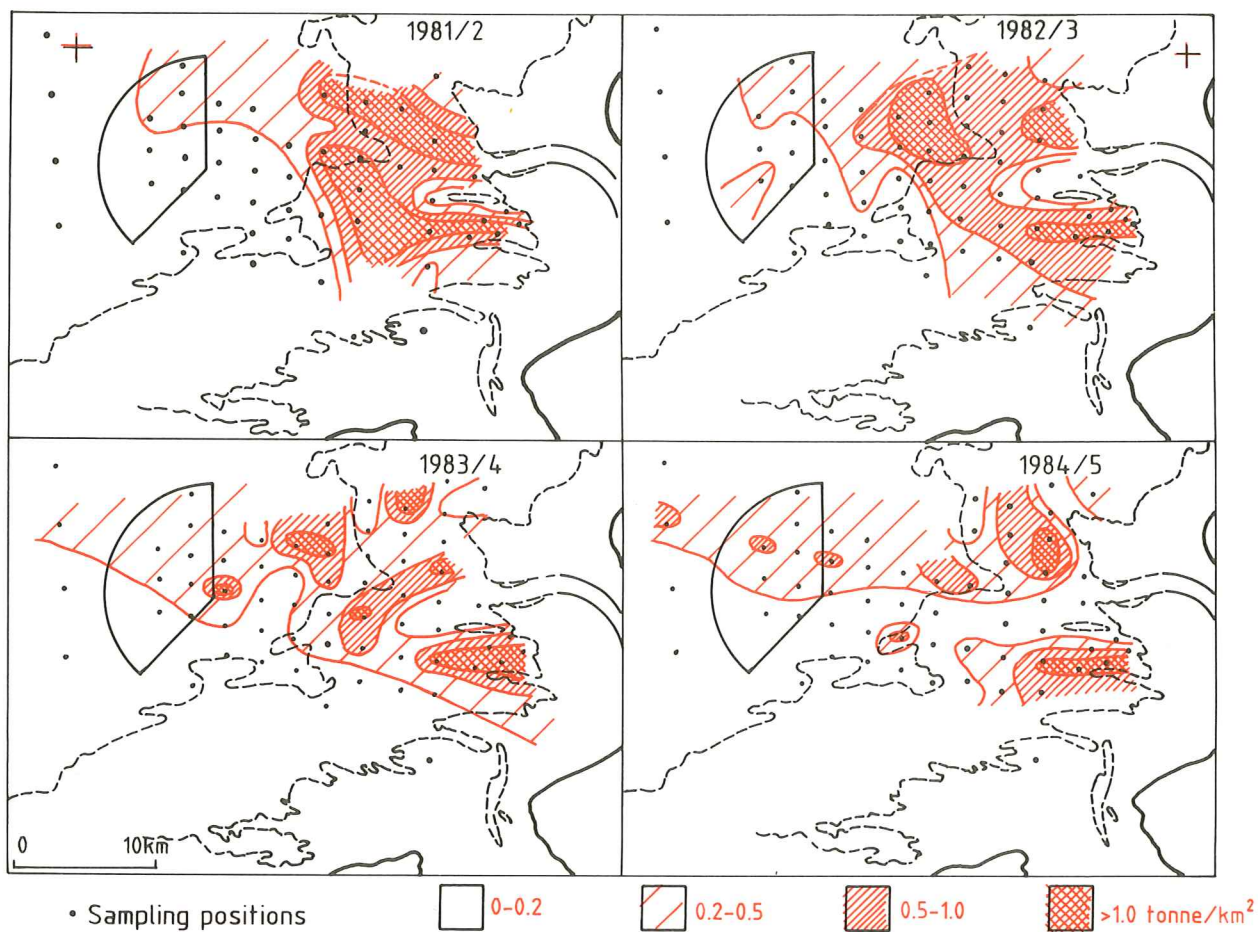


Fig 13 Total lead in mud from the top 25mm of bed



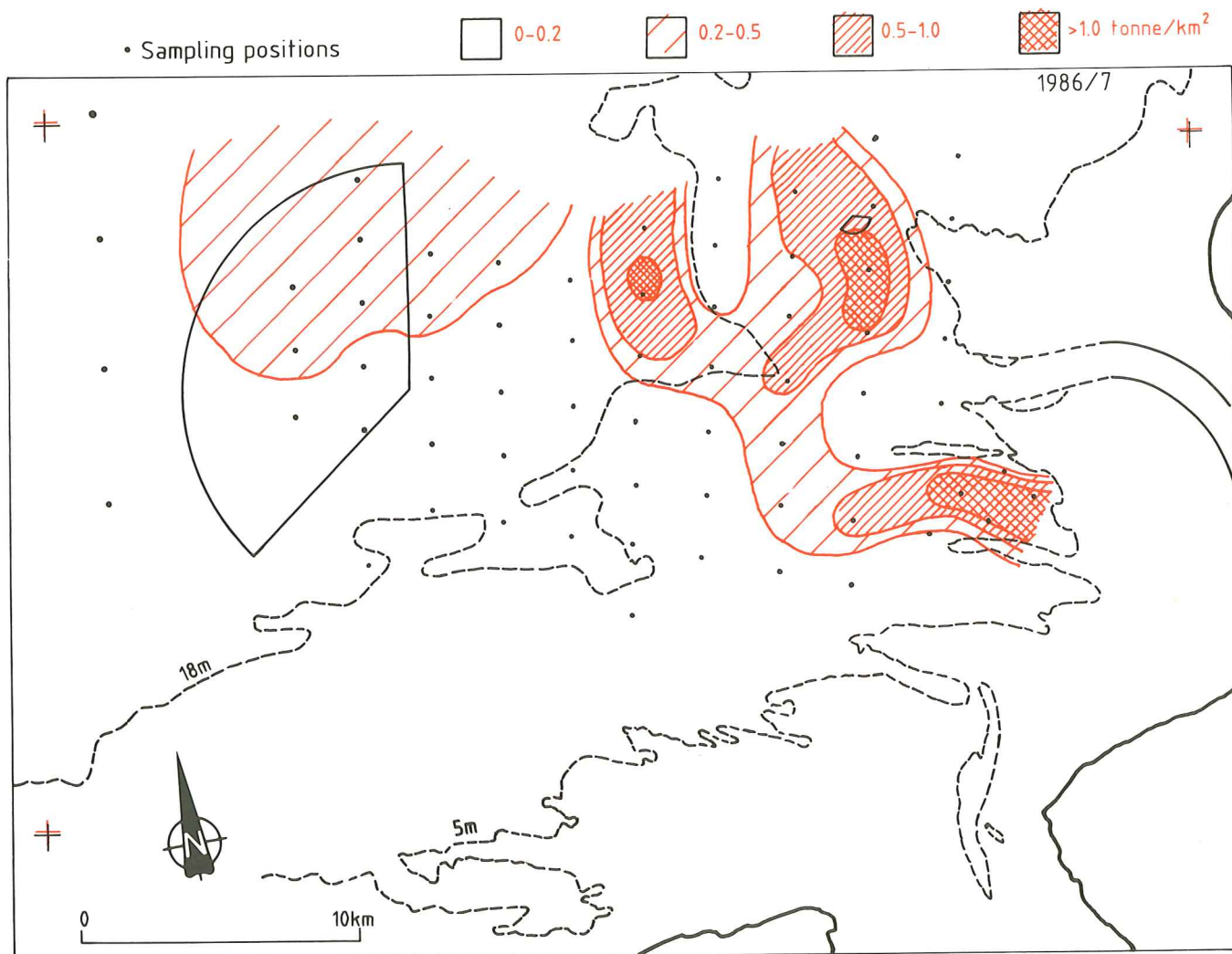
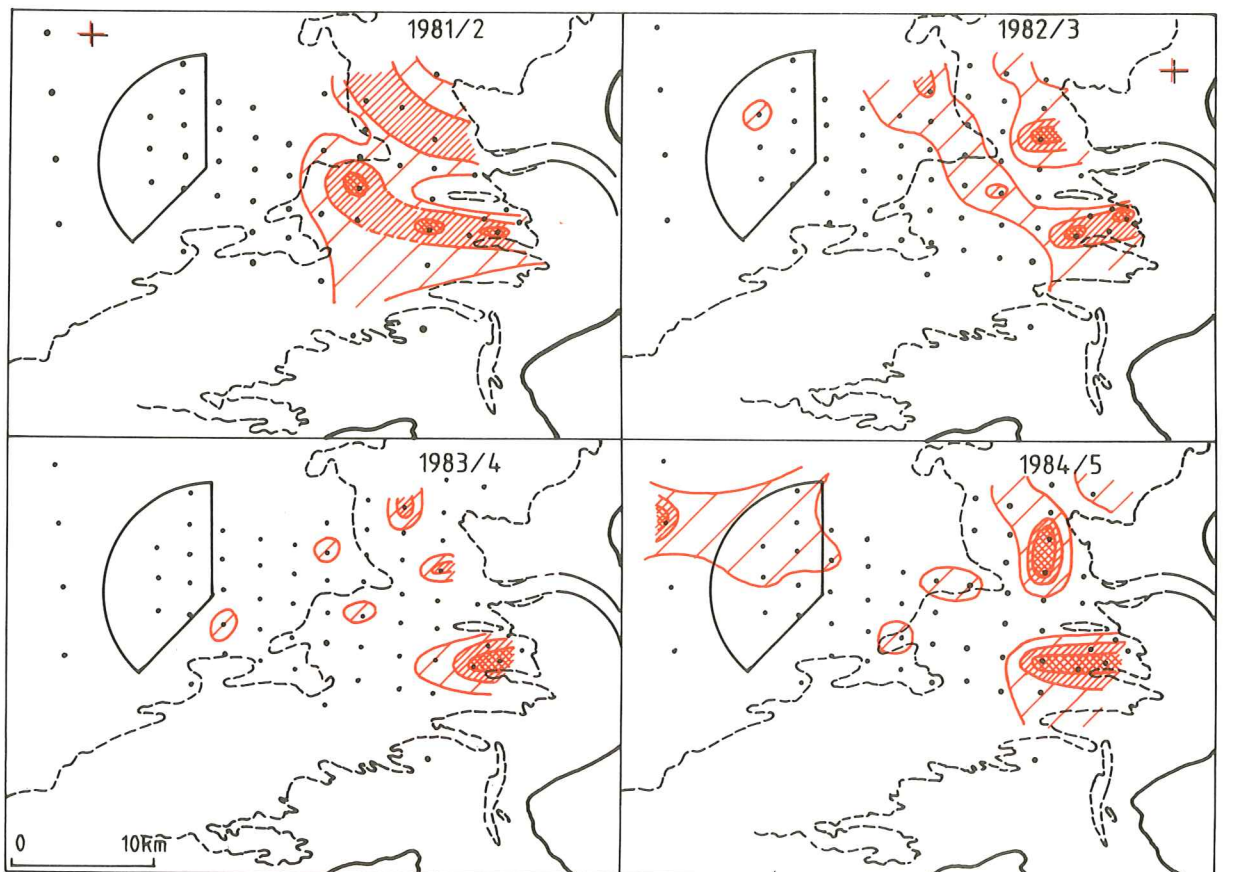


Fig 13 Total lead in mud from the top 25mm of bed



• Sampling positions

0-0.2

0.2-0.5

0.5-1.0

>1.0 tonne/km<sup>2</sup>

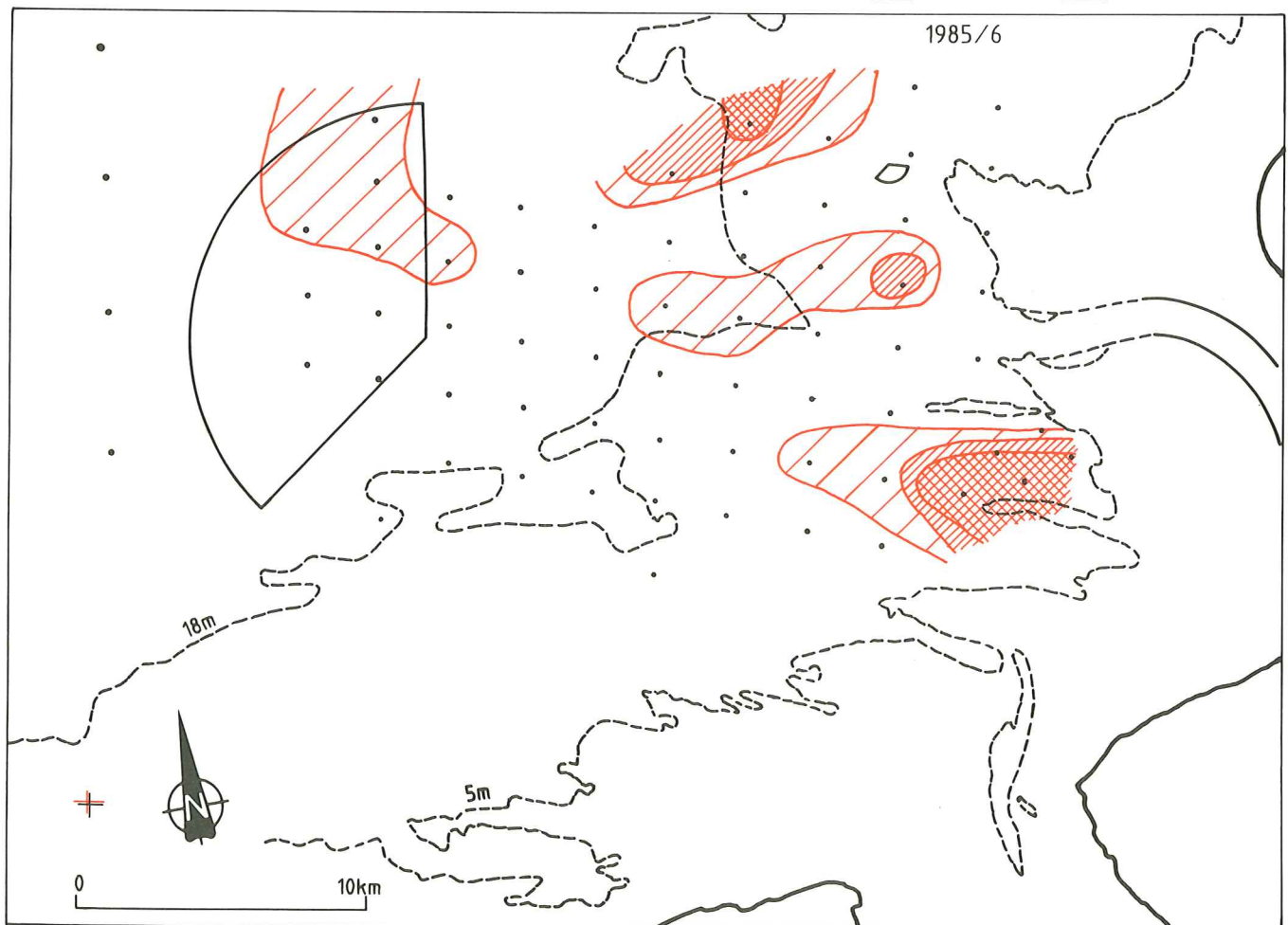


Fig 14 Total nickel in mud from the top 25mm of bed

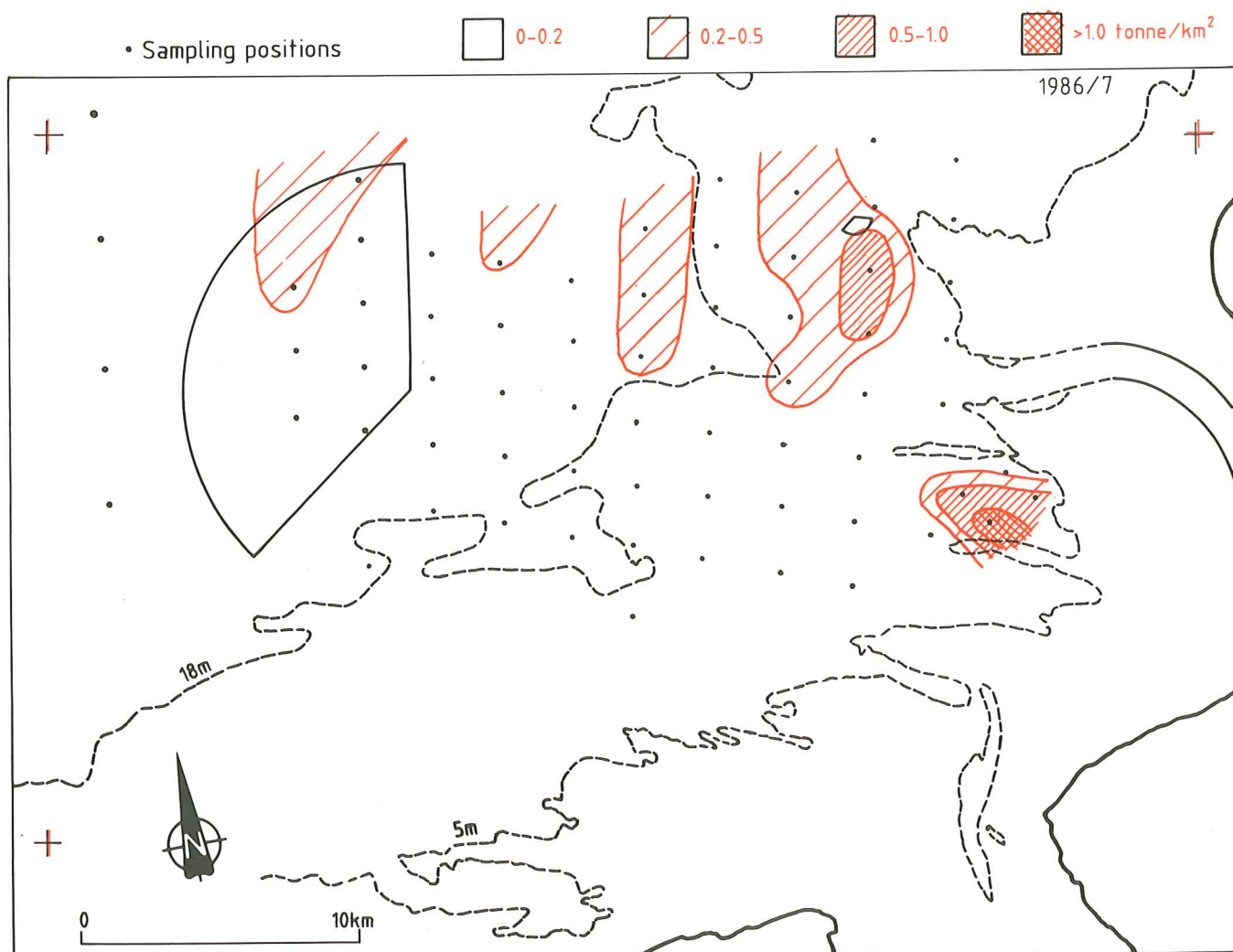


Fig 14 Total nickel in mud from the top 25mm of bed

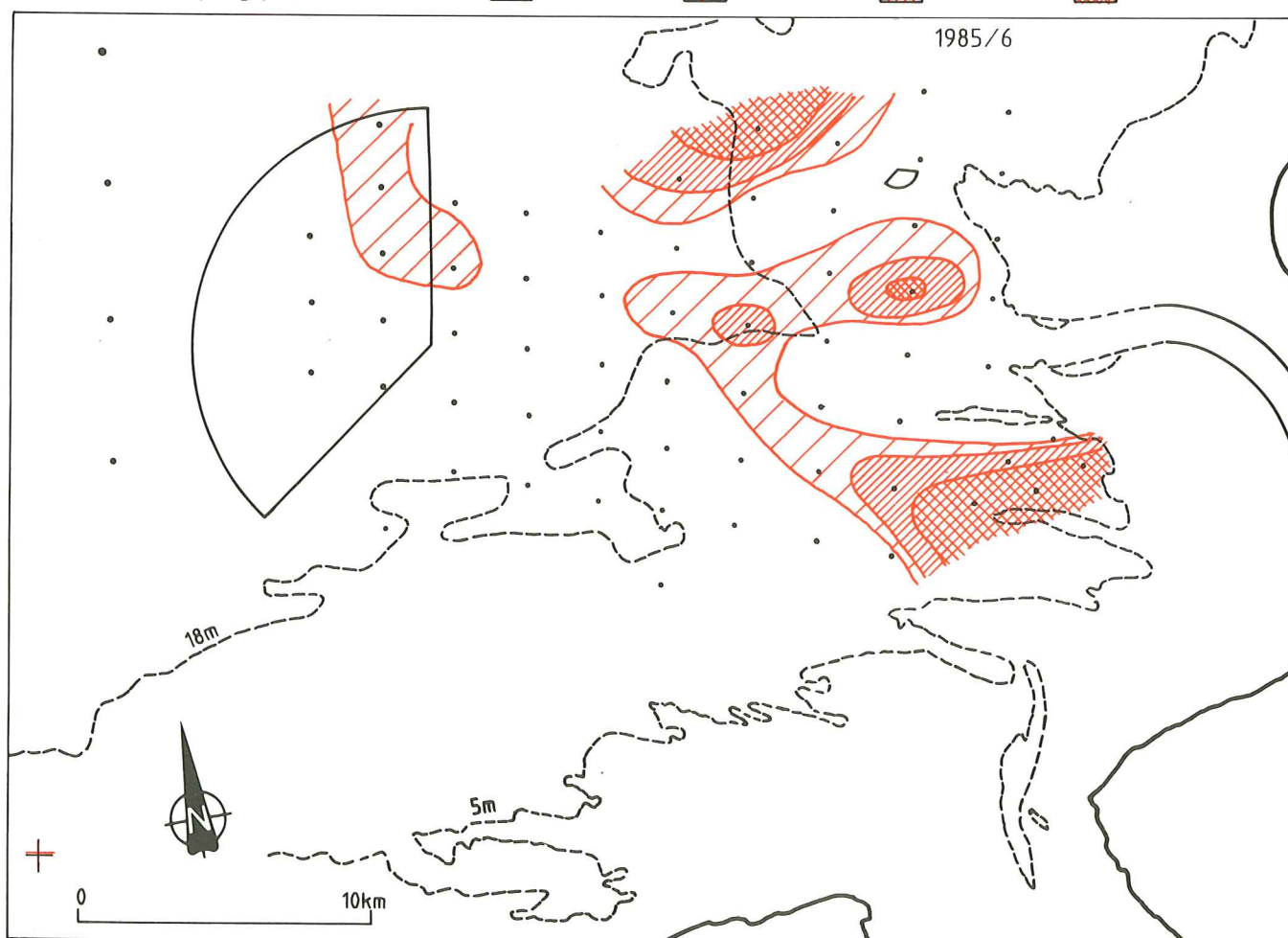
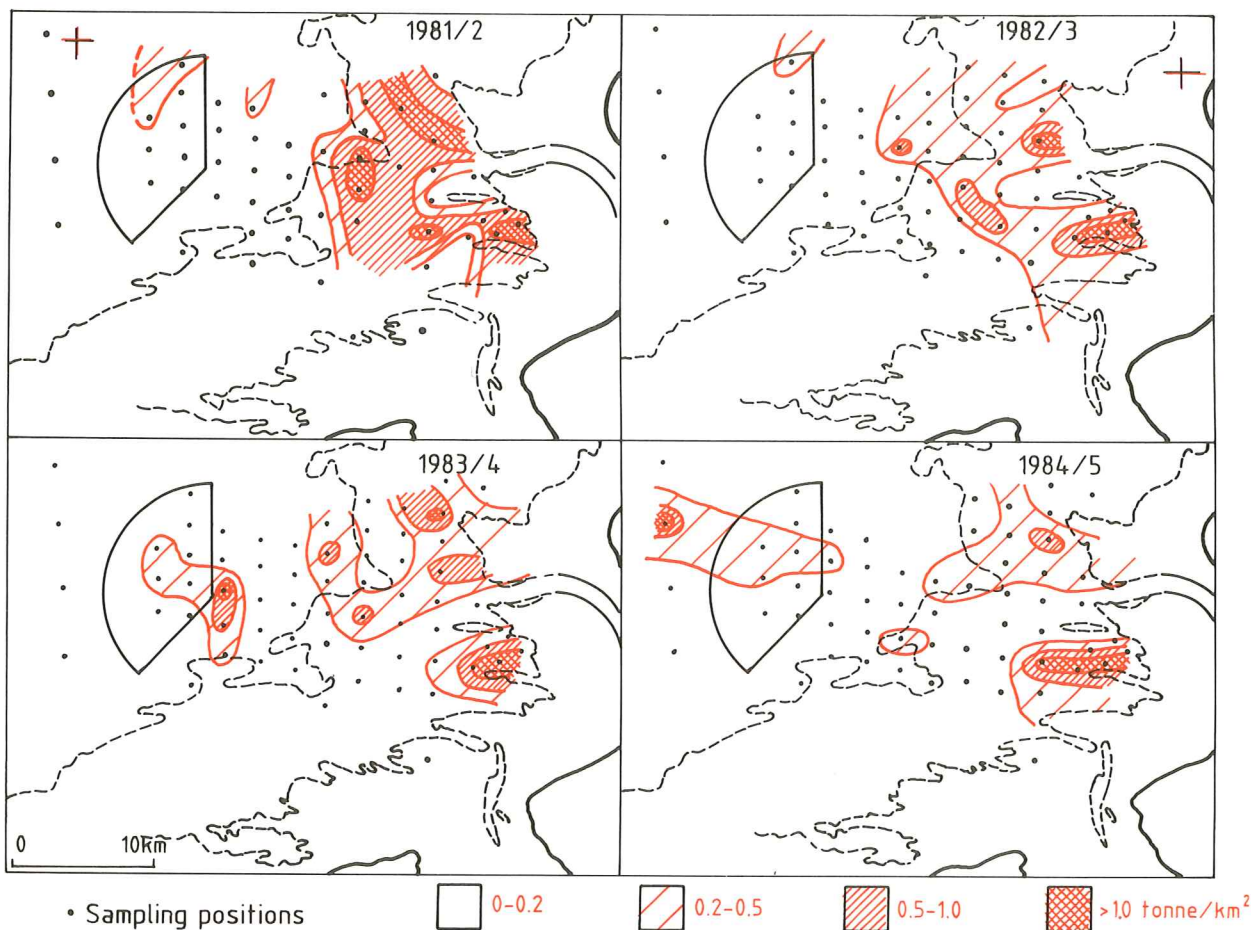


Fig 15 Total copper in mud from the top 25mm of bed



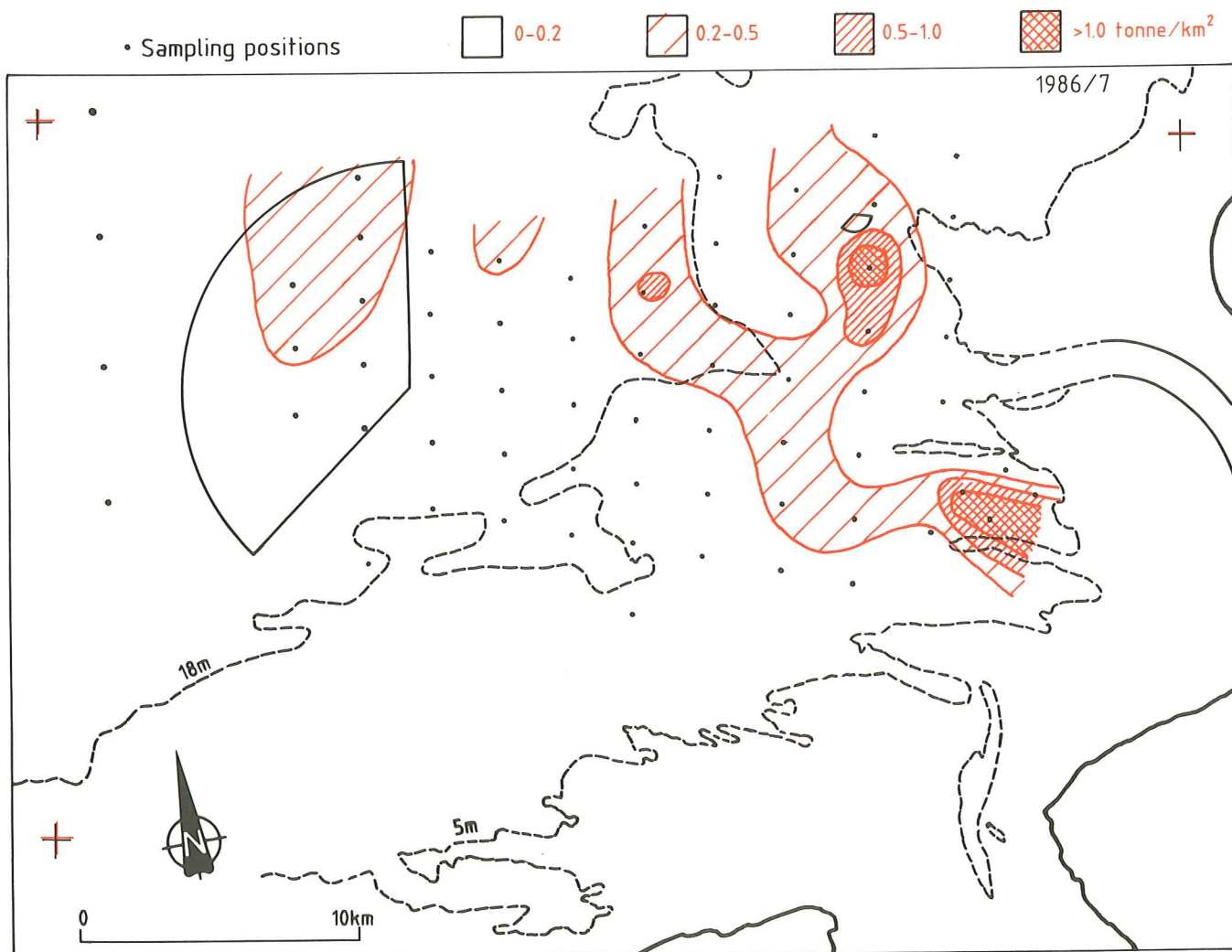


Fig 15    Total copper in mud from the top 25mm of bed

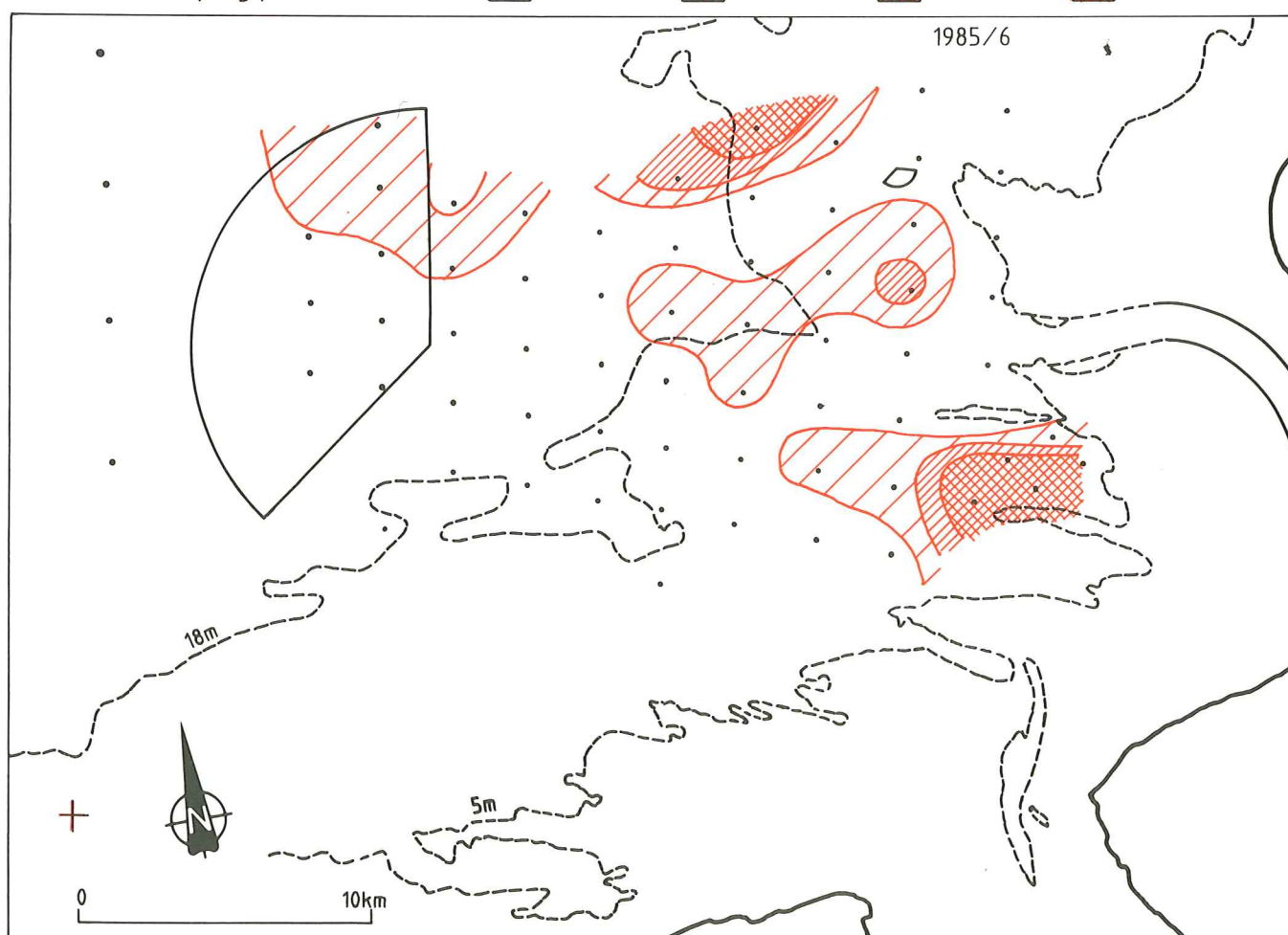
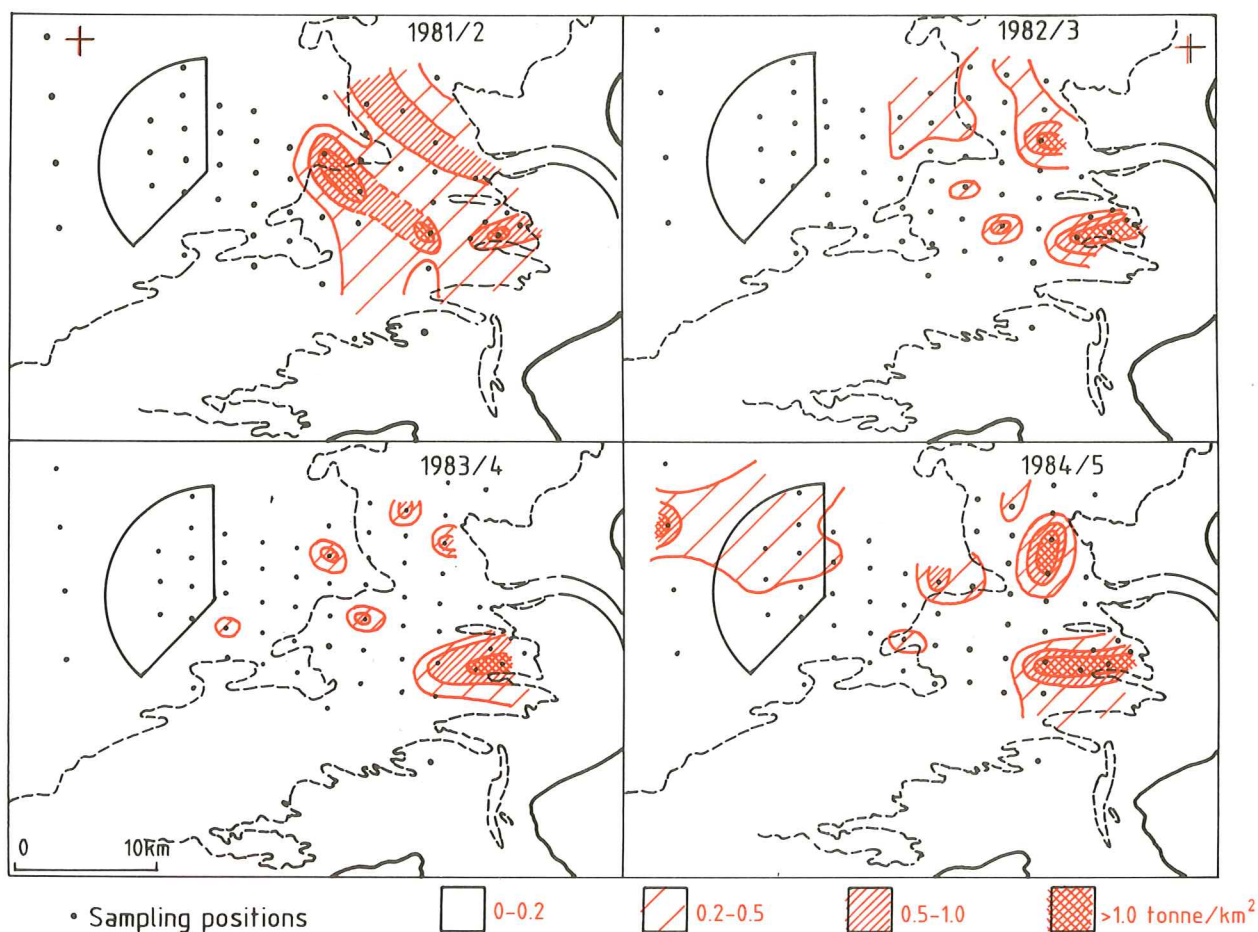


Fig 16 Total chromium in mud from the top 25mm of bed

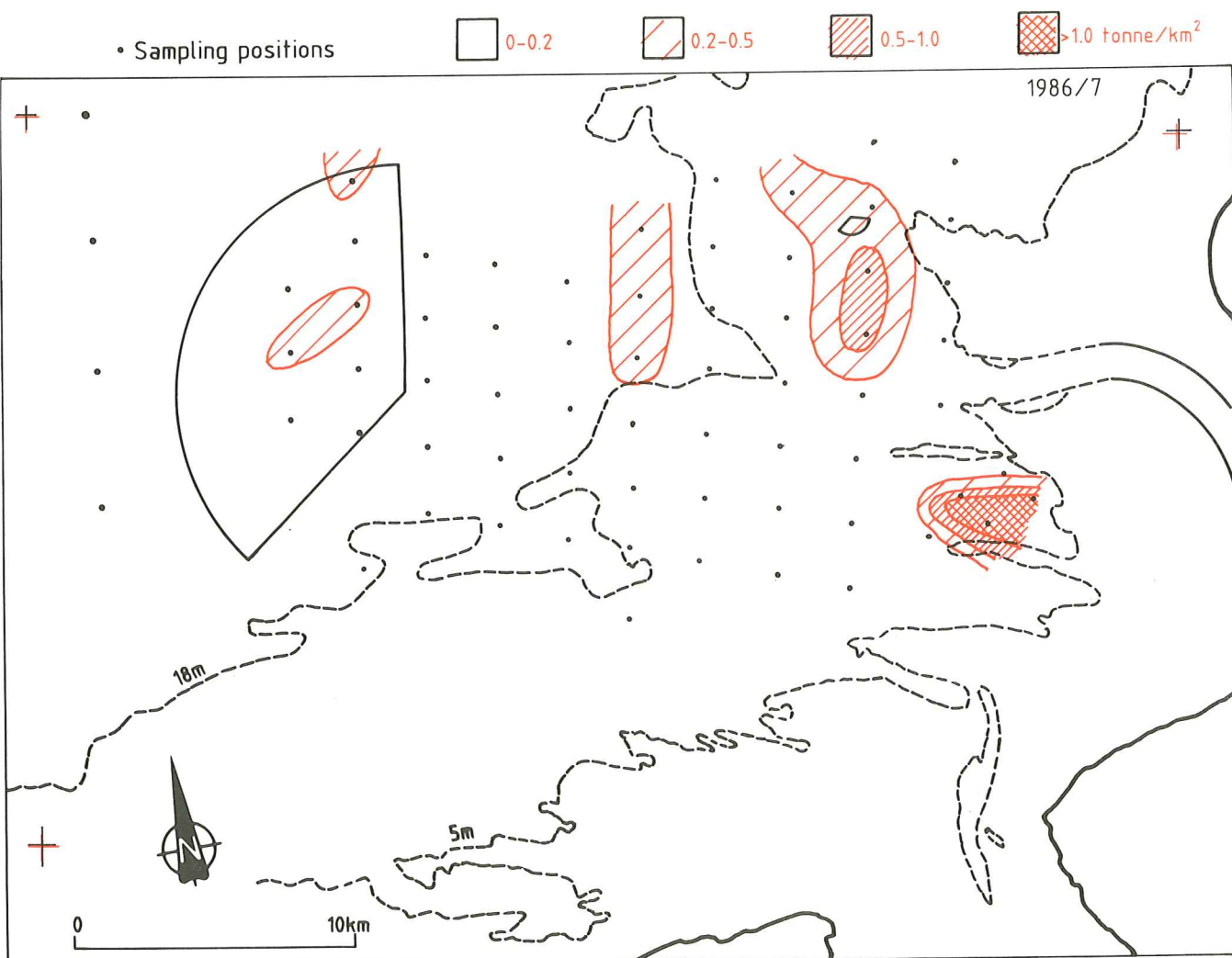
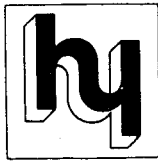


Fig 16 Total chromium in mud from the top 25mm of bed







**Hydraulics Research**  
Wallingford

**SLUDGE DISPOSAL IN LIVERPOOL BAY**

**Vertical profiles of heavy metals and  
organic carbon in bed sediments:  
addendum to report of fourteenth survey  
November 1986**

**P R Kiff BSc**

**Report No. SR 134 (Addendum)  
October 1987**

*Corrected*

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## **ABSTRACT**

This report is an addendum to that of the fourteenth bed monitoring survey conducted in November 1986. Eight cores were taken in addition to the grab samples previously reported and these have been analysed to give further background information as to the depth of sediment enriched by heavy metals present in the eastern half of Liverpool Bay. The basal unpolluted strata was reached in three of the sites visited, the remaining four indicating a depth of at least 1m of polluted mud. These depth profiles augment those of three previous surveys and, with the horizontal distribution of heavy metals and organic matter in the top 25mm of bed sediment derived from the annual monitoring surveys, help to give a more complete picture of the movement and deposition pattern of sewage sludge particulates.



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### TABLE 1

Depth profiles of mud, organics and metals

### FIGURES

- 1 Coring positions
- 2 Depth profiles



## 1 INTRODUCTION

The report of the fourteenth bed monitoring survey in Liverpool Bay (Ref 1) included the statement that core as well as grab samples were taken on that occasion and the results of the core sample analyses were to be reported later. This report contains the results of the core analyses and is presented as an addendum to that previous report. Objectives and analytical procedures are closely similar to those of the three earlier "long-core" surveys of 1983, 1985 and 1986 (Refs. 2, 3, 4).

These previous surveys had indicated that the basal "unpolluted" strata in the eastern area was of the order of 1 metre or more below the surface and so the HR 2-metre vibro-corer was used as on the April 1986 survey. Although this corer is capable of penetrating 1.8m under favourable conditions, the nature of the bed sediments often precludes full penetration (large pebbles, shells or consolidated mud) or occasionally loosely compacted sediment can be lost on withdrawal of the core tube from the bed. The maximum core length obtained on this survey was 1.5m with a minimum of 0.5m (repeated to give 1.0m on the second attempt).

Of the seven sites visited at which the cores were taken, six were at the same sites as on previous surveys (T10, T14, U9, YY1, YY3 and YY4) and one at a new position (T 13.5) adjoining the dredging spoil disposal ground off Jordans Spit. The basal strata was reached at three of these (T13, U9 and YY1) whilst the remaining four had not penetrated the polluted sediment down to depths ranging from 1.0 to 1.4m.

## 2 RESULTS

For the first time, sludge standards were obtained from the Community Bureau of Reference (Reference materials BCR 144, 145 and 146) and sub-samples of these in addition to our normal standards, were submitted for analysis in the normal way. Agreement between the results of our commercial laboratory and the quoted metal concentrations for these additional reference materials was very good apart from the results on BCR 144 and 146, that were high in chromium ( $> 500 \mu\text{g/g}$ ). Our laboratory gave significantly lower concentrations of chromium for these two "Eurosludge" standards. However, the difference is to be expected because the analytical method of the Community Bureau calls for digestion with aqua regia instead of nitric acid. Their more vigorous extraction procedure could lead to greater dissolution of chrome minerals.

The analytical results for each individual core stratum are listed in Table 1 and shown graphically as vertical profiles in Fig 2. Both the organic matter percentages and heavy metal concentrations relate to the mud fraction only ( $< 63 \mu\text{m}$ ) and not to their abundance in the total sediment.

### 2.1 Mud Distribution

Compared with previous surveys the stations in the vicinity and to the north of Newcome Knoll (ie. U9, YY3, YY4) feature the most muddy beds. Many of the cores exhibited layering, sometimes with alternate mud and fine sand of millimetre thickness. In these cases the tabulated and plotted average values for the 100mm strata mask the true vertical microstructure of the bed. Where there is a macro change in bed composition, then the strata have been separated at that point although in this survey, the few macro changes observed have coincided with the standard 100mm sampling intervals.

### 2.2 Organic matter in the mud fraction

Surface concentrations of organic matter are consistent with those given by the regular monitoring surveys ranging between 4 and 6%. The core at U9 differs from those previously taken at this position in 1985 and 1986 in that it appeared to reach the basal unpolluted strata below 200mm as regards metal contents but retained 2 to 2.5% organics below this level. The fact that the organics do not decrease with depth implies that



either the bacterial and other decomposition of the remaining organic matter has ceased entirely or that the basal strata was all laid down at the same time and is decomposing uniformly. The explanation of uniform organic content given in the 1986 survey report (Ref 4) of remixing of surface sediments cannot apply in this case as the metal contents are so low. It is most likely that the 2% organic content is also a basal concentration of resistant organic matter as in T12 of the last report (Ref 4) and differs from the results found from the west of Liverpool Bay where the organics decrease with depth. The coarser nature of the bed in this western area would increase its porosity and possibly assist in the oxidation of the organic matter.

### 2.3 Heavy metals in the mud fraction

Only three (T13, U9 and YY3) of the seven cores taken show the abrupt decrease in heavy metals with depth (although at YY1 the background may just have been reached). The mean "natural background" concentrations have been derived from 18 strata taken from these three cores and have been included in the following table together with the 1983 and April 1986 values (Ref 4).

	Concentration $\mu\text{g/g}$					
	Mercury	Copper	Zinc	Lead	Nickel	Chromium
1983	0.09 (0.05)	19 (8)	98 (30)	51 (33)	36 (6)	25 (6)
1986 (Apr)	0.04 (0.03)	24 (10)	78 (11)	27 (16)	43 (6)	47 (14)
1986 (Nov)	0.07 (0.04)	18 (4)	87 (11)	24 (6)	41 (11)	53 (17)

(figures in brackets = standard deviation)

The core YY3 is unusual because, although there is an abrupt decrease at 500mm for mercury, lead and zinc, copper shows only a small decrease, nickel no change and chromium an abrupt increase. The striking increase in chromium with depth ( $72 \mu\text{g/g}$  above 400mm compared to  $378 \mu\text{g/g}$  below) has been seen before: the YY3 core from the April 1986 exercise gave a marked increase below 560 mm ( $65$  compared to  $277$ ). This increase in chromium

is paralleled by an almost equally abrupt decrease in mud content (52% to 1% and 32% to 1.4% respectively). This implies a change in deposition pattern at a specific time when an vast increase in mud deposition occurred, absorbing more chromium from solution but not reaching the same absolute concentration as previously. The average organic matter content for the basal strata of the three cores in which the true background was reached was 2.4% compared with 5.0% for the surface 100m of the same cores.

The present exercise confirms and adds to our previous findings on the depth of penetration of obvious metal enrichment. In the Newcombe Knoll area, the basal strata was reached at U9 only 0.2m below the surface compared with 0.8m in 1986. This is more likely to be due to local variability rather than any overall reduction in the depth of enrichment. North of the Mersey outflow at T13 enrichment extended to 1m. South of the Mersey outflow the basal strata was probably reached at the same depth, but at both YY3 and YY4, coring to 1.1 and 1.2m failed to penetrate below the enriched layer.

Mean enrichment factors have been calculated for the upper strata of the cores as in Ref. 4.

Zone	1987 Cores	No. of strata	Mean enrichment factor					
			Mercury	Copper	Zinc	Lead	Chromium	Nickel
North of Mersey Outflow	T13	11	37	9.1	13.3	16.5	3.9	2.6
	T13.5A	6	47	5.0	5.3	6.9	1.7	1.0
	T13.5B	11	60	5.5	5.5	7.5	2.0	1.3
	T14	15	53	5.9	6.2	11.4	2.0	1.7
South of Mersey Outflow	U9	3	17	2.4	2.9	3.9	1.0	1.1
	YY1	12	31	3.7	3.7	7.4	1.5	1.2
	YY3	6	36	4.3	4.5	6.4	1.8	1.4
	YY4	13	37	4.5	5.1	7.0	1.7	1.2

Of the four cores (3 positions) north of the Mersey outflow T13 shows particularly high enrichment for all metals except mercury. This is possibly due to the dumping of dredging spoil in the vicinity. T13.5 and T14 show increased mercury but a noticeable reduction in the other metals.

To the south of the Mersey, YY1, 3 and 4 are very similar. In comparison with the other six cores U9 is low in all metals although with only 0.2m above the background, there are only three strata results available.

- 1 The sediments of the eastern part of Liverpool Bay show considerable surface enrichment in five of the six heavy metals studied. Even nickel, found previously to be reasonably uniform over the sampled depth showed an increase at T13, close to the dredged spoil dumping ground to a depth of 0.9m. Chromium also showed the same pattern although high chromium figures are found elsewhere. By virtue of its low natural background, mercury shows the greatest proportional enrichment throughout the survey area.
- 2 The longer cores recovered by the 2-metre vibrocorer reached the basal strata in three of the sites visited, YY1 being reached for the first time. A much shallower depth of metal enrichment was found at U9 on this occasion (0.2m as against 0.8m in April 1986). The projection of the tongue of Newcombe Knoll itself is very close to U9 and bed depths vary considerably in that area.
- 3 Heavy metal concentrations found in the basal strata below the enriched zone are thought to represent the natural geological background, free from man-made contaminants. Values are reasonably in accord with those obtained in 1983 and April 1986.

The anomalous enrichment with chromium at lower levels observed at YY3 suggests that a change in regime took place at some time in the past.

#### 4      **ACKNOWLEDGEMENTS**

We wish to thank Mr Jonathan Binks of HR's Field Studies Section for his successful completion of the coring programme. We are also pleased to acknowledge the valuable assistance given to Mr Binks on the cruise by the crew of M V Branding.

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## **Tables**



TABLE 1 - Depth profiles of mud, organics and metals

T 13

No.	Position depth (mm)	Mud %	Organics %	$\mu\text{g/g}$					
				Mercury	Copper	Zinc	Lead	Nickel	Chromium
0	0 - 25	14.14	4.91	2.83	162	1289	521	118	301
1	25 - 100	9.91	5.81	3.25	194	1258	431	115	262
2	100 - 200	18.40	4.84	3.20	206	1289	372	113	209
3	200 - 300	12.80	4.65	4.51	264	1742	515	118	219
4	300 - 400	10.90	5.32	3.57	216	1876	477	121	222
5	400 - 500	15.44	3.66	1.44	121	765	335	109	175
6	500 - 600	7.50	8.17	2.68	141	1382	431	117	151
7	600 - 700	14.31	3.83	2.30	126	1289	362	107	242
8	700 - 800	18.41	3.27	2.44	146	797	323	105	212
9	800 - 900	15.72	3.98	1.33	156	737	372	106	205
10	900 - 1000	1.89	4.09	1.21	73	289	221	49	79
11	1000 - 1100	15.21	1.84	0.09	28	89	28	42	54
12	1100 - 1200	4.43	1.71	0.01	18	71	28	35	92
13	1200 - 1300	12.91	1.80	0.01	18	81	18	41	57
14	1300 - 1390	10.41	1.99	0.06	18	82	20	41	74

TABLE 1 (cont'd)

T 13.5A

No	Position depth (mm)	Mud %	Organics %	µg/g					
				Mercury	Copper	Zinc	Lead	Nickel	Chromium
0	0 - 25	7.92	6.01	1.95	83	379	192	40	79
1	25 - 100	17.22	5.00	2.28	80	395	141	47	97
2	100 - 200	7.65	4.77	4.08	92	420	153	48	124
3	200 - 300	24.10	6.19	3.92	104	558	187	52	102
4	300 - 400	12.97	2.29	4.22	90	486	157	44	72
5	400 - 520	12.79	7.82	3.29	90	530	167	35	74

TABLE 1 (cont'd)

T 13.5B

No.	Position depth (mm)	Mud %	Organics %	u g/g					
				Mercury	Copper	Zinc	Lead	Nickel	Chromium
0	0 - 25	1.19	5.11	3.94	83	325	197	40	134
1	25 - 100	4.73	4.06	3.63	106	462	190	56	155
2	100 - 200	67.08	5.55	5.91	106	524	192	54	107
3	200 - 300	28.81	4.99	3.59	109	402	167	61	96
4	300 - 400	16.23	5.77	3.89	88	448	155	47	87
5	400 - 500	15.40	5.56	4.76	90	493	172	52	103
6	500 - 600	14.13	5.67	3.57	95	385	148	50	78
7	600 - 700	15.87	5.81	4.33	93	500	192	52	80
8	700 - 800	14.22	5.99	4.12	105	540	186	51	105
9	800 - 900	13.57	4.92	4.42	109	586	205	58	112
10	900 - 1030	14.10	5.18	4.37	100	591	182	57	108

TABLE 1 (cont'd)

T 14

No.	Position depth (mm)	Mud %	Organics %	$\mu$ g/g					
				Mercury	Copper	Zinc	Lead	Nickel	Chromium
0	0 - 25	1.32	5.71	3.73	131	471	524	72	143
1	25 - 100	6.93	6.61	2.46	73	371	138	39	95
2	100 - 200	9.82	5.56	2.86	77	405	154	47	76
3	200 - 300	2.64	4.92	3.85	104	495	234	62	104
4	300 - 400	6.59	5.76	3.89	100	512	226	52	95
5	400 - 500	6.86	6.02	4.65	131	723	264	70	120
6	500 - 600	13.67	6.44	4.14	114	613	200	44	95
7	600 - 700	27.13	6.18	5.05	104	515	200	61	107
8	700 - 800	10.80	5.89	4.52	98	544	176	58	111
9	800 - 900	8.12	6.06	3.89	109	572	205	68	105
10	900 - 1000	4.58	5.44	2.94	126	617	248	81	122
11	1000 - 1100	0.88	5.66	7.13	184	1134	1023	195	139
12	1100 - 1200	12.46	5.13	2.58	86	403	214	78	89
13	1200 - 1300	5.37	4.25	2.40	83	376	165	69	121
14	1300 - 1410	7.87	5.58	1.33	63	309	128	57	72



TABLE 1 (cont'd)

U.9

No.	Position depth (mm)	Mud %	Organics %	µg/g					Nickel	Chromium
				Mercury	Copper	Zinc	Lead			
0	0 - 25	8.36	2.71	0.52	33	177	57	43	55	
1	25 - 100	3.79	6.45	2.40	70	400	152	52	65	
2	100 - 200	18.19	3.29	0.73	30	167	74	43	42	
3	200 - 300	26.30	1.90	0.08	15	80	25	42	46	
4	300 - 400	49.94	2.36	0.08	13	76	20	37	40	
5	400 - 500	36.63	2.40	0.07	20	107	25	65	73	
6	500 - 600	47.61	2.52	0.04	20	105	30	55	52	
7	600 - 700	48.84	2.40	0.01	15	91	20	45	43	
8	700 - 800	42.21	2.20	0.02	15	79	25	8	34	
9	800 - 900	45.76	2.69	0.01	27	103	18	36	60	
10	900 - 1000	39.82	2.20	0.02	18	81	25	38	37	
11	1000 - 1100	34.92	2.92	0.10	17	85	25	42	37	
12	1100 - 1200	35.33	4.27	0.10	18	88	23	41	55	
13	1200 - 1300	36.15	2.39	0.11	15	92	23	51	50	
14	1300 - 1400	43.16	3.06	0.13	13	75	20	32	39	
15	1400 - 1530	52.47	2.29	0.14	15	85	25	35	36	

TABLE 1 (cont'd)

YY 1

No.	Position depth (mm)	Mud %	Organics %	$\mu\text{g/g}$					
				Mercury	Copper	Zinc	Lead	Nickel	Chromium
0	0 - 25	50.68	5.67	2.73	63	309	128	42	62
1	25 - 100	72.19	4.26	1.90	45	258	96	35	54
2	100 - 200	69.55	7.08	3.67	60	348	131	45	70
3	200 - 300	43.09	5.83	3.38	63	351	131	42	62
4	300 - 400	29.55	5.11	3.20	89	481	186	53	92
5	400 - 500	16.68	4.47	2.22	73	371	153	49	86
6	500 - 600	5.60	5.54	3.43	85	462	175	53	101
7	600 - 700	24.13	5.19	2.03	75	412	170	60	100
8	700 - 800	38.52	3.68	1.33	55	242	113	45	53
9	800 - 900	23.34	3.34	0.73	50	189	136	52	55
10	900 - 1000	1.62	3.75	0.87	73	256	431	65	104
11	1000 - 1100	0.78	3.12	0.85	60	204	268	51	105
12	1100 - 1180	9.83	2.52	0.10	23	101	42	44	77

TABLE 1 (cont'd)

YY 3

No.	Position depth (mm)	Mud %	Organics %	$\mu$ g/g					
				Mercury	Copper	Zinc	Lead	Nickel	Chromium
0	0 - 25	61.57	4.84	2.19	65	338	128	63	58
1	25 - 100	89.54	5.87	2.50	60	329	116	55	56
2	100 - 200	71.76	7.64	1.67	58	332	118	57	52
3	200 - 300	32.84	3.65	2.67	68	363	108	51	73
4	300 - 400	3.12	4.88	2.96	121	552	241	64	119
5	400 - 500	1.61	5.06	3.28	90	457	205	61	214
6	500 - 600	0.92	2.50	0.75	57	182	71	58	598
7	600 - 700	1.04	2.52	0.39	50	136	52	51	347
8	700 - 800	1.00	2.96	0.47	53	151	52	70	346
9	800 - 900	0.91	2.65	0.45	50	128	37	54	295
10	900 - 1000	0.55	2.73	0.47	53	124	37	51	496
11	1000 - 1100	0.93	2.37	0.50	45	123	34	54	349

TABLE 1 (cont'd)

YY 4

No.	Position depth (mm)	Mud %	Organics %	µg/g					Nickel	Chromium
				Mercury	Copper	Zinc	Lead			
0	0 - 25	51.31	3.90	1.24	65	448	215	55	158	
1	25 - 100	74.72	5.15	2.10	50	302	126	44	105	
2	100 - 200	59.73	5.73	2.43	65	418	153	48	107	
3	200 - 300	65.22	5.14	3.73	80	479	167	49	77	
4	300 - 400	59.20	6.99	5.09	65	438	136	38	48	
5	400 - 500	44.52	5.83	4.29	104	608	202	51	63	
6	500 - 600	49.91	6.82	4.22	131	698	251	57	78	
7	600 - 700	71.43	4.72	2.01	98	572	175	51	90	
8	700 - 800	20.10	4.91	1.97	78	397	155	52	95	
9	800 - 900	22.12	5.03	2.50	83	474	170	46	87	
10	900 - 1000	30.90	1.24	1.95	70	371	159	50	74	
11	1000 - 1100	27.69	4.14	1.22	58	263	126	44	52	
12	1100 - 1200	10.24	3.45	0.49	100	302	143	67	143	

**Figures**





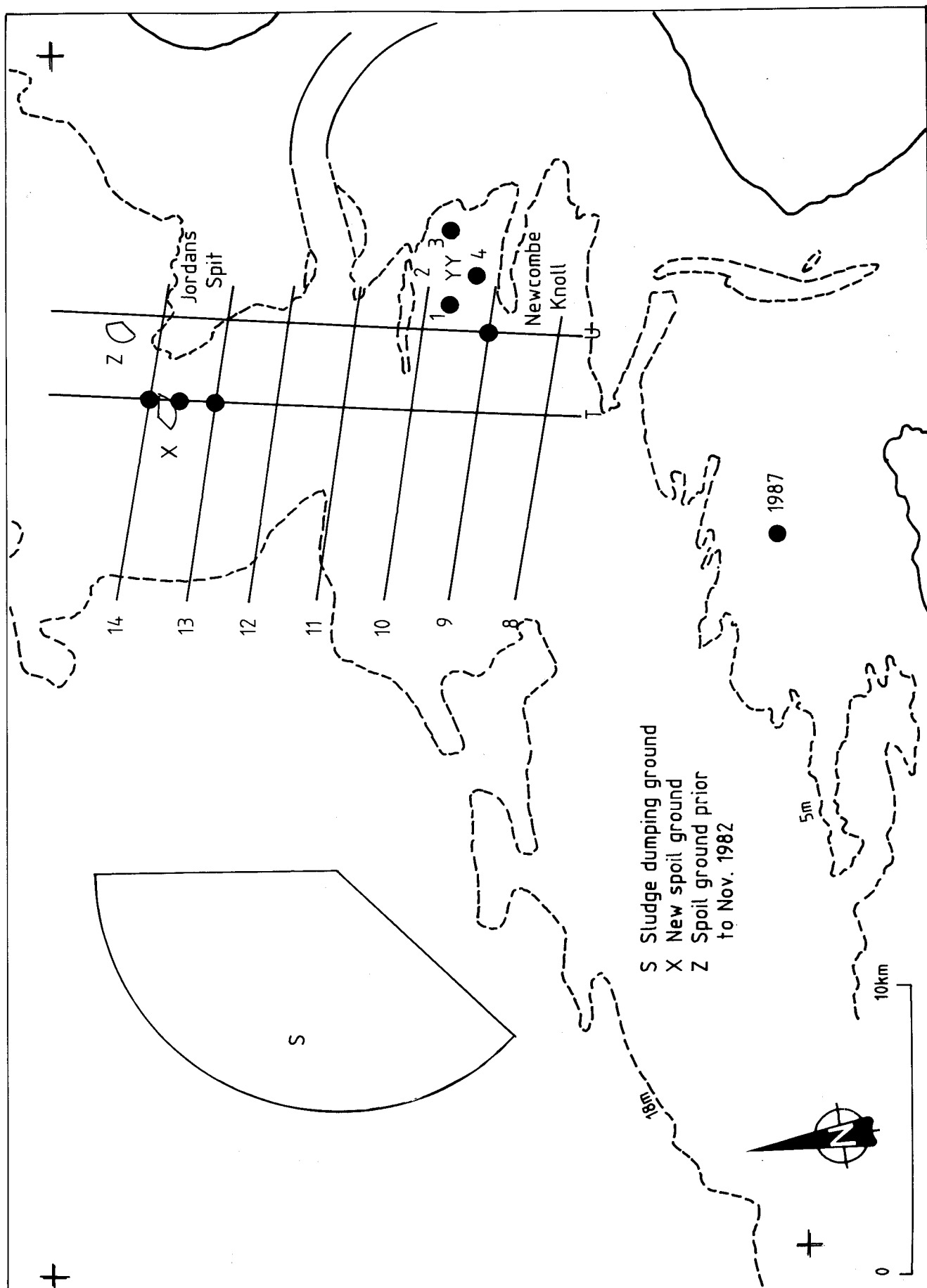


Fig 1 Monitoring positions



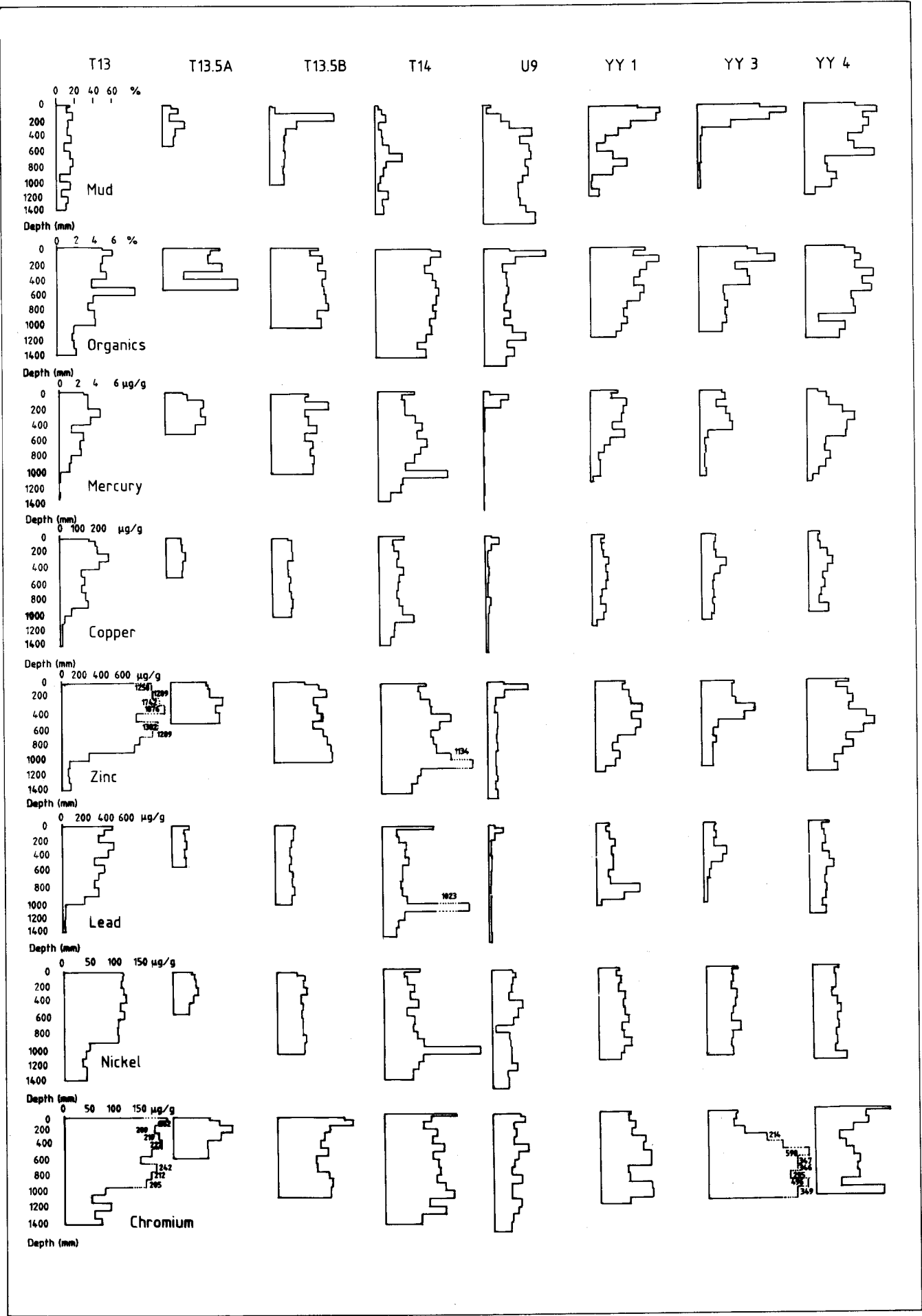
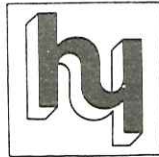


Fig 2 Depth profiles





**Hydraulics Research**  
Wallingford

**SLUDGE DISPOSAL IN LIVERPOOL BAY**

**Vertical profiles of heavy metals and  
organic carbon in bed sediments:  
addendum to report of fourteenth survey  
November 1986**

**P R Kiff BSc**

**Report No. SR 134 (Addendum)  
October 1987**

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## **ABSTRACT**

This report is an addendum to that of the fourteenth bed monitoring survey conducted in November 1986. Eight cores were taken in addition to the grab samples previously reported and these have been analysed to give further background information as to the depth of sediment enriched by heavy metals present in the eastern half of Liverpool Bay. The basal unpolluted strata was reached in three of the sites visited, the remaining four indicating a depth of at least 1m of polluted mud. These depth profiles augment those of three previous surveys and, with the horizontal distribution of heavy metals and organic matter in the top 25mm of bed sediment derived from the annual monitoring surveys, help to give a more complete picture of the movement and deposition pattern of sewage sludge particulates.



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### TABLE 1

Depth profiles of mud, organics and metals

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- 1 Coring positions
- 2 Depth profiles



## 1 INTRODUCTION

The report of the fourteenth bed monitoring survey in Liverpool Bay (Ref 1) included the statement that core as well as grab samples were taken on that occasion and the results of the core sample analyses were to be reported later. This report contains the results of the core analyses and is presented as an addendum to that previous report. Objectives and analytical procedures are closely similar to those of the three earlier "long-core" surveys of 1983, 1985 and 1986 (Refs. 2, 3, 4).

These previous surveys had indicated that the basal "unpolluted" strata in the eastern area was of the order of 1 metre or more below the surface and so the HR 2-metre vibro-corer was used as on the April 1986 survey. Although this corer is capable of penetrating 1.8m under favourable conditions, the nature of the bed sediments often precludes full penetration (large pebbles, shells or consolidated mud) or occasionally loosely compacted sediment can be lost on withdrawal of the core tube from the bed. The maximum core length obtained on this survey was 1.5m with a minimum of 0.5m (repeated to give 1.0m on the second attempt).

Of the seven sites visited at which the cores were taken, six were at the same sites as on previous surveys (T10, T14, U9, YY1, YY3 and YY4) and one at a new position (T 13.5) adjoining the dredging spoil disposal ground off Jordans Spit. The basal strata was reached at three of these (T13, U9 and YY1) whilst the remaining four had not penetrated the polluted sediment down to depths ranging from 1.0 to 1.4m.

## 2 RESULTS

For the first time, sludge standards were obtained from the Community Bureau of Reference (Reference materials BCR 144, 145 and 146) and sub-samples of these in addition to our normal standards, were submitted for analysis in the normal way. Agreement between the results of our commercial laboratory and the quoted metal concentrations for these additional reference materials was very good apart from the results on BCR 144 and 146, that were high in chromium ( $> 500 \mu\text{g/g}$ ). Our laboratory gave significantly lower concentrations of chromium for these two "Eurosludge" standards. However, the difference is to be expected because the analytical method of the Community Bureau calls for digestion with aqua regia instead of nitric acid. Their more vigorous extraction procedure could lead to greater dissolution of chrome minerals.

The analytical results for each individual core stratum are listed in Table 1 and shown graphically as vertical profiles in Fig 2. Both the organic matter percentages and heavy metal concentrations relate to the mud fraction only ( $< 63 \mu\text{m}$ ) and not to their abundance in the total sediment.

### 2.1 Mud Distribution

Compared with previous surveys the stations in the vicinity and to the north of Newcome Knoll (ie. U9, YY3, YY4) feature the most muddy beds. Many of the cores exhibited layering, sometimes with alternate mud and fine sand of millimetre thickness. In these cases the tabulated and plotted average values for the 100mm strata mask the true vertical microstructure of the bed. Where there is a macro change in bed composition, then the strata have been separated at that point although in this survey, the few macro changes observed have coincided with the standard 100mm sampling intervals.

### 2.2 Organic matter in the mud fraction

Surface concentrations of organic matter are consistent with those given by the regular monitoring surveys ranging between 4 and 6%. The core at U9 differs from those previously taken at this position in 1985 and 1986 in that it appeared to reach the basal unpolluted strata below 200mm as regards metal contents but retained 2 to 2.5% organics below this level. The fact that the organics do not decrease with depth implies that



either the bacterial and other decomposition of the remaining organic matter has ceased entirely or that the basal strata was all laid down at the same time and is decomposing uniformly. The explanation of uniform organic content given in the 1986 survey report (Ref 4) of remixing of surface sediments cannot apply in this case as the metal contents are so low. It is most likely that the 2% organic content is also a basal concentration of resistant organic matter as in T12 of the last report (Ref 4) and differs from the results found from the west of Liverpool Bay where the organics decrease with depth. The coarser nature of the bed in this western area would increase its porosity and possibly assist in the oxidation of the organic matter.

### 2.3 Heavy metals in the mud fraction

Only three (T13, U9 and YY3) of the seven cores taken show the abrupt decrease in heavy metals with depth (although at YY1 the background may just have been reached). The mean "natural background" concentrations have been derived from 18 strata taken from these three cores and have been included in the following table together with the 1983 and April 1986 values (Ref 4).

	Concentration $\mu\text{g/g}$					
	Mercury	Copper	Zinc	Lead	Nickel	Chromium
1983	0.09 (0.05)	19 (8)	98 (30)	51 (33)	36 (6)	25 (6)
1986 (Apr)	0.04 (0.03)	24 (10)	78 (11)	27 (16)	43 (6)	47 (14)
1986 (Nov)	0.07 (0.04)	18 (4)	87 (11)	24 (6)	41 (11)	53 (17)

(figures in brackets = standard deviation)

The core YY3 is unusual because, although there is an abrupt decrease at 500mm for mercury, lead and zinc, copper shows only a small decrease, nickel no change and chromium an abrupt increase. The striking increase in chromium with depth ( $72 \mu\text{g/g}$  above 400mm compared to  $378 \mu\text{g/g}$  below) has been seen before: the YY3 core from the April 1986 exercise gave a marked increase below 560 mm ( $65$  compared to  $277$ ). This increase in chromium

is paralleled by an almost equally abrupt decrease in mud content (52% to 1% and 32% to 1.4% respectively). This implies a change in deposition pattern at a specific time when an vast increase in mud deposition occurred, absorbing more chromium from solution but not reaching the same absolute concentration as previously. The average organic matter content for the basal strata of the three cores in which the true background was reached was 2.4% compared with 5.0% for the surface 100m of the same cores.

The present exercise confirms and adds to our previous findings on the depth of penetration of obvious metal enrichment. In the Newcombe Knoll area, the basal strata was reached at U9 only 0.2m below the surface compared with 0.8m in 1986. This is more likely to be due to local variability rather than any overall reduction in the depth of enrichment. North of the Mersey outflow at T13 enrichment extended to 1m. South of the Mersey outflow the basal strata was probably reached at the same depth, but at both YY3 and YY4, coring to 1.1 and 1.2m failed to penetrate below the enriched layer.

Mean enrichment factors have been calculated for the upper strata of the cores as in Ref. 4.

Zone	1987 Cores	No. of strata	Mean enrichment factor					
			Mercury	Copper	Zinc	Lead	Chromium	Nickel
North of Mersey Outflow	T13	11	37	9.1	13.3	16.5	3.9	2.6
	T13.5A	6	47	5.0	5.3	6.9	1.7	1.0
	T13.5B	11	60	5.5	5.5	7.5	2.0	1.3
	T14	15	53	5.9	6.2	11.4	2.0	1.7
South of Mersey Outflow	U9	3	17	2.4	2.9	3.9	1.0	1.1
	YY1	12	31	3.7	3.7	7.4	1.5	1.2
	YY3	6	36	4.3	4.5	6.4	1.8	1.4
	YY4	13	37	4.5	5.1	7.0	1.7	1.2



Of the four cores (3 positions) north of the Mersey outflow T13 shows particularly high enrichment for all metals except mercury. This is possibly due to the dumping of dredging spoil in the vicinity. T13.5 and T14 show increased mercury but a noticeable reduction in the other metals.

To the south of the Mersey, YY1, 3 and 4 are very similar. In comparison with the other six cores U9 is low in all metals although with only 0.2m above the background, there are only three strata results available.

### 3 CONCLUSIONS

- 1 The sediments of the eastern part of Liverpool Bay show considerable surface enrichment in five of the six heavy metals studied. Even nickel, found previously to be reasonably uniform over the sampled depth showed an increase at T13, close to the dredged spoil dumping ground to a depth of 0.9m. Chromium also showed the same pattern although high chromium figures are found elsewhere. By virtue of its low natural background, mercury shows the greatest proportional enrichment throughout the survey area.
- 2 The longer cores recovered by the 2-metre vibrocorer reached the basal strata in three of the sites visited, YY1 being reached for the first time. A much shallower depth of metal enrichment was found at U9 on this occasion (0.2m as against 0.8m in April 1986). The projection of the tongue of Newcombe Knoll itself is very close to U9 and bed depths vary considerably in that area.
- 3 Heavy metal concentrations found in the basal strata below the enriched zone are thought to represent the natural geological background, free from man-made contaminants. Values are reasonably in accord with those obtained in 1983 and April 1986.

The anomalous enrichment with chromium at lower levels observed at YY3 suggests that a change in regime took place at some time in the past.

#### 4      **ACKNOWLEDGEMENTS**

We wish to thank Mr Jonathan Binks of HR's Field Studies Section for his successful completion of the coring programme. We are also pleased to acknowledge the valuable assistance given to Mr Binks on the cruise by the crew of M V Branding.

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## Tables



TABLE 1 - Depth profiles of mud, organics and metals

No.	Position depth (mm)	Mud %	Organics %	μg/g					
				Mercury	Copper	Zinc	Lead	Nickel	Chromium
0	0 - 25	14.14	4.91	2.83	162	1289	521	118	301
1	25 - 100	9.91	5.81	3.25	194	1258	431	115	262
2	100 - 200	18.40	4.84	3.20	206	1289	372	113	209
3	200 - 300	12.80	4.65	4.51	264	1742	515	118	219
4	300 - 400	10.90	5.32	3.57	216	1876	477	121	222
5	400 - 500	15.44	3.66	1.44	121	765	335	109	175
6	500 - 600	7.50	8.17	2.68	141	1382	431	117	151
7	600 - 700	14.31	3.83	2.30	126	1289	362	107	242
8	700 - 800	18.41	3.27	2.44	146	797	323	105	212
9	800 - 900	15.72	3.98	1.33	156	737	372	106	205
10	900 - 1000	1.89	4.09	1.21	73	289	221	49	79
11	1000 - 1100	15.21	1.84	0.09	28	89	28	42	54
12	1100 - 1200	4.43	1.71	0.01	18	71	28	35	92
13	1200 - 1300	12.91	1.80	0.01	18	81	18	41	57
14	1300 - 1390	10.41	1.99	0.06	18	82	20	41	74

TABLE 1 (cont'd)

T 13.5A

No	Position depth (mm)	Mud %	Organics %	Mercury	Copper	Zinc	Lead	Nickel	Chromium
				μg/g					
0	0 - 25	7.92	6.01	1.95	83	379	192	40	79
1	25 - 100	17.22	5.00	2.28	80	395	141	47	97
2	100 - 200	7.65	4.77	4.08	92	420	153	48	124
3	200 - 300	24.10	6.19	3.92	104	558	187	52	102
4	300 - 400	12.97	2.29	4.22	90	486	157	44	72
5	400 - 520	12.79	7.82	3.29	90	530	167	35	74



TABLE 1 (cont'd)

T 13.5B

No.	Position depth (mm)	Mud %	Organics %	µ g/g				
				Mercury	Copper	Zinc	Lead	Nickel Chromium
0	0 - 25	1.19	5.11	3.94	83	325	197	40 134
1	25 - 100	4.73	4.06	3.63	106	462	190	56 155
2	100 - 200	67.08	5.55	5.91	106	524	192	54 107
3	200 - 300	28.81	4.99	3.59	109	402	167	61 96
4	300 - 400	16.23	5.77	3.89	88	448	155	47 87
5	400 - 500	15.40	5.56	4.76	90	493	172	52 103
6	500 - 600	14.13	5.67	3.57	95	385	148	50 78
7	600 - 700	15.87	5.81	4.33	93	500	192	52 80
8	700 - 800	14.22	5.99	4.12	105	540	186	51 105
9	800 - 900	13.57	4.92	4.42	109	586	205	58 112
10	900 - 1030	14.10	5.18	4.37	100	591	182	57 108

TABLE 1 (cont'd)

T 14

No.	Position depth (mm)	Mud %	Organics %	μ g/g					Nickel	Chromium
				Mercury	Copper	Zinc	Lead			
0	0 - 25	1.32	5.71	3.73	131	471	524	72	143	
1	25 - 100	6.93	6.61	2.46	73	371	138	39	95	
2	100 - 200	9.82	5.56	2.86	77	405	154	47	76	
3	200 - 300	2.64	4.92	3.85	104	495	234	62	104	
4	300 - 400	6.59	5.76	3.89	100	512	226	52	95	
5	400 - 500	6.86	6.02	4.65	131	723	264	70	120	
6	500 - 600	13.67	6.44	4.14	114	613	200	44	95	
7	600 - 700	27.13	6.18	5.05	104	515	200	61	107	
8	700 - 800	10.80	5.89	4.52	98	544	176	58	111	
9	800 - 900	8.12	6.06	3.89	109	572	205	68	105	
10	900 - 1000	4.58	5.44	2.94	126	617	248	81	122	
11	1000 - 1100	0.88	5.66	7.13	184	1134	1023	195	139	
12	1100 - 1200	12.46	5.13	2.58	86	403	214	78	89	
13	1200 - 1300	5.37	4.25	2.40	83	376	165	69	121	
14	1300 - 1410	7.87	5.58	1.33	63	309	128	57	72	

TABLE 1 (cont'd)

U.9

No.	Position depth (mm)	Mud %	Organics %	μg/g					Nickel	Chromium
				Mercury	Copper	Zinc	Lead			
0	0 - 25	8.36	2.71	0.52	33	177	57	43	55	
1	25 - 100	3.79	6.45	2.40	70	400	152	52	65	
2	100 - 200	18.19	3.29	0.73	30	167	74	43	42	
3	200 - 300	26.30	1.90	0.08	15	80	25	42	46	
4	300 - 400	49.94	2.36	0.08	13	76	20	37	40	
5	400 - 500	36.63	2.40	0.07	20	107	25	65	73	
6	500 - 600	47.61	2.52	0.04	20	105	30	55	52	
7	600 - 700	48.84	2.40	0.01	15	91	20	45	43	
8	700 - 800	42.21	2.20	0.02	15	79	25	8	34	
9	800 - 900	45.76	2.69	0.01	27	103	18	36	60	
10	900 - 1000	39.82	2.20	0.02	18	81	25	38	37	
11	1000 - 1100	34.92	2.92	0.10	17	85	25	42	37	
12	1100 - 1200	35.33	4.27	0.10	18	88	23	41	55	
13	1200 - 1300	36.15	2.39	0.11	15	92	23	51	50	
14	1300 - 1400	43.16	3.06	0.13	13	75	20	32	39	
15	1400 - 1530	52.47	2.29	0.14	15	85	25	35	36	

TABLE 1 (cont'd)

YY 1

No.	Position depth (mm)	Mud %	Organics %	$\mu\text{g/g}$					
				Mercury	Copper	Zinc	Lead	Nickel	Chromium
0	0 - 25	50.68	5.67	2.73	63	309	128	42	62
1	25 - 100	72.19	4.26	1.90	45	258	96	35	54
2	100 - 200	69.55	7.08	3.67	60	348	131	45	70
3	200 - 300	43.09	5.83	3.38	63	351	131	42	62
4	300 - 400	29.55	5.11	3.20	89	481	186	53	92
5	400 - 500	16.68	4.47	2.22	73	371	153	49	86
6	500 - 600	5.60	5.54	3.43	85	462	175	53	101
7	600 - 700	24.13	5.19	2.03	75	412	170	60	100
8	700 - 800	38.52	3.68	1.33	55	242	113	45	53
9	800 - 900	23.34	3.34	0.73	50	189	136	52	55
10	900 - 1000	1.62	3.75	0.87	73	256	431	65	104
11	1000 - 1100	0.78	3.12	0.85	60	204	268	51	105
12	1100 - 1180	9.83	2.52	0.10	23	101	42	44	77

TABLE 1 (cont'd)

YY 3

No.	Position depth (mm)	Mud %	Organics %	$\mu$ g/g					
				Mercury	Copper	Zinc	Lead	Nickel	Chromium
0	0 - 25	61.57	4.84	2.19	65	338	128	63	58
1	25 - 100	89.54	5.87	2.50	60	329	116	55	56
2	100 - 200	71.76	7.64	1.67	58	332	118	57	52
3	200 - 300	32.84	3.65	2.67	68	363	108	51	73
4	300 - 400	3.12	4.88	2.96	121	552	241	64	119
5	400 - 500	1.61	5.06	3.28	90	457	205	61	214
6	500 - 600	0.92	2.50	0.75	57	182	71	58	598
7	600 - 700	1.04	2.52	0.39	50	136	52	51	347
8	700 - 800	1.00	2.96	0.47	53	151	52	70	346
9	800 - 900	0.91	2.65	0.45	50	128	37	54	295
10	900 - 1000	0.55	2.73	0.47	53	124	37	51	496
11	1000 - 1100	0.93	2.37	0.50	45	123	34	54	349



TABLE 1 (cont'd)

YY 4

No.	Position depth (mm)	Mud %	Organics %	$\mu\text{g/g}$					Chromium
				Mercury	Copper	Zinc	Lead	Nickel	
0	0 - 25	51.31	3.90	1.24	65	448	215	55	158
1	25 - 100	74.72	5.15	2.10	50	302	126	44	105
2	100 - 200	59.73	5.73	2.43	65	418	153	48	107
3	200 - 300	65.22	5.14	3.73	80	479	167	49	77
4	300 - 400	59.20	6.99	5.09	65	438	136	38	48
5	400 - 500	44.52	5.83	4.29	104	608	202	51	63
6	500 - 600	49.91	6.82	4.22	131	698	251	57	78
7	600 - 700	71.43	4.72	2.01	98	572	175	51	90
8	700 - 800	20.10	4.91	1.97	78	397	155	52	95
9	800 - 900	22.12	5.03	2.50	83	474	170	46	87
10	900 - 1000	30.90	1.24	1.95	70	371	159	50	74
11	1000 - 1100	27.69	4.14	1.22	58	263	126	44	52
12	1100 - 1200	10.24	3.45	0.49	100	302	143	67	143

## Figures





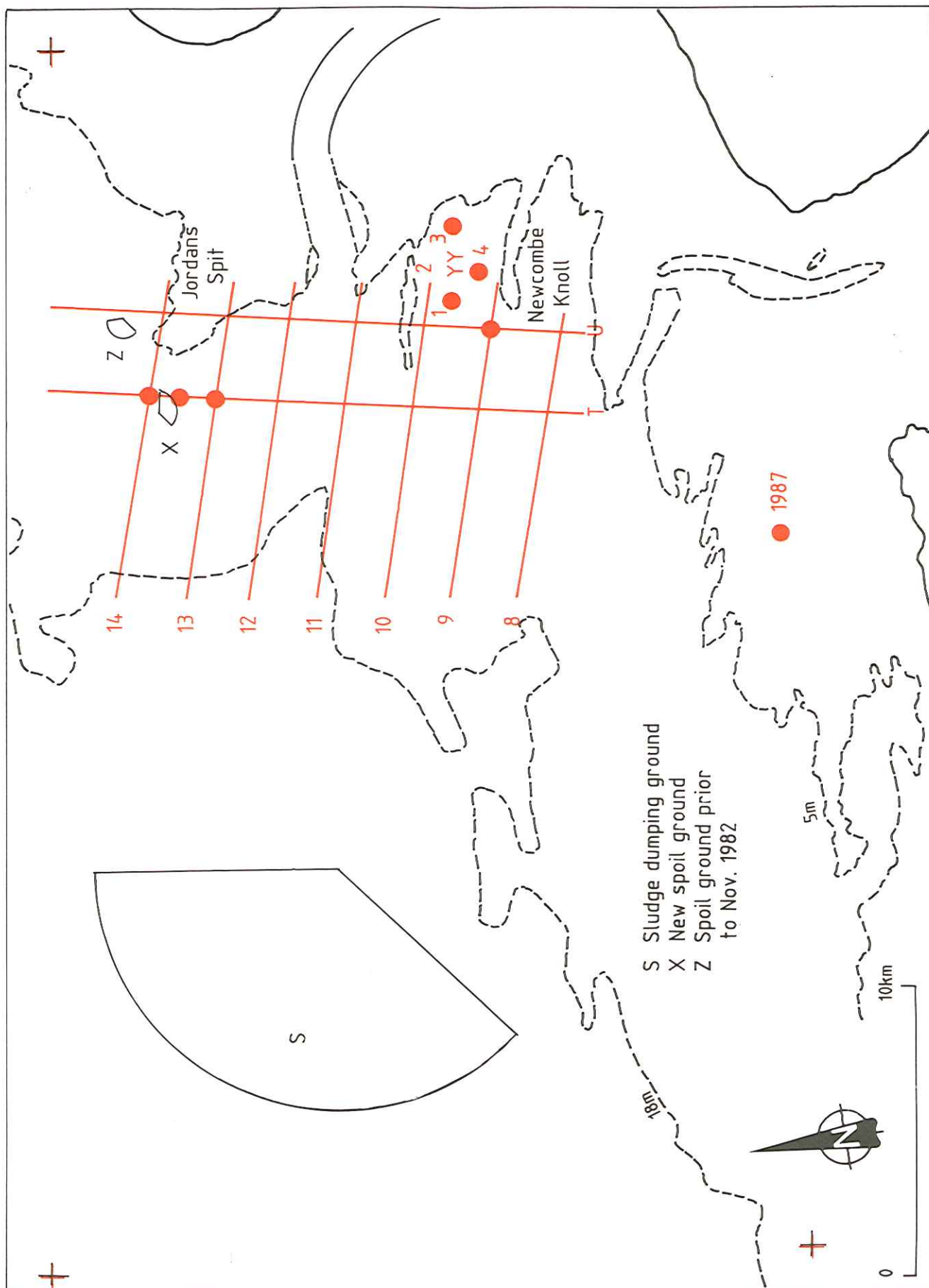


Fig 1 Monitoring positions



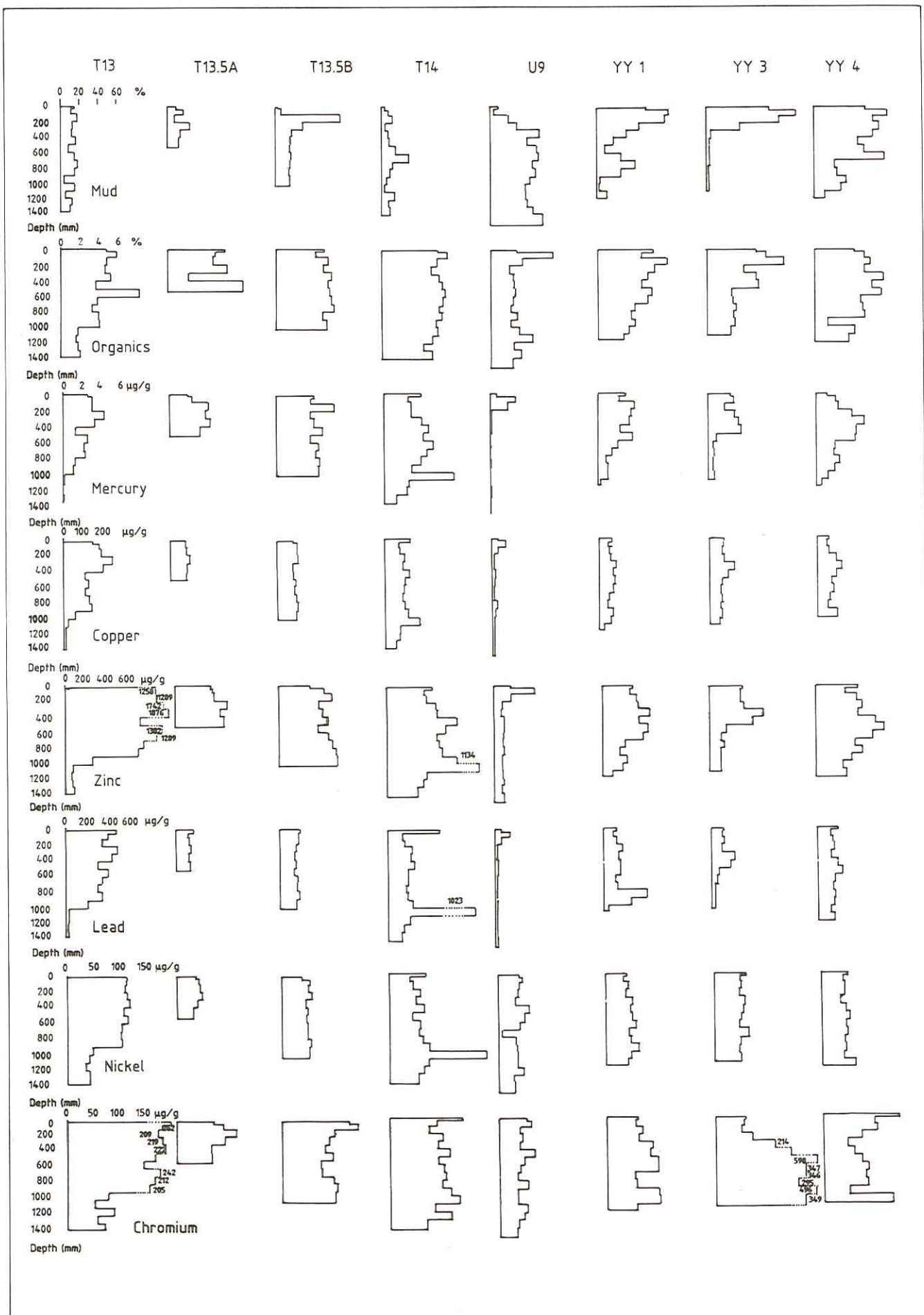


Fig 2 Depth profiles

