

Contract 420

Mercury and Methylmercury in the River Yare, Norfolk (1986 - 1992)

Main Report

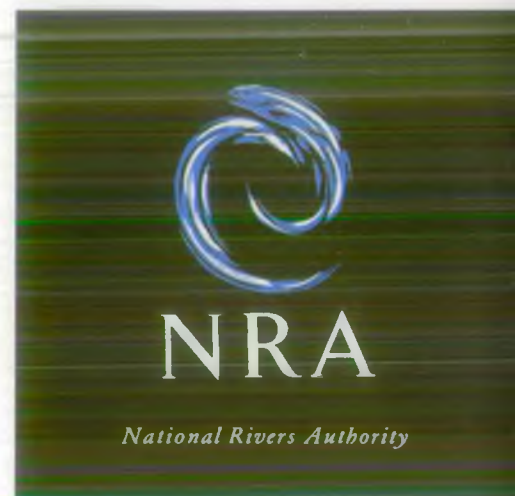



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Anglian Region Operational Investigation

OI 420/8/A



**Mercury and Methylmercury in the River
Yare, Norfolk.**

**Report to the National Rivers Authority,
Anglian Region.**

NRA Report No OI/420/8/A

December 1992

***Environmental and Water Resource Engineering Section,
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1. SUMMARY

This is the second report submitted by Imperial College of Science, Technology and Medicine, London, to the National Rivers Authority on mercury contamination in the River Yare, Norfolk. It describes the research undertaken since 1986, concerning the magnitude, fate and behaviour of sediment bound total and methylmercury within the Yare river system and considers the environmental factors that may govern mercury accumulation and availability.

Annual monitoring of surficial sediments has identified a 17 km mercury enrichment zone stretching from Trowse, at the upper tidal limit, to Hassingham in the west, including the interconnecting Broad (Surlingham, Wheatfen and Rockland) and pinpoints Whitlingham STW as the contaminative source. Total mercury concentrations in surficial sediments have undergone a significant decline since 1986, culminating in a 7 fold decrease by 1990. Surficial sediment concentrations currently lie at $<6.7 \text{ mg kg}^{-1}$ (1992 levels). The burial of contaminated sediment beneath a cleaner overlay is the dominant sedimentological process responsible for this observed decrease. Total mercury concentrations of up to 36.9 mg kg^{-1} have been detected within sediment cores, the precise depth being dependent upon sedimentation rates, as dictated by hydrology, sediment supply and channel morphology. Disturbance of these contaminated sediment layers can stimulate an increase in total mercury concentrations in the downstream environment and it is recommended that all dredging operations be halted until completion of the environmental impact assessment.

Although emission controls have been effective in promoting a decline in surficial sediment total mercury loadings, methylmercury has not undergone a similar response. Since methylmercury is the most available mercury species its continued synthesis within the sediment compartment is a cause for concern. The complex interplay between methylation and demethylation reactions govern net methylmercury concentrations. These processes are controlled by temperature, dissolved oxygen, sulphur and the nature of sediment bacterial communities. Maximum methylmercury production occurred in the warm summer months when conditions were optimised for the formation and subsequent retention of methylmercury within the sediment system (high temperatures, low oxygen availability) and were lowest in the autumn under cold temperature conditions. Methylmercury was routinely detected at concentrations of up to $25\text{-}33 \text{ } \mu\text{g kg}^{-1}$ during the summer months and declined by 30-50% in the autumn. Methylmercury concentrations consequently vary seasonally. Active methylmercury synthesis was confined to the uppermost sediment layers with maximum loadings usually prevailing at depths of 4-8 cm. Undetectable levels of methylmercury occurred below $\approx 40 \text{ cm}$.

List of Contents

Page No.

1. SUMMARY	1
List of Contents	2
List of Tables	4
List of Figures	5
List of Appendices	7
Glossary	8
2. INTRODUCTION	9
3. OBJECTIVES	10
4. MATERIALS and METHODS	11
4.1. Study Area	11
4.2. An Assessment of the Spatial Distribution of Mercury and Methylmercury within the River Yare Surficial Sediments	13
4.2.1. Sampling strategy: The River Yare sediment surveys	13
4.2.1.1. Sample collection	15
4.2.1.2. Sample processing	15
4.2.2. An Evaluation of the Methylmercury Anomaly in the River Yare Sediments at Cantley	17
4.3. An Assessment of the Vertical Extent of Total and Methylmercury Contamination within the Shallow Broad Systems Bordering the River Yare	17
4.3.1. The Broads surveys (Rockland, Surlingham and Wheatfen Broads)	17
4.3.2. Sampling strategy	19
4.4. To Assess the <i>In situ</i> Seasonal Variations in Methylmercury Production and Elucidate the Factors Controlling Methylation	19
4.4.1. Rockland Broad <i>in situ</i> seasonal experiments	19
4.4.1.1. Study area	19
4.4.1.2. Sampling strategy	19
4.4.1.3. Sample processing and characterisation	22
4.5. Laboratory Based Tank Experiments Designed to Evaluate the Movement of Mercury from Buried Contaminated Layersto Cleaner Surficial Sediments	22
4.5.1. Sampling strategy	22
4.5.2. The effect of temperature upon methylmercury synthesis	23
4.6. Analytical Methods	23
4.6.1. Total mercury analysis	23
4.6.2. Methylmercury analysis	24
4.6.2.1. Instrumentation and analysis	24
4.6.2.2. Standards preparation	25
4.6.2.3. Methylmercury extraction procedure	25
4.6.3. Copper determination	26
4.6.4. Sulphide determination	26
4.6.5. Sulphate determination	27
4.6.6. Chloride determination	27

4.6.7.	Total and volatile solids determination	27
4.6.8.	Viable counts on mercury and non-mercury amended agar plates	27
4.7.	Equipment	28
4.8.	Analytical Quality and Control	28
5.	RESULTS	30
5.1.	River Yare Surficial Sediments	30
5.1.1.	Assessment of the temporal and spatial changes in the distribution of total mercury within the River Yare surficial sediments	30
5.1.2.	Copper within the River Yare system	34
5.1.3.	The temporal and spatial distribution of methylmercury within the River Yare surficial sediments	36
5.1.4.	The effect of environmental factors upon surficial sediment metal concentrations	42
5.1.4.1.	<i>The influence of sediment type and organic matter content on metal distribution within the Yare surficial sediment</i>	42
5.1.4.2.	<i>Hydrological controls upon sediment and metal accumulation tendencies</i>	44
5.1.4.3.	<i>The effect of sediment pH, temperature and chloride upon mercury accumulation tendencies</i>	45
5.2.	River Yare Sediment Core Record	46
5.2.1.	The vertical distribution and historic loading of mercury within the River Yare's sediment compartment (1992)	46
5.2.2.	Laboratory based experiments to ascertain mercury mobility in contaminated sediment buried beneath a cleaner overlay	50
5.2.3.	The vertical distribution and historic loading of copper within the River Yare's sediment compartment (1992)	55
5.3.	Broads Sediment Surveys	58
5.3.1.	Concentration and distribution of mercury in Broad surficial sediments	58
5.3.2.	<i>In-situ</i> seasonal variations in methylmercury and related physiochemical parameters in the sediment of Rockland Broad	64
5.3.3.	Seasonal variations in total viable bacterial communities in Rockland Broad sediment	74
6.	DISCUSSION	78
6.1.	The Fate and Behaviour of Total mercury within the River Yare (1986-1992)	78
6.2.	Controls, Fate and Behaviour of Methylmercury within the River Yare's Surficial Sediments	85
7.	RECOMMENDATIONS	94
8.	CONCLUSIONS	96
9.	REFERENCE LIST	98
10.	APPENDICES	103

List of Tables

	Page No.
Table 1. River Yare sampling strategies for surficial sediments (1986-1992).	17
Table 2. The accuracy of sediment digestions and AAS analysis for total mercury and copper.	29
Table 3. Summary of total and methylmercury levels found within the River Yare surficial sediments between 1986-1992.	30
Table 4. Summary of total copper levels found within the River Yare surficial sediments between 1986-1992.	36
Table 5. The effect of sediment type upon mean metal concentrations and solid loadings in the River Yare surficial sediment.	43
Table 6. Correlation coefficients and significance levels for mercury and copper as a function of sediment type in the River Yare.	43
Table 7. Summary of surficial sediment environmental parameters.	45
Table 8. Summary of mercury and copper concentrations in cored sediment samples from the River Yare, 1992.	48
Table 9. Methylmercury summary data for the laboratory based tank experiments.	55
Table 10. Spearman's ranked correlations table derived for core depth versus metal and physicochemical parameters in River Yare sediment cores (1992).	56
Table 11. Mean surficial mercury concentrations in the Broads (1990).	58
Table 12. The seasonal variations in total mercury and percentage volatile solids in Rockland Broad, coring site 5.	67
Table 13. Seasonal variation in metals and physicochemical parameters averaged over core depth.	68
Table 14. Methylmercury concentrations following a 10°C change in sediment temperature.	72
Table 15. Mercury concentration in fish flesh taken from the River Yare between Thorpe and Rockland Broad.	84
Table 16. Mercury concentrations in British Rivers.	85
Table 17. Methylation and demethylation of mercury by bacteria.	88

List of Figures

	Page No.
Figure 1. Sample transect locations on the River Yare.	12
Figure 2. Plan and cross section showing field sampling technique.	14
Figure 3. <i>In situ</i> determination of sediment temperature and pH in surficial grab sample	16
Figure 4. Cantley sample site.	18
Figure 5. Sampling sites in Surlingham, Wheatfen and Rockland Broads.	20
Figure 6. Sampling sites for the seasonal survey of Rockland Broad (1991-1992).	21
Figure 7. Longitudinal distribution of mean transect total mercury loadings in River Yare surficial sediments.	31
Figure 8. Comparison of the low level tailing of total mercury within River Yare surficial sediments, 1987 and 1992.	33
Figure 9. Comparison of mean transect copper concentrations in surficial sediments from 1986, 1987 and 1992.	35
Figure 10. Longitudinal distribution of mean transect loadings of methylmercury in River Yare surficial sediments.	37
Figure 11. Percentage ratio of methyl/total mercury plotted against distance from Whitlingham sewage treatment works.	39
Figure 12. Methylmercury concentrations in surficial sediments in proximity to Cantley, 1990 survey results.	41
Figure 13. The depth distribution of total mercury in River Yare sediment cores (1992 data).	47
Figure 14. Total mercury concentrations over time. Laboratory based tank experiments.	51
Figure 15. Temporal variability in methylmercury concentrations under controlled temperature conditions (12°C).	52
(i) Contaminated sediment: Rockland Broad control.	52
(ii) Contaminated overlain by a clean sediment: Ormsby overlying Rockland.	53
iii) Contaminated overlying clean sediment: Rockland overlying Ormsby.	54
Figure 16. The depth distribution of total copper in River Yare sediment cores (1992 data).	57
Figure 17. Spatial distribution of total and methylmercury in surficial sediments from Rockland, Wheatfen and Surlingham Broads.	59
Figure 18. (i) Vertical distribution of total and methylmercury in five cores from Rockland Broad (1990).	61
(ii) Vertical distribution of total and methylmercury in cores from Wheatfen Broad	62

	Page No
Figure 18. (iii) Vertical distribution of total and methylmercury in cores from Surlingham Broad.	63
Figure 19. Differences in the vertical distribution of total mercury in Rockland Broad sediment cores.	65
Figure 20. Within site variability of total mercury concentrations (Coring site 5, Rockland Broad).	66
Figure 21. Seasonal variations in the vertical distribution of methylmercury, redox, sulphate and sulphide in Rockland Broad sediments.	69
(i) Coring site 2	69
(ii) Coring site 3	70
Figure 22. Seasonal changes in sediment temperature with core depth.	71
Figure 23. Seasonal variations in mercury resistant bacteria and methylmercury in Rockland Broad sediments.	76
Figure 24. Concentrations of total mercury in final effluent from Whitlingham STW, 1976-1990.	81

List of Appendices

		Page No.
Appendix 1.	The behaviour of methylmercury in sediment samples during storage.	103
Appendix 2.	Diagrammatic representations of Rockland Broad seasonal survey depth distribution of physicochemical parameters.	105
	(i) Core 1	105
	(ii) Core 2	107
	(iii) Core 3	109
	(iv) Core 5	110
	(v) Core 6	113
Appendix 3.	Seasonal variations in mercury resistant bacteria and methylmercury in Rockland Broad sediments.	115
	(i) Core 1	115
	(ii) Core 2	116
	(iii) Core 3	117
	(iv) Core 5	118
	(v) Core 6	119

GLOSSARY

Abiotic	Non living part of an ecosystem.
Aerobic	Presence of free oxygen (oxic).
Anaerobic	Absence of free oxygen and inorganic substances.
Anoxic	The absence of free oxygen but the existence of inorganic substances which can provide oxygen (eg sulphate, nitrate).
Bioaccumulate	The ability of a living organism to concentrate, accumulate and biomagnify a chemical substance either from the surrounding medium (bioaccumulation) or via the food chain (biomagnification).
Biosorption	The adhesion of substances to biological cells.
Biotic	Living part of an ecosystem, pertaining to life.
Demethylation	Ability of Hg resistant bacteria to metabolize methylmercury to elemental mercury.
Facultative anaerobes	Organisms capable of growth in the presence or absence of oxygen.
Heterotrophic	Organism which utilizes organic matter as an energy source.
Lipophilic	Affinity for fat.
Methylation	Addition of methyl groups to metal (Hg, As, Se, Pb) by means of enzymatic activity.
Microaerophilic	An organism that can exist in very little free oxygen.
Oxidation	The gain of oxygen or loss of electrons by a compound.
Redox potential	The electromotive force in mV set up in a solution between standard electrodes due to the concentration of oxidizing or reducing substances. Aerobic (oxidising systems) +200 to +600 mV. Anaerobic processes (-100 to -200 mV)
Reduction	The loss of oxygen or gain of electrons by a compound.
Reducing/oxidising	Conditions in sediment can be defined as either reducing or oxidising depending on the availability of oxygen. A reducing environment is deficient in free oxygen, while in an oxidising environment oxygen is readily available.

2. INTRODUCTION

Imperial College of Science, Technology and Medicine, London, was commissioned by the National Rivers Authority (formerly Anglian Water Authority) to undertake annual surveys of the River Yare to monitor the magnitude and spatial distribution of total and methylmercury within surficial sediment layers. This followed the discovery in 1985 that eels taken from the River Yare contained mean mercury concentrations of 0.57 mg kg^{-1} wet weight, almost twice the 0.3 mg kg^{-1} limit set by the 1984 EEC Directive (Council of European Communities, 1984). This was of particular concern since eels are fished commercially on the Yare for human consumption.

The contamination was historical, originating from an industrial source that discharged (under licence) quantities of mercuric halides and copper to the public sewer during the late 1960s to mid 1970s. The original discharge consent for the chemical company permitted the emission of 2000 kg a^{-1} of mercury to the sewer, this limit was set by Norwich City Council; the regulatory authority at that time. The consent was subsequently reduced in the light of work published in the mid 1970s that highlighted the potential health effects associated with mercury and its organic derivatives (Smith and Smith, 1975). The consent limit currently stands at 48 kg a^{-1} and effective in-house pollution control means that actual emissions are well below this value. Discharge controls however, are likely to become increasingly stringent as measures are introduced to try and obtain a 50-70% reduction in the amount of priority pollutants discharged into the North Sea by 1995 (based upon 1985 levels). This is in line with recommendations made by the 2nd and 3rd Ministerial Conferences on the North Sea in November 1987 and March 1990.

An effluent discharges from the chemical company are conveyed via the public sewerage system to Whitlingham sewage treatment works (STW). Average mercury removal efficiencies across the works are in the order of 83% (Goldstone *et al.*, 1990). Final effluent is subsequently discharged to the River Yare. A significant reduction in the amount of mercury released from Whitlingham STW has occurred in the last 17 years. Current final effluent mercury concentrations are $<0.1 \text{ } \mu\text{g l}^{-1}$ and fall below the EEC List I criterion for dangerous substances in surface waters. Despite substantial reductions in emission levels in recent years, the River Yare has undergone considerable cumulative loading of mercury, the majority of which now resides within bottom sediments.

Sediment analysis undertaken in 1986 revealed the existence of a mercury contamination plume originating at Whitlingham sewage treatment works (Bubb *et al.*, 1991). Mercury concentrations ranged from $0.05\text{-}32.9 \text{ mg kg}^{-1}$ producing mean enrichment 2-30 times greater than catchment background levels. The discovery of methylmercury within the sediments

(0.7-13.2 $\mu\text{g kg}^{-1}$) was of particular concern because methylmercury has the potential to bioaccumulate and was the major causative agent responsible for 784 official cases of Minamata disease in the Minamata bay district, Japan, during the late 1950's and early 1960's. Inorganic and methylated forms of mercury were discharged into the bay from the Chrisso Corporation chemical factory following the use of mercuric sulphate for acetaldehyde production. Methylmercury subsequently synthesized in the sediments, accumulated in fish and shellfish and then in the local population, for whom fish formed a significant proportion of the diet. Over a hundred people died, 21 within the first year of the disease and many people are still suffering subacute and chronic symptoms, such as neurological and renal disturbances, forty years after the incident was first diagnosed (Smith and Smith, 1975). The occurrence of significant quantities of both inorganic and methylmercury within the Yare sediments is consequently of concern since it too appears to be potentially available to indigenous aquatic organisms increasing the mercury body burden in eels and roach significantly above background. The Ministry for Agriculture, Fisheries and Food, however, calculated that an individual could consume 0.5 kg (≈ 16 oz) of eel flesh, taken from the contaminated reach of the River Yare, before any risk was posed to human health (Pers. comm. from MAFF, 1987). Although mercury within the River Yare was therefore perceived not to be a direct threat to human health, fears were still expressed over long term effects on water quality. It was in response to these concerns that Imperial College was commissioned to undertake further research into mercury within the River Yare system. A routine monitoring programme was set up to assess temporal and spatial changes in the distribution of total and methylmercury within the sediment system, while *in-situ* and laboratory based experiments were employed to elucidate the factors controlling the behaviour and fate of mercury within the system. The ultimate aim is to formulate management strategies for the River Yare that will safeguard water quality.

This report describes the research to date undertaken by Imperial College of Science, Technology and Medicine on mercury within the River Yare system. The information contained herein supersedes and subsumes all reports presented to the National Rivers Authority by Imperial College since the January 1987 report; *'Heavy metals' in the River Yare, Norfolk, and its associated Broads; Survey and Modelling*.

3. OBJECTIVES

To coalesce the information currently available on mercury contamination within the River Yare since 1986, in order to:

1. Assess the temporal changes in the magnitude and spatial distribution of total- and methyl-mercury within the sediments of the River Yare and associated Broad systems (Surlingham, Rockland and Wheatfen).

2. Clearly define the area and extent of mercury contamination.
3. Determine the absolute depth of mercury contamination in order to clearly define the nature of historical mercury loadings and recent temporal trends in mercury accumulation.
4. Identify the main environmental variables governing the synthesis and retention of methylmercury within the sediment compartment.
5. Predict the consequences of sediment disturbance upon methylmercury production and the implications for bioavailability.
6. Ascertain the mobility of mercury contained at depth within the sediment compartment, to determine if contaminated deposits at depth form a potential source of total and methylmercury for surficial sediments.

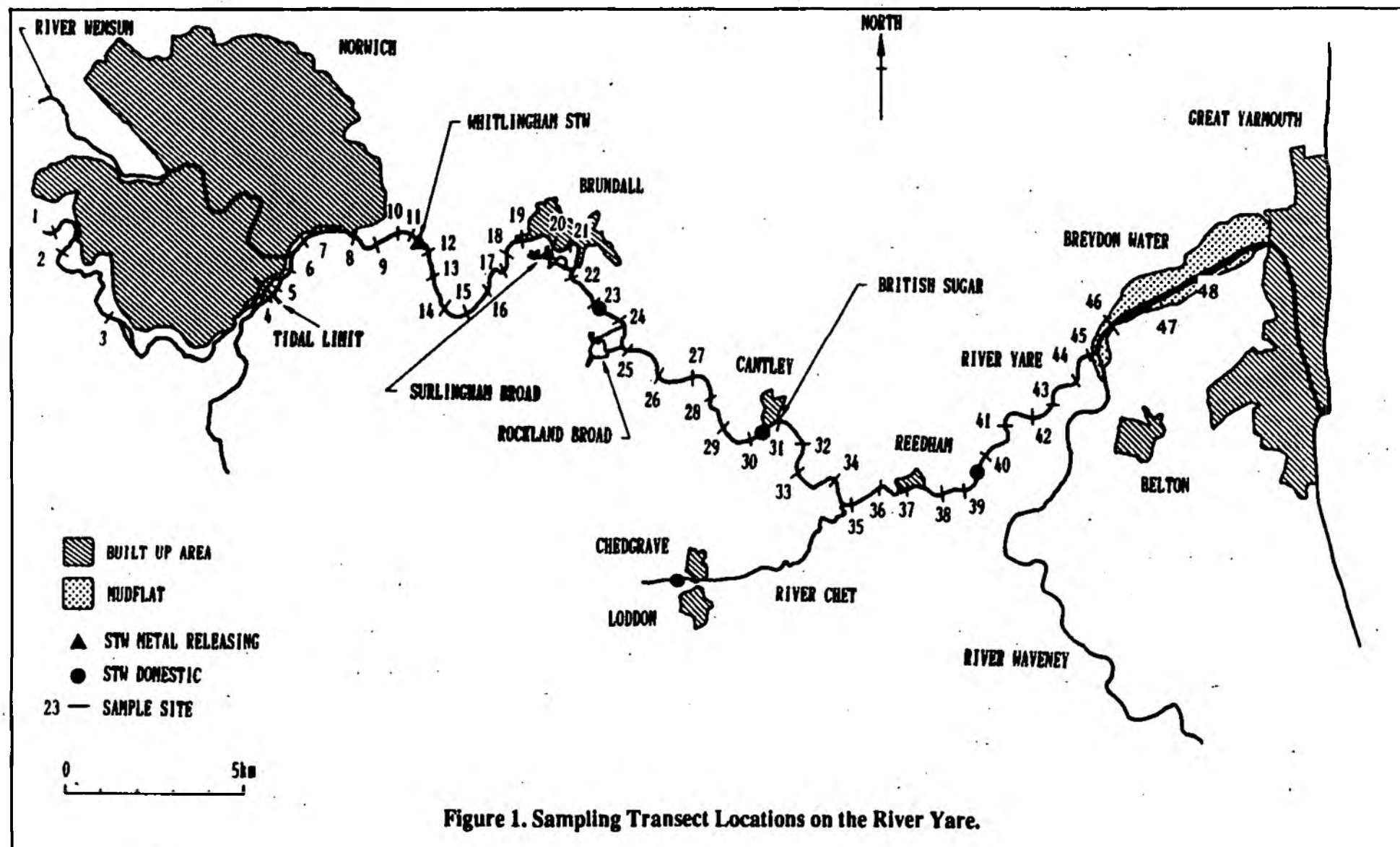
4. MATERIALS AND METHODS

4.1. Study Area

The River Yare and its major tributaries, the Wensum and Tas, drain an area of 988 km² across a low-lying plateau, standing 30-50 m above sea level. The river flows in an east-south-easterly direction until it enters Breydon water at the confluence to the River Waveney and hence flows to the North Sea at Great Yarmouth (Figure 1).

The Yare is characterized by a stable flow regime as dictated by its shallow bed gradient (approximately 3 cm fall per km) together with the moderating capacity of the Broad's, which produces a mean daily flow of 6.74 m³ s⁻¹. The tidal limit reaches upstream as far as Norwich, but the saline interface occurs at Cantley, with conductivity readings in the upstream reach in the range 540-950 μ S cm⁻², but exceeds 21,000 μ S cm⁻² in the estuarine zone. Dissolved oxygen concentrations vary seasonally in the range 54-140% saturation. The occurrence of algal blooms in the eutrophic waters can reduce the dissolved oxygen to 27%.

The geology of the area comprises Cretaceous chalk covered in mixed drift, boulder clays and fluvio-glacial sand and gravel. The excavation of the Brushwood Peats in the alluvial plain during the 12th-14th centuries resulted in the development of small water filled depressions or Broad's, which are now rapidly filling with soft uncompacted organic, calcareous mud at a rate of approximately 1 cm a⁻¹ (Garrad, 1984). The area maintains an extensive tourist industry based mainly on boating holidays and angling (Bell, 1980).



4.2. An Assessment of the Spatial Distribution of Mercury and Methylmercury within the Yare Surficial Sediments

4.2.1. Sampling strategy: The River Yare sediment surveys.

The initial sediment survey conducted in July 1986 covered a 16 km reach of the River Yare, from the Norwich New Cut (TG 254 081), situated 3.35 km above Whitlingham STW outfall, to Rockland Broad (TG 349 045) some 12 km downstream. The results identified a heavy metal contaminated zone centred upon the Whitlingham STW outfall but the study reach failed to encapsulate the entire downstream tailing of contaminants. The sampling strategy employed for the 1987 spatial survey extended the limits of the 1986 survey to encompass this downstream reach, and stretched from Colney in the west (grid reference TG 179 079) to Breydon water in the east (grid reference TG 491 068) covering some 52 km. This straddles the transects defined in the 1986 survey and divided the river into three main reaches:

- i) An upstream reach (Sites Y₁₋₆), located above the upper limit of the 1986 survey commencing at grid reference TG 189 082.
- ii) A middle contaminated zone, consistent with the 1986 survey transects (Sites Y₇₋₂₆).
- iii) A downstream reach, which covered the remaining 22 km into Breydon Water, (Sites Y₂₇₋₄₈).

Sediment samples: one per transect, were collected by means of a Burke Ekman grab from the upstream and middle study reaches. This allowed upper catchment background levels to be calculated from mean concentrations at sites situated above the tidal limit (Sites Y₁₋₄). Samples from the 'middle' section were used to compare contaminant levels with those defined in the 1986 sediment survey.

The downstream reach was characterised by a more detailed sampling programme which emulated the sampling strategy employed for the 1986 survey. Transects were set approximately 1 km apart as seen in Figure 2 and were aligned perpendicular to the flow, being fixed by distinctive landmarks on each bank and a centrally placed buoy. Five sediment samples were taken on each transect (bottom conditions allowing). These transect lines formed the basis for all subsequent surveys, the location of each is depicted in Figure 1.

With each successive survey a more detailed picture arose of the distribution and behaviour of mercury within the River Yare system. This allowed the sampling strategy to be rationalised, enabling research efforts to concentrate upon the main contaminated zone which stretched from Trowse in the west (Site Y₄) to Cantley in the east (Site Y₃₄). The number of samples per transect was reduced from 5 to 3 (see Fig. 2). This sampling strategy was utilised for both the 1990 and 1991 sediment surveys and was initially perceived to form the basis for all

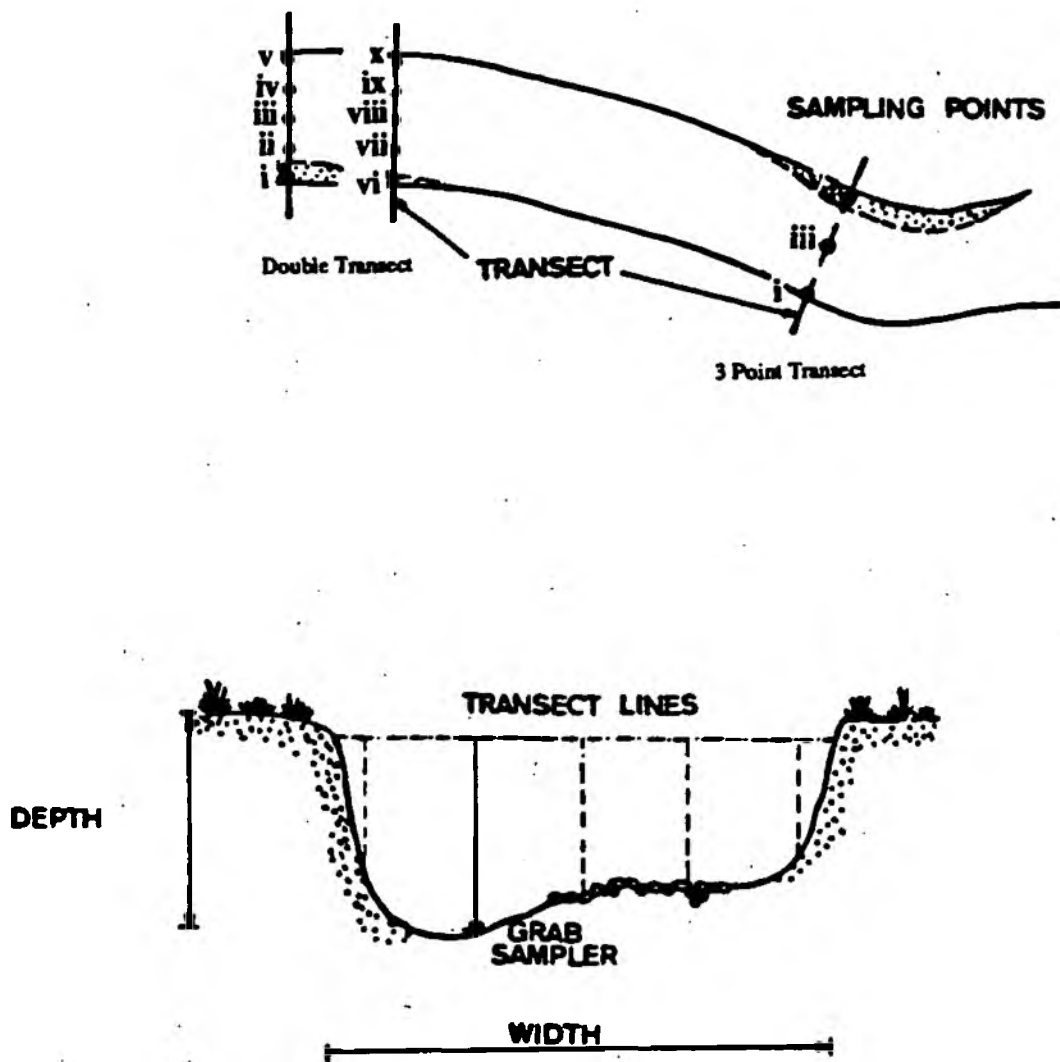


Figure 2. Plan and Cross Section showing Field Sampling Technique.

subsequent surveys. However, results from successive surveys revealed a significant decline in total mercury concentrations in surface sediments between 1986-1990. The 1992 annual River Yare survey was designed to evaluate the reason for this decline through the combined use of sediment cores, which would elucidate the vertical distribution of contaminants within the sediment compartment, combined with an extensive spatial survey of surficial sediments. The latter allowed an evaluation of the extent of downstream contaminant transport. Three samples per transect were collected over a 52 km reach, consistent with the 1987 sample transects. Ten sediment cores from the main contaminated stretch were used to assess the depth of mercury contamination. The position of the cores was based upon the 1986 sediment core sample locations, but extended the coring study area further downstream to Site Y₂₈. A summary of the sampling strategies employed in respective surveys is given in Table 1.

4.2.1.1. Sample collection.

All sampling procedures have been described in full in the 1987 report (Imperial College, 1987). In brief, surficial sediment samples were obtained using a stainless steel Burke Ekman grab and were placed in air tight high density polyethylene bottles which were completely filled to exclude all air, thus preventing oxidation of the sample. Sediment cores collected during the 1992 survey were obtained using a simple drainpipe corer designed by Imperial College workshop. This consisted of a 1.8 m length of plastic drainpipe of approximately 10 cm dia. split over half its length to allow core extrusion which was sealed by tape during use. The sediment was held in place by the suction supplied by a bung inserted into the lid which was removed prior to inserting the corer into the sediment. Cores were subdivided into 2.5 cm intervals over the top 20 cm, then at 5 cm intervals to the base of the core. *In-situ* temperature, pH and redox were determined using a portable probe (ELE International, Hemel Hempstead, UK) as illustrated in Figure 3 and the sediment appearance and texture logged. The samples were returned to the laboratory as soon as possible after collection, and processed in a manner to preserve their *in-situ* mercury concentrations.

4.2.1.2. Sample processing

All samples were subdivided to obtain separate samples for heavy metal analysis, methylmercury and physico-chemical determinants. Subsamples were placed in acid leached high density polyethylene bottles. Total mercury samples were preserved by the addition of 1% (v/w) Aristar grade HNO₃ and 0.05 % (w/v) K₂Cr₂O₇ according to recommended methods (Comm. Anal. Qual. Control, 1984). Samples for methylmercury analysis were frozen on the day of collection following an evaluation of a number of different preservation schemes which proved that freezing of sediment best preserved the intrinsic properties of the sample (experimental results are presented in Appendix 1).

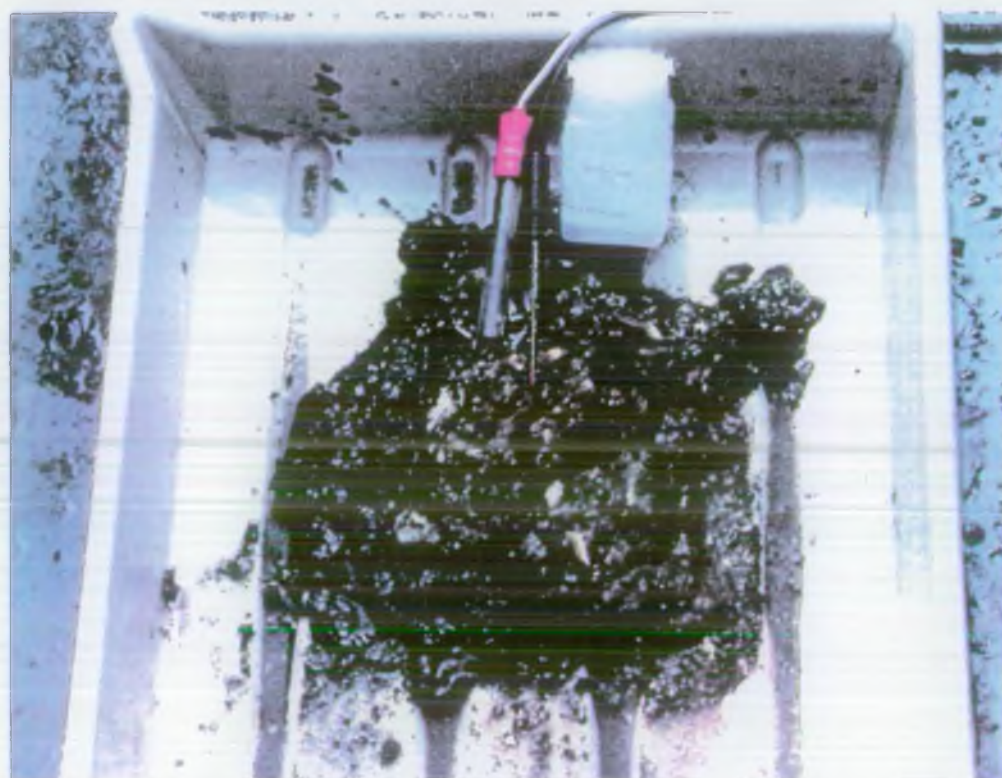


Figure 3. Insitu determination of sediment temperature and pH in surficial grab samples.

Table 1. River Yare sampling strategies for surficial sediments (1986-1992).

Year	Month	Site numbers	Sample reach (km)	Samples per transect
1986	7-14 May	7-26	16	5
1987	10-24 Oct	1-26	30	1
		27-48	21	5
1989	16-18 July	4-46	40	1
1990	16-19 July	4-34	28	3
1991	3-7 June	4-34	26	3
1992	29 June-3 July	1-49	52	3

4.2.2. An Evaluation of the Methylmercury Anomaly in the River Yare Sediments at Cantley.

Results from the 1987 and 1989 River Yare spatial survey revealed intermittently high loadings of methylmercury in the vicinity of Cantley (Site Y30-32), despite low total mercury concentrations. A detailed survey of the Cantley area was undertaken in July 1990 to pinpoint the main zone of methylmercury enrichment and to assess the effect of pH, temperature and organic loading upon methylation in this particular area. A number of additional sample transects were incorporated into the overall River Yare sampling framework. Two samples were taken on each additional transect and *in-situ* measurements were obtained for sediment pH and temperature. Sample site locations are shown in Figure 4.

4.3. An Assessment of the Vertical Extent of Total and Methylmercury Contamination within the Shallow Broad Systems Bordering the River Yare.

4.3.1. The Broads surveys (Rockland, Surlingham and Wheatfen Broads).

The initial 1987 Imperial College report contained information on the vertical distribution of metal contaminants within the sediment compartments of Rockland and Surlingham Broads. Data interpretation was however hindered by the subdivision of cores into stratigraphic rather than depth integrated units. The amalgamation of 50 cm or so of mercury contaminated sediment could have led to the dilution of the more heavily contaminated layers and prohibited an accurate assessment of the historic loading sequence of mercury within the system. Rockland and Surlingham Broad were re-sampled in May and June 1990, together with Wheatfen, an offshoot of Rockland Broad, to assess the magnitude and vertical extent of mercury contamination within these shallow lakes. Wheatfen Broad was added to the sampling scheme for two reasons:

1. Wheatfen Broad is a relatively isolated body of water which is inaccessible to motor cruisers and should therefore be a relatively undisturbed system.

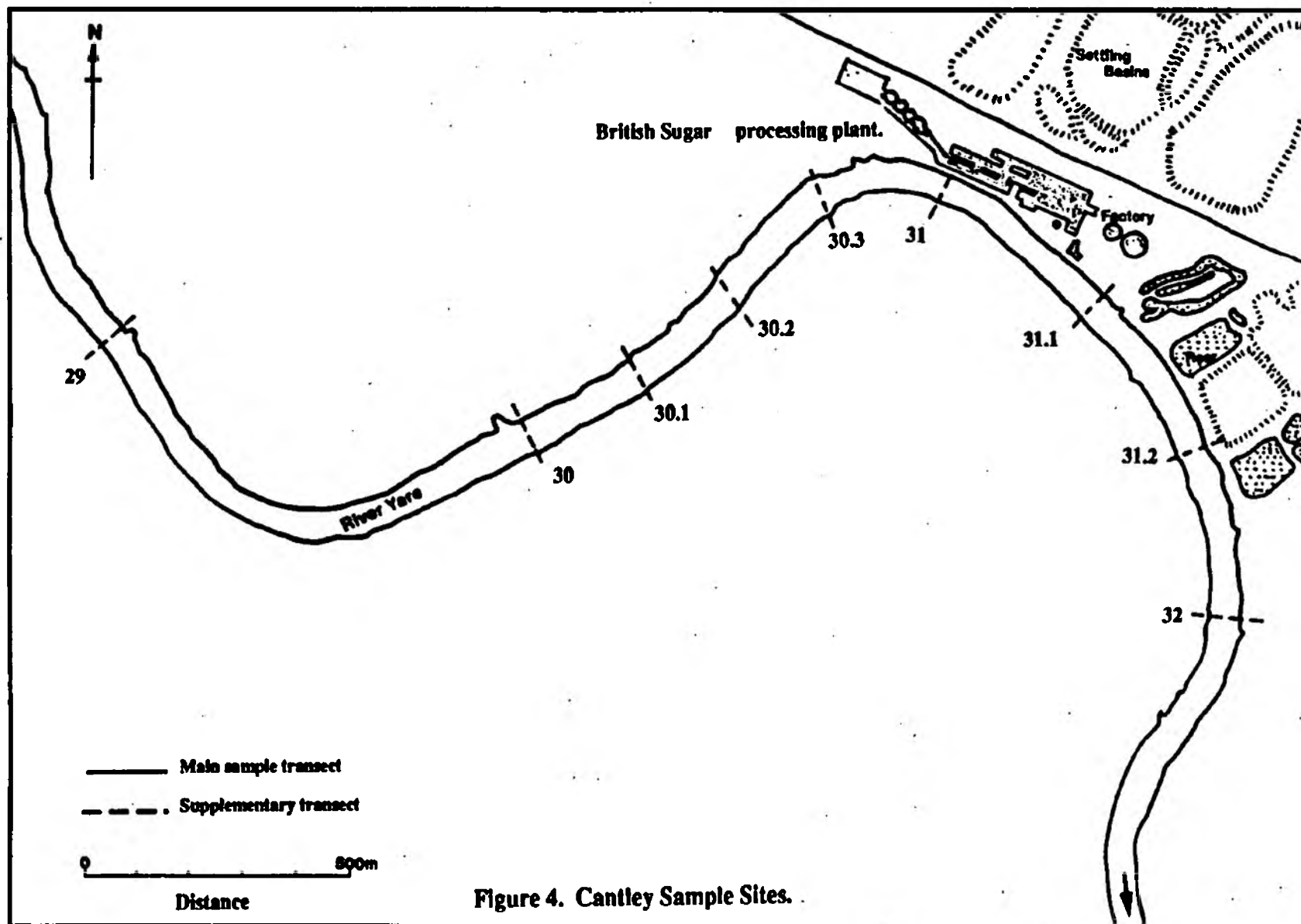


Figure 4. Cantley Sample Sites.

2. Analysis of spot sediment samples by the NRA showed that Wheatfen sediments contained elevated levels of mercury and a more detailed investigation of this area was called for.

4.3.2. Sampling strategy

Cores and surficial sediments were obtained from the Broads as shown in Figure 5, the cores sampling strategy was based on the 'W' shaped pattern previously employed in the 1986 Broads surveys. The cores were divided into 4 cm intervals, or every 2 cm for short cores and processed as described in Section 4.2.1.2.

4.4. To Assess the *In-situ* Seasonal Variations in Methylmercury Production and Elucidate the Factors Controlling Methylation.

4.4.1. Rockland Broad *in-situ* seasonal experiments

4.4.1.1. Study site

Rockland Broad lies to the north-east of Norwich and approximately 9 km downstream from Whitlingham sewage treatment works at ordinance survey co-ordinates TG 30, 333 053. Access to the Broad is gained from the River Yare via an 800 m long dyke; 'The Fleet', and the Broad drains back into the Yare approximately 400 m further downstream via two small dykes. The 'Short Dyke' is the main exit channel for boat traffic. Rockland Broad supports a large and varied population of aquatic wildlife. There is a single navigation channel bisecting the Broad at its shortest edge, leaving the majority of the Broad relatively undisturbed by boat traffic.

Rockland Broad was chosen to be the study site because of its relatively undisturbed nature, having many quiet, sheltered areas hidden behind islands of reed beds supported in the sediments. Rockland Broad was also known to act as a 'sink' for mercury and other heavy metal contaminants which caused an elevation in loadings compared to adjacent river channel sites (Imperial College, 1987).

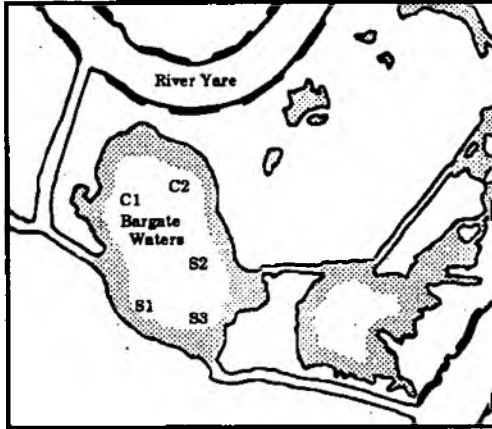
4.4.1.2. Sampling strategy

Sediment cores were obtained from Rockland Broad from five pre-designated sample sites (Figure 6) which were marked by wooden poles to facilitate sample positioning on subsequent surveys and fixed with compass bearings to distinctive marker points. Samples were collected on a 3 monthly basis over 1 year:

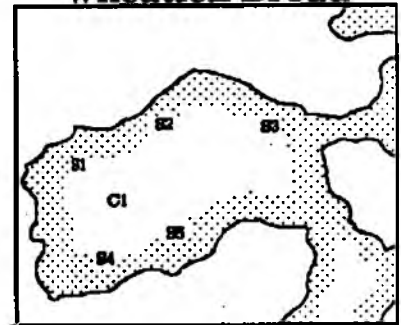
- i) Spring survey 28th May 1991
- ii) Summer survey 6th August 1991

Figure 5 : Sampling Sites In Surlingham, Wheatfen and Rockland Broads

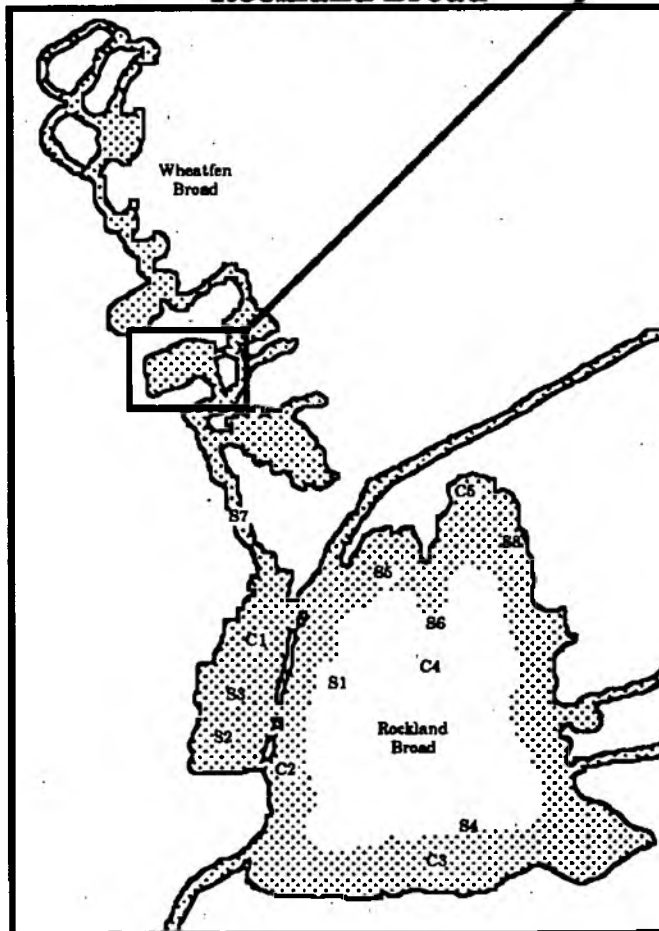
Surlingham Broad (Bargate Waters)



Wheatfen Broad



Rockland Broad



c = core.
s = surficial.

0 500
metres

- ii) Autumn survey 25th November 1991
- iii) Winter survey 17th March 1992

A sixth site was sampled in the first spring survey (Site 4 in Fig. 6), but its proximity to the navigation channel produced a core profile with little vertical stratification and consistently low total mercury concentrations which negated the relevance of the site for further seasonal monitoring.

The cores were obtained using a simple drainpipe corer designed by Imperial College as described previously. Care was taken to ensure, that where possible, sample cores extended down to the basement stratum, so an absolute depth of contamination could be defined. The *in-situ* temperature of the core was measured immediately on taking the core using a temperature probe (ELE International, Hemel Hempstead, UK). The cores were subdivided into 4 cm intervals and placed with minimal disturbance in acid washed polyethylene bottles which were filled completely to exclude all air, sealed and stored out of direct sunlight.

A study of bacterial populations present in the sediments of Rockland Broad has been undertaken to assess the relationship between mercury resistance in bacteria and methylmercury concentrations with depth. Jenkins cores were taken at each site which preserved the intrinsic chemical and bacterial properties of the sediment. The Jenkins corer (Freshwater Biological Association, Ambleside, UK) also facilitated fine subdivisions (2 cm) of sediment layers to be taken which gives a more accurate picture of the distribution of determinands in surface samples.

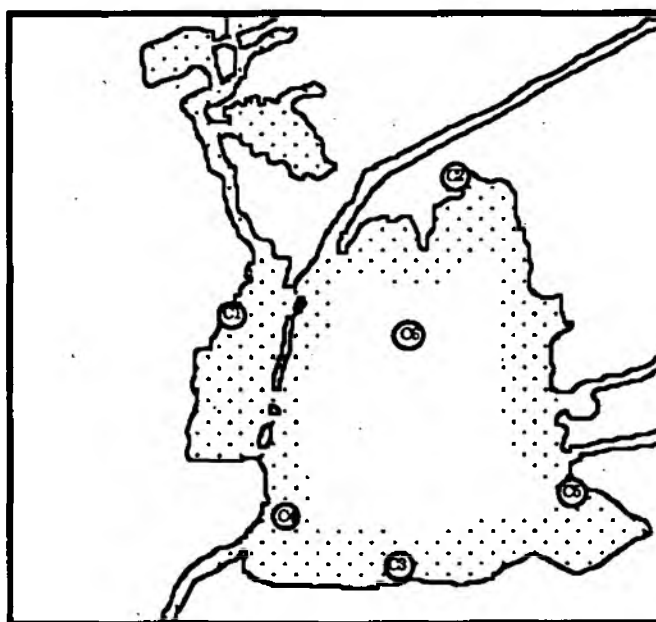


Figure 6 . Sampling sites for the seasonal survey of Rockland Broad (1991-1992).

4.4.1.3. *Sample processing and characterisation*

Samples were returned to the laboratory on the day of collection and stored overnight at 14°C. Sediments were analysed for total and methylmercury, total and volatile solids, sulphide and sulphate, chloride, pH, redox potential, bacterial numbers and resistance to inorganic mercury. Analytical methods and procedures for these determinands are detailed in Section 4.6.

4.5. Laboratory Based Tank Experiments Designed to Evaluate the Movement of Mercury from Buried Contaminated Layers to Cleaner Surficial Sediments

Three different sediment types of varying degrees of mercury contamination were employed to ascertain the mobility of buried mercury in a static undisturbed system. The experiment was conducted in a series of 60 litre cylindrical tanks which contained various combinations of contaminated and uncontaminated sediment; overlain by river water. Rockland Broad sediment was designated as a 'contaminated' stratum since its silty matrix was shown from the 1990 Broads survey to contain mercury concentrations of up to 30 mg kg⁻¹. Clay sediment from the Yare at Cantley provided an alternate sediment source and was chosen principally because of the intermittent presence of methylmercury in the surface sediment, despite low total mercury concentrations. Sediment obtained from Ormsby Broad was utilised as an uncontaminated control.

The six tanks contained the following combinations of sediment:

- | | |
|--------|--|
| Tank 1 | - Rockland sediment only. |
| Tank 2 | - Cantley sediment only. |
| Tank 3 | - Ormsby sediment overlying Cantley sediment. |
| Tank 4 | - Ormsby sediment overlying Rockland sediment. |
| Tank 5 | - Rockland sediment overlying Ormsby sediment. |
| Tank 6 | - Cantley sediment overlying Ormsby sediment. |

The tanks were made of 'food grade' medium density polyethylene and were cleaned according to standard procedures as defined in Section 4.7.

4.5.1. Sampling strategy

The sediments were collected on the 19th March 1991. Sediments from Cantley and Rockland Broad were collected using a dredger. Care was taken to collect only surficial sediments. The shallow nature of Ormsby Broad allowed the use of a Burke Ekman grab to obtain surficial sediment. All sediments were placed in new reinforced plastic builders bags and returned to the laboratory on the day of collection and stored overnight at 12 °C.

The tanks were set up within 24 h. Water from Ormsby Broad was added to each of the sediment filled bags to facilitate mixing and was added until a pasty consistency was obtained. The mixture was then thoroughly homogenised by stirring. The homogenized sediment was poured into the tanks. The upper layers in tanks 3 to 6 were poured carefully from a jug to minimise intermixing between contrasting sediment types. The tanks were kept in a temperature controlled room at 12 °C.

Cored samples were taken from the tanks on a pre-designated grid pattern, initially on a daily basis, then at increasing intervals up to one month apart over a 1 year period. The coring apparatus was designed to minimise sample disturbance within the cored sample and the tanks. The corer comprised two close fitting concentric tubes. The inner tube (o.d. 38 mm, i.d. 32 mm) was split along almost its entire length to facilitate core extraction, the sections being taped during sample extraction. The outer core (o.d. 45 mm, i.d. 39 mm) remained in place following core acquisition, to prevent sediment collapse within the tank. The cores were subdivided into a number of segments to highlight movements in total and methylmercury between and within the layers. Samples were obtained from the surface, middle and bottom portions of the control tanks (tanks 1 and 2), while four samples were taken from the layered tanks, the middle portion straddling the two sediment types was characterised by two samples, one immediately above and one immediately below the divide. Sediment samples for methylmercury determination were frozen in acid washed polyethylene sample bottles as a means of preservation. Sediment samples for total mercury were digested within one hour of collection, eliminating the need for sample preservation. The samples were also analysed for total and volatile solids.

4.5.2. The effect of temperature upon methylmercury synthesis

The importance of temperature as a control upon sediment mercury methylation was evaluated by subjecting tanks containing Rockland Broad sediment (Tanks 1,4 and 5) to an $\sim 10^{\circ}\text{C}$ rise in temperature following their transfer to a room at 22°C . Cores were extracted on day 1 (12°C), on day 4, after the tanks had attained temperature (22°C) and finally after acclimatisation, on day 10 (22°C). Sediment temperature was measured using an electronic thermocouple. Sample collection, processing and pH and redox measurements were undertaken as previously described (Section 4.5.1).

4.6. Analytical Methods

4.6.1. Total mercury analysis

Sediment samples for total mercury analysis were digested in aqua regia (1 part HNO_3 , 3 parts HCl) according to the procedure recommended by Anglian Water Authority (Imperial College,

1987). Sediments obtained during the 1992 sampling campaign were digested in a Milestone, MLS 1200 Mega microwave digester (Roth Scientific Ltd, Farnborough, UK) in accordance with the manufacturers operating instructions, utilising 2 g of wet sediment and 5 ml aqua regia.

Total mercury determinations were carried out using a Perkin Elmer FIAS-200 Flow Injection Atomic Spectrometry System with AS-90 autosampler linked to a Perkin Elmer 5100 AAS (Perkin Elmer Ltd, Beaconsfield, UK). Analytical conditions were as specified by the manufacturers, utilising 0.2% NaBH₄ in 0.05% NaOH as the reductant and 10% HCl as the carrier solution. The NaBH₄ requires filtration to eliminate undissolved reagents and was made up daily. Anti-foaming agent (Dow Corning Silicone DC anti foaming emulsion) was added to the NaBH₄ to minimise foaming in the FIAS chemifold and carry over into the quartz cell. A few drops of 5% (w/v) potassium permanganate were added to both standards and samples to prevent rapid reduction of the mercury. Standard solutions were prepared from Spectrosol 1000 mg l⁻¹ mercuric nitrate via three serial dilutions. The system was calibrated on 2, 5, 10 and 30 µg l⁻¹ solutions. Digested samples, standards and reagent blanks were analysed in replicate. The results were recorded as mg kg⁻¹ dry weight of sediment.

4.6.2. Methylmercury analysis

4.6.2.1. Instrumentation and analysis

A Hewlett Packard model 5710 gas chromatograph (Hewlett Packard, Bracknell, UK) coupled with a Perkin Elmer Model 1100 atomic absorption spectrophotometer (Perkin Elmer Ltd, Beaconsfield, UK) was used in accordance with the following chromatographic conditions:

Injection temperature:	200°C
Detector temperature:	200°C
Temperature program:	80°C for 4 min 180°C for 2 min
Carrier Gas:	High purity argon
Make up Gas:	High purity argon
Flow rates:	Carrier Gas 25 ml min ⁻¹ Overall 60 ml min ⁻¹
Column:	15 m DB wax wide bore Capillary column 1 µm film thickness (J&W Scientific, Folsom, California, USA)
Sample volume injected:	5 µl

The column was conditioned by injecting methylmercuric chloride standards and a silanising agent; dimethyldichlorosilane (Sigma Chemicals Ltd, Poole, UK) until the mercury peaks stabilised. Once stable the column gave very good repeatability. A slow reduction in efficiency of the column occurred over time due to the build up of organic contaminants, which caused tailing of peaks. Further injections of silanising agent usually corrected this. However if

efficiency did not improve, the column was removed and the contaminated injector end of the column was cut away (about 30 cm). The column was then back washed with methanol and toluene. Once dry the column was replaced and reconditioned, returning its original efficiency.

4.6.2.2. *Standards preparation*

Extraction of organomercury compounds from sediment utilizing CuSO_4 and KBr converts all species into the methylmercuric bromide form and consequently elutes only one analyte peak. Since the retention time of methylmercuric chloride (MeHgCl) is the same as for MeHgBr and is inherently more stable, standards were prepared with MeHgCl . Approximately 25 mg of MeHgCl (weighed to the nearest 0.1 mg) was weighed into an 'A' grade 10 ml volumetric flask, dissolved with double glass distilled toluene (Rathburns, Walkerburn, U.K.) and made up to the mark. Intermediate standards were prepared by 100 fold dilutions of the stock solution. This solution was then serially diluted to give working calibration standards in the required range.

4.6.2.3. *Methylmercury extraction procedure*

Extraction methods are required to remove organomercurials from the sample matrix and concentrate them to within the limits of detection (Ealy *et al.*, 1973). Organomercury compounds in sediment samples are extracted with a solvent after treatment with copper sulphate and an acidified potassium bromide solution. The method detailed below is a modified version of the procedure presented in the 1987 Imperial College report.

A thoroughly mixed wet sediment sample (10g) was accurately weighed (to the nearest 0.01g) into a Nalgene teflon centrifuge tube. A 2 ml volume of 0.5 M CuSO_4 and 5 ml of 3 M KBr in 1 M Aristar H_2SO_4 were added. The screw caps were placed firmly into the tubes and were shaken vigorously on a automatic rotary flask shaker (Gallenkamp Ltd., Loughborough, UK) for 30 min. A 3 ml volume of double glass distilled toluene was then added and the mixture shaken vigorously by hand for 5 min, after which it was centrifuged at 3000 rpm for 10 min using a benchtop centrifuge (Gallenkamp Ltd., Loughborough, UK). The addition of CuSO_4 saturated the mercury binding sites releasing MeHg (CH_3Hg^+). KBr then transformed the free methylmercury into methylmercuric bromide. The toluene layer was transferred by micropipette into 1 ml graduated Wheaton V-vials (Phase Separations Ltd., Deeside, UK) the volume being recorded to the nearest 0.01 ml. The extract was heated to 70°C in a precision Multi-Block heater supplied by Alltech Associates (Carnforth, UK) and modified by Imperial College workshop to hold 9 vials. The extract was evaporated to approximately 0.1 ml, one tenth of its initial volume, the precise volume was later determined with a microlitre syringe.

4.6.3. Copper determinations

Sediment total copper concentrations were determined according to the procedures described in the Imperial College report (1987) utilising a $\text{HNO}_3/\text{H}_2\text{O}_2$ digestion prior to analysis by Flame AAS on a Perkin Elmer model 5000 AAS (Perkin Elmer Ltd, Beaconsfield, UK). For the 1992 samples however, 2 g of sediment was acid digested in a Milestone 1200 microwave digestion system (Roth Scientific Ltd, Farnborough, UK) and analysed by flame AAS utilising a Perkin Elmer Model 5100 system in conjunction with an AS 90 autosampler according to the analytical conditions specified by the manufacturer.

4.6.4. Sulphide determination

The water soluble sulphide content of the sediments (which is thought to be the most important sulphide fraction in terms of binding mercury) was determined using a sulphide ion specific electrode, combining and modifying methods developed by Craig and Moreton (1982). Standards were prepared from a stock solution of sodium sulphide, (1 ml of saturated sodium sulphide solution in 50 ml of sulphide antioxidant buffer (SAOB), made up to the mark in a 100 ml volumetric with distilled water). SAOB prevents oxidation of the sulphide by reducing any oxygen present and stabilizing the redox potential at a value at which sulphide oxidation is unfavourable. The high alkalinity of the SAOB also converts undetectable hydrogen sulphide and hydrosulphide ions into detectable divalent sulphide ions (Craig and Moreton, 1982).

The concentration of stock sulphide was determined by electrode titration with 0.1 M cadmium nitrate prior to calibration curve construction. The titrand (50 ml of stock sulphide solution) was added to 25 ml of SAOB and 25 ml of distilled water. The concentration of stock sulphide in mg l^{-1} (c) is given by:

$$c = (\text{ml of titrant}) \times 64$$

The volume of titrant used was taken as the point of inflection of the curve on a graph plotting volume of titrant used (ml) against potential recorded (mV).

Standards were made up in the following concentrations:

Standard A	=	0.05 c
Standard B	=	0.01 c
Standard C	=	0.001 c
Standard D	=	0.0005 c

where c equals the concentration of stock sulphide solution in mg l^{-1} .

The slope of the electrode was checked before analysis and a calibration curve constructed by immersing the sulphide and the double junction reference electrodes (EDT Analytical Ltd.,

London, UK) into each standard in turn, starting with the lowest. The standards were stirred at constant speed without a vortex until a stable reading was obtained.

The samples were prepared by accurately weighing 3 g of sediment into a beaker and adding 50 ml of SAOB and 50 ml distilled water. The mixture was stirred vigorously until the sediment was thoroughly dispersed and the samples were left to stand for 20 min prior to potentiometric measurement. All analyses were carried out in a temperature controlled room at 14°C under fluorescent lighting. Concentrations were calculated as mg kg⁻¹ dry weight of sediment.

4.6.5. Sulphate determination

Sediment 2.5 g was shaken for 30 min with 25 ml of milli-Q water, filtered through 0.45 µm Whatman filter paper prior to sulphate detection by Waters HPLC (IC-Pak A column and a borate/gluconate eluent) with conductivity detection (Millipore (UK) Ltd., Watford, UK).

4.6.6. Chloride determination

Chloride concentrations were analysed using a solid state chloride electrode Model 94-17B and a double junction reference electrode, Model 90-02 (Orion Research Ltd., Forest Row, UK) according to the Standing Committee of Analysts (1985) procedure. Standards were prepared from a NaCl 1000 mg l⁻¹ stock solution. Sediment samples (30 g) were accurately weighed into polyethylene bottles together with 75 ml of distilled water and mechanically shaken for 10 min. The sediment was left to settle and the supernatant decanted into a beaker. Ionic strength adjuster (ISA) (2 ml 5M NaNO₃) was added to each sample prior to analysis.

4.6.7. Total and volatile solids determination

These were carried out in accordance with standard methods (Standing Committee of Analysts, 1980). The measurement of organic content by 'loss on ignition' has its limitations, but a good relationship has been observed for organic carbon measured in this way and by total organic carbon analysis (Luoma and Bryan, 1981; Brennan, 1989).

4.6.8. Viable counts on mercury and non-mercury amended agar plates

Viable bacterial counts were undertaken on the Jenkins core samples to assess the relationship between sediment organomercury concentrations and aerobic mercury resistant bacteria, using the method of Olson *et al.*, (1991). This involved plating aqueous sediment extracts onto both mercury amended and non-amended plates. The Jenkins cores were stored at 14°C overnight before being extruded. Once extruded the sediment samples were processed immediately. All glassware was dry heat sterilised prior to use for 4 h at 180°C in a 'Hot Box' oven

(Gallenkamp Ltd., Loughborough, UK). Diluent and media were steam sterilised in a gas autoclave (121°C for 15 min).

Sediment material (10 g wet wt.) was added to 90 ml of phosphate buffer (American Public Health Association, 1985) in a 250 ml flask and shaken for 60 min on a flat bed shaker at ambient temperature and allowed to settle. Serial dilutions were spread plated either on to Plate Count Agar (PCA) amended with 50 mg l⁻¹ filter sterilised Hg as HgCl₂, or onto non-amended PCA (control). Colonies were counted using an illuminated colony counter (Gallenkamp Ltd., Loughborough, UK) after 7 days incubation at 22°C. Although mercury resistance in this study was determined on mercuric chloride amended plates, it is generally acknowledged that resistance to one type of mercury compound confers a generalised resistance to different types and concentrations of mercury species. The measurement of mercury resistance in bacterial communities therefore provides a measure of the real, or potential, ability of a contaminated system to promote mercury transformations from a variety of different mercury substrates.

4.7. Equipment

All glassware was of borosilicate glass to minimise adsorptive losses of mercury. All apparatus was cleaned by soaking in 5% v/v Decon 90 detergent (BDH Chemicals Ltd., Dagenham, UK) for 24 h to remove organic contamination, followed by 24 h in 10% v/v GPR grade nitric acid to reduce metallic contamination. Items were then thoroughly rinsed three times with distilled water and air dried.

4.8. Analytical Quality and Control

Precision and accuracy assessments were used to quantify experimental and instrumental errors associated with the analytical techniques and to validate the data generated. The precision of total mercury analysis was evaluated at three levels. Firstly, instrumental variation was quantified by five replicate analyses of 0.01 mg l⁻¹, 0.02 mg l⁻¹, 0.04 mg l⁻¹ and 0.06 mg l⁻¹ standards of mercuric nitrate which gave relative standard deviations (RSD) of 2-3 %. Secondly, five replicate analyses of a single sediment digestate were made, resulting in an RSD of <1.0%. Thirdly, experimental variation associated with the digestion process was assessed on duplicate analyses of five independently digested subsamples for the "hot plate" digestion method (described in the 1987 Imperial College report). An RSD value of 10.3% was obtained. Comparative RSD for the microwave digestion procedure were 7.6%. Certified reference materials were used to assess the accuracy of the total metal analytical procedure. The results are presented in Table 2 and compare well with the certified and guideline values. Detection limits for mercury were well below average sample background levels at 0.01 mg kg⁻¹.

Table 2. The accuracy of sediment digestions and AAS analysis for total mercury and copper.

Reference Material	Mercury			Copper	
	Measured	Certified	Uncertified	Measured	Certified
NBS 1645	1.3± 0.5	1.1 ± 0.5	-	106± 1.4	109±19
IAEA Soil 5	0.65	-	0.79	-	-
IAEA SL-1	0.20	-	0.13	-	-
CRM 277	1.66-1.72*	1.77±0.06	-	-	-
ABSS	-	-	-	56±4	50

NBS = National Bureau of Standards, standard river sediment.

IAEA = International Atomic Energy Agency.

CRM = Community Bureau of Reference, Certified reference material 277, estuarine sediment.

ABSS = Arkona Basin standard sediment. Ratified by 20 international laboratories (ICES).

* = microwave digested sample.

Precision of methylmercury analysis was evaluated on five replicate analyses of 0.24 ng, 0.72 ng and 1.20 ng standards of methylmercuric chloride which gave RSD's of 2.0%, 3.8%, and 4.6% respectively. The five replicate analyses of a single sediment extract resulting in an RSD of 3.8%. Analysis of five subsamples of independently extracted, methylmercuric chloride spiked sediment gave an RSD of 6.4% and an overall recovery >95%. Detection limits for methylmercury in real terms was 0.1 ng, which corresponds to about 0.1 µg kg⁻¹ in field samples.

5. RESULTS

5.1. River Yare Surficial Sediments

5.1.1. Assessment of the temporal and spatial changes in the distribution of total mercury within the River Yare surficial sediments

The magnitude and longitudinal distribution of inorganic mercury within the River Yare surficial sediments is depicted in Figure 7 for sampling campaigns undertaken between 1986-1992. The 1986 survey clearly identified the existence of a 14 km contaminant plume emanating from Whitlingham STW which, due to tidal reversals, distributed mercury both up and downstream of the outfall. Sediment mercury loadings failed to return to catchment background levels at the ends of the study reach which inferred the existence of a low level tailing of mercury beyond the limits of the 1986 survey reach. Average transect concentrations (a mean of 10 samples) ranged from 0.81-11.9 mg kg⁻¹ which represented a 2-30 fold increase over published background levels for non-contaminated sediments, while individual or 'spot' samples ranged from 0.05-32.9 mg kg⁻¹. Maximum mercury loadings occurred 1-2 km downstream from the outfall which inferred the rapid deposition of particulate bound mercury. If this 1986 data is taken as 'baseline datum', a significant decline in the concentration of inorganic mercury is readily apparent from Figure 7, particularly between 1986 and 1990. Table 3 provides a summary of mercury concentrations for individual surveys. Concentrations in spot samples obtained from the 1990 survey ranged from 0.01-4.68 mg kg⁻¹, compared to 0.05-32.9 mg kg⁻¹ in 1986 which represents a 7 fold decrease in maximum surficial sediments mercury loadings over this time period and a 4 fold reduction in mean study reach concentrations.

Table 3. Summary of total and methylmercury levels found within the River Yare surficial sediments between 1986-1992.

Date	Total Mercury (mg kg ⁻¹)				Methylmercury (µg kg ⁻¹)		
	Mean	Range	n	Enrichment ^a	Mean	Range	n ^b
May 1986	5.4	0.05-32.9	197	82	5.3 ^c	0.7-13.2	10 ^c
Oct. 1987	3.0	0.19-15.2	103	38	1.8	0.5- 6.4	26
July 1989	2.5	0.11-15.9	28	40	3.3	0.3-13.7	28
July 1990	1.3	0.01-4.68	78	12	7.7	0.7-29.5	74
June 1991	1.3	0.02-4.59	78	11	7.3	0.1-22.2	69
July 1992	1.7	0.01-6.89	125	17	3.8	0.1-21.8	62

^a Maximum level of enrichment compared to background levels of 0.4 mg kg⁻¹.

^b Number of samples containing detectable concentrations of methylmercury, all samples were analysed.

^c Preliminary study to assess the presence of methylmercury within the bottom sediments. Analysis was undertaken on a limited number of samples from the contaminated reach.

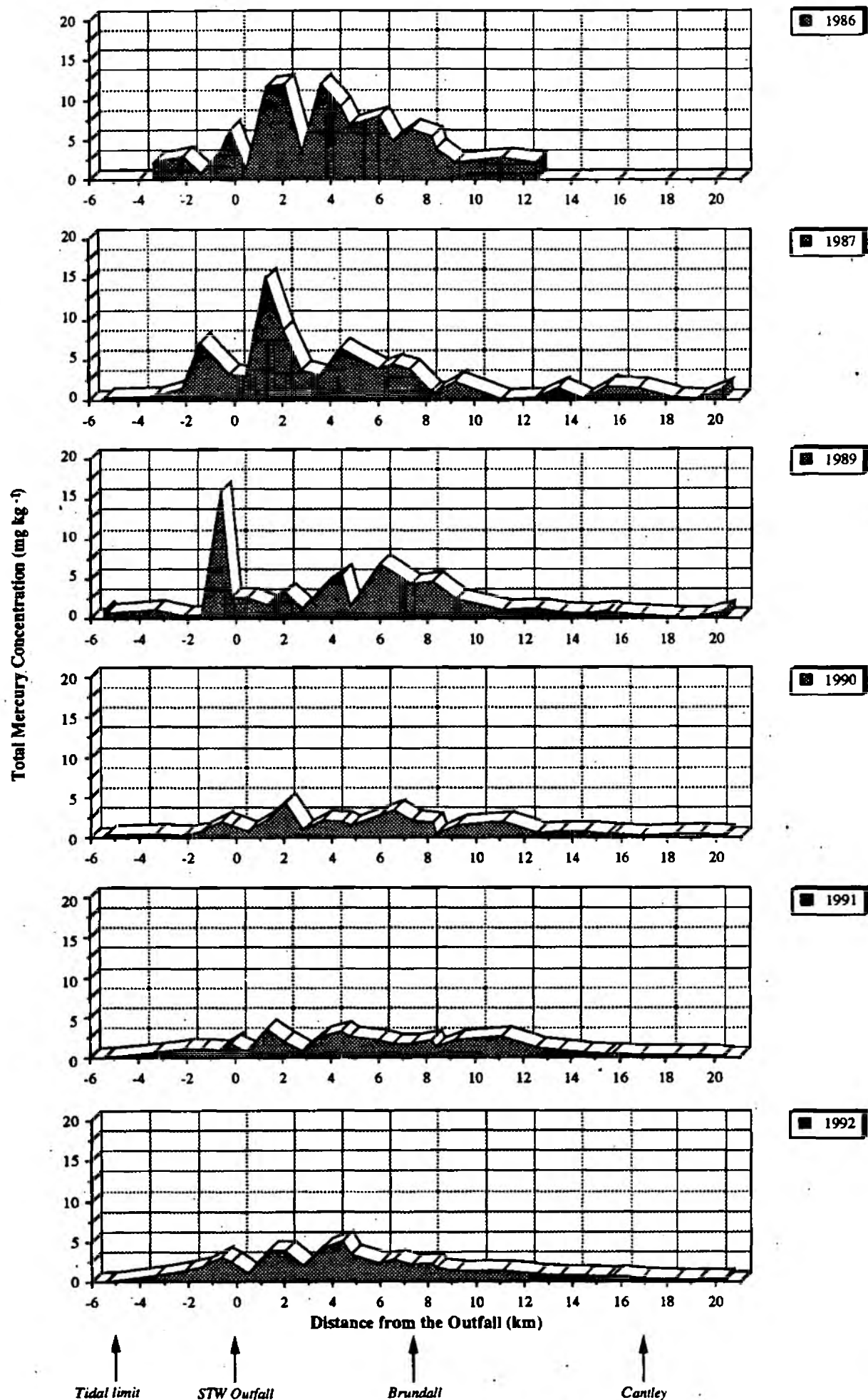


Figure 7. Longitudinal Distribution of Mean Transect Total Mercury loadings in River Yare Surficial Sediments.

Sediment total mercury concentrations appeared to have stabilised by 1990 since mean study reach concentrations remained fixed at 1.3 mg kg^{-1} for both the 1990 and 1991 surveys and comparative analysis using standard unpaired 't' test procedures failed to highlight a statistically significant difference between the data sets. The 1992 survey results revealed a slight increase in surficial sediment mercury concentrations above 1991 levels which was reflected in the increase in study reach means from 1.3 to 1.7 mg kg^{-1} . Eight sediment samples collected in 1992 contained concentrations $>4.59 \text{ mg kg}^{-1}$, the 1991 study reach maximum, all these samples were confined to a 5 km reach adjacent to Whitlingham STW (Sites Y₁₀₋₁₈). Statistical analysis, however, failed to uphold the presumption that the 1992 mercury loadings were significantly different from surficial sediment concentrations detected in the previous year. Student 't' test results revealed that the 1991/1992 population means were essentially the same ($\mu_1=\mu_2$), although when the analysis was rerun for samples confined to the 1986 survey reach, the area of greatest enrichment, the significance level assigned to this 't' statistic (0.1)¹ nearly caused the rejection of the hypothesis that $\mu_1=\mu_2$. What is emphatically evident from the succession of survey results is that total mercury concentrations in surficial sediments have undergone a substantial decline since 1986. There has however been little alteration to the overall shape of the contaminant plume. Peak loadings occurred consistently 1-2 km below the outfall and the main contaminated zone, which was redefined in the 1987 survey, has remained confined to a 17 km reach stretching from Site Y₅ to Site Y₂₇. If particulate bound contaminants were being transported downstream, mercury concentrations in the lower reaches would be expected to increase.

The possibility of downstream migration of contaminated particulates was first investigated in 1987 and was subsequently readdressed in 1992. The former study was employed to define the downstream tailing of contaminants which was inferred from the 1986 survey results, while the latter addressed the hypothesis that the observed decline in surficial sediment mercury concentrations was attributed to the downstream movement of particulate bound contaminants. Samples were obtained from a 52 km reach which stretched from the east of Norwich, westwards into Breydon Water. Results from these surveys are depicted graphically in Figure 8. The 1987 data revealed that the lower study reach was characterised by fairly low mercury concentrations which were on average 4 times lower than the means associated with the middle contaminated zone. A low level tailing of mercury was evident which produced a decline in mean transect loadings from 1.6 mg kg^{-1} at Site Y₂₇, (13.5 km below the outfall) to $<0.2 \text{ mg kg}^{-1}$ within Breydon Water. The low metal concentrations observed in Breydon Water, which are comparable to those obtained for similar sediments types in the upper catchment, implied that the estuarine zone was not a major sink for mercury. Intermittent 'pockets' of mercury enrichment were, however, evident within this lower study reach, as exemplified by

¹ A significance level of <0.05 would require rejection of the null hypothesis of $\mu_1=\mu_2$.

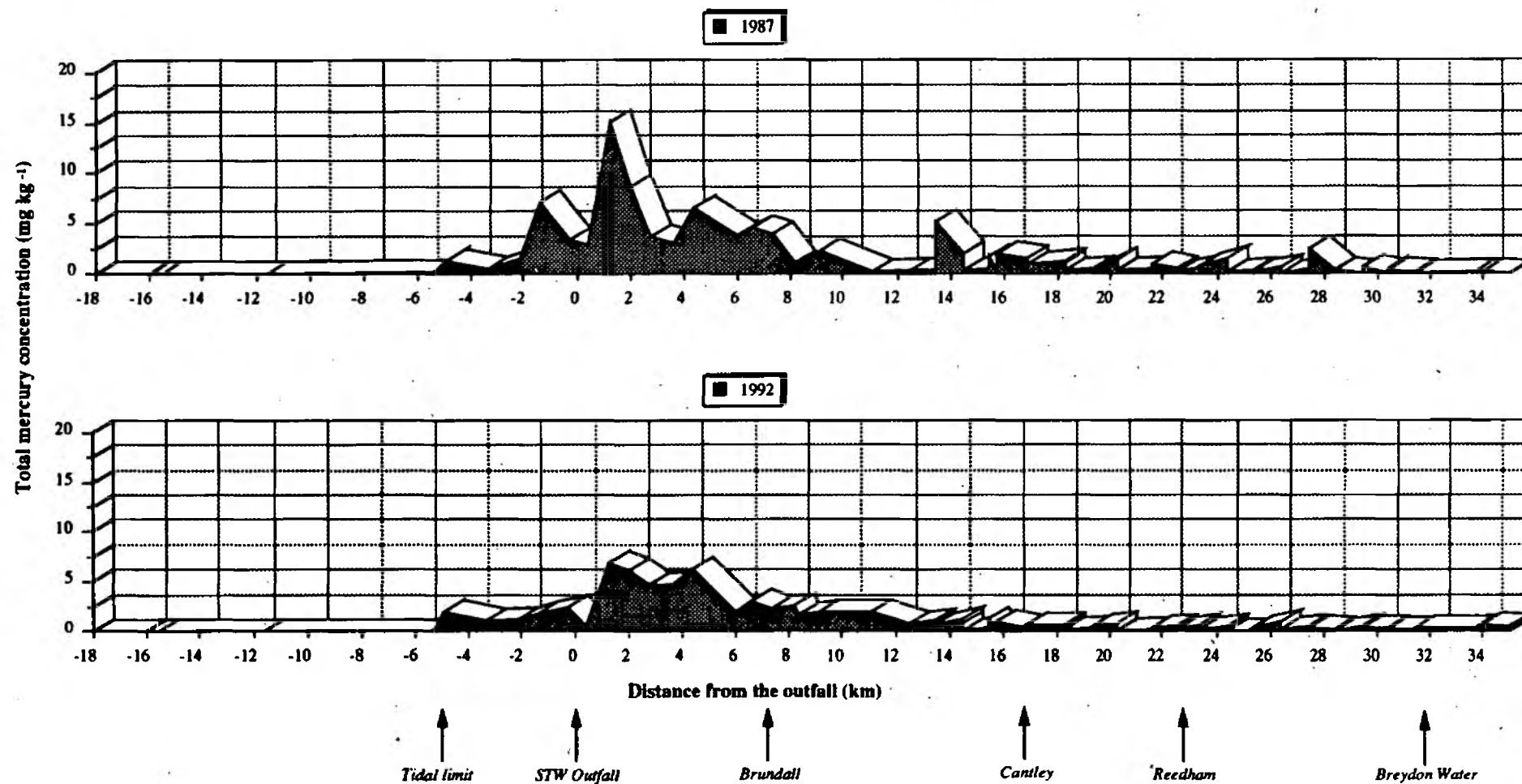


Figure 8. Comparison of the Low Level Tailing of Total Mercury within River Yare surficial Sediments, 1987 and 1992.

the 5.14 mg kg⁻¹ loading at Site Y_{27(v)} and the 2.38 mg kg⁻¹ at Site Y_{41(v)}, 27.4 km below the outfall, which were well in excess of average loadings for the lower catchment, but in general the major distribution pattern of mercury was one of small fluctuations about the mean. The lower study reach was characterised by a small decline in total mercury concentrations between the 1987 and 1992 surveys, mimicking the temporal mercury trend previously reported for the contaminated section. Concentrations remained low, approximating to catchment background levels but, unlike the 1987 profile, showed no enrichment anomalies.

Although this information implies that the downstream transport of mercury is not responsible for the decline in surficial sediment mercury loadings further verification was sought through inter-comparisons with the distribution and behaviour of copper. The status of copper as a co-pollutant with mercury from the industrial process, makes it an expedient surrogate for tracer studies within the Yare, particularly since the behaviour of both metals is governed, to a large extent, by particulate interactions. Both copper and mercury are therefore expected to behave in a similar manner.

5.1.2. Copper within the River Yare system

The longitudinal distributions of mean transect copper loadings within the Yare surficial sediments are depicted in Figure 9 for those sampling campaigns in which copper analysis was undertaken. The magnitude and spatial distribution of copper within the River Yare system has essentially remained unchanged since 1986. A summary of the copper data is given in Table 4 and illustrates similarities in sample means and ranges, a fact verified by 't' test analysis. The longitudinal profiles infer the existence of a point source contamination plume originating from Whitlingham STW. Peak copper concentrations occurred approximately 2 km below the STW outfall and gradually declined with increased distance downstream.

Copper loadings in the lower study area (below Site Y₂₇) have declined slightly since 1987, from a mean of 27.2 mg kg⁻¹, to a 1992 mean of 24.5 mg kg⁻¹, but perhaps the most salient point is that copper loadings have become more uniform over this time period. Copper concentrations ranged from 3.9-150.8 mg kg⁻¹ in 1987 to 2.1-50.0 mg kg⁻¹ in 1992, greatly reducing the degree of spatial variability in copper loadings. This 'damping down' effect was restricted to the lower study reach and could arise if non-contaminated particulate matter, derived perhaps from bank erosion or tributary inflows, was introduced into the lower reach, effectively diluting surficial copper concentrations.

The behaviour of copper and mercury are therefore markedly different. A comparison of Figures 8 and 9 reveals that the distribution of both metals mirrored each other in 1986 and 1987, implying that mercury and copper were controlled by similar hydrological and

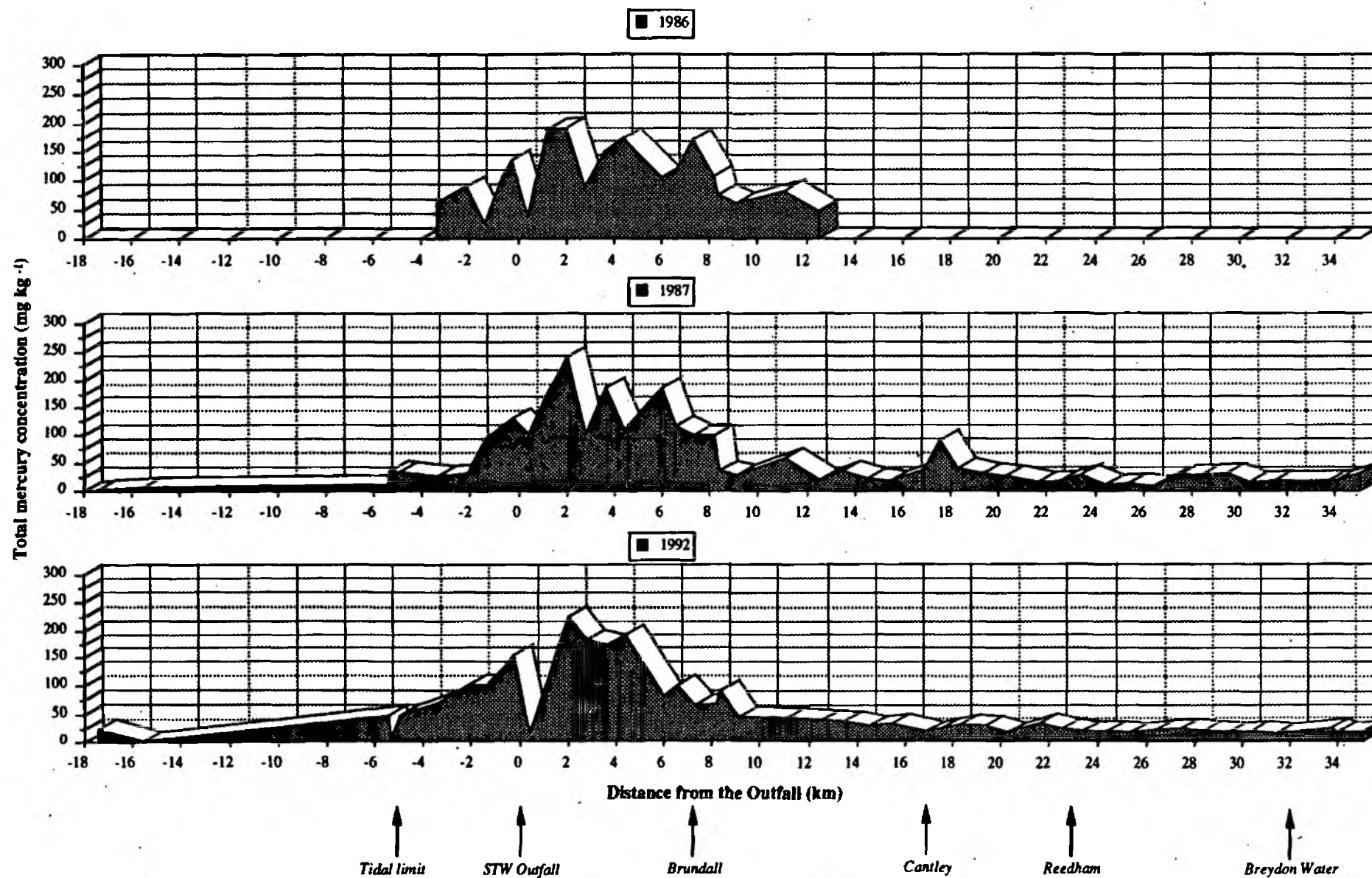


Figure 9. Comparison of Mean Transect Copper Concentrations in Surficial Sediments from 1986, 1987 and 1992.

Table 4. Summary of total copper levels found within the River Yare surficial sediments between 1986-1992.

Survey Date	Distance (km)	Study Reach Cu Conc. (mg kg ⁻¹)	
		Mean	Range
1986	16	106.2	4.6-375
1987	16	103.3	17.4-239
1992	16	107.6	14.1-290
1987	52	58.4	2.2-239
1992	52	56.8	2.1-290

sedimentological factors. From 1987 onwards, however, differences emerged in the nature of the concentration profiles, principally due to the decline in surficial total mercury concentrations in the zone adjacent to Whitlingham STW. The peak of both the copper and mercury contaminant plumes remained fixed at ≈ 2 km below the STW outfall, implying identical input sources, and despite a reduction in total mercury concentrations, the overall shape of the pollution plumes have remained constant since 1986. This implies that these differences are attributed to changes in input and not due to contaminant export downstream. This fact combined with the knowledge that concentrations in the lower study reach have not increased over time, negates the original hypothesis that the downstream movement of contaminated particulates was responsible for the observed decline in total mercury concentrations downstream of Whitlingham STW.

5.1.3. The temporal and spatial distribution of methylmercury within the River Yare surficial sediments

The longitudinal profile of mean transect methylmercury concentrations is depicted in Figure 10 for the Yare surficial sediments and summary data is provided in Table 3. Methylmercury loadings exhibited a large degree of variability, which unlike its inorganic counterpart, failed to display many schematic spatial or temporal trends. Methylmercury concentrations ranged from $<0.1 \mu\text{g kg}^{-1}$ (below the analytical detection limit) to $29.5 \mu\text{g kg}^{-1}$, which even at its maximum, is 3 orders of magnitude lower than surficial sediment total mercury concentrations. Elevated levels of methyl-mercury were not restricted to the main inorganic mercury 'contaminated' zone but displayed marked enrichments outside the influence of the mercury plume, such as the $22.2 \mu\text{g kg}^{-1}$ loading at Site Y₂₇, in 1990 (distance 13.5 km) and the $6.42 \mu\text{g kg}^{-1}$ detected at Site Y₃₁ in the October 1987 survey, 16.9 km below Whitlingham STW outfall. Methylmercury did not reflect the pattern exhibited by total mercury concentrations, as comparisons with Figures 7

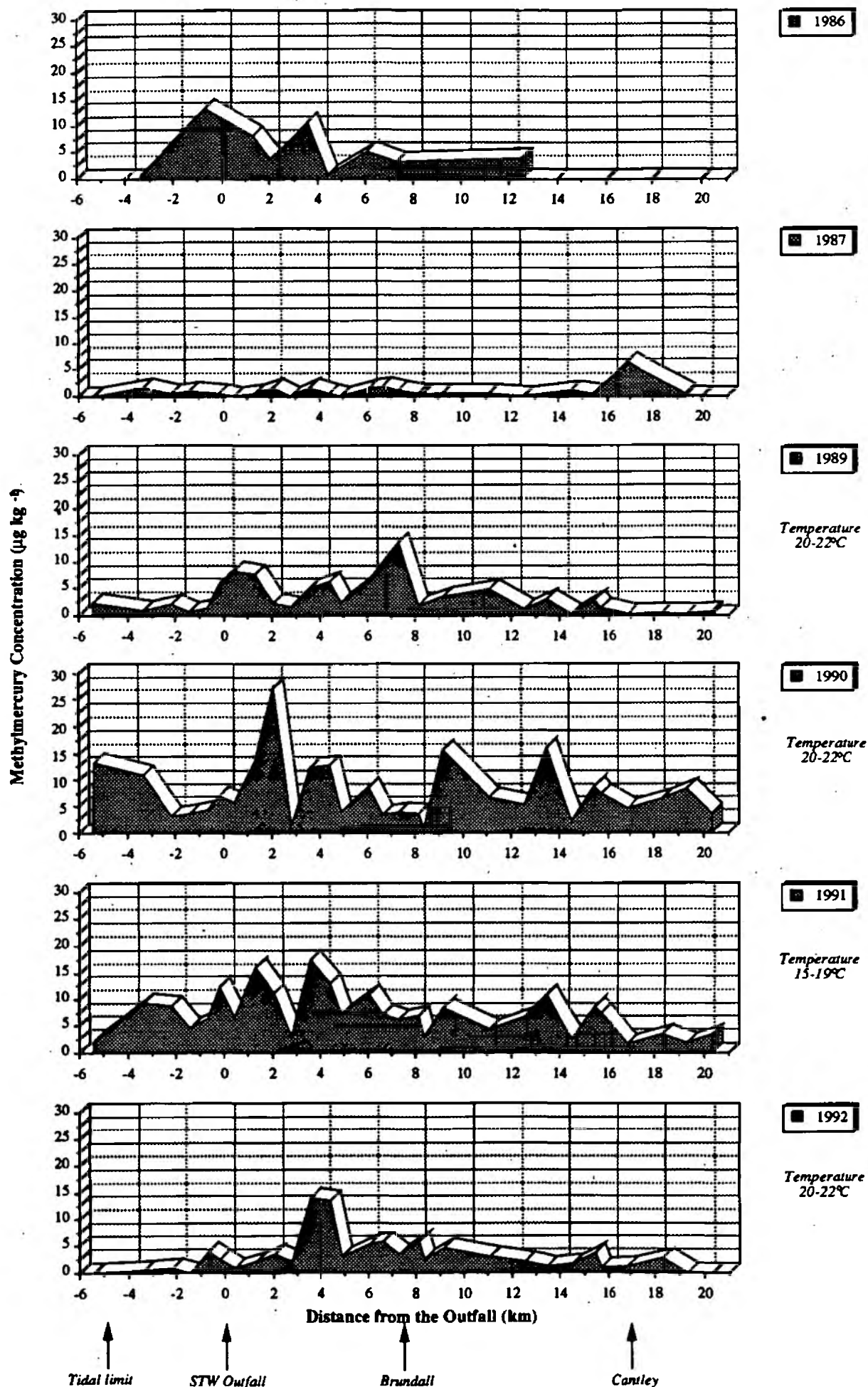


Figure 10. Longitudinal Distribution of Mean Transect Loadings of Methylmercury in River Yare Surficial Sediments.

and 10 reveal and the occurrence of high methylmercury loadings in areas where levels of total mercury approached background (e.g. Site Y₅, 1991, Site Y₄, and Y₃₀, 1990), suggests that inorganic mercury was not a limiting factor for the methylation process.

One of the most striking features which manifests from Figure 10 is the low level of methylmercury enrichment observed for the 1987 survey data. Concentrations ranged from $<0.5 - 6.42 \mu\text{g kg}^{-1}$, the maximum for which is lower than both the 1990 and 1991 study reach means. Only 24% of the samples analysed for methylmercury in 1987 contained quantifiable levels and most of these bordered on the limit of analytical detection. This forms a stark contrast to the prolific occurrence of methylmercury in samples obtained from the other annual surveys, where greater than 70% of the samples contained quantifiable amounts of methylmercury, reaching 94% in the 1990 survey. The most obvious difference between the 1987 and other annual surveys is the time of year in which sampling was carried out. The 1987 samples were collected in mid to late October, when conditions were cool and wet, while all other sampling campaigns took place in the summer months under hot and dry conditions. Maximum methylmercury enrichment occurred in the July 1990 survey where average concentrations over a 25 km study reach were $7.7 \mu\text{g kg}^{-1}$ and sediment temperatures ranged $20-22^\circ\text{C}$ which implies that temperature is an important control upon net methylation. Temperature can not, however, be solely responsible for the observed behaviour of methylmercury since comparable sediment temperatures prevailed during the July 1990 and June 1992 sampling campaigns but net organo-mercury measurements were on average 40% lower in 1992. Likewise comparable study reach methylmercury means between the 1990 ($7.7 \mu\text{g kg}^{-1}$) and 1991 data ($7.3 \mu\text{g kg}^{-1}$) occurred in spite of a $3-5^\circ\text{C}$ difference in sediment temperature. What may be important is the proceeding temperature regime over weeks or even months, rather than prevailing conditions.

The occurrence of the hurricane on 15th October 1987 may also be partially responsible for the low levels of organomercury detected in surficial sediment layers. High flows experienced on the River Yare ($19.8 \text{ m}^3\text{s}^{-1}$, compared to average discharge of $6.74 \text{ m}^3\text{s}^{-1}$ (NRA data archive)) may have reworked sediment deposits, releasing methylmercury to the water column and reducing organomercury concentrations in the sediment. Conversely, environmental conditions may have promoted demethylation activities. This aspect is dealt with in greater detail in Section 6.2.

Information on the sediment methylmercury burden can be gained from calculating the percentage ratio of methyl/total mercury. Figure 11 plots this ratio against distance downstream and reveals an enhancement from 1990 onwards. Ratio values range from 0 (no methylation ability) to a maximum of 10.5% (Site Y₄, July 1990), but the vast majority of sediments exhibited ratios of $<1\%$. This $<1\%$ category encompasses all the samples from the 1986, 1987 and 1989 surveys, and the majority of sediments from 1990 onwards, but with two exceptions,

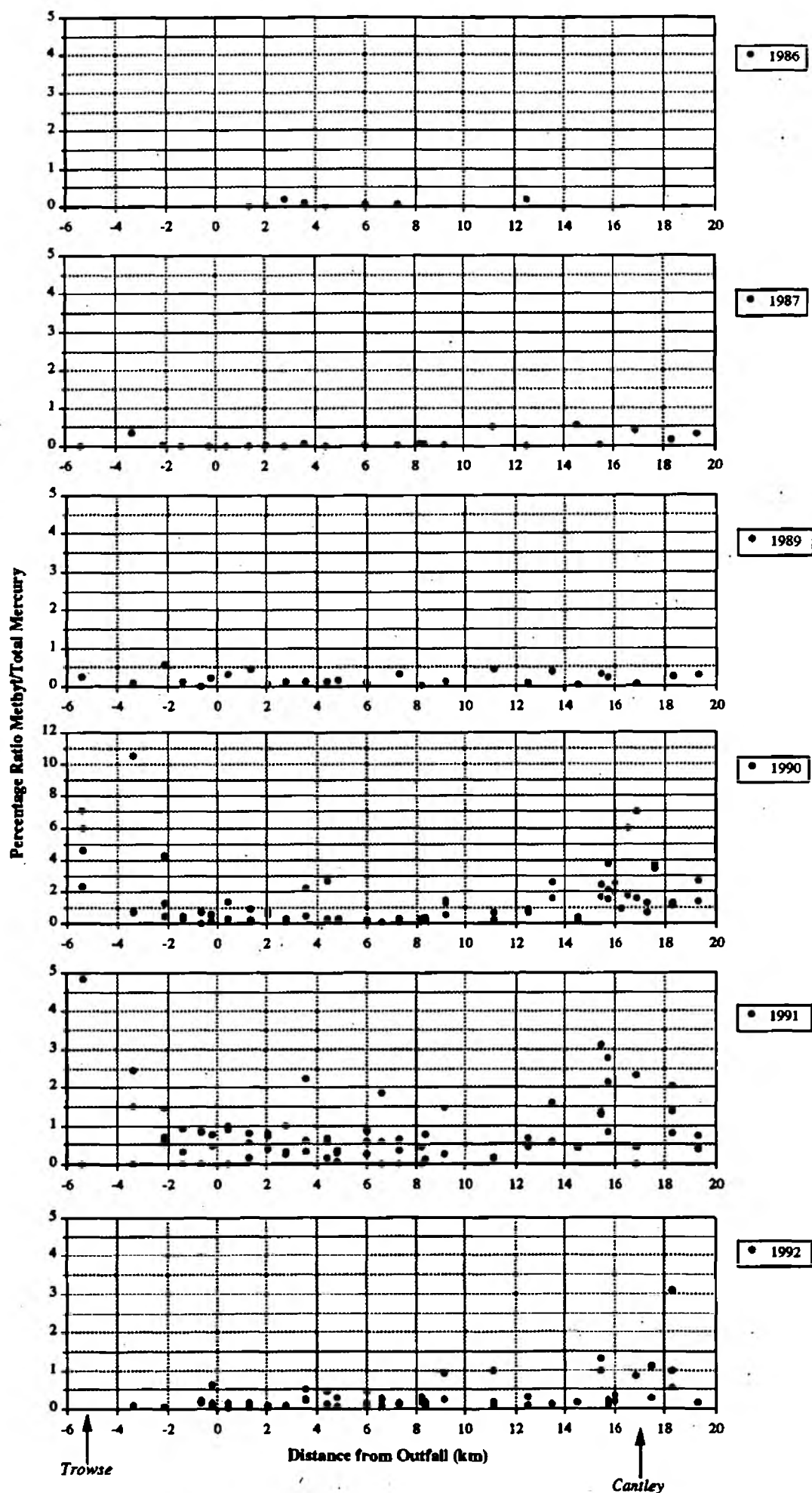


Figure 11. Percentage Ratio of Methyl/Total Mercury plotted against Distance from Whitlingham Sewage Treatment Works.

clusters of high methyl/total mercury ratios at Trowse (Site Y₄) and around Cantley (Site Y₃₁). This infers that these sediments have a high methylating capacity despite low total mercury concentrations. The 1990 methylmercury concentration at Site Y₄, for example, was $\approx 13 \mu\text{g kg}^{-1}$ compared to a total mercury loading of 0.25 mg kg^{-1} , which is equivalent to catchment background levels. Likewise at Site Y_{32(iii)} in 1992, a methylmercury loading of $3.36 \mu\text{g kg}^{-1}$ occurred from a sediment containing only 0.11 mg kg^{-1} of inorganic mercury. Methylmercury production therefore appears not to be totally dependent upon total mercury levels.

The intermittent occurrence of high methylmercury levels at Cantley, within the vicinity of the British Sugar processing plant, prompted an investigation to more clearly define the area affected and to elucidate the reasons behind the enrichment in organomercury. A number of additional transects were incorporated into the 1990 survey framework; the results, which are presented in Figure 12, proved disappointing.

Methylmercury concentrations were highly variable and not confined to specific areas, or morphologically similar locations. High loadings were evident at meander apexes (Site Y_{32v}) as well as at point bar localities on the inside of meander bends (Site Y_{32(iii)}), and were not restricted to areas of known anthropogenic inputs (Cantley STW, British Sugar cooling water discharges). The occurrence of methylmercury proved to be independent of sediment type, since it was found in diverse deposits, from fine grained clays (Site Y_{31.2ii}) to coarser grained gravel, sand and grit deposits (Site Y_{30ii}). Correlation analysis also failed to identify any statistically significant relationships between methylmercury concentrations, sediment pH, temperature or volatile solids. Results from subsequent Yare surveys in 1991 and 1992 have verified the existence of an area of enhanced methylating capacity, but have also been unsuccessful in identifying the controlling factors, despite the introduction of chloride analysis into the monitoring protocol. The factors responsible for the presence of elevated organomercury loadings in the vicinity of Cantley therefore remain elusive.

The enhanced methylation capacity at Trowse is perhaps a little easier to explain, particularly for the 1990 results, where the concomitant occurrence of high volatile solids (18-23%) and elevated methylmercury loadings infers a causal link between these two factors. Methylating activity could be enhanced in the shallow water and higher temperature conditions which characterise this site. This is reiterated by the spurious methylmercury loading of $2.42 \mu\text{g kg}^{-1}$ at Trowse in the 1991 survey, which coincided with a maximum study reach sediment temperature of 19.6°C in an area characterised by background concentrations of total mercury. This implies that temperature and organic matter content are important controls upon methylation.

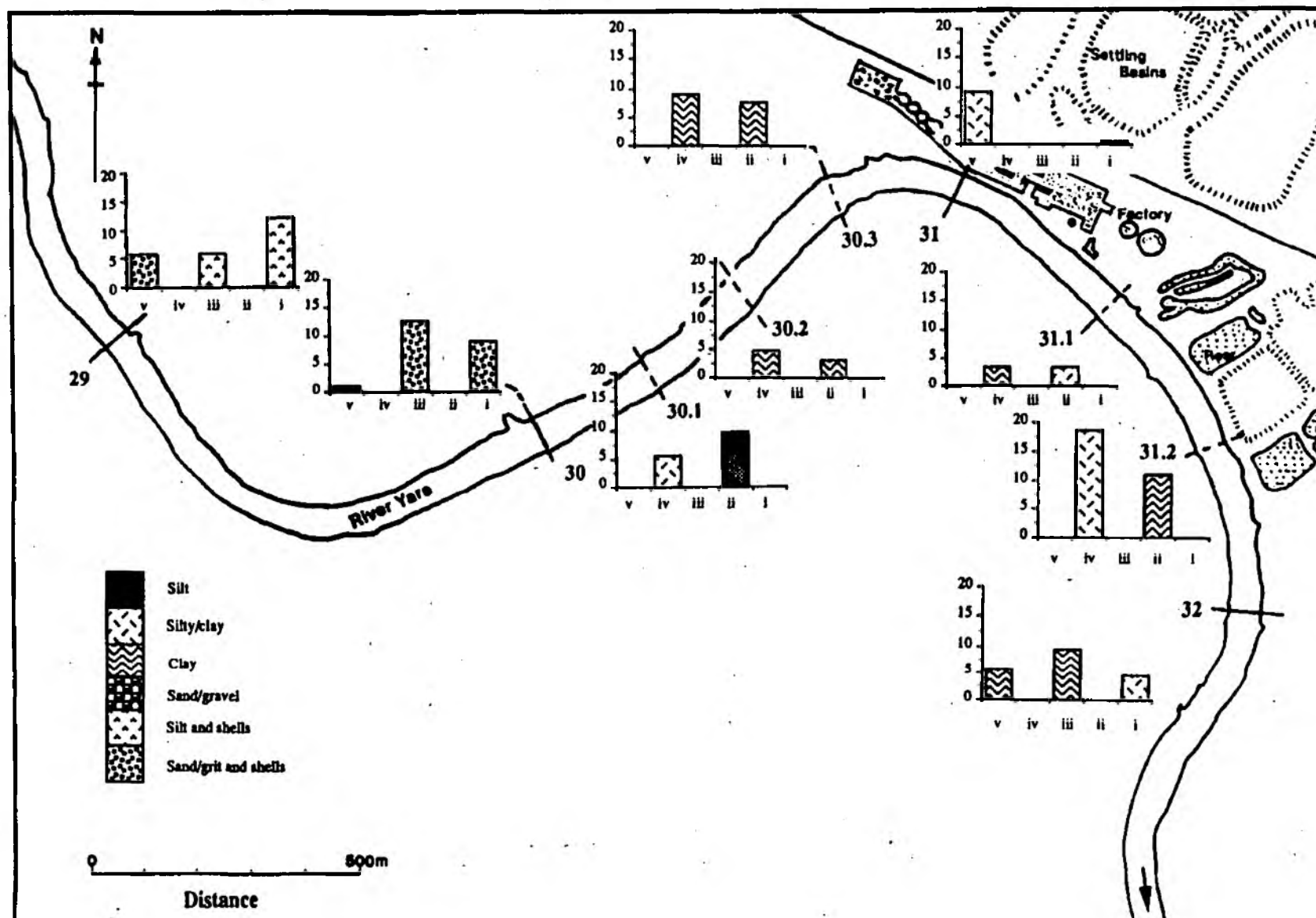


Figure 12. Methylmercury concentrations in surficial sediments in proximity to Cantley ($\mu\text{g kg}^{-1}$).

(Roman numerals indicate sampling position in the river. Refer to Figure 2).

5.1.4. The effect of environmental factors upon surficial sediment metal concentrations

Total mercury and copper had quite distinctive downstream trends which implicated distance from the source as being a major determinant in controlling their distribution. However, a degree of spatial variability was still inherent in their distribution. A detailed comparison of the profiles displayed in Figure 7 reveal that certain channel reaches, such as at Sites Y₁₂ and Y₁₅, 0.45 and 2.8 km below the outfall respectively, consistently exhibited low metal loadings despite their proximity to the contaminant source. The outcrop of chalk and the concomitant occurrence of coarse grained flint, gravel and sand deposits and low metal loadings at these sites, compared to the presence of fine silts which occupy adjacent channel reaches, infer that sediment type and texture may be important controls upon metal accumulation tendencies. Crystalline sand size particulates may prohibit the adsorption of contaminants, reducing metal concentrations in specific reaches. Correlation analysis was used to identify the main environmental factors which may have influenced the distribution of metals within surficial sediments. The following discussion is based upon the 1987 data but holds true for the other annual surveys.

Preliminary analysis produced significant correlations ($p = 0.001$) between heavy metals and the total solids (TS) component (a measure of sediment weight and density) and to a lesser extent with the proportion of volatile constituents (%VS). These fundamental relationships implied that finer grained, silt type sediments, which were typically characterized by lower TS and comparatively high organic loadings (>10% VS), contained higher metal loadings than coarser grained sand/gravel deposits with high TS values and relatively low volatile solids (<2%). Such associations may, however, be coincidental, with the discharge of metal laden effluents occurring in channel reaches which were naturally occupied by finer grained bottom deposits. Closer examination of scatter plots derived between the metals and sedimentary variables, however, revealed that outlying values were significantly influencing the strength of these relationships. The highly organic peat sediment of the underlying basement rock, for example, contained very low quantities of metals and was strongly influencing the otherwise positive correlation between organics and metal content. In an attempt to reduce or eliminate this type of influence, the surficial sediment data was re-evaluated according to sediment type.

5.1.4.1. *The influence of sediment type and organic matter content on metal distribution within the Yare surficial sediment*

Sediments were subjectively classified into silt, gravel, clay or peat in order to assess the significance of sediment type in determining metal accumulation tendencies. Mean metal concentrations for each sediment category are listed in Table 5. Although mean values may be subject to undue influence from extreme values, they still provide a convenient indicator of

Table 5. The effect of sediment type upon mean metal concentrations and solid loadings in the River Yare surficial sediment: Data based on the 1987 survey.

PARAMETER	SEDIMENT TYPE				
	PEAT n=5	GRAVEL n=7	CLAY n=27	SILT n=56	COMBINED n=103
Hg (mg kg ⁻¹)	0.31	0.41	0.26	1.85	1.20
Cu (mg kg ⁻¹)	19.5	43.6	22.6	50.3	39.8
% V.S	61.4%	5.7%	7.5%	10.3%	12.0%

n Number of observations.

general trends. Correlation analysis was carried out for each sediment type, to investigate the relationships between metal concentrations and environmental parameters (Table 6).

Fine grained, highly organic silt sediments were associated with high loadings of metals. Mean concentrations of mercury, for example, were 4.5 times higher in silts than in other sediment types. Highly significant relationships ($p=0.001$) were observed between the concentrations of these metals with distance, TS, and %VS. Distance from Whitlingham and percentage organic matter accounted for as much as 68% of the observed variation in silt mercury concentrations over the study reach, although the simultaneous release of organic-rich effluents and mercury compounds from Whitlingham STW may indicate a degree of autocorrelation between these two variables.

Table 6. Correlation coefficients and significance levels for mercury and copper as a function of sediment type in the River Yare.

Sed. Type	Metal	Distance	% TS	%VS
Silt	Hg	-0.69*	-0.63*	0.71*
	Cu	-0.63*	-0.56*	0.71*
Clay	Hg	0.44#	0.67*	0.38°
	Cu	0.42#	0.70*	0.53§
Gravel	Hg	0.77#	-0.82°	0.74#
	Cu	0.84§	-0.77#	-
Peat	Hg	-	-	-
	Cu	-	-	-
Combined	Hg		0.56*	0.41*
	Cu		0.55*	0.43*

Significance levels * = 0.001; § = 0.01; ° = 0.02; # = 0.05

The clay fraction was characterised by low metal concentrations which approximated to geochemical baseline levels.

Metal concentrations and the significance of the correlation coefficients derived between metals and the physical components of the gravel deposits, were intermediate between those in the silts and those in the peat and clay sediments. The difference in enrichment between silt and gravel was presumably due to reduced organic loadings and the dilution effect of coarser size fractions within gravel deposits.

Peat type sediments were characterised by low metal concentrations which approximated to natural background levels and no significant correlations were obtained. This low level of correlation may be attributed to the small number of samples in this category (n=5) which reduced the efficiency of Spearman's rank correlation.

For both gravel and clay, TS appeared to be more significant as an indicator of metal concentration than % VS. The weak correlations observed for all sediments, other than silts, probably reflected the smaller number of samples in these categories and the fact that their occurrence tended to be confined to particular sections of the study reach. Most clay type sediments, for example, were restricted to an area downstream of Cantley which lay beyond the main contaminated reach, while gravel deposits were either located at the control sites, or at isolated locations in the lower study reach. Consequently neither sediment was exposed to direct inputs of anthropogenic wastes.

Correlation analysis does, however, indicated the significance of sediment texture, in particular the proportion of organic matter, in influencing the ability of sediments to concentrate metals.

5.1.4.2. Hydrological controls upon sediment and metal accumulation tendencies

Channel morphology and associated flow dynamics tended to dictate metal enrichment patterns by controlling the rate and zones of sedimentation. High total metal loadings were consistent with areas of fine particulate deposition under more quiescent flow conditions, such as at channel margins and point bar localities. This was highlighted by the decrease in metal loadings from marginal to mid-channel regions. This reflected the textural gradation towards coarser sediments in central channel areas (as seen at Site Y₃₀, 1987 survey) or conversely the exposure of the peat and clay bedrock in scour zones (Sites Y₃₄, Y₃₉, 1987). Lower metal concentrations were also characteristic of the outer edges of meander bends, where flow velocities may have been sufficient to scour bottom deposits and inhibit fine particulate deposition, while transverse currents caused the active accumulation of finer silt fractions in inner channel reaches (Site Y₃₁).

5.1.4.3. *The effect of sediment pH, temperature and chloride upon mercury accumulation tendencies*

Metal accumulation tendencies in surficial sediments can be partly explained by the interaction between hydrological factors, sediment type and distance from pollution sources, but the chemical properties of bottom deposits may also exert an influence. Sediment pH has been determined routinely for all surficial samples since 1987, but sediment temperature and chloride were added at later stages (temperature from 1989 onwards and sediment chloride from 1991) in response to concerns about their effect upon total and organo-mercury loadings within the Yare. The range of values obtained for individual surveys are listed in Table 7.

Surficial sediment temperature is very closely linked to the temperature of the overlying water (20-22.5°C to 21-23 °C, respectively) but exhibits greater variability, with the occurrence of lower temperatures in deeper waters where light and heat penetration are reduced. This explains the consistent fall in temperatures on approach to Breydon Water. A slight increase in sediment temperatures was apparent immediately downstream of Whitlingham STW outfall in 1990, increasing temperatures by 1°C from a study reach mean of 20.5°C and the 1991 surficial sediment temperatures were generally lower than has been observed in the other annual surveys.

Table 7. Summary of surficial sediment environmental parameters.

Date	Temp (°C)	pH	Cl: (mg kg ⁻¹)
1986	-	-	-
1987	-	6.9-7.8	-
1989	20-22.5	6.9-7.8	-
1990	20-22.7	6.8-8.0	-
1991	15-19.6	6.9-8.0	24-1074
1992	17.2-22.1	6.5-7.6	34-14,683*

* Elevated chloride loadings occur within Breydon Water, in the estuarine zone.

Sediment pH is slightly alkaline, reflecting the calcareous basement rock which underlies the area, and generally ranges from 6.8-8.0 pH units, although pH does reach a low of pH 6.5. Sediment pH fails to display a significant spatial trend and probably reflects the underlying geology, although a slight elevation in the 1990 pH readings which increased from a study reach mean of 7.4 to 7.8 occurred just upstream of Cantley and may be significant in terms of its influence upon methylmercury production, although correlation analysis failed to implicate an association between these two variables.

Chloride ion concentration in sediments displayed a steady increase downstream from Trowse, in the freshwater portion, to Cantley where the demarcation between fresh and saline water lies. Concentrations ranged between 34 mg kg^{-1} to $14,683 \text{ mg kg}^{-1}$ reflecting this transition from fresh to saline waters. Chloride concentrations remained fairly consistent above Cantley with mean loadings of 274 mg kg^{-1} compared to an average of 6107 mg kg^{-1} further downstream which increased dramatically as the estuarine conditions in Breydon Water were reached. Correlation analysis undertaken between total/methylmercury and copper with sediment pH and chloride failed to produce any statistically significant relationships. This implies that other factors were controlling the distribution of these metallic elements within the River Yare's sedimentary compartment.

5.2. River Yare Sediment Core Record

5.2.1. The vertical distribution and historic loading of mercury within the River Yares sediment compartment (1992)

The vertical distribution of mercury in sediment samples taken from cores collected in the summer of 1992 examined whether burial of contaminated sediments by a cleaner overlay could account for falling mercury levels in surficial sediments. Ten cores were collected from the 'contaminant' reach of the Yare to elucidate the temporal trends of mercury accumulation in sediments and are shown in Figure 13. Summary data is presented in Table 8.

Total mercury concentrations in the core samples varied between 0.04 mg kg^{-1} (core 10, 14.5 km below the outfall) to 18.6 mg kg^{-1} (core 3, 1.30 km downstream), which represents a 46 fold increase over the River Yare background level. Concentrations averaged over the entire core depth ranged between 0.71 mg kg^{-1} (core 10, 14.5 km downstream) to 5.86 mg kg^{-1} (cores 6 and 7, approximately 7 km below the outfall). Difficulties experienced in obtaining cores in deep waters restricted the vertical extent of some of the cores and even the length of the largest core, which was 105 cm long (core 6, 6 km downstream), failed to extend to the base stratum. Background mercury levels at depth were only determined in cores 3, 8 and 10 where coring reached the base stratum. This failure to encapsulate the entire contaminative episode in some of the cores inhibits the derivation of a complete contaminant history, particularly at those locations characterised by high sediment accumulation rates. Never-the-less, the information attained from this coring exercise has been invaluable in understanding the behaviour of total mercury within the River Yare system.

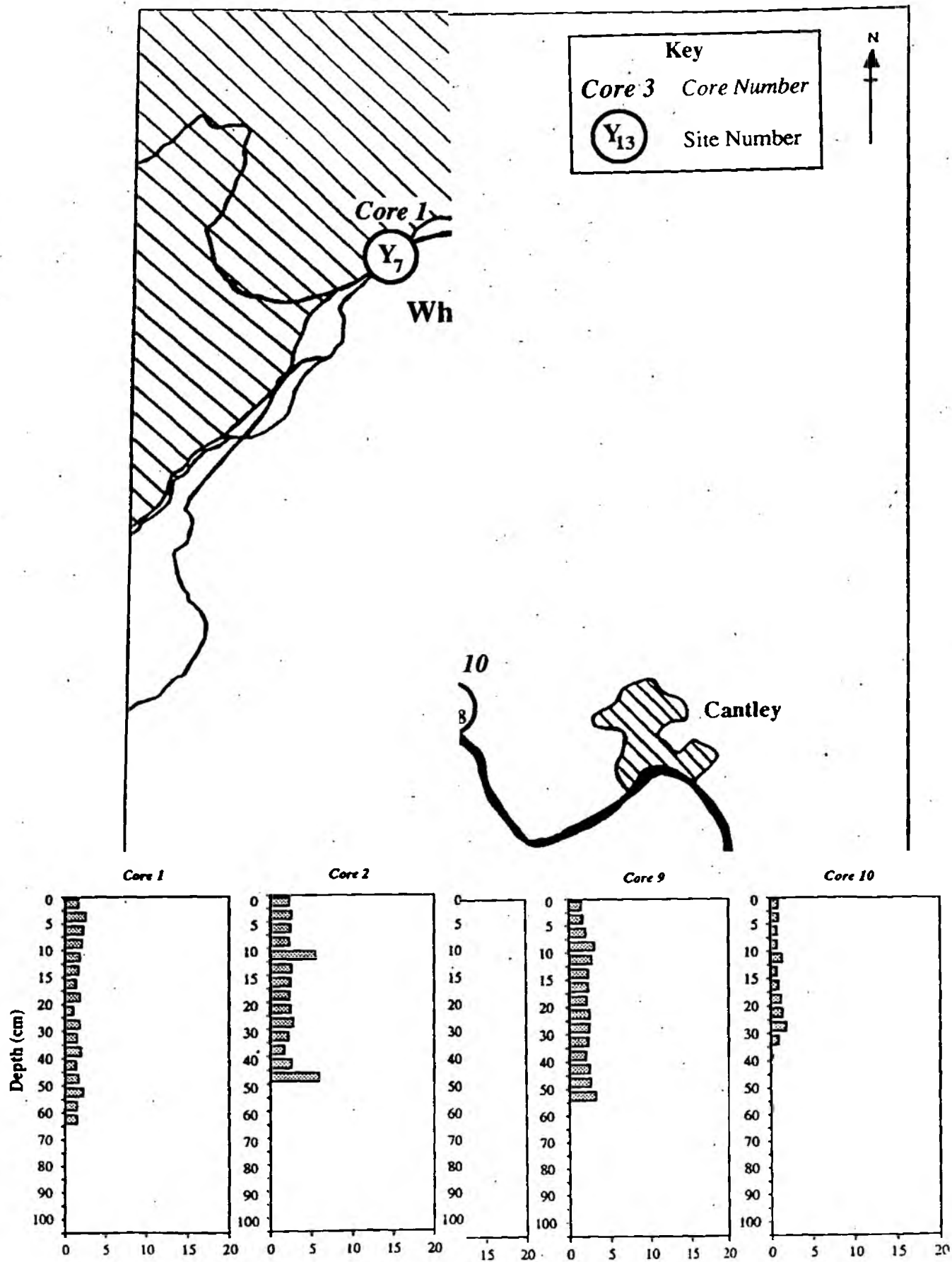


Fig 992 data).

Table 8. Summary of mercury and copper concentrations in cored sediment samples from the River Yare, 1992.

Core	Site	Distance from STW Outfall	Metal Concentration (mg kg ⁻¹)			
			Mercury		Copper	
			\bar{x}	Max.	\bar{x}	Max.
1	7	-3.35	1.74	2.6	99.3	120.3
2	10	-0.65	2.82	5.91	195.8	232.3
3	13	1.30	4.58	18.6	145.4	308.5
4	14	2.05	4.04	10.0	238.6	376.1
5	16	3.60	3.10	7.2	320.4	391.6
6	19	6.00	5.86	17.6	195.0	335.0
7	21	7.3	5.86	18.0	114.7	208.5
8	24	9.15	1.46	2.4	52.2	73.1
9	26	12.5	2.23	3.1	70.2	113.1
10	28	14.5	0.71	1.8	41.6	67.7

Two cores were taken to characterise the area upstream of Whitlingham STW (core 1, at Site Y₇, 3.35 km upstream and core 2, at Site Y₁₀, 0.65 km upstream). Mercury loadings averaged over the core depth were 1.74 mg kg⁻¹ and 2.82 mg kg⁻¹ respectively, and reflected the influence of tidal reversals which distributed contaminated sediments upstream of the point source. Mercury levels in core 1 revealed no significant trends with depth, remaining fairly constant at ≈ 2 mg kg⁻¹. Core 2 contained elevated levels of mercury at depth, with maximum values of 5.38 and 5.91 mg kg⁻¹ occurring at 12.5 and 50 cm respectively. The high mercury loading at 12.5 cm corresponds to the lowest percentage total solids value for the core and highest percentage volatile solids value. A high degree of organic binding may therefore account for the mercury loading at this depth although correlation analysis failed to highlight such an association in this instance.

Cores taken immediately downstream of Whitlingham STW (cores 3 and 4, located at Sites Y₁₃ and Y₁₄, 1.30 and 2.05 km downstream, respectively) contained elevated mercury loadings at depth. Maximum mercury concentrations in core 3 (18.6 mg kg⁻¹) occurred at 7.5 cm and tailed off to background levels with increased depth, reaching 0.5 mg kg⁻¹ at 25 cm. The zone of mercury enrichment (7.5-20 cm) coincided with the occurrence of low sediment redox potentials (-242 to -314 mV) which could promote the formation of mercury sulphides of low solubility in this reduced zone. This assertion was backed up by the negative correlation between mercury and sediment redox ($p=0.001$), so as redox declined (became more anoxic) mercury concentrations increased. Core 4 displayed elevated mercury loadings with increasing depth to a maximum of 10 mg kg⁻¹ at 70 cm. Core 4 was too shallow to encapsulate the entire depth of sediment down to the underlying uncontaminated base stratum and the acquisition of a deeper core could provide more detail on the historic loading of mercury at this site.

Core 5 (Site Y₁₆, 3.6 km downstream) was characterised by moderate concentrations of total mercury with few observable trends in the mercury distribution. Sediment disturbance via boating activities or dredging may be responsible for the apparent homogeneity of the core profile. Maximum levels of 7.2 mg kg⁻¹ occurred in the top 2.5 cm but average core concentrations over a depth of 60 cm were ≈3.1 mg kg⁻¹.

In general those cores taken 4 km either side of Whitlingham STW (cores 1-5) displayed higher mercury loading in the uppermost 12.5 cm of sediment. Further downstream there was a tendency for sub-surface enrichment (cores 6-10). This is exemplified at core 6 (Site Y₁₉, 6 km below the outfall) where a clear trend of increasing mercury loadings with depth was apparent. Maximum concentrations of 17.6 mg kg⁻¹ occurred at a depth of 100 cm, the magnitude of which is approximately three times greater than the maximum concentration observed for surficial sediments in 1992. Despite the depth of this core it failed to reach the stratigraphic base. Core 6 was consequently extracted from an area of high sedimentation. Low redox potentials were observed over the entire core depth (-233 mV to -255 mV) which pertains to the existence of insoluble mercury sulphides in this reduced zone which are capable of effectively immobilising mercury within the sediment compartment.

Core 7, located at Site Y₂₁, 7.3 km downstream of Whitlingham STW outfall, displayed peak mercury loadings at a depth of 45-55 cm, producing a maximum concentration of 18.0 mg kg⁻¹, with much lower concentrations both above (3.7 mg kg⁻¹) and below (2.5 mg kg⁻¹) this divide. Mercury concentrations, however, failed to return to background levels at the base of the core despite the occurrence of the underlying peat base. A speculative reason for this apparent paradox could lie in the exposure of this highly organic stratum by dredging activities during the main period of mercury emissions in the early 1970s. This could have elevated mercury loadings above background.

Mercury loadings in core 8 (Site Y₂₄, 9.15 km below the outfall) displayed an abrupt decline to 0.15 mg kg⁻¹ as the basement clay was reached at a depth of 30 cm. Average concentrations above this stratigraphic unit were 1.75 mg kg⁻¹ and exhibited only a minor increase from surface to bottom deposits. Cores 9 (Site Y₂₆, 12.5 km) and 10 (Site Y₂₈) exhibited fairly low mercury concentrations throughout, with average core concentrations of 2.23 and 0.71 mg kg⁻¹ respectively, the latter being only marginally above background levels. Both cores displayed a slight increase in mercury loading with depth with core 9 reaching a maximum mercury loading of 3.1 mg kg⁻¹ at 55 cm, while background levels were encountered below 40 cm in core 10.

The existence of elevated mercury loadings at depth within the main 'contaminated' zone implies that the burial of contaminated stratum beneath a cleaner overlay is the main process responsible for the decline in surficial sediment levels since monitoring began in 1986. Some

core profiles clearly reflected the historic accumulation of mercury within the Yare's sediments, but the shape of the vertical contaminant profiles was closely linked to the sedimentation rate and the effects of past dredging activities.

5.2.2. Laboratory based experiments to ascertain mercury mobility in contaminated sediment buried beneath a cleaner overlay

A series of tanks were set up to ascertain if mercury contaminated sediment contained at depth presented a potential source of total and methylmercury to the overlying sedimentary and aqueous system. The experiment was designed to simulate an undisturbed system and to highlight the effect of diagenetic processes upon the movement and subsequent methylation of mercury within the sediment profile. No physical mixing was applied once the tanks had been established, although bioturbation occurred in the upper sediment layers. The results from the laboratory based tank experiments can be seen in Figures 14 and 15(i)-(iii).

Total mercury concentrations ranged from 4.19 mg kg^{-1} in Rockland Broad sediment, the contaminated stratum, to $\approx 0.25 \text{ mg kg}^{-1}$ in Cantley and Ormsby sediments. The Cantley sediment was originally envisaged to contain a moderate degree of mercury enrichment, however, mercury contamination of the Yare at Cantley is known to exhibit great spatial variability and it was unfortunate that the bulk sample obtained for this experiment contained a low concentration of mercury, which bordered upon geochemical background levels. The original intention was to use the clay sediment at Cantley as a means of comparing the mobility of mercury within different sediment types. The tanks containing Cantley sediment (Tanks 2 and 3) were analysed for methylmercury but all values were below the analytical detection limit and are consequently not discussed further. The assessment into the movement of mercury from the contaminated to uncontaminated stratum was consequently restricted to Tank 1 (Rockland Broad contaminated control), Tank 4 (Ormsby overlying Rockland) and Tank 5 (Rockland overlying Ormsby).

Total mercury concentrations did not display any significant changes during the 365 day sampling period (Figure 14) and there was no evidence to infer the movement of mercury from contaminated stratum to overlying or underlying uncontaminated sediment. A degree of variability in total mercury concentrations was apparent in the Rockland sediment (Tank 1) where concentrations ranged from 3.41 to 5.27 mg kg^{-1} (mean 4.19 mg kg^{-1}). This probably reflected localised 'pockets' of mercury which persisted in spite of initial sediment homogenisation.

Methylmercury concentrations, in contrast, displayed temporal variability in both the buried and surface samples obtained from the Rockland Broad sediment (Figure 15(i-iii)). Methylmercury

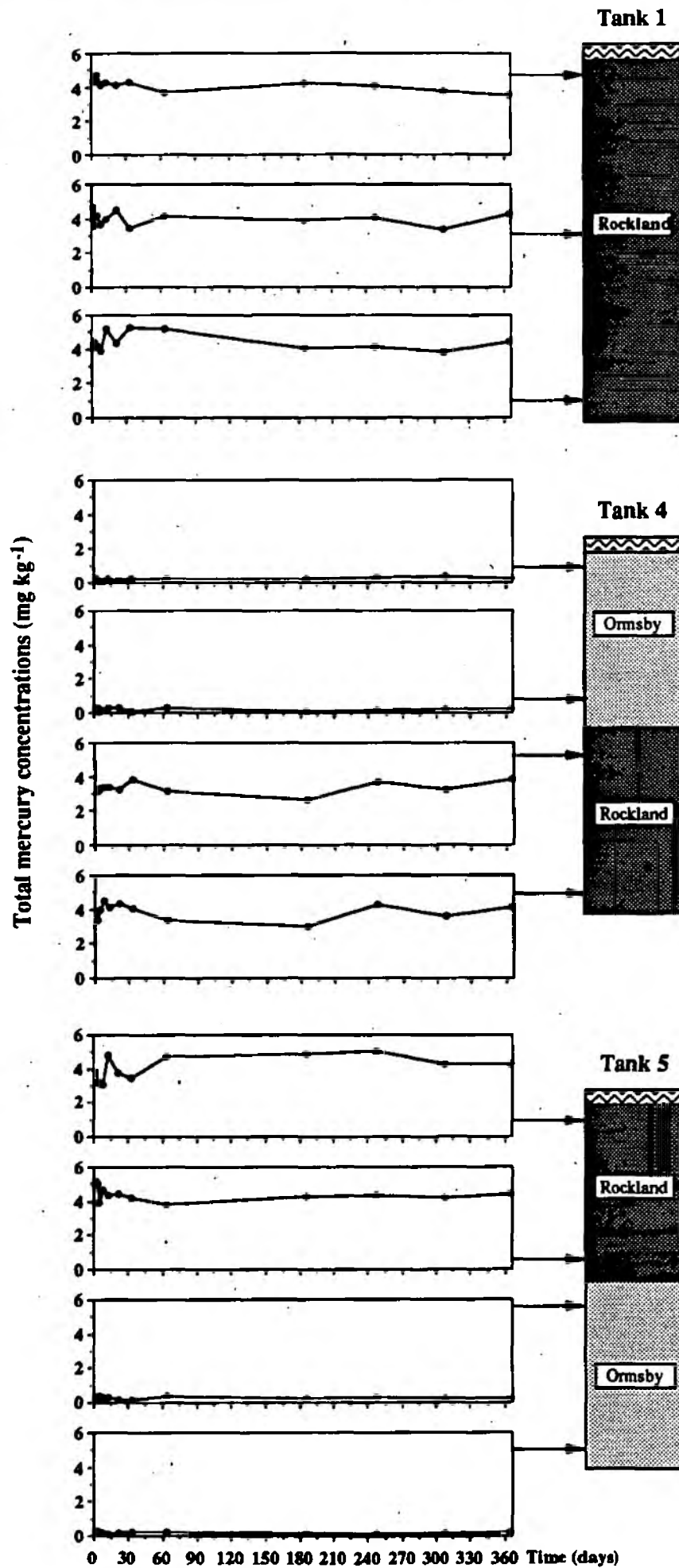


Figure 14. Total mercury concentrations over time. Laboratory based tank experiments.

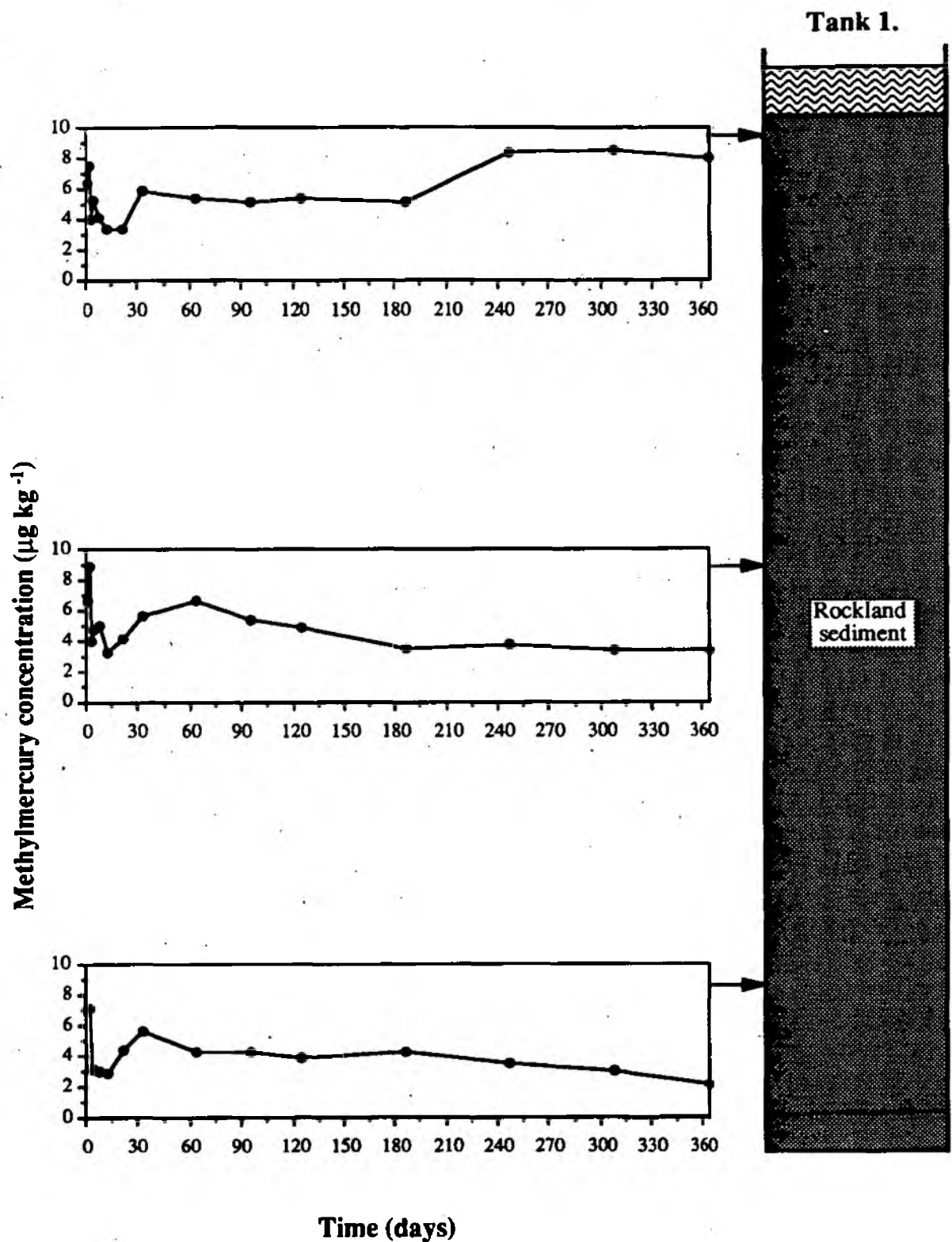


Figure 15. Temporal Variability in Methylmercury Concentrations under Controlled Temperature Conditions (12°C).

(i) Contaminated sediment. Rockland Broad control.

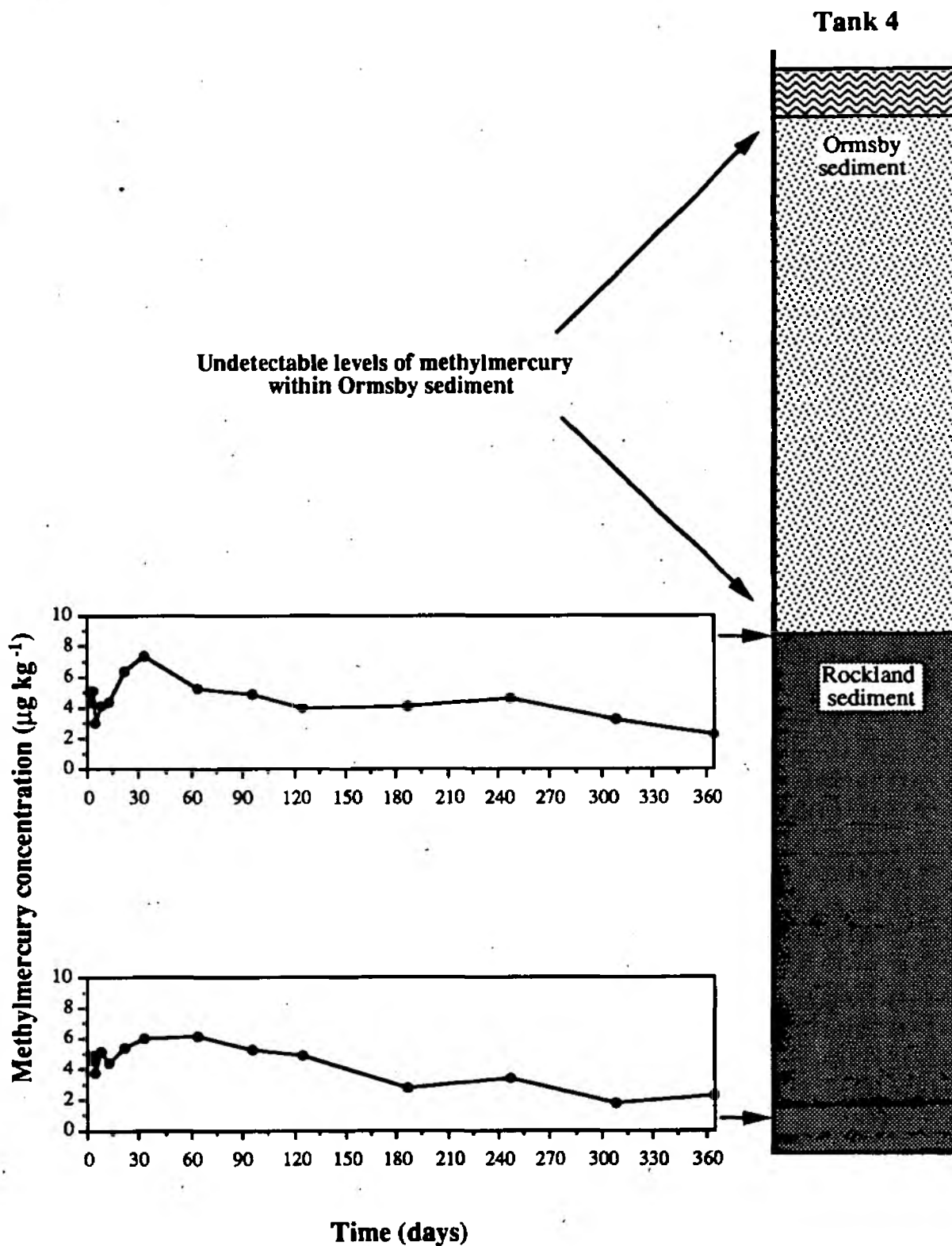


Figure 15. Temporal Variability in Methylmercury Concentrations under Controlled Temperature Conditions (12°C).

(ii) Contaminated overlain by a clean sediment: Ormsby overlying Rockland.

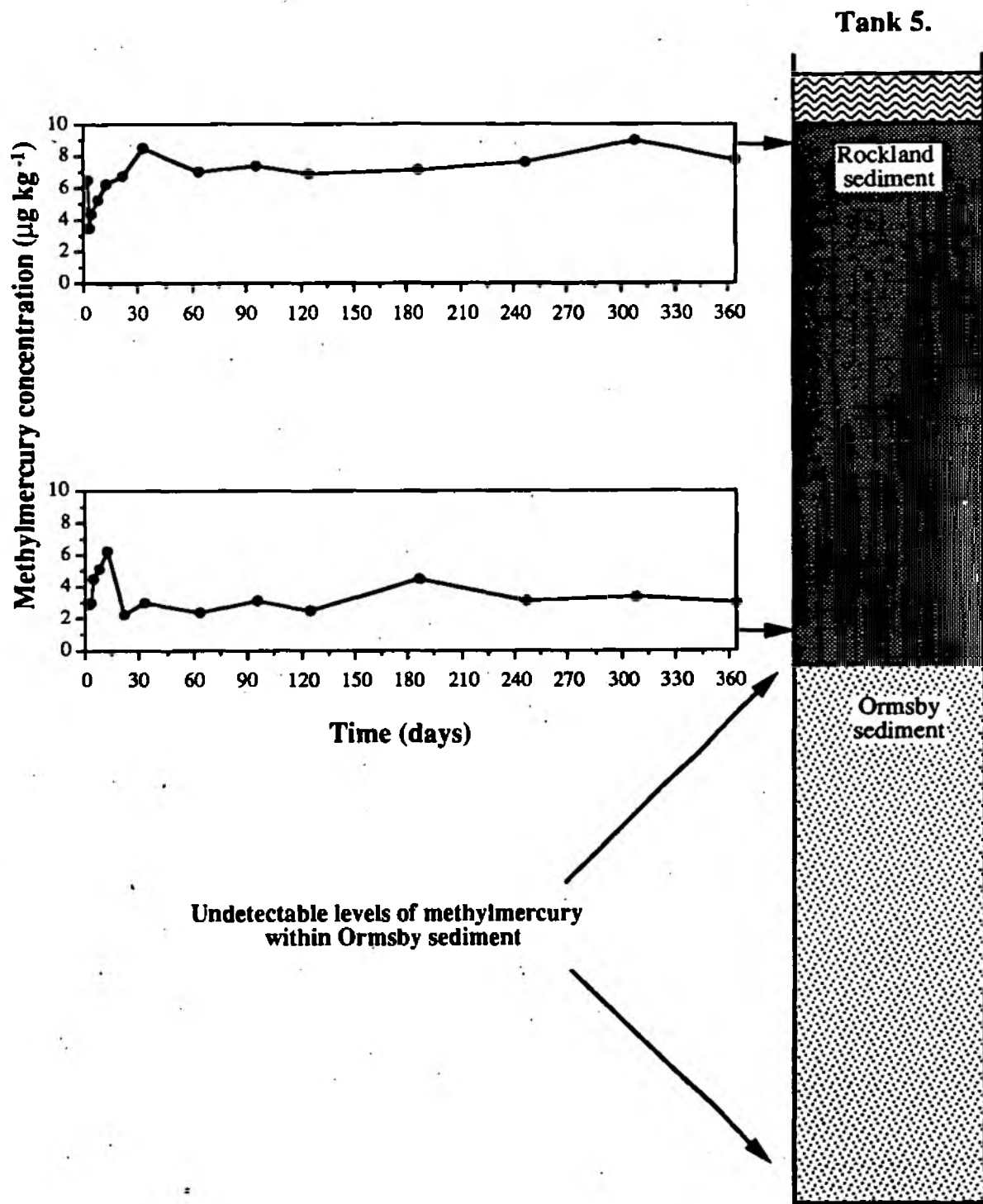


Figure 15. Temporal Variability in Methylmercury Concentrations under Controlled Temperature Conditions (12°C).

(iii) Contaminated overlying clean sediment: Rockland overlying Ormsby.

concentrations initially displayed a large degree of fluctuation irrespective of the location within the tank. This can be attributed to the effects of handling and sediment mixing as the experiment was being set up. A lag period of between 2-13 days existed before conditions became favourable for mercury methylation and concentrations started to gradually increase, reaching a high at day 33 before concentrations stabilised. In surficial sediments the concentration of methylmercury increased slightly over time (Tanks 1 & 5) reflecting the active synthesis of methylmercury which reached a maximum on day 308. In buried sediment, however, methylmercury concentrations declined over time. In Tank 4, for example (Ormsby overlying Rockland), methylmercury loadings in the buried Rockland sediment declined from 7.34 $\mu\text{g kg}^{-1}$ at day 33 to 2.21 $\mu\text{g kg}^{-1}$ at day 365, for samples taken just below the intersect of the two sediment layers (Table 9). This implied that methylmercury was slowly degraded in deeper sediment layers.

Samples obtained from the layers immediately adjacent to the contaminated sediment failed to contain detectable levels of methylmercury. There was consequently no evidence of the vertical translocation of methylmercury, either upwards from buried contaminated sediment or via leaching from surface contaminated stratum to buried uncontaminated deposits. The results from these tank experiments therefore indicate that the mobility of inorganic and organic mercury buried at depth is limited in a static environment.

Table 9. Methylmercury summary data for the laboratory based tank experiments.

Tank	≈Depth (cm)	Maximum ($\mu\text{g kg}^{-1}$)	Minimum ($\mu\text{g kg}^{-1}$)	Average ($\mu\text{g kg}^{-1}$)
1	0-5	8.52 (Day 308)	3.32 (Day 22)	5.72
	20-24	8.87 (Day 2)	3.24 (Day 13)	4.90
	48-50	7.07 (Day 2)	2.09 (Day 365)	4.11
4	25-30	7.34 (Day 33)	2.21 (Day 365)	4.51
	48-52	6.14 (Day 64)	1.70 (Day 308)	4.33
5	0-5	8.96 (Day 308)	3.48 (Day 3)	6.69
	20-24	6.22 (Day 13)	2.43 (Day 64)	3.52

5.2.3. The vertical distribution and historic loading of copper within the River Yare's sediment compartment (1992)

The vertical distribution of copper in River Yare sediment cores was used to assess whether source emission reductions of mercury or enhanced sedimentation of 'uncontaminated' particulates to the study reach was responsible for the observed decline in surficial sediment mercury concentrations.

The vertical distribution of copper in sediment cores from the Yare is shown in Figure 16 and are similar to those previously described for mercury, with cores above Whitlingham STW displaying fairly constant metal concentrations with depth, while those below the STW outfall exhibited sub-surface maxima. Copper concentrations varied between 19 mg kg⁻¹ (core 10, Site Y₂₈, 14.5 km downstream) and 391.6 mg kg⁻¹ (core 5, Site Y₁₆, 3.6 km downstream) with the highest concentration representing a 14.5 fold enrichment over catchment background levels. Average copper concentrations in the cores varied between 41.6 mg kg⁻¹ (site 10, 14.5 km downstream) and 320.4 mg kg⁻¹ (Site 5, 3.6 km downstream) and are shown in Table 8. Maximum copper concentrations occurred ≈2 km downstream of Whitlingham STW, consistent with the findings of the surficial survey.

The similarity in the vertical profiles for copper and mercury imply that both metals are controlled by similar processes. Spearman's correlation analysis (Table 10) highlighted the strong association between metals and sediment depth for cores 3, 4-6 and 9-10, implying that the vertical distribution of copper and mercury were controlled, to a large extent, by depositional processes. Mercury and copper concentrations in cored sediment were significantly correlated with one another ($p=0.05$) with the exception of cores 2, 4 and 5 implying that different processes were responsible for the vertical metal distribution of individual metals in these instances. Core 5, for example, revealed surface enrichment for mercury (0-2.5 cm) compared to subsurface enrichment for copper (>10 cm). The reason for this divergence in the vertical metals profiles is not immediately apparent. Some cores displayed an abrupt decline in copper loadings due to changes in sediment type. Core 3, for example, showed a decline in concentrations from 227.3 mg kg⁻¹ to 46.2 mg kg⁻¹ at the transition between a black peaty silt deposit and a clay-silt layer at a depth of 25 cm. This transition was defined from the core field

Table 10. Specimens ranked correlations table for core depth versus metal and physico-chemical parameters in River Yare sediment cores (1992).

CORE	TS	%VS	pH	Redox	Cu	Hg	Temp
1	0.82*	-0.68§	-0.50#	0.64§	-	-	-0.99*
2	0.81*	-	-0.61#	-	-	-	0.99*
3	0.92*	-0.82*	-0.56#	0.77§	-0.63°	-0.91*	-0.99*
4	0.81*	-	-	-	0.48#	0.50#	-0.99*
5	0.94*	-	-	-	0.69§	-	-1.00*
6	0.93*	-	-0.79*	-	0.82*	0.88*	-0.66§
7	-0.50#	-	-0.71*	0.75*	-	-	-0.99*
8	0.61#	-	-	-	-	-	-0.99*
9	0.57°	0.70§	-0.72§	-0.54#	0.76*	-	-0.97*
10	0.94*	-	-0.61°	0.75*	-0.57#	-0.50#	-0.98*

Significance levels * = 0.001 § = 0.01 ° = 0.02 # = 0.05

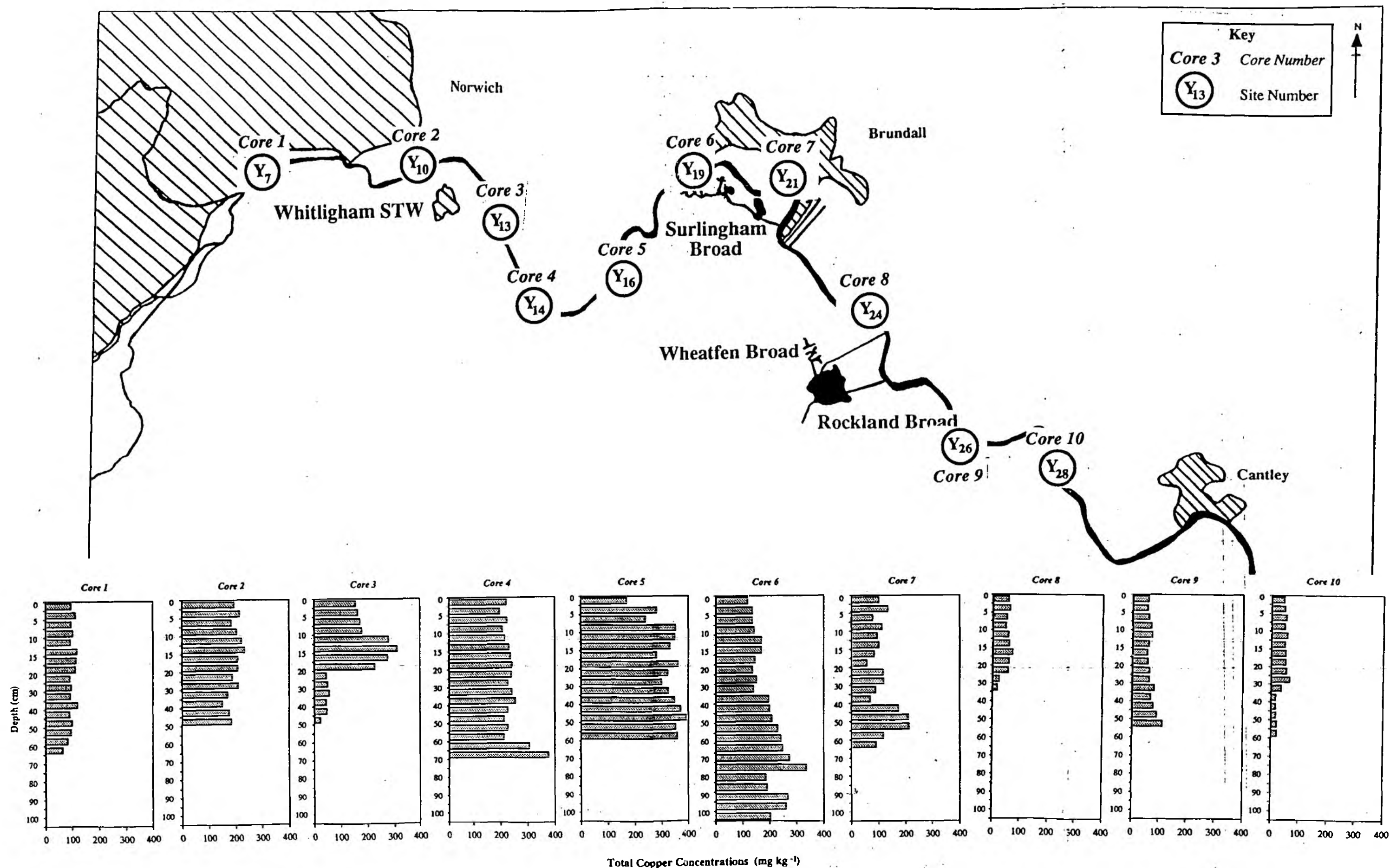


Figure 16. The Depth Distribution of Total Copper in River Yare Sediment Cores (1992 data).

descriptions and confirmed by the reduction in %VS from 22% above this intersection to 16 % below the divide and the positive correlation ($p=0.02$) between %VS and the metal components. At core 10 a decline from 51.4 to 20.0 mg kg⁻¹ at 40 cm was reflected by an increase in %TS as more compact clay sediment was reached. Correlation analysis highlighted the importance of total solids in dictating gross metal accumulations ($p=0.02$). Sediment pH and redox may have influenced the distribution of metals at certain sites but their influence was by no means universal. Significant correlations were restricted to cores 3 and 10 for redox and cores 3, 4 and 6 for pH. All correlations for redox were negative, implying that a decline in redox potential was concomitant with an increase in metal concentrations, while both positive and negative correlations were apparent for sediment pH. These results indicate that sediment stratigraphy plays an important role in defining the nature of contaminant profiles.

5.3. Broads Sediment Surveys

5.3.1. Concentration and distribution of mercury in Broad surficial sediments

The spatial distribution of surficial sediment total mercury and methylmercury concentrations in Rockland, Wheatfen and Surlingham Broads (Bargate Water) is given in Figure 17 and summary data is presented in Table 11. It is evident that these relatively undisturbed shallow lakes tended to act as a sink for mercury, producing 4 to 10 fold increases in mean total mercury loadings over adjacent river sites. Wheatfen Broad proved to be the least contaminated of the Broads investigated, but even this Broad contained surface mercury concentrations which were nearly twice those found in the main contaminated zone of the River Yare, just below Whitlingham STW. Loadings of methylmercury were also elevated within the Broads surface sediment, producing 1.5-3 fold enrichments over adjacent channel reaches, again with Wheatfen displaying the lowest degree of enrichment.

Table 11. Mean surficial mercury concentrations in the Broads (1990).

Broad System	Mean Total Mercury Conc. (mg kg ⁻¹)	Mean Methylmercury Conc. (µg kg ⁻¹)
Surlingham Broad	17.6	19.1
Adjacent Yare Sites Y ₁₉₋₂₂	2.40	5.69
<i>Enrichment over main River</i>	<i>7 fold</i>	<i>3 fold</i>
Rockland	16.9	19.7
Adjacent Site Y ₂₄₋₂₅	1.73	11.2
<i>Enrichment over main River</i>	<i>~10 fold</i>	<i>~2 fold</i>
Wheatfen	7.44	18.4
Adjacent Site Y ₂₄₋₂₅	1.73	11.2
<i>Enrichment over main River</i>	<i>4 fold</i>	<i>1.5 fold</i>
Max. Yare Conc. (Site Y ₁₄)	4.68	29.5

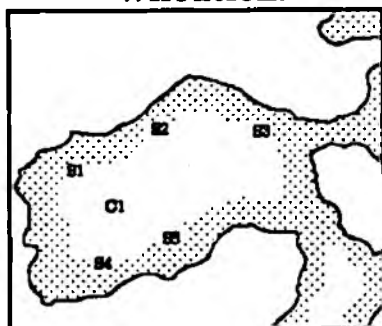
Figure 17. Spatial Distribution of Total and Methylmercury in surficial Sediments from Rockland, Wheatfen and Surlingham Broads.

Rockland.



Core	THg (mg/kg)	MeHg (µg/kg)
R1	31.15	-
R2	19.60	-
R3	13.29	-
R4	21.17	-
R5	8.65	21.38
R6	9.80	23.48
R7	5.98	18.53
R8	7.35	16.97

Wheatfen.



Core	THg (mg/kg)	MeHg (µg/kg)
W1	3.98	16.66
W2	7.38	15.69
W3	7.65	16.47
W4	9.56	21.93
W5	9.56	21.38

Surlingham.



Core	THg (mg/kg)	MeHg (µg/kg)
S1	13.90	-
S2	14.80	-
S3	24.02	-

The vertical extent of mercury contamination was assessed from sediment cores obtained from strategic locations in each Broad, results for which are depicted in Figure 18(i-iii). Total mercury concentrations were seen to increase with depth, reaching a maximum at around 20-24 cm. At some sites total mercury loadings at depth were 10 times higher than surface concentrations found within the main river channel. A degree of variability was inherent in the vertical profiles some of which can be attributed to geographical siting of the cores. Cores 1, 3, 4 and 5 from Rockland Broad (situated ≈ 9 km below Whitlingham STW outfall) were obtained from undisturbed yet open areas of the water and displayed subsurface maxima (27.4 mg kg⁻¹, 36.9 mg kg⁻¹, 29.8 mg kg⁻¹ and 15.0 mg kg⁻¹ respectively) with a tailing in concentrations both above and below the divide. Peak concentrations occurred at different depths (≈ 30 cm in core 1, 8-10 cm core 2, and 20-24 cm in cores 4 and 5) illustrating the importance of sedimentation rate in determining the nature of the concentrations profiles. Concentrations reach a low plateau of ≈ 3 mg kg⁻¹ below 36-40 cm in cores 4 and 5. Core 3, taken in a lily bed close to the navigation channel, displayed comparatively low concentrations (mean 7.88 mg kg⁻¹) producing a fairly uniform vertical profile. Disturbance by boat traffic or the removal of contaminated sediment by past dredging activities could explain this type of vertical stratification.

Wheatfen Broad displayed a lower degree of total mercury enrichment with a maximum loading of 11.2 mg kg⁻¹ occurring at a depth of 20-24 cm, consistent with the vertical distribution of mercury in Rockland Broad. The core extended down to the underlying marl base sediments and therefore incorporated the full contaminant sequence. Concentrations within the marl base layer were low, containing 0.1 mg kg⁻¹ mercury.

Methylmercury concentrations in Rockland and Wheatfen were fairly similar with high concentrations to a depth of about 10 cm before tailing off to undetectable levels at around 30 cm. The similarity of methylmercury concentrations in Rockland and Wheatfen Broads is in contrast to the significant difference in total mercury concentrations, which would suggest that once above a certain threshold concentration total mercury levels are no longer a limiting factor for methylmercury formation.

The total mercury concentrations in Surlingham Broad (6.5 km downstream from Whitlingham STW outfall) were generally higher than those of Rockland and Wheatfen, but due to the deeper body of water overlying the sediment the coring device only permitted the acquisition of fairly shallow cores which prohibited a full evaluation of the vertical extent of contamination. Maximum concentrations occurred at depth although the concentrations in Surlingham core 1 were fairly uniform throughout (mean 25 mg kg⁻¹). Methylmercury concentrations revealed surface maxima (0-4 cm) which decreased rapidly with depth, to undetectable levels at 16 cm and 10 cm for cores 1 and 2, respectively. The consistent occurrence of maximum

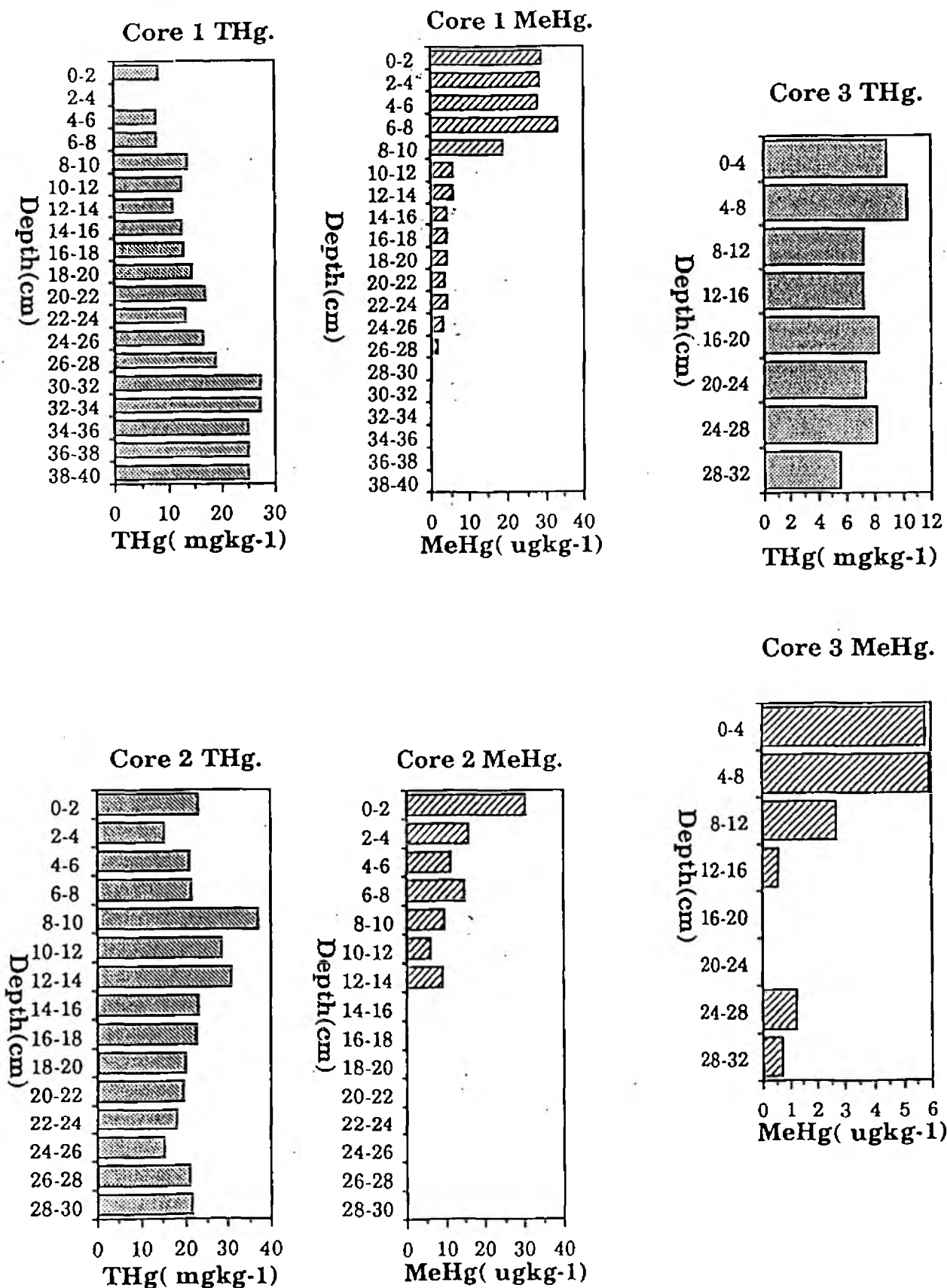
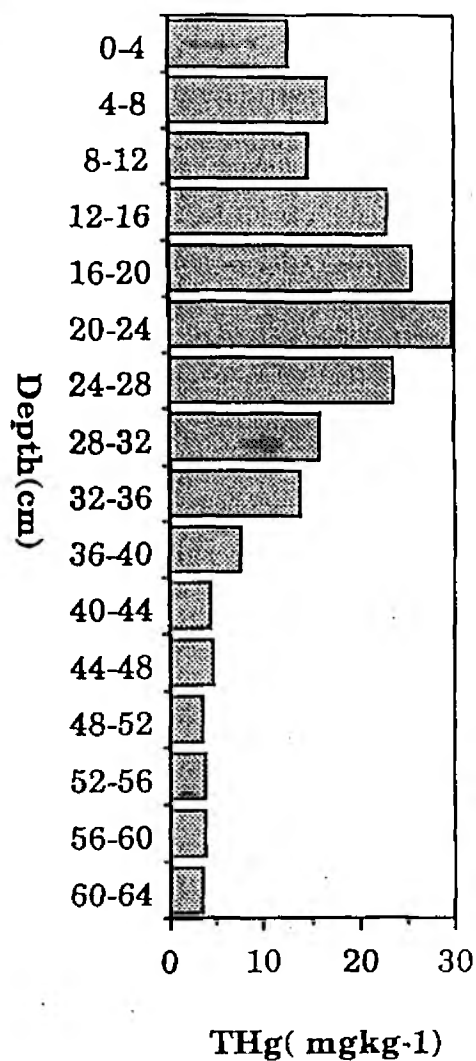
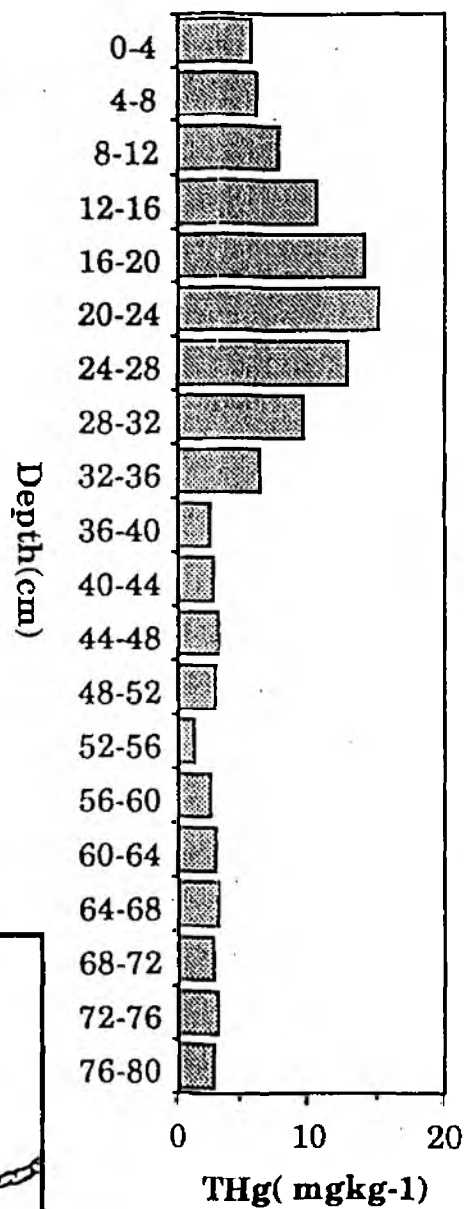


Figure 18(i). Vertical Distribution of Total and Methylmercury in five Cores from Rockland Broad

Core 4 THg.



Core 5 THg.



Core 5 MeHg.

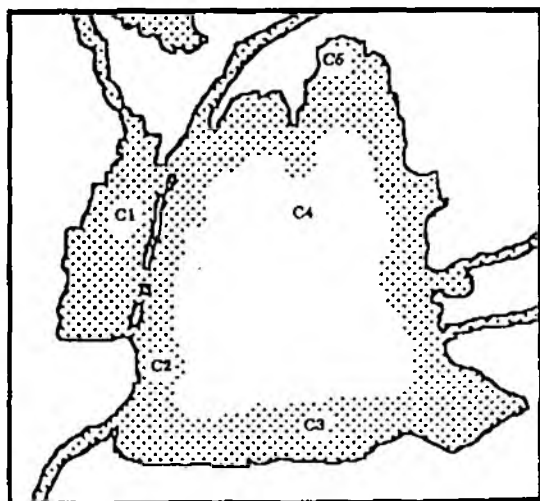
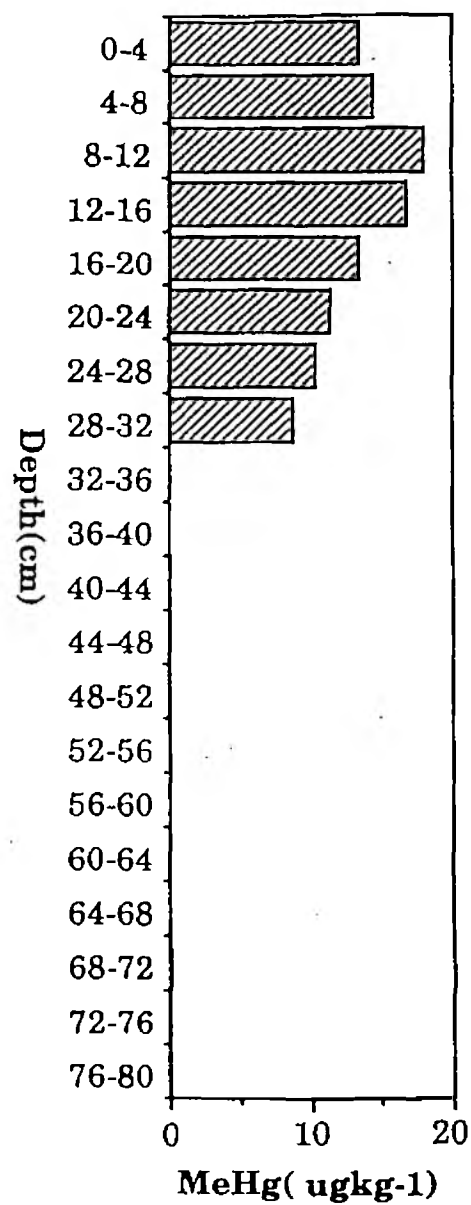
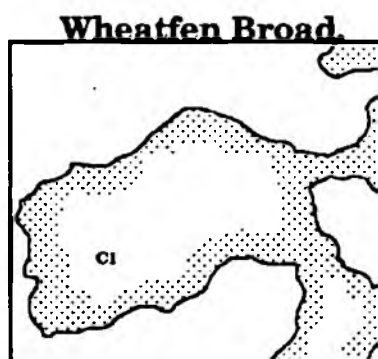
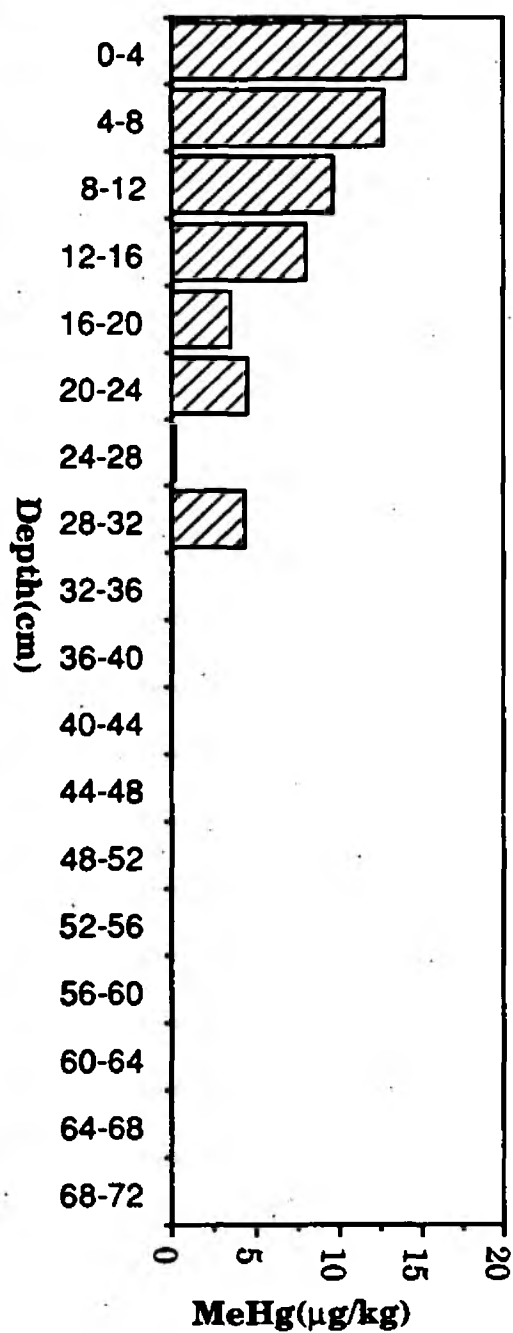


Figure 18(ii) : Vertical distribution of Total and Methylmercury in cores from Wheatfen Broad.



Wheatfen Core Methylmercury.



Wheatfen Core Total Mercury

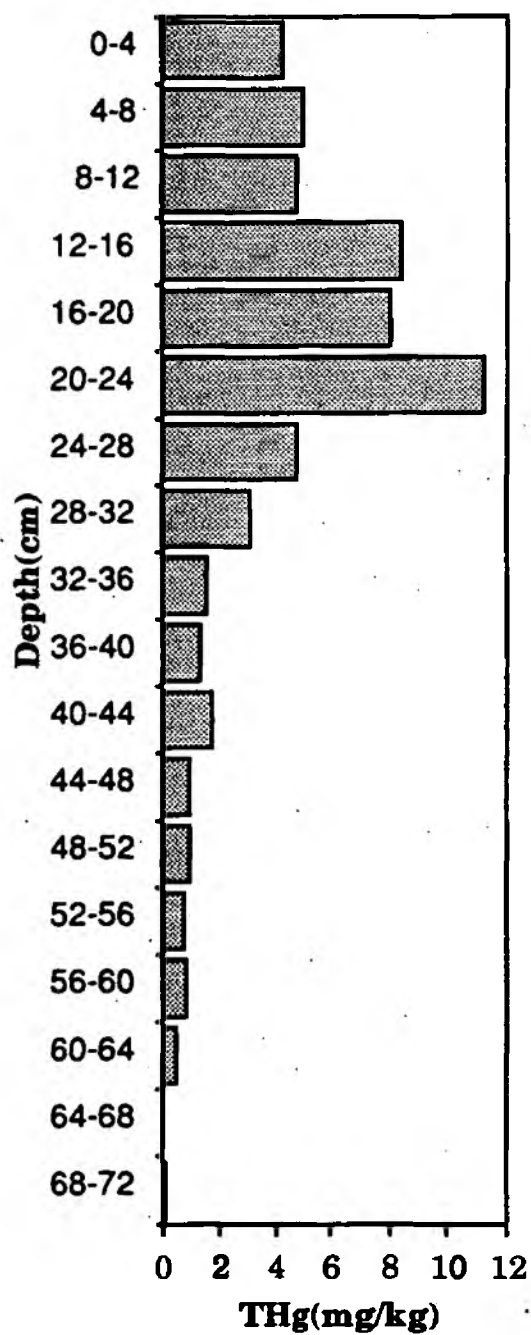
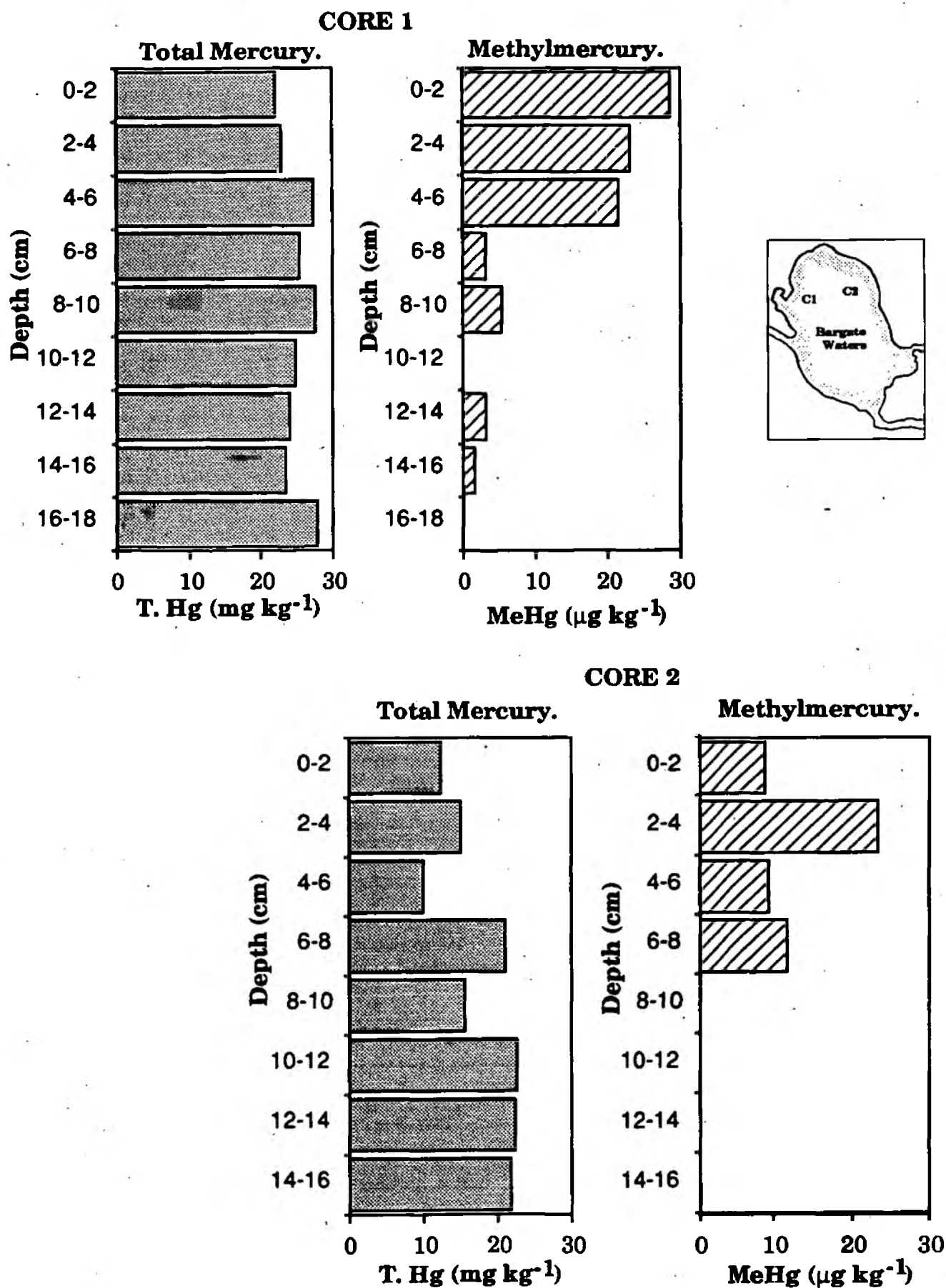


Figure 18(iii). Vertical distribution of Total and Methylmercury in cores from Surlingham Broad.



methylmercury mercury enrichment in surface sediment layers infers a dependence upon a particular set of environmental conditions which promote methylmercury formation and persistence. A more detailed longer term study was instigated in 1991 to evaluate the role of bacteria and sediment physico-chemistry upon the methylating ability of the sediments.

5.3.2. *In-situ* seasonal variations in methylmercury and related physiochemical parameters in the sediment of Rockland Broad

Sediment cores were obtained from 5 predesignated sampling points in Rockland Broad, on a three monthly basis, the timing of which was set to maximise seasonal variability. Samples were collected in May (Spring), August (Summer) and November (Autumn) 1991, and March 1992 (Winter). The seasonal profiles, which are depicted in Appendix 2 for individual cores, illustrate temporal changes in the magnitude and vertical distribution of methylmercury and associated determinands.

The total mercury profiles closely mirror those previously seen in Rockland Broad revealing subsurface enrichment to depths in excess of 30 cm, with detectable levels extending down to >80 cm in some of the cores. Maximum loadings generally occurred at depths of ≈ 20 -24 cm and a gradual reduction in concentrations was apparent both above and below this subsurface maximum. Mercury concentrations generally returned to background levels at the base of the cores indicating that this coring exercise effectively encapsulated the entire mercury contamination sequence in Rockland Broad.

Differences were however evident in the vertical extent of contamination both within and between sites (Figure 19). Certain sites revealed a compact sequence of accumulation history where maximum loadings occurred at depths of 8-12 cm (*coring site 3*), while other sites (*coring site 5*) revealed subsurface maxima at 36-40 cm. This implies that disparities in sedimentation rates were responsible for some of the variability in total mercury concentrations.

Sample location also influenced the rate and nature of particulate and contaminant deposition with low mercury concentrations in sheltered backwaters (e.g. *core site 1*) and greater accumulations in fairly open, but remote corners of the Broad, away from the main boating channel (cores 2 and 5). Figure 19 illustrates the relative position of the coring sites and shows that although Core 1 is sited in proximity to the main inlet, it is partially separated from the main expanse of Rockland Broad by a line of small islands which have built up adjacent to the main navigation channel. The presence of this barrier, due it is presumed to the active deposition of suspended sediment, may have inhibited the transportation and subsequent deposition of particulate bound contaminants at this site, reducing average core concentrations to $\approx 2 \text{ mg kg}^{-1}$,

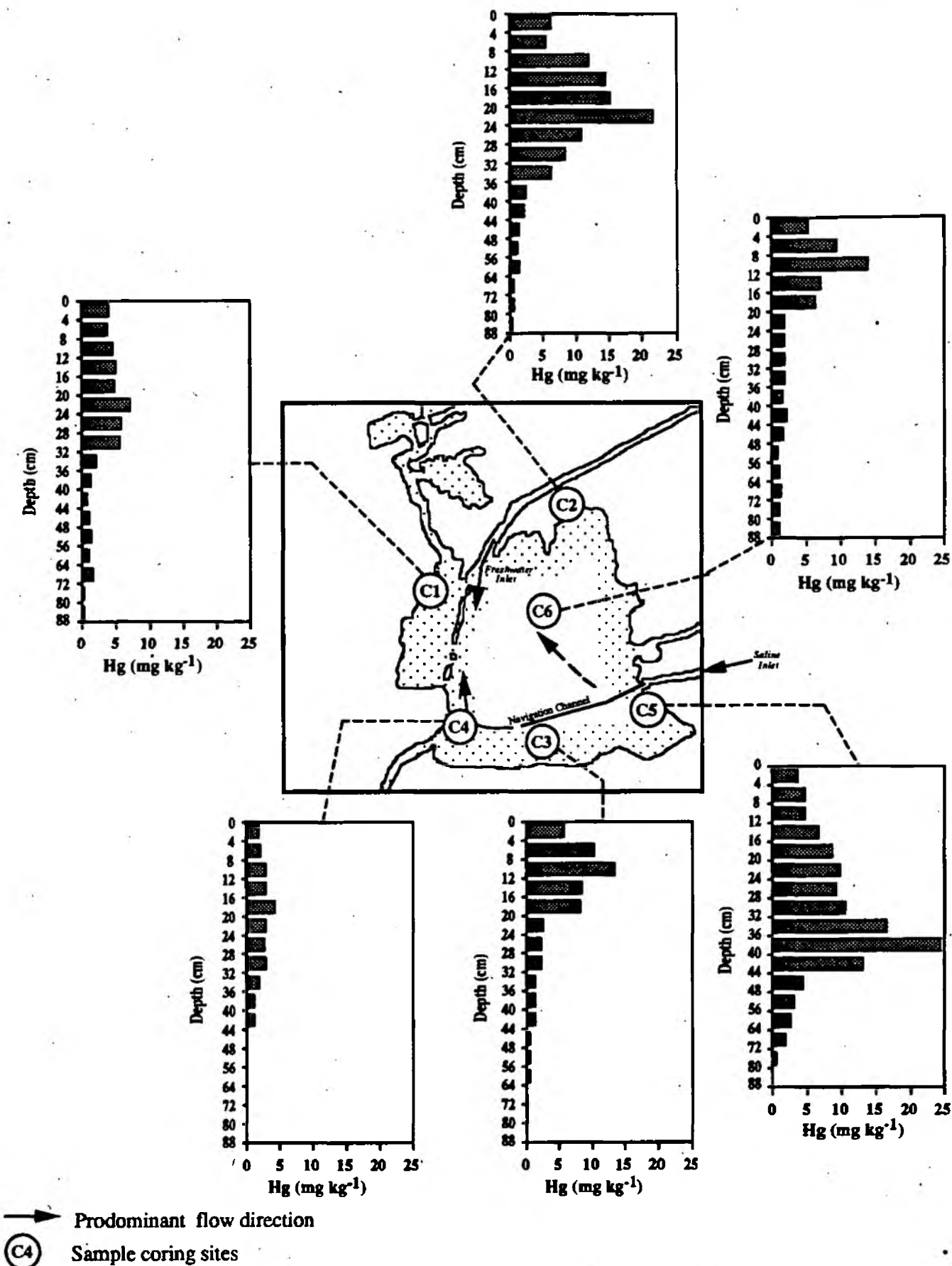


Figure 19. Differences in the Vertical distribution of Total Mercury in Rockland Broad Sediment Cores.
(Results from the Spring 1991 survey).

less than a third of the loadings experienced in cores 2 and 5. The comparatively shallow depth of the mercury concentration maximum in core 1 also infers a lower degree of sedimentation at this site.

Sediment disturbance may also be responsible for some of the observed variability in the total mercury contamination profiles, particularly for those sites situated in proximity to the main navigation channel, where past dredging activities and disturbance by boat traffic could have radically altered the vertical profiles. This appears to be the case in Core 4 where the spring 1991 mercury concentration profile exhibited little vertical stratification and low loadings (2.36 mg kg^{-1}). There consequently seemed to be little merit in continuing the seasonal monitoring programme at this site and research efforts concentrated upon the remaining 5 sampling sites.

Within site variability was evident at a number of the coring sites. Core 6, for example, exhibited peak total mercury concentrations at the 28-32 cm depth interval in the winter survey compared to $\approx 12-16 \text{ cm}$ for all the other seasonal surveys (Appendix 2) and a similar situation is apparent in core 5 as depicted in Figure 20. This infers the existence of localised zones of deposition even within short distances (1 m). Likewise, similarities between the depth of maximum mercury enrichment and sediment %VS in the summer-winter and spring-autumn

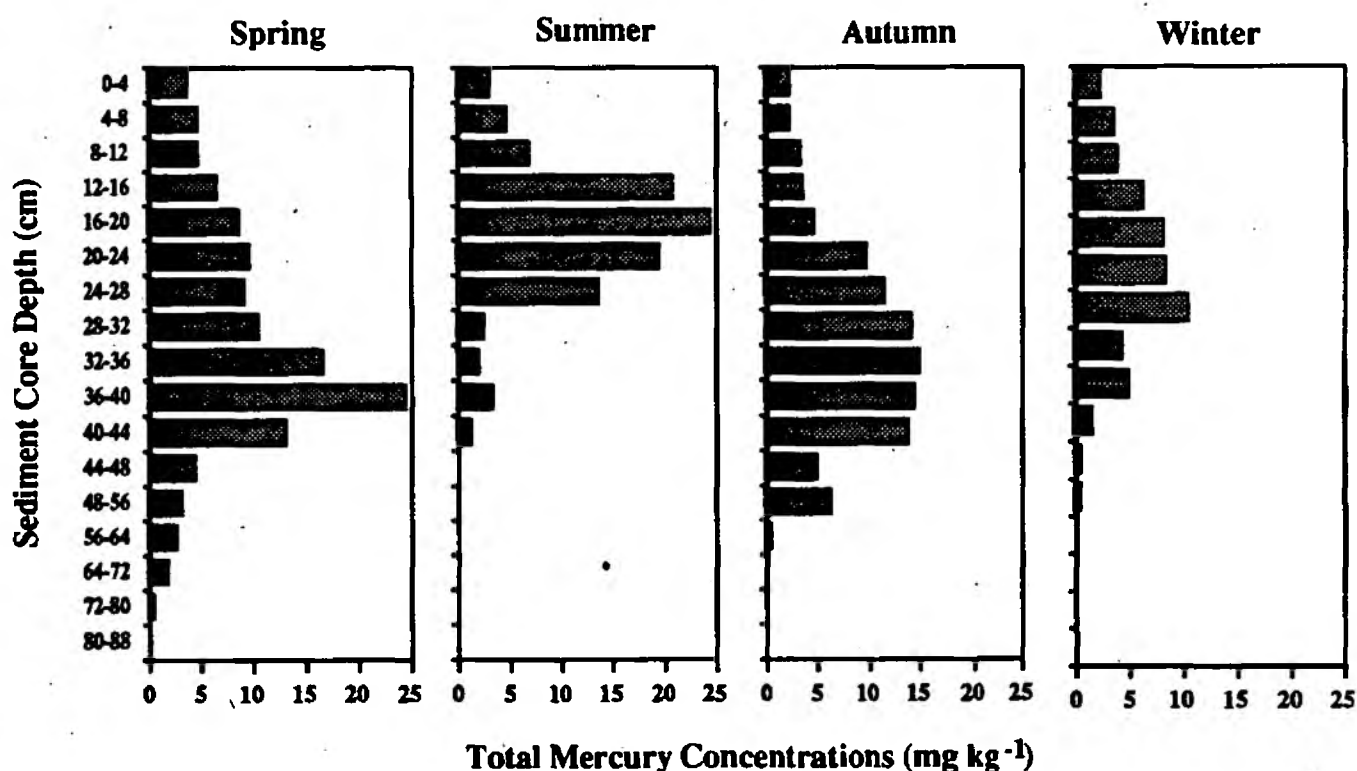


Figure 20. Within Site Variability in Total Mercury Concentrations (Coring Site 5, Rockland Broad).

Table 12. The seasonal variation in total mercury and percentage volatile solids in Rockland Broad, coring site 5.

Season	Depth of peak T. Hg	T. Hg conc. (mg kg ⁻¹)		%VS Core mean
		Max.	Core mean	
Spring	36-40 cm	24.37	7.78	20.0
Autumn	32-36 cm	15.02	6.71	22.3
Summer	16-20 cm	24.41	7.47	36.6
Winter	24-28 cm	10.46	4.60	41.2

surveys for core 5 (Table 12) implies that the summer-winter cores were acquired from a different stratigraphic zone to spring-autumn cores. Part of the reason for the apparent change in stratigraphy at coring site 5 could pertain to sampling difficulties experienced during the summer survey which necessitated core acquisition a short distance (2 m) from the assigned site marker.

The vertical distribution of contaminants therefore appears to be governed to a large extent by sample locality, through the effects of flow regime, sedimentation rates and surface disturbance which results in a degree of spatial variability. Even so, total mercury concentrations remained fairly consistent over the 12 month sampling period. Unpaired Student 't' tests failed to highlight any statistically significant difference between the mercury concentration means calculated for successive seasonal surveys. The exception being between the spring and summer results at core 1, where average core total mercury loadings of 2.94 and 1.17 mg kg⁻¹, respectively, caused the null hypothesis of comparable population means to be rejected.

The behaviour of methylmercury within cored sediment profiles was strikingly different from that previously described for inorganic mercury, in that the magnitude, vertical extent and nature of the contamination profiles changed between sampling campaigns. Concentrations of methylmercury ranged from undetectable (<0.1 µg kg⁻¹) to a maximum of 23.74 µg kg⁻¹ (core 2, spring survey at 8-12 cm), with cores 2 and 5 generally displaying the greatest enrichment (see Table 13). The depth penetration of methylmercury was greatest in the spring and lowest in the autumn as exemplified in cores 2 and 6 where detectable levels of methylmercury occurred in the uppermost 28 and 48 cm in the spring but were confined to the top 16 and 32 cm, respectively, in the autumn. In general, maximum concentrations prevailed in the spring and summer months, the exception being for Core 6, where elevated methylmercury loadings occurred in the autumn with a maximum loading of 13.9 µg kg⁻¹ and a mean core concentration of 6.65 µg kg⁻¹.

Table 13. Seasonal variations in metals and physiochemical parameters averaged over core depth.

Determinand	Survey	Mean core loadings				
		Core 1	Core 2	Core 3	Core 5	Core 6
Total Mercury (mg kg ⁻¹)	Spring	2.94	6.48	4.34	7.78	3.54
	Summer	1.17	5.46	2.14	7.47	3.56
	Autumn	1.42	7.89	3.21	6.71	3.38
	Winter	2.43	5.71	2.78	4.6	4.59
Methylmercury (µg kg ⁻¹)	Spring	3.21	7.36	6.86	9.56	3.32
	Summer	9.37	11.8	5.04	8.01	4.29
	Autumn	0.00	10.9	5.56	5.77	6.65
	Winter	4.07	10.4	6.02	4.52	5.89
Sulphide (mg kg ⁻¹)	Spring	197	107	123	305	128
	Summer	750	703	122	183	134
	Autumn	173	115	118	195	185
	Winter	293	280	142	290	239
Temperature (°C)	Spring	9.4	11.0	10.6	11.3	10.7
	Summer	15.6	19.2	15.7	17.9	17.6
	Autumn	8.5	7.2	7.5	7.1	6.9
	Winter	9.5	8.6	7.81	7.8	8.1
Chloride (mg kg ⁻¹)	Spring	137	149	145	302	308
	Summer	96.2	215	131	198	453
	Autumn	382	658	635	571	1008
	Winter	320	357	217	436	395
pH	Spring	7.4	7.4	7.5	7.4	7.3
	Summer	7.5	7.5	7.5	7.5	7.3
	Autumn	7.2	7.2	7.3	7.0	7.2
	Winter	7.3	7.4	7.5	7.1	7.6
Sulphate (mg kg ⁻¹)	Autumn	595	949	716	550	538
	Winter	3533	3850	3594	3905	3601
Redox (mV)	Autumn	-315	-284	-284	-288	-349
	Winter	-309	-256	-219	-193	-209

This seasonal change in the vertical extent of methylmercury was accompanied by changes in its distribution within the sedimentary compartment (Figure 21). Maximum methylmercury concentrations normally prevailed in the uppermost sediment layers, producing a subsurface maximum just below the sediment/water interface which gave way to a rapid decline in concentrations with depth. Only low levels of methylmercury were detected at depths in excess of 28 cm. The methylmercury maximum generally resided at the 4-8 cm or 0-4 cm depth intervals, but in some instances this peak occurred in deeper sediment layers, extending to 20 cm in the case of the winter core 2. The methylmercury peak tended to reside higher up in the sediment profile in the summer (0-8 cm) and extended to greater depths in the winter, although there were exceptions to this generalised rule, such as cores 1 & 6 in the winter survey where the highest concentrations occurred at the sediment surface. Despite this discrepancy the overall



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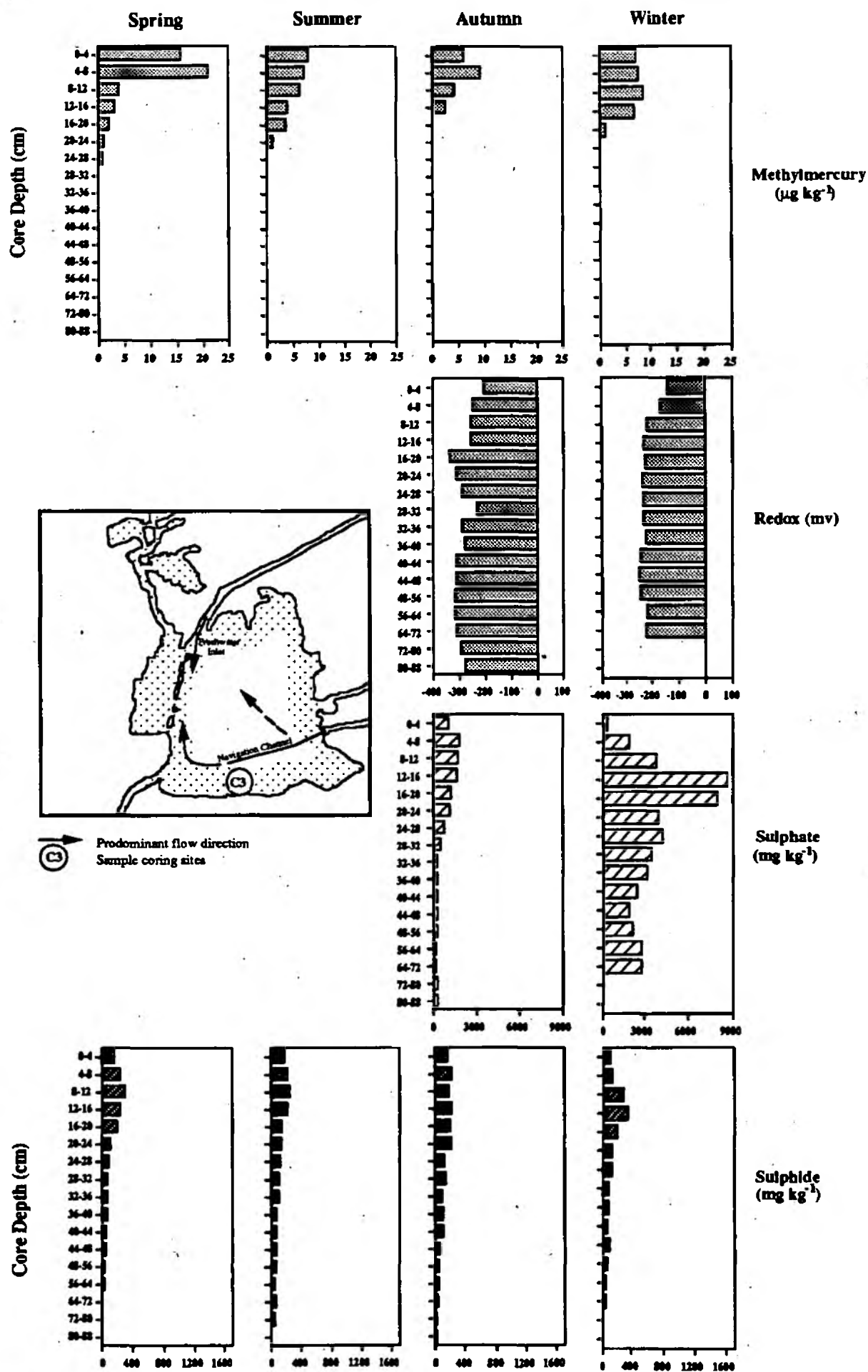


Figure 21(ii). Seasonal Variations in the Vertical Distribution of Methylmercury, Redox, Sulphate and Sulphide in Rockland Broad Sediments. Coring Site 3.

trend seems to indicate that alterations in sediment conditions confine methylmercury to a narrow band in the upper sediment during the summer months.

The analysis of sediment temperature, sulphide, sulphate and redox may help to explain the behaviour of methylmercury within the sediment compartment of Rockland Broad, although their effect upon the net mercury methylation ability appear, in certain instances, to be site specific. Surficial sediment temperatures followed a predictable pattern with higher temperatures ($\approx 20^{\circ}\text{C}$) prevailing during the summer and lower temperatures during the autumn ($\approx 6^{\circ}\text{C}$). A seasonal temperature gradient within the sediment compartment was evident from the vertical profiles in Figure 22 caused by surface heating during the spring and summer and cooling during the autumn. This resulted in high surface sediment temperatures in the summer which declined with depth and a reversal in the autumn where warmer temperatures were experienced at depth. This seasonal pattern was consistent for all the cores. The degree of surface heating will depend on site location, in terms of aspect, shading by aquatic/terrestrial vegetation and water depth. Shading by reeds during the summer at site 3, for example, could account for relatively low surface temperatures at this site (18°C) which were 3°C cooler than the other sites. Temperature will undoubtedly have a positive influence upon the methylating ability of bacteria. The concomitant occurrence of high summer temperature and elevated methylmercury concentrations infers a causative link between these two parameters particularly for cores 2 and 5 where elevated methylmercury loadings coincided with the existence of high sediment temperatures.

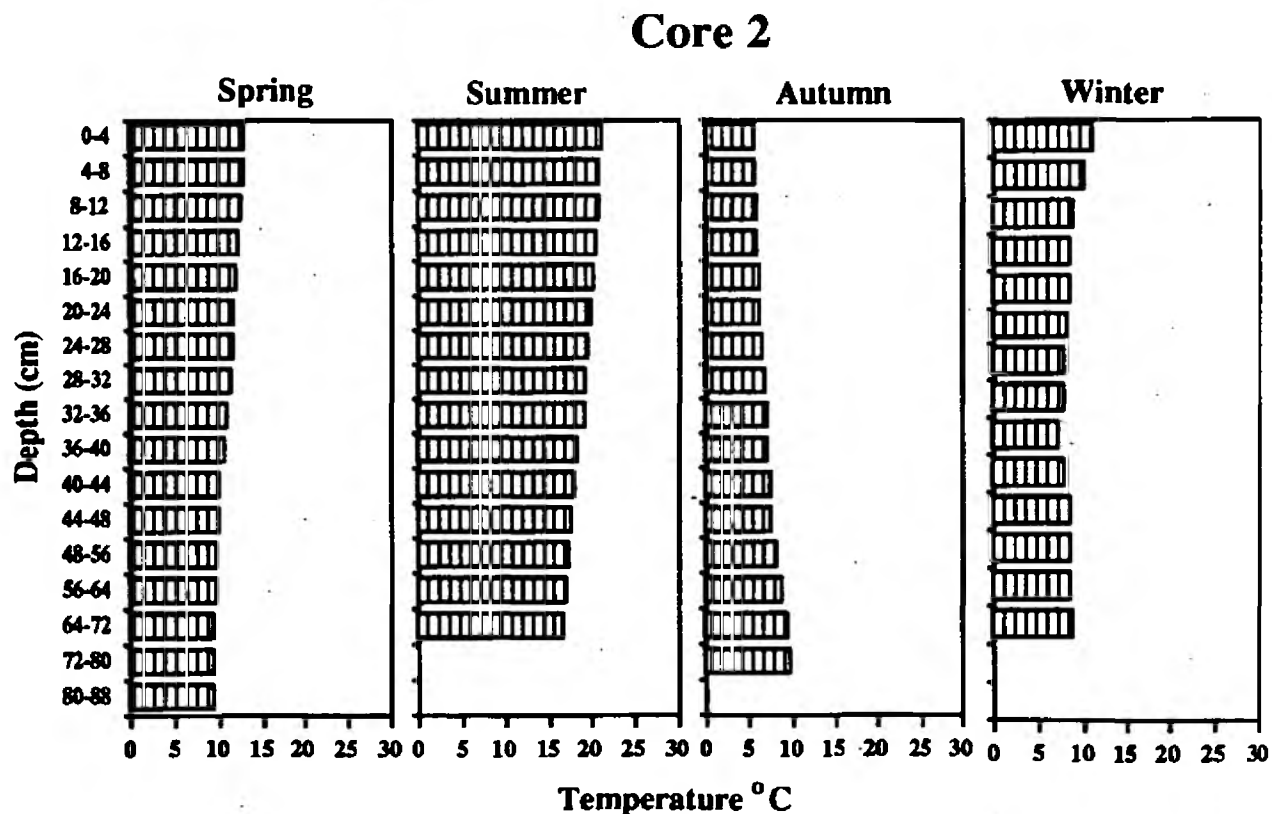


Figure 22. Seasonal changes in sediment temperature with core depth.

The importance of temperature as a control upon mercury methylation was investigated under laboratory controlled temperature conditions by subjecting mercury contaminated sediment to a 10°C rise in temperature, consistent with the temperature difference stimulated by seasonal change (12°C to 22°C). The results are presented in Table 14 and indicate a 17-31% increase in methylmercury concentrations following a 6 day acclimatisation period to elevated temperatures in the upper most sediment layers (\approx top 30 cm). Increased temperature, however, failed to stimulate a positive response in deeper sediment layers, but instead exhibited signs of methylmercury degradation. This implies that an increase in temperature elevates methylmercury production in the upper sediment layers, but promotes methylmercury degradation at depth.

Temperature effects alone cannot however account for all the differences in methylmercury loadings since methylmercury concentrations also appears to be intrinsically linked to the chemical cycling of sulphur and oxygen. Sediment sulphide concentrations, which refer to water soluble, rather than acid soluble forms, revealed similar depth profiles to those observed for total mercury, as can be seen by comparing the Figures in Appendix 2. The major trend was one of subsurface enrichment with levels declining above and below the peak concentration. Values near the base of the cores were generally lower than surface and subsurface concentrations despite the occurrence of black anaerobic sediments at these depths, suggesting the presence of more strongly bound (acid soluble) sulphide. Average core concentrations in the spring remained fairly low (see Table 13) and although levels remained comparable in cores 3, 5 and 6 during the summer, a 4-6 fold enrichment was apparent in cores 1 and 2. The majority of this increase occurred in the 0-32 cm zone and it is assumed that the rapid reduction of sulphate in the upper sediment layers was responsible for the large increase in pore water

Table 14. Methylmercury concentrations following a 10°C change in sediment temperature.

Tank	Depth (cm)	Total Mercury (mg kg ⁻¹)			Methylmercury (µg kg ⁻¹)			% Increase Methylmercury	
		12°C	22°C	22°C	12°C	22°C	22°C	Temp. increase 12-22 °C	
		Day 1	Day 4	Day 10	Day 1	Day 4	Day 10	(day 1-4)	(day 1-10)
1	0-5	3.74	3.59	3.69	7.14	7.92	9.39	+11	+31
	25-29	4.01	3.78	4.34	3.02	3.48	3.97	+15	+31
	50-54	4.29	4.20	4.04	2.41	2.28	2.10	-6	-12
4	0-5	0.28	0.15	0.17	nd	nd	nd	-	-
	22-26	0.30	0.21	0.19	nd	nd	nd	-	-
	26-30	3.61	3.29	3.40	2.39	2.68	2.50	+12	+5
	48-52	4.07	3.69	3.85	3.01	2.44	2.26	-20	-25
5	0-5	4.59	4.17	4.17	7.54	7.59	8.84	-	+17
	24-28	4.18	3.84	3.96	3.12	3.48	3.51	+11	+12
	28-32	0.31	0.24	0.25	nd	nd	nd	-	-
	52-56	0.21	0.18	0.27	nd	nd	nd	-	-

nd - not detectable.

sulphide. [This observation prompted an expansion of the experimental protocol in the later surveys to include sediment sulphate and redox in the routine determinands]. Sulphide concentrations in the autumn were roughly comparable to those observed in the spring for all cores but increased 1.2-2.4 fold between the autumn and winter.

The confinement of methylmercury to the upper sediment layers during the summer could be related to elevated sulphide loadings at depth particularly in cores 1 and 2. Sulphide has the ability to complex inorganic mercury making it comparatively unavailable for microbial synthesis so its presence at depth may have inhibited methylmercury production. Conversely the presence of sulphide may have altered the microbial population to non-methylating bacteria, or demethylating bacteria, both mechanisms would have stimulated the same response, the absence of methylmercury at depth. Statistical analysis, however, failed to highlight a relationship between water soluble sulphide and methylmercury due, most probably, to the limited number of methylmercury values which reduces the efficiency of the statistical test.

Redox, a measure of the oxidation-reduction potential, was negative in all sediment cores with values ranging from -15 mV to -397 mV, with more oxic conditions prevailing in surface layers. Rockland Broad sediments are therefore reducing in nature but seasonal changes in redox were apparent, with a trend towards slightly less anoxic conditions in the winter. Cores 2, 3, 5 and 6 displayed a progressive trend towards more oxic conditions in the upper 30 cm which could occur following an influx of dissolved oxygen to the sediment compartment during the colder winter months. The presence of more oxygenated conditions in the winter coincides with an increase in the depth penetration of methylmercury. Methylmercury in core 2, for example, was confined to the upper 16 cm in the autumn but extended down to 32 cm in the winter (Figure 21 (i)). Similarly in core 1, the complete absence of methylmercury in the autumn gave way to detectable levels down to 12 cm in the winter. This implies that dissolved oxygen is an important control upon the distribution and behaviour of methylmercury within the sediment system.

This trend towards more oxygenated conditions in the winter may also have stimulated the universal increase in sediment sulphate which displayed 4-7 fold enrichment in average core loadings over autumn levels. At core 2, for example, mean core concentrations increased from 949 mg kg⁻¹ to 3850 mg kg⁻¹. This increase is unlikely to be from the oxidation of water soluble sulphide in the more oxic conditions since the magnitude of the increase is too great and was by no means reflected in a change in sediment sulphide values. It could however be due to the oxidation of precipitated forms of sulphide or conversely the influx of sulphate in surface waters. The enrichment of sulphate at intermediate depths producing peaks at depths of 12-20 cm (cores 1 & 3), 16-28 cm (core 5) and 28-36 cm (cores 2 & 6), implies that the dissolution of

solid components at depth is probably the main cause of the observed increase in winter sulphate values.

Chloride has been utilised in this study as a surrogate measure for salinity. Concentrations were generally less than 400 mg kg^{-1} but displayed a significant enrichment in the autumn survey where 2-5 fold increases were observed. Highest autumn concentrations (as core averages) occurred in core 6 (1008 mg kg^{-1}) and the lowest (382 mg kg^{-1}) at site 1. This degree of enrichment could occur with the influx of saline water to the system prior to the autumn sampling. Chloride exhibited subsurface enrichment particularly in the autumn cores and could therefore be partially responsible for the autumn reduction in the concentration and vertical extent of methylmercury. Correlation coefficients identify a negative association between sediment chloride and methylmercury loadings in core 6 ($p = <0.05$) but no further correlations were evident. In general, however, the nature of the chloride depth profiles differed from those described for these other parameters in so much as the chloride maxima failed to coincide with the total mercury, sulphide or methylmercury peak concentrations. The profiles showed marked differences between cores and exhibited little pattern with depth. So even though chloride may have been instrumental in initiating the decline in methylmercury in the autumn, following the influx of saline water, it seems unlikely that chloride regulates the ordinary synthesis of methylmercury within Rockland Broad.

While the behaviour of sediment methylmercury appears to be dictated to a certain degree by sulphate, sulphide, redox, temperature and total mercury, other parameters seem to exert little or no direct control upon net methylmercury concentrations. Sediment pH ranged from 6.8-7.8, indicating neutral to slightly basic sediment conditions. pH remained fairly consistent down the core, although surface layers tended to display a slight reduction in pH when compared to deeper sediment. This could speculatively be linked to the formation of weak sulphuric acid solution in the presence of sulphate and hydrogen ions under the more oxic conditions experienced in the surface layers which locally lowered pH. This assumption, however, is not backed up by correlation analysis, apart from the derivation of a significant correlation between pH and sulphate ($r=0.72$) and redox ($r=0.58$) in the winter core 2 sample. Percentage volatile solids, a surrogate measure for organic loading, displayed a decline in loadings with core depth but did not show any significant temporal variation and could therefore not be of paramount importance in controlling the synthesis of methylmercury.

5.3.3. Seasonal variations in total viable bacterial communities in Rockland Broad sediment

Perhaps the most important factor, which has yet to be directly addressed, is the role that bacteria play in synthesising methylmercury within aquatic sediments. An investigation into the effects of seasonality upon bacterial numbers and their resistivity to inorganic mercury was

conducted through the use of Jenkins cores. These cores allow the acquisition of undisturbed surface sediments covering the top 8 to 14 cm of sediment and facilitated the subdivision of sediment layers into discrete 2 cm intervals. The relationship between bacterial colony counts and methylmercury is illustrated in Figure 23 for coring site 1, but this relationship holds true for the other sediment cores. The results are presented in diagrammatic form in Appendix 3.

The distribution of aerobic bacteria within the sediment compartment was influenced by depth and seasonality with the highest number of colonies occurring in the uppermost sediment layers and during the spring sampling. Numbers declined with core depth and compared to the spring were less prolific in the summer and reached a minimum in the winter. This implies that sediment conditions were most favourable for the survival of the aerobic bacteria during spring. The vertical extent of these aerobic colonies differed between the cores but increased significantly in the winter, as can be seen from core 1 where their depth penetration increased from 8-10 cm to 14-16 cm between the autumn and winter surveys.

The distribution of mercury resistant colonies differed to that previously described for the total number of aerobic bacterial colonies, in that mercury resistance peaked in subsurface layers. Maximum resistance occurred at 4-8 cm in the spring, autumn and winter but shifted to surface deposits in the summer (0-4 cm). The distribution of mercury resistant aerobic bacteria mirrored that of methylmercury loadings in some instances, although this association was by no means universal and digressions were apparent, such as at core 2 in the spring and autumn. It does however imply an association between these two parameters.

The degree of mercury resistance was also expressed as a percentage of the total colony count and their depth distribution reveals a subsurface maximum at 4-8 cm, although some cores displayed surface enrichment (core 1, summer, 0-4 cm), while others peaked at depth (autumn core 5, 8-12 cm). The highest degree of mercury resistance occurred in the spring (90-109%) and summer (71-115%) and was lowest in the autumn (12.3-78.1%) which indicates a dependence on seasonality. Correlation analysis failed to infer a consistent association between percentage mercury resistance and methylmercury concentrations and although these two parameters are undoubtedly correlated other factors must also be dictating methylmercury synthesis and demethylation characteristics.

Methyl- and total mercury concentrations within these Jenkins core sediment profiles displayed a wide range of values but generally pertained to the vertical distribution previously described for the larger cores. Methylmercury concentrations were elevated in the spring ($9.93\text{--}23.70\ \mu\text{g kg}^{-1}$) and summer ($2.38\text{--}29.74\ \mu\text{g kg}^{-1}$) but were much lower in the autumn and tended to reside in surface deposits in the summer but at subsurface locations at other times of the year. Total mercury levels generally increased with depth and displayed a similar degree of

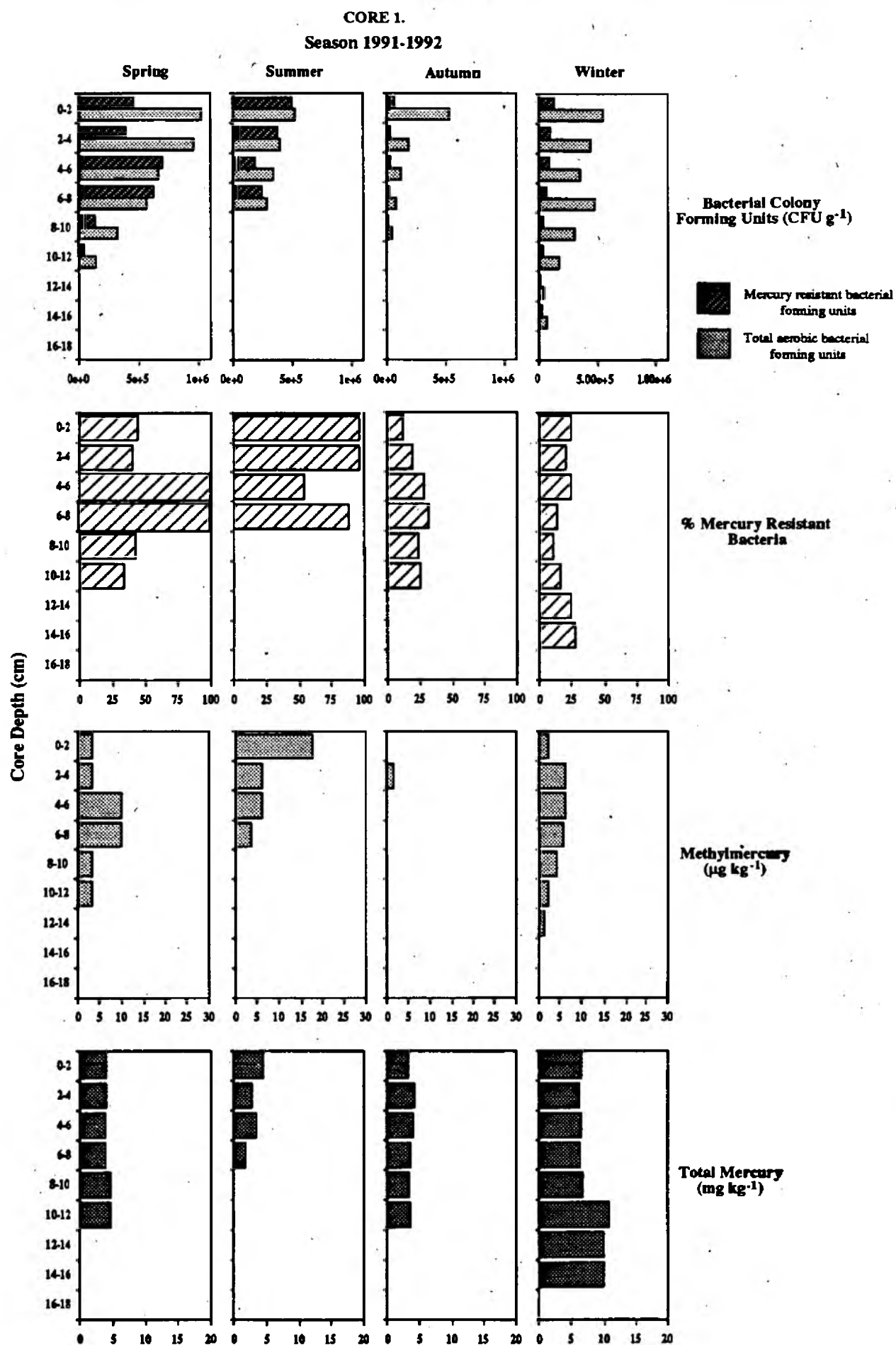


Figure 23 Seasonal variations in mercury resistant bacteria and methylmercury in Rockland Broad sediments.

enrichment and variability as previously stipulated for the larger cores, with loadings ranging from 1.06-18.1 mg kg⁻¹. There was no seasonal change in the distribution of total mercury and the lack of significant correlation between this inorganic substrate and methylmercury and the percentage of mercury resistant bacteria implies that total mercury is not the principal control upon mercury methylation within the Rockland Broad system.

6. DISCUSSION

6.1. The Fate and Behaviour of Total Mercury within the River Yare (1986-1992)

Past industrial discharges of persistent and non-biodegradable substances can have a deleterious effect upon the receiving environment long after abatement of the original pollution source. During the 1960s and early 1970s the River Yare received substantial quantities of mercuric halides and copper, of industrial origin, which were discharged to the aquatic environment following conventional two stage sewage treatment at Whitlingham STW. Despite average removal efficiencies of approximately 83% across the sewage treatment works (Goldstone *et al.*, 1990) the River Yare still underwent a considerable cumulative loading of mercury within the bottom sediments. The majority of the sediment bound mercury is confined to a 17-18 km reach stretching from Trowse in the west, at the upper tidal limit, to Hasingham in the east, (Site Y₂₇) located downstream of Rockland Broad and includes the interconnecting Broad systems.

The spatial distribution of inorganic mercury within the River Yare sediments forms a classic point source pollution plume which is centred 1-2 km downstream of Whitlingham STW and identifies Whitlingham as the source of contamination. The occurrence of elevated loadings ≈ 4 km above the point source reflected the effect of tidal reversals which swept contaminants upstream. A quantitative assessment of the magnitude of mercury enrichment was gained by comparisons to average catchment background levels derived from morphologically similar sediment materials. Although mercury background levels in the River Yares upper catchment are generally $<0.1 \text{ mg kg}^{-1}$, the coarse nature of these sand and gravel deposits precludes their use as geochemical background indices for finer silt and clay deposits. Background levels have consequently been defined from 'uncontaminated' sediments in the lower study reach producing a value of 0.4 mg kg^{-1} . This is consistent with Turekian and Wedepohl's (1961) average shale value, which is often used as a global baseline average for particulate associated metals (Salomons *et al.*, 1987). Surface sediments exhibited significant degrees of enrichment in the initial 1986 surficial sediment survey, where mean transect loadings ($0.81\text{--}11.9 \text{ mg kg}^{-1}$) displayed 2-30 fold elevations over catchment background levels which increased to an 82 fold enrichment when the maximum observed concentration of 32.9 mg kg^{-1} was considered. Since 1986, however, a systematic decline in total mercury concentrations has greatly reduced surficial sediment loadings, culminating in a 7 fold decline in maximum surficial sediment mercury loadings by 1990 with concentrations ranging $0.01\text{--}4.68 \text{ mg kg}^{-1}$.

The reasons for this temporal decline in surface mercury concentrations can be attributed to one, or a combination, of the following processes:

- (i) The downstream movement and dispersion of particulate bound mercury by natural sediment transport processes, with subsequent dilution by 'fresh' unpolluted particulate matter.
- (ii) The burial of mercury contaminated sediment beneath a 'cleaner' overlay of fresh uncontaminated sediment.
- (iii) Remobilization of mercury from surficial sediments due to the action of complexing agents (chlorides, organics etc.), changes in pH and/or redox, or the conversion of the mercuric ion (Hg^{2+}) to volatile elemental mercury which may then be lost to the atmosphere.
- (iv) Uptake by biota.

From the information currently available, fluvial transportation of mercury contaminated particulates out of the study area is unlikely to be a dominant process operating within the River Yare system. If the movement of contaminated particulates were responsible for the decline in surficial concentrations, a downstream shift in the pollution plume and enhanced loadings in the downstream reach should have accompanied such a process. Instead the location and shape of both the mercury and copper contaminant plumes has remained fairly constant since monitoring began in 1986 and concentrations in the lower reach continued to approximate to geochemical background levels with no evidence of additional metal enrichment. These results are entirely consistent with the conclusions drawn from the hydrological modelling exercise computed for the River Yare in 1986, which predicted that the dominant fluvial process was one of net particulate deposition, so once deposited, contaminated particulates are essentially fixed within the sediment compartment (Imperial College, 1987). Some downstream transport of mercury bound particulates is expected during periods of turbulence but this process is considered of minor importance compared to sediment burial.

Sediment cores obtained from the main river channel and the interconnecting Broads revealed significant subsurface enrichment of total mercury which infers that net deposition of particulates has caused the burial of contaminated sediments beneath a cleaner overlay. Most of the sediment cores collected in 1992 displaying >2 fold mercury enrichments in buried sediments compared to surficial loadings, extending to a 7 fold increase in some instances (*coring site 7*). Mercury concentrations of up to 18.6 mg kg^{-1} were observed at depth (*coring site 3*) which represents a 46 fold enrichment over catchment background levels. The depth of maximum mercury accumulation was highly variable, particularly on the main river where hydrological processes and local sediment disturbance by boat traffic, dictated the zones of sediment accumulation and erosion. Subsurface enrichment, for example, occurred at 7.5 cm in core 3, but at a depth of 100 cm in core 6. Comparisons of the 1986² and 1992 mercury depth profiles however indicate that at some localities more contaminated mercury deposits may

² Imperial College (1987).

reside at even greater depths since some of cores revealed maximum loadings at the base of the cores. At coring site 4, for example, maximum mercury loadings of 10 mg kg^{-1} occurred at the core base (65-70 cm) in 1992, but greater depth penetration was apparent in 1986 when levels of 22 mg kg^{-1} occurred between 62-100 cm. Likewise at core 6, 33 mg kg^{-1} of mercury was detected in 1986 at 8-22 cm, but only half this amount was found in 1992 (17.6 mg kg^{-1}) despite the acquisition of a 1 m core in this instance. A more accurate definition of the absolute depth of contamination is therefore hindered by the limited depth of some of the cores. Coring of fluidised river silt sediments has proved problematic in the past because the unconsolidated nature of the material prohibits effective plugging of the corer, with the consequential loss of sample. Endeavours should however be made in the future to obtain sample cores which are 1-1.5 m deep, sediment type permitting.

If maximum sediment mercury loadings are assumed to correspond to peak discharges of mercury laden wastewaters during the mid to late 1960s, then average sedimentation rates of between $0.3\text{-}4.5 \text{ cm a}^{-1}$ can be calculated for the main river channel, depending upon location. This implies that in zones of high sedimentation, such as point bar localities on the inside of meander bends (*coring site 4*), or under quiescent flow conditions (*coring site 6*), contaminated sediment is rapidly buried by less contaminated particulate matter to depths in excess of 1 m. In the shallow, less disturbed areas of the Broads however, a more uniform depth of enrichment was evident with the majority of cores displaying maximum mercury concentrations at 20-24 cm, although peaks occurred at depths ranging from 4-8 cm to 36-40 cm. This corresponds to approximate sedimentation rates of $0.5\text{-}1.8 \text{ cm a}^{-1}$ for the Broad systems and compares well with the sedimentation rates of 1 cm a^{-1} quoted by Garrad (1984) for the Norfolk Broads. The Broads tended to act as efficient contamination traps, concentrating mercury to concentrations of up to 37 mg kg^{-1} in places. Mercury loadings in the majority of cores exhibited a gradual decline towards surface deposits, implying that the reduction in mercury inputs to the system has been effective in promoting a corresponding decline in recent sediments.

The release of mercury to the River Yare is known to have declined dramatically since 1974. Prior to the establishment of the Water Authorities by the 1973 Water Act, Norwich City Council, who were responsible for granting discharge licences, consented to a limit of $2000 \text{ kg Hg a}^{-1}$ for the discharge of mercury compounds from the local chemical/pharmaceutical factory. With the introduction of the Control of Pollution Act (COPA) in 1974, regulatory control for industrial discharges passed to the Water Authorities who gradually reduced the consent limit for mercury as awareness of the potential health risks and environmental impact came to light. Effective in-house pollution control of industrial wastewaters has now reduced emissions to well below their legal consent limit of 0.1 mg l^{-1} or 48 kg a^{-1} and the enforcement of stricter discharge controls at source is reflected in a reduction in emissions from Whitlingham STW which have declined by $>97\%$ since 1974 (Figure 24). The dramatic reduction in mercury

inputs is reflected in the cored sediment profiles which display subsurface mercury enrichments, but the magnitude of the decline is not adequately reflected by surface loadings. Assuming maximum sediment concentrations of $\approx 30 \text{ mg kg}^{-1}$ and a 97% reduction in mercury inputs, current surface deposits should contain $\approx 0.9 \text{ mg Hg kg}^{-1}$. In reality mercury loadings within the main contaminative reach are over 5 times this level. This implies that sediment reworking of older contaminated deposits is adding to the surficial mercury burden.

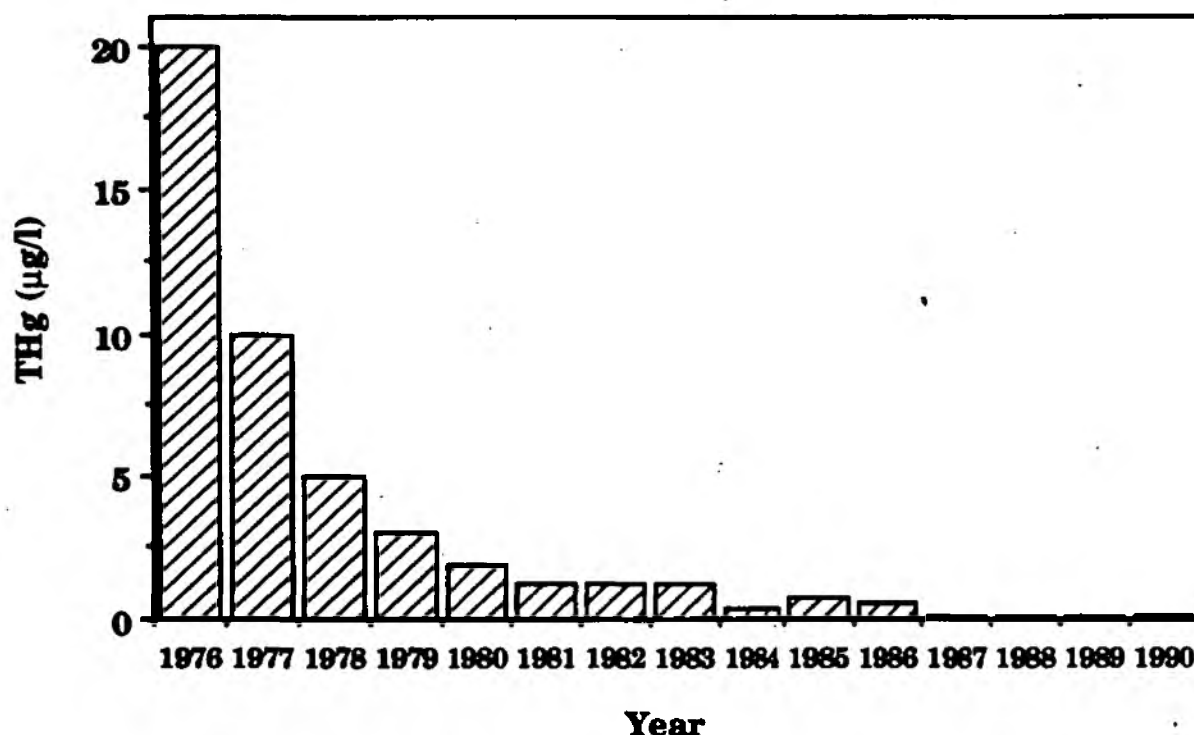


Figure 24. Concentration of total mercury in final effluent from Whittingham STW 1976-1990.

Episodic turbulent events such as storms and boat traffic are capable of stirring up and redistributing sediment. Bank undercutting by boating activity can cause accelerated sedimentation rates, burying contaminated deposits to depths greater than 15 cm according to Müller and Förstner (1975) and can greatly increase the turbidity of water through which they pass (Garrahd and Hay, 1987; Bell, 1980). An additional factor responsible for the reworking, homogenisation and chemical nature of aquatic sediments is bioturbation (the stirring or movement of sediment by the burrowing and feeding activities of benthic organisms (Reynoldson, 1987)). Benthic macroinvertebrates, such as oligochaete worms, chironomid midges and bivalve molluscs, have been shown to increase oxygen penetration, enhance microbial activity, shift pH levels and alter sediment particle size and pore spaces in actively worked substrates (Krantzberg, 1985). This may result in the redistribution of physico-chemical forms and promote the flux of nutrients and pollutants to the overlying water column.

Jernelöv (1970) for example, demonstrated that the release of methylmercury from sediments was intensified in the presence of benthic invertebrates and similar conclusions have been drawn by Wood (1975) and Karickhoff and Morris (1985) for other trace constituents. Although most bioturbation is confined to depths of 0-20 cm (minimal disturbance occurs below this depth according to Petr (1977)), this represents an important mixing mechanism which could promote the transfer of pollutants from bottom to surface sediments.

The possibility that mercury contained at depth could be a potential source of total mercury to overlying sedimentary and aqueous phases was evaluated in a number of experimental tanks. The tanks simulated an 'undisturbed' sediment system, in that no physical agitation was applied to them once they had been set up. The results showed no movement of total mercury from contaminated strata to overlying, or underlying, uncontaminated sediment despite active bioturbation in the upper sediment layers throughout the 12 months of the experiment.

This implies that the major processes responsible for intermixing from buried contaminated layers is not bioturbation but the larger scale physical agitation induced by boating activities, dredging and/or scour under high flow conditions. Dredging of the Yare used to be undertaken routinely by the Great Yarmouth Port and Haven Commissioners to maintain navigational channels, but uncertainty over the long term environmental impact of large scale sediment disturbance in mercury contaminated sediments has resulted in restrictions being placed upon dredging activities (NRA, pers. comm., 1992). There is evidence, however, which indicates that even small scale, localised dredging may have a marked affect upon downstream total mercury concentrations.

Results from the monitoring surveys conducted since 1990 indicate that the previous trend, of declining surficial sediments mercury concentrations over time has been effectively halted or even reversed. Between 1990 and 1991, maximum mercury concentrations remained fixed at $\approx 4.6 \text{ mg kg}^{-1}$, although marginal increases over 1990 levels were evident at some localities. A site by site comparison of the 1992 total mercury levels however, highlighted enrichment above 1991 levels in one or more samples taken from all transects lying between Site Y₁₀ and Y₂₂ and identified eight sediment samples which contained loadings in excess of the 1991 study reach maximum. This enrichment could be attributed to a number of factors, including sediment reworking of buried contaminated sediment, the removal of surface sediments by natural or man induced processes which exposed more heavily contaminated layers, and additional mercury inputs.

The areas affected by elevated mercury loadings were however confined to specific river reaches which are known to have undergone large scale sediment disturbance. This implies that sediment reworking is responsible for the recent elevation in surficial sediment total mercury concentrations. The first zone of enrichment, identified in the 1991 survey, involved a stretch

of some 2 km, upstream of Surlingham Ferry (Site Y₁₆) where flood defence work in 1990-1991 necessitated the use of dredge spoil to increase bank height. The second enrichment area was located around Site Y₁₁, where bridge construction for the A11 Norwich southern bypass may have substantially disturbed the river bed. The 1992 survey data highlighted a 9 km reach downstream of the new A11 road bridge (Site Y₁₀₋₂₂) which contained loadings above those detected in 1991. This infers that the exposure and disturbance of contaminated sediment can have a marked affect upon downstream concentrations. This has important implication for future dredging activities.

Burial of mercury contaminated sediment by a cleaner overlay in the wake of tightened emission controls, is undoubtedly the main process responsible for the observed decline in surface sediment mercury loadings. But the remobilization of metals from sediments can occur following changes in the physicochemical characteristics of the aqueous and sedimentary systems. Of particular concern, in a tidal system such as the Yare, is the effect of salinity, or more specifically, the presence of chloride which has an ability to form strong complexes with mercuric ions.

In the presence of increasing chloride ion (Cl⁻) concentrations, Hg²⁺ forms HgCl⁺, HgCl₂, HgCl₃⁻ and HgCl₄²⁻ complexes, each of which reaches maximal proportions at specific Cl⁻ concentrations (Hahne and Kroontje, 1973). At salinities of 3.5‰ (full strength sea water) soluble mercury exists as HgCl₃⁻ and HgCl₄²⁻, while a combination of mercuric chloride and mercury hydroxide complexes coexist in fresh water environments (Bodek, 1988). In the presence of chloride ions however the solubility of other inorganic mercury complexes can increase markedly. Hahne and Kroontje (1973) showed that a 1 M chloride solution (35,460 ppm) enhanced the solubilities of Hg(OH)₂ and HgS by factors of 10⁵ and 3.6x10⁷, respectively. Even at low chloride concentrations (3.5 ppm) the solubility of Hg(OH)₂ and HgS increased by a factor of 55 and 408, respectively. Remobilization potential through the formation of mercury-chloro complexes can therefore increase the solubility of mercury hydroxides and sulphides, but chloride ions are also known to desorb mercury from clays through competition of mercuric chlorides with adsorption sites (Newton *et al.*, 1976; Lodenius *et al.*, 1987). Several studies have noted significant declines in mercury concentrations in estuarine sediments (Reimers *et al.*, 1974) while in sea and estuarine waters the competition from Cl⁻ can also alter mercury speciation, greatly decreasing the proportion of Hg²⁺ bound to humic substances (Bodek, 1988). This has important implications on the Yare which in recent years has seen saline intrusions pushing further inland. Evidence from the seasonal monitoring surveys indicates that saline waters reached inland as far as Rockland Broad in November 1991 and it is expected that they may extend even further inland. This trend is likely to continue with the projected rise in sea level and may be augmented by lower freshwater flows. There is

consequently real potential for mercury remobilization if saline waters interact with mercury contaminated sediment.

The importance of pH, organic complexation agents (e.g. humic and fulvic acids), microbial transformations and biota uptake, as causative agents for mercury desorption remains to be addressed but it is unlikely that any of these factors could promote large scale mercury desorption from the River Yare sediment compartment. pH generally plays a significant role in determining partitioning coefficients between the soluble and particulate phases in water and sediments, with lower pH favouring soluble ionic species. The measurements of surface water and sediment pH however, indicate that the Yare is a well buffered, moderately alkaline system, as dictated by the high buffering capacity of the calcareous bedrock which underlies the Yare catchment. pH has also not changed significantly over the past five years, nor, it is assumed, has the type and quantity of organic complexing agents which preclude these factors as causative agents in the decline in total mercury loadings since 1986. Volatilisation and methylation represent an additional pathway for loss of mercury from the sediment system but these are generally considered as minor processes when compared to sediment transport in terms of large scale mercury losses from contaminated sediments (Bothner *et al.*, 1980). Likewise, uptake by biota normally accounts for only a small percentage of the total mercury within aquatic systems, 0.2%, as opposed to 97% within the sediments (Kudo *et al.*, 1978). Biological uptake could potentially be enhanced, in an eutrophic system such as the Yare, following biosorption by algal communities. Phytoplankton are capable of accumulating metal species into (absorption), or onto (adsorption) their cells from dilute aqueous solutions. Since algae are a major food source for primary consumers, they form the first step in the biomagnification process which could lead to elevated mercury loadings in higher trophic levels. Fish taken from the contaminated reach of the River Yare do contain body burdens of total mercury (Table 15) but bioaccumulation of mercury is unlikely to represent a significant pathway for mercury removal from the system. Fish flesh mercury concentrations have actually decreased over time and mean loadings now reside below the 0.3 mg kg⁻¹ wet fish flesh limit specified in EC legislation (Council of European Community, 1984). Biota uptake

Table 15. Mercury concentration in fish flesh taken from the River Yare between Thorpe and Rockland Broad.

	Date of Survey	Nº of Specimens	Mean (mg kg ⁻¹ wet wt.)	Range (mg kg ⁻¹ wet wt.)
Eel	June 1991	28	0.18	0.04-0.63
	Oct. 1989	18	0.16	0.01-0.44
	Dec. 1985	99	0.46	0.06-1.08
Roach	May 1991	17	0.10	0.05-0.22
	Dec. 1986	9	0.19	0.11-0.47
	June 1971	13	0.71	

National River Authority Data.

consequently could not account for the magnitude of the decline in surficial sediment total mercury concentrations. Although all these processes may play a minor role in repartitioning mercury from the solid to aqueous phase, the information currently available indicates that burial is by far the most important processes in operation in the River Yare.

6.2. Controls, Fate and Behaviour of Methylmercury within the Yares Surficial Sediments

Methylmercury concentrations within the River Yare's sediment compartment were highly variable and failed to display any systematic spatial or temporal trends, in strict contrast to the 'predictability' of inorganic mercury loadings. The occurrence of elevated methylmercury loadings at sites with low or undetectable concentrations of inorganic mercury implies that the sediment accumulation of methylmercury is relatively independent of total mercury concentrations. Since a prerequisite for methylation is the presence of the Hg^{2+} ion this lack of correlation could indicate that the majority of the inorganic mercury is complexed and therefore not readily available for methylation reactions. Sediment methylmercury concentrations obtained from the River Yare and associated Broad, ranged from <0.1 - $33.4 \mu\text{g kg}^{-1}$, which is consistently higher than values reported for other river and estuarine systems in the British Isles (Table 16). Methylmercury, however, contributed only a small fraction to the overall mercury burden, generally accounting for $<1\%$ of the total mercury present, which is in agreement with Jernelöv and Åsell (1975) and Barlett and Craig (1981) who respectively quoted ≈ 1 and $<1\%$ for aquatic sediments. Two areas of the main river channel consistently displayed a high percentage of methyl to total mercury of 1-10%. The first occurred at Trowse, upstream of Whitlingham STW, the second at Cantley, in the vicinity of a sugar reprocessing factory.

Table 16. Mercury concentrations in British Rivers.

River	Total Mercury (mg kg^{-1})	Methylmercury ($\mu\text{g kg}^{-1}$)
Exe	<0.05 -2.2	<0.5 -2.2
Dart	0.33-4.46	0.6-3.8
Plym	0.08-0.35	0.1-4.0
Tamar	0.07-0.66	0.5-1.7
Lynher	0.61-0.83	1.5-3.0
Restronghet	0.15-0.45	1.1-3.5
Truro	0.30-0.42	1.6-1.8
Teign	0.11-0.67	2.7-3.6
Hayle	0.26-0.36	0.6-0.8
Gannel	<0.05 -0.20	0.4-0.5
Clyde	<0.05 -3.68	<0.5 -17.0
Mersey	<0.05 -4.01	<0.5 -24.0
Yare (1986)	0.05-32.9	<0.5 -13.2
Yare (1987)	0.01-15.2	<0.5 -6.4
Yare (1989)	0.09-15.9	<0.35 -13.7
Yare (1990)	0.04-4.68	<0.7 -29.5
Yare (1991)	0.02-4.59	<0.1 -22.2
Yare (1992)	0.01-6.89	<0.1 -21.8

(after Craig and Moreton, 1986)

The simultaneous occurrence of high methylmercury loadings and low total mercury at Trowse dissociates the net rate of methylation from the characteristic pollution plume of inorganic mercury and implies that methylmercury formation and subsequent retention in the sediment compartment is not solely dependent on total mercury concentrations. The high methylation capacity at this location could be linked to light penetration in shallow water conditions. Photochemical methylation has been cited as an important methylation pathway, accounting for a 3% per day conversion of mercuric acetate to methylmercury, which is reported to be 2 orders of magnitude greater than microbial methylation rates (Summers and Silver, 1972). This process was however inhibited by 99.9% if HgCl_2 and acetic acid replace the mercuric acetate, which could discount the role of photochemical methylation in saline waters. Shallow water conditions would also facilitate heat penetration and elevated sediment temperatures. Callister and Winfrey (1986) observed clear increases in mercury methylation with increased temperatures, which was consistent with the observations in the Tank experiments which saw a 30% increase in methylmercury concentrations as sediment temperatures increased from 12-22°C (Section 4.5.2). The shallow water conditions combined with higher sediment temperatures at Trowse may consequently favour both abiotic and biotic mercury transformations. A similar situation may prevail in the shallow Broads, some areas of which may even be exposed at low tide, thereby increasing the potential for photochemical and biological methylation processes.

Temperature induced methylation phenomena could also account for the sporadic occurrence of elevated methylmercury loadings at Cantley, since this stretch of the river receives cooling water from the sugar processing factory at a temperature of 25°C (NRA, Pers. Comm. 1988). It is also possible that the release of nutrients from this plant or Cantley STW could encourage bacterial activity. A study by Wright and Hamilton (1982) reports increased mercury synthesis from inorganic mercury upon the addition of Tryptic soya broth nutrient medium while Callistry and Winfrey (1986) found increased methylation in organically enriched compared to less eutrophic sediments.

Apart from the existence of these two anomalies, the distribution of methylmercury in the rest of the river system appeared to be fairly random. Methylmercury concentrations appeared to be independent of sediment type, although high concentrations tended to prevail in the finer, more organic fine silt type matrices, but there was by no means a universal trend. Methylmercury tended to accumulate in low energy 'sinks', concentrating it in the shallower Broad systems and in quiescent areas of the main river. Hydrology could partially control the retention of methylmercury within the system since lower concentrations in the 1987 annual sediment survey coincided with the existence of high flow conditions which may have agitated bottom sediments, releasing methylmercury to the water column. Parks and Hamilton (1987) however, predicted that high flows would temporarily raise the concentration of methylmercury,

presumably through the oxidation of anaerobic sulphide bound mercury and the release of Hg^{2+} , the methylation substrate but then the disturbance of upper sediment layers would facilitate the release of buried methyl- and total mercury to the water column, reducing sediment loadings.

The Yare sediments are known to actively synthesise methylmercury since detectable concentrations have been found in all the River Yare surveys undertaken by Imperial College since 1986. Large variations in the concentration of methylmercury, on both a spatial and temporal scale, implies that seasonal factors and localised differences in the physico-chemical environment affected the net methylation rate. The *in-situ* seasonal monitoring of methylmercury and associated physico-chemical determinants in Rockland Broad has helped to elucidate the factors controlling the distribution and accumulation of methylmercury within the Yare's sediment compartment. Microbial activity and sediment diagenetic reactions appear to be the key to methylation/ demethylation processes.

Organic rich sediments, such as those which underlie Rockland Broad, support large and active populations of micro-organisms. The nature of the experimental method used to characterise microbial populations within this present study meant that bacterial colonies were primarily aerobic and microaerophilic in nature, although some facultative anaerobes may also have been present. The universal decrease in total aerobic bacterial numbers with increasing core depth can therefore be attributed to the transition towards more anaerobic conditions and the resultant ecological succession to facultative anaerobes. The population of aerobic bacteria was consequently highest at the sediment/water interface, where oxygen was freely available, and decreased rapidly with depth, confirming the findings of Regnell and Tunlid (1991). Higher numbers of aerobic bacteria and greatest depth penetration prevailed in the spring with reduced colony counts in the winter. This periodicity is linked to changes in environmental conditions (redox, temperature, nutrient supply etc.) which maximise aerobic bacterial growth in the spring. Total aerobic bacterial numbers, however bore little relationship to the seasonal or spatial distribution of methylmercury within the sediment compartment which instead closely mirrored the occurrence of mercury resistant bacteria.

Mercury resistant strains of bacteria are widely distributed amongst bacterial communities taken from sites containing inorganic mercury (Olson *et al.*, 1989) and infers the ability of bacteria to detoxify Hg^{2+} ions by metabolic transformations. Methylation and demethylation have both been cited as detoxification mechanisms. The precise mechanism for mercury methylation remains unclear but appears to involve the transfer of methyl groups from methyl cobalamin (vitamin B_{12}) to the mercuric ion (Hg^{2+}) by enzymatic or non enzymatic transfer (Craig, 1986). This process produces water soluble monomethylmercury (CH_3Hg^+) which may be further methylated by methyl cobalamin to dimethylmercury (CH_3HgCH_3); an insoluble volatile

compound which remains undissociated in solution and is rapidly lost from the aquatic system. Monomethylmercury is consequently the predominant organomercury form in the environment. Although both abiotic (Lee *et al.*, 1985) and biotic (Jefferies, 1982; Wood *et al.*, 1968) pathways for methylation have been demonstrated, the net production of methylmercury is generally believed to be biologically controlled and some 16 genera of aerobic and anaerobic micro-organisms have been shown to methylate mercury (Table 17). Biological methylation has been observed under aerobic (Bisogni and Lawrence, 1973) and anaerobic conditions (Bisogni and Lawrence, 1975; Olson and Cooper, 1974; Compeau and Bartha, 1984) but maximum rates seem to occur in moderately anaerobic zones where redox potentials exist in the -100 to -150 mV range and methylating bacterial activity and Hg^{2+} availability are optimised (Bisogni, 1979; Bartlett and Craig, 1981). Demethylation, in contrast, causes the degradation of methylmercury following cleavage of the mercury-carbon bond by aerobic and facultative-anaerobic mercury resistant bacteria to produce elemental mercury (Hg^0) (Compeau and Bartha, 1984). Methylation/demethylation reactions govern the net accumulation of monomethylmercury within the sedimentary compartment so the factors controlling these processes are ultimately responsible for the presence and behaviour of methylmercury within the River Yare system.

Mercury resistance in aerobic heterotrophic bacterial colonies displayed marked periodicity in Rockland Broad sediments reaching a maximum in the spring with declining numbers in proceeding months, identical to the findings of Colwell and Nelson (1975) for Chesapeake Bay sediments, USA. Maximum resistance occurred just below the sediment/water interface at a

Table 17. Methylation and demethylation of mercury by bacteria.

Species capable of HgCl_2 methylation	Species capable of demethylation of CH_3Hg^+
<i>Pseudomonas fluorescens</i> <i>Microbacter phlei</i> <i>Bacillus megaterium</i> <i>Escherichia coli</i> <i>Lactobacilli</i> sp. <i>Aerobacter aerogenes</i> <i>Bifidobacteria</i> <i>Enterobacter aerogenes</i> <i>Clostridium cochlearium</i> <i>Aspergillus niger</i> <i>Scopulariopsis brevicaulis</i> Human intestinal microflora: (streptococci sps., staphylococci sps., <i>E. coli</i> , <i>Sacchomyces</i> sp.)	<i>Serratia marcescens</i> <i>Providencia</i> sp. <i>Pseudomonas fluorescens</i> <i>Citrobacter freundii</i> <i>Proteus mirabilis</i> <i>Enterobacter aerogenes</i> <i>Enterobacter cloacae</i> <i>Paracolonobacterium coliforme</i> <i>Achromobacter pestifer</i> <i>Serratia plymuthica</i> <i>Staphylococcus</i> sp. <i>Pseudomonas aeruginosa</i> <i>Bacillus subtilis</i> <i>Flavobacterium marino typicum</i> <i>Citrobacter intermedius</i> <i>Pseudomonas fragi</i> <i>Desulfovibrio desulfuricans</i> (anaerobe)

(Source: Craig, 1986).

depth of 4-8 cm but shifted to surface deposits (0-4 cm) in the summer when their vertical extent was also significantly reduced. This behaviour closely mirrored that of the methylmercury in some instances but was by no means universal and can be linked to changes in temperature and redox within the system.

Rockland Broad supports populations of aerobic bacteria which were capable of methylating mercury in surficial sediments. During the spring, warm weather (25°C) and well oxygenated clear water encouraged aerobic bacteria to flourish. These are predominantly demethylators (Compeau and Bartha, 1984). In the late summer months (mid-July to September) however, elevated temperatures and prolific microbial activity cause oxygen depletion and a deepening of anaerobic sediment conditions near the sediment surface. Such anoxic conditions would inhibit the survival of aerobic/microaerophilic micro-organisms and promote less oxygen dependent and anaerobic communities like the sulphate reducers which have also been identified as a mercury methylators under sulphate limiting conditions (Compeau and Bartha, 1985, 1987; Gilmour *et al.*, 1992). Their presence may have stimulated rapid reduction of sulphate in oxygen deficient zones causing the observed 4-6 fold increase in pore water sulphide in cores 1 and 2 in the summer sampling. The presence of deoxygenated conditions and free sulphide would have inhibited the survival of aerobic demethylating bacteria and stimulated methylmercury production in the upper sediment layers where Hg^{2+} ions remain uncomplexed, the net result being the accumulation of methylmercury within the sediments during the summer, which produced concentrations in excess of $20 \mu\text{g kg}^{-1}$.

In the autumn numbers of mercury resistant bacteria and methylmercury concentrations displayed a marked decline compared to summer values despite consistent numbers of total aerobic bacteria. This could well be linked to changes in the temperature regime which appears to play a significant role in dictating the behaviour of methylmercury. Work undertaken by Wright and Hamilton (1982), suggested that methylmercury production declined by 50-70% as the temperature declined from 20°C to 4 °C, due to lower rates of growth and metabolic activity. Data obtained *in-situ* from Rockland Broad revealed a 30-50% decline in net methylmercury concentrations between the spring and autumn samplings with respective temperatures of $\approx 25^\circ\text{C}$ and $\approx 6^\circ\text{C}$. This decline in sediment methylmercury concentrations was consistent with the results obtained from the laboratory based tank experiments which displayed a 17-30% difference in methylmercury loadings as the temperature increased from 12-22°C, all other parameters being equal. This implies that methylmercury production is approximately halved in colder months and that this decline is solely temperature induced.

The reduction in microbial activity in colder weather slows down or halts bacterial conversions including the reduction of sulphate to sulphide. This would allow sulphate to build up within the sediment compartment and could account for the 4-7 fold increase in sediment sulphate

concentrations during the winter sampling. This would facilitate oxygen penetration in the sediments (as seen by the winter shift in redox towards more oxic conditions) and stimulate a change in bacterial succession favouring aerobic and microaerophilic species which resided at depth within the sediment cores in more oxygenated zones. Lower temperatures and the dominance of demethylating bacteria would combine to reduce the concentration of methylmercury within the sediment compartment in the autumn and winter.

Net methylmercury concentrations within aquatic sediments is therefore dependent upon the equilibrium between methylating and demethylating mechanisms which appear to be largely governed by seasonal variations in dissolved oxygen, temperature and microbial populations. The distinct subsurface maxima in sediment accumulations of methylmercury and mercury resistant bacteria can also be ascribed to opposing methylation/demethylation mechanisms. Work carried out by Ormeland *et al.* (1991) and Korthals and Winfrey (1987) found demethylating activity to be greatest at the sediment surface and noted a decline in methylating activity with depth. The decline in methylating activity was correlated with the known depth distribution of microbial activity within the sediments (Korthals and Winfrey, 1987). Active degradation of methylmercury by aerobic demethylating bacteria can therefore simulate a reduction in net methylmercury concentrations in upper sediment layers. The inability of the demethylators to degrade under moderately anaerobic conditions encourages methylmercury to accumulate in subsurface layers (4-8 cm) where conditions are optimised for its formation and subsequent retention. Peaks in mercury methylation therefore correspond to alterations in demethylating activity stimulated by changes in environmental conditions (Korthals and Winfrey, 1987). The decline in levels of methylmercury at the sediment/water interface could also infer the diffusion of monomethylmercury into the water column, which represents a potential pathway for accumulation in aquatic biota.

In addition to methylation and demethylation, the enzymatic reduction of Hg^{2+} to volatile elemental mercury (Hg^0) in mercury resistant bacteria is also widely acknowledged to be a detoxification mechanism (Barkey *et al.*, 1985; Baldi *et al.*, 1989; Robinson and Tuovinen, 1984). Enzymatic reduction is usually the most common and rapid mode of mercury transformation. Summers and Silver (1972) reported that a plasmid bearing strain of *E. Coli* could reduce 95% of 10^{-5} M Hg^{2+} over 24 hours. This is in comparison to reported conversion efficiencies of 0.005-0.9% for biological methylation (Jensen and Jernelöv, 1969). It can therefore be assumed that the majority of mercury resistance is mediated by genes coded for the reduction of Hg^{2+} rather than for methylation. Baldi *et al.* (1989) isolated 37 strains of mercury resistant aerobic bacteria from the Fiora River sediments, Tuscany, which drains a cinnabar deposit (HgS). All mercury resistant strains were capable of producing elemental mercury following bioreduction and seven degraded methylmercury. None of the strains isolated produced detectable levels of methylmercury. This implies that mercury methylation was not a

mechanism of aerobic mercury resistance in the environment studied. Although many studies have documented the aerobic and anaerobic production of methylmercury by bacteria and fungi (Handy and Noyes, 1975; Olson *et al.*, 1979) enzymatic methylation has never been conclusively demonstrated and it is hard to explain why a resistance mechanism would produce a bi-product which is at least as toxic to the micro-organisms as the inorganic Hg^{2+} substrate. The biological function of methylation therefore remains unclear but the dominance of the bioreduction pathway in mercury resistance populations could partially explain both the lack of statistically significant correlations observed in this study between the numbers of aerobic mercury resistant bacterial colonies and methylmercury concentrations and the surface decline in mercury resistant numbers which would thrive at depth under more anoxic conditions.

Methylation/demethylation reactions are also governed by mercuric ion availability and those factors which effect Hg^{2+} concentrations. The formation of reduced sulphur compounds exerts a controlling influence upon the chemistry of mercury in anoxic sediments. The mercuric ion has an extremely high capacity to form strong complexes with donor atoms such as sulphur (Craig and Moreton, 1983). Under reducing conditions and in the presence of free-sulphide ligands, mercury is stabilised in the mercuric state as extremely insoluble mercury sulphide precipitates or bound as surface complexes with organic material containing sulphhydryl (-SH) donor atoms (Kerston, 1988). The presence of mercuric sulphide (cinnabar) can restrict Hg^{2+} availability, the component required for methylation (Olson and Cooper 1976).

Inhibition of mercury methylation in the presence of sulphide has been demonstrated, even when levels of total mercury exceed 1000 mg kg^{-1} (Berman and Bartha, 1986). Craig and Moreton (1985) noted a curtailment of mercury methylation when sulphide concentrations exceeded 1.8 mg g^{-1} . Concentrations of sediment sulphide in Rockland Broad were however well below this threshold value, but our utilisation of water soluble sulphide as a measure of 'available' sulphide means that no account was taken of other more recalcitrant sulphide forms, in particular iron pyrite (FeS_2), the dominant sulphide species in aquatic sediments. The combined sum of all the sulphide species may well exceed this limit.

The chemistry of iron and manganese could also exert a controlling influence upon the behaviour of trace metals and methylmercury within aquatic sediments, particularly in temperate environments where sediment physico-chemical conditions vary seasonally in response to alterations in temperature regimes and microbial activity. This can stimulate the cycling of iron together with coprecipitated and adsorbed trace elements in response to changes in the dissolved oxygen regime. In highly oxidised environments, such as in surface sediments, Fe^{3+} and Mn^{4+} hydroxides and oxides exist alongside the microbial degradation of organic matter. As sedimentation continues, compaction and dewatering processes together with enhanced degradation of organic matter causes a downward depletion of oxygen which lowers redox

potential and causes the reduction of Fe^{3+} , Mn^{4+} oxides/hydroxides to soluble Fe^{2+} and Mn^{2+} forms, releasing coprecipitated and adsorbed trace elements, including mercury. In anoxic zones this process occurs concurrently with the reduction of sulphate to sulphide and results in the formation of iron pyrite which can occur in surface sediment layers in eutrophic environments. This equilibrium shifts in the opposite direction in the presence of oxygen, stimulating the reoxidation of FeS, releasing sulphate and Fe^{2+} . Ferrous ion (Fe^{2+}) is subsequently oxidized to Fe^{3+} which has the capability of oxidising pyrite, overtaking the initial role of oxygen (Salomons and Förstner, 1984). Reoxidation of FeS has been observed during colder months due to enhanced oxygen penetration in the absence of microbial activity (Hines *et al.*, 1984; Jørgensen, 1977). The large increase in sulphate for Rockland Broad sediments during the winter sampling infers that a similar process is in operation within the Yare's sediment compartment. A separate study undertaken on the more oxygenated Yare sediments adjacent to Whitlingham STW reveals that over 80% of the Fe exists as iron oxides/hydroxides (as operationally defined by sequential extractions) and that a significant proportion of the copper and lead were associated with this 'moderately reduced' geochemical phase (Bubb, 1992). Iron is consequently an important binding substrate for metals within the Yare's sedimentary compartment, which it is assumed includes mercury. Wang *et al.* (1989) states that the dissolution of iron and manganese oxides releases mercury into the sediment porewaters when dissolved oxygen is sufficiently depleted. Alternatively, the conversion of mercuric sulphide to water soluble mercury compounds by iron oxidizing bacteria in the presence of iron sulphates has also been cited as a control upon mercury in the sediment environment (Yamada and Tomomura, 1972). Both mechanisms would periodically increase Hg^{2+} availability for further chemical interactions and for biological uptake. The behaviour of mercury is therefore interlinked with the seasonal behaviour of iron and sulphur as dictated by temperature and dissolved oxygen availability.

Salinity may be an additional factor limiting methylation. In normal circumstances the saline/freshwater interface on the Yare occurs at Cantley, 6 km downstream of Rockland Broad, but the 2-5 fold increase in sediment Cl^- concentrations in the Broads' autumn survey infers the intrusion of saline waters into Rockland Broad. Sediment chloride loadings increased from $<400 \text{ mg kg}^{-1}$ to a $\approx 1000 \text{ mg kg}^{-1}$ between the summer and autumn sampling which is comparable to the changes normally seen at Cantley, the transition from fresh to brackish waters. Tidal flow data supplied by the NRA (Pers. Comm., 1992) infers the gradual build up of saline conditions in the tidal reaches between 3-12 November 1991, peaking around 6th November, some 3 weeks prior to our autumn sampling. The occurrence of such a saline intrusion could account for the build up of chloride within Rockland Broad sediments in the November survey.

The long term effect of periodic saline intrusions is hard to predict for although evidence supplied in the literature points to enhanced remobilization tendencies, elevated water column concentrations and the potential for biotic uptake and food chain biomagnification (Salomons and Förstner, 1979, Hahne and Kroontje, 1973), chloride has also been shown to reduce the rate of methylation, the major uptake pathway. Blum and Bartha (1980) in a study of Chesapeake Creek, New Jersey, demonstrated a strong negative correlation between the salinity of anaerobic sediments and their ability to form monomethylmercury from Hg^{2+} , for salinities up to 2‰. They postulated that sulphide, derived by microbial reduction of sea salt sulphate, interferes with Hg^{2+} methylation by forming HgS which is not readily methylated (Compeau and Bartha, 1983). Other factors may also be at play; instability of methylmercury in the presence of H_2S , interference of sea salt anions with the methyl transfer from cobalamin to Hg^{2+} and shifts in populations or activity of methylating and demethylating bacteria in response to salinity. Compeau and Bartha (1983) confirmed that sulphides in anaerobic sediments reduces the availability of Hg^{2+} for the abiotic methylation by methylcobalamin, but also found that mercury bicarbonate complexes (HgCO_3) were more inhibitory to the methyl transfer process than Cl^- . Since bicarbonate is an important component of sea salt and estuarine sediments this, rather than the Cl^- agent, could be responsible for methylation inhibition in saline environments. Since most sites with detectable levels of methylmercury were located upstream of Reedham and no methylmercury was found within Breydon Water, the true estuarine zone, salinity or chloride concentrations may well inhibit methylation within the River Yare system.

7. RECOMMENDATIONS

The findings of the research conducted to date has important implications for the environmental management of the River Yare system. Any attempt to remove contaminated sediment for navigational or flood defence purposes may inadvertently increase downstream total mercury concentrations and enhance the potential for methylmercury synthesis. Careful management of the river system is therefore necessary to prevent, or minimise large scale sediment disturbance.

The following recommendations are directed solely to activities within the main contaminated reach. No special restrictions need apply downstream of Cantley (grid reference TG 387032).

The contaminated reach is defined as; *the River Yare from Trowse (grid reference TG 244068) to Hassingham (TG 360045) and encompasses all the intervening Broads systems and Fleet areas.*

1. The main recommendation is to refrain from all dredging operations unless they are essential.
2. If dredging activity is unavoidable then the following precautions should be taken:
 - 2.1. Dredging should be undertaken in the late autumn or winter periods following a prolonged period of cold weather. This will minimise the activity of methylating and sulphate reducing bacteria and may help to minimise methylmercury formation.
Do not undertake dredging activities in:
 - The spring and summer, or at other times of the year if temperatures are high.
 - During period of saline intrusions.
 - During periods of algal blooms.
 - 2.2. Remove **all** contaminated sediments. This may require site investigations to determine the absolute depth of contamination at specific sites.
 - 2.3. Attempts should be made to minimise sediment remobilization during the dredging operations by the adoption of appropriate dredging technologies.
 - 2.4. **All** dredge spoil derived from the 'contaminated reach' should be properly disposed of in a licensed, fully clay lined, disposal site. This includes sediments from the Broads and small inlets and moorings. It **should not** be placed on the river banks, even for flood defence purposes. Uncontaminated sediment from the lower river reaches can be used for this purpose if necessary.

- 2.5. Prior notification of dredging operations should be made to the Broads Authority and a detailed log should be kept of all dredging operations undertaken on the contaminated reach. This should include:
- i) reasons for dredging.
 - ii) written notification to the dredging contractor authorising the dredging operation, detailing any operational restrictions.
 - iii) definitive location of dredging.
 - iv) quantity and depth of sediment removed.
 - v) details of precautions taken to minimise remobilization and sediment re-entry into the system.
 - vi) precise location of dredge spoil disposal at the licensed disposal site.
3. An additional precaution that could be taken if the 'do nothing strategy' is subsequently adopted, is to minimise reworking of upper sediment layers by reducing disturbance by boating traffic in shallow water areas, such as the Broads. The options could range from a total ban on boat traffic through the Broads to a review of speed limit restrictions. This may help to reduce surface concentrations of total mercury by encouraging the deposition of clean sediment overlay.
4. Instrumental surveying of bottom sediments types should be undertaken to provide a detailed picture of bottom sediment characteristics. This would be invaluable for estimating the depth of contamination in specific river reaches and the mercury burden in the sediment compartment.
5. To undertake an additional coring exercise in the light of Point 4 to define the depth of contamination in areas of high particulate sedimentation.

Points 4 and 5 will be invaluable for ensuring that future dredging activities remove all mercury contaminated sediment.

6. To continue the annual monitoring of surficial sediments using the pre-designated transects and sampling strategy employed on former Yare surveys. Monitoring should be undertaken in July to minimise seasonal influences.
7. Routine monitoring to track the extent and frequency of saline intrusions on the River Yare is required in order to predict the impact of saline intrusions upon mercury remobilization from the sediment to the overlying water.
8. Further research to assess the impact of large scale sediment disturbance upon mercury mobility and availability needs to be undertaken, together with an assessment on the long term consequences of dredge spoil disposal.
9. To more fully elucidate the role of bacteria as methylating agents and to more clearly evaluate the links with the seasonal cycling of sulphur and iron.

8. CONCLUSIONS

1. Historically the River Yare in Norfolk, has received a considerable loading of heavy metals, particularly of inorganic mercury, of industrial source, which together with copper were released to the public sewer and treated at Whitlingham STW prior to discharge to the River Yare. The majority of metals discharged within the final effluent now reside within a 17-18 km enrichment zone centred upon Whitlingham sewage outfall.
2. The 'contaminated reach' is defined as the River Yare from Trowse (grid reference TG 244068) (Site Y₄) to Hasingham (TG 360045) (Site Y₂₇) and encompasses all the intervening Broads systems and Fleet areas.
3. Surficial sediment mercury concentrations have undergone a consistent decline since 1986, reducing loadings from a 1986 level of 0.05-32.9 mg kg⁻¹ to 0.01-4.68 mg kg⁻¹ in 1990. Surveys conducted since 1990 however, have seen a slight increase in surface mercury loadings due, it is believed, to sediment disturbance following civil engineering works.
4. The dominant fluvial process is one of net deposition of particulates rather than downstream transport, which has caused the burial of contaminated strata beneath a cleaner overlay, to depths in excess of 1 m in places. The absolute depth of burial is controlled by local sedimentation rates as dictated by channel morphology, flow dynamics and sediment supply, with greater sedimentation rates at point bar localities (on the inside of meander bends), in wider channel reaches and under quiescent flow conditions such as the Broads.
5. Disturbance of these buried more highly contaminated layers can elevate downstream sediment concentrations and, it is assumed, increase methylmercury production and the potential for the biological uptake following the oxidation of reduced metal forms as sediment layers are exposed to oxygenated surface waters.
6. The occurrence of saline intrusions on the River Yare could increase the mobility of inorganic mercury through the formation of soluble mercury-chloro complexes. This could in theory increase water column concentrations and bioaccumulation tendencies, but this premise needs to be verified by more research. It is recommended that salinity data be routinely collected for the upper Yare, in the vicinity of Whitlingham STW to aid data interpretation.
7. Methylmercury concentrations ranged between <0.1-33.4 µg kg⁻¹ which accounted for only a small proportion of the total sediment mercury burden (generally <1%). The highly toxic and lipophilic properties of methylmercury however make it readily assimilated by aquatic organisms and therefore of real environmental significance.
8. Net methylation appears to be governed by the nature of the bacterial communities, temperature and the availability of dissolved oxygen rather than total mercury

concentrations. Methylmercury concentrations displayed large seasonal variations, with maximum loadings occurring during the summer and low net productivity in the colder autumn months. This could have direct operational benefits if dredging operations could be timed to minimise methylmercury synthesis by restricting dredging activities to the colder autumn and winter months.

9. The occurrence of elevated methylmercury loadings in sediment characterised by low concentrations of total mercury implies that inorganic mercury is not a limiting factor for methylation within the Yare system. Although emission controls at source have been fairly effective in reducing total mercury concentrations in River Yare surface sediments this has not stimulated a corresponding response in methylmercury loadings or alleviated the problems of the past accumulations of inorganic mercury within buried sediment.
10. Further research into the environmental impact of dredging, the consequences of dredge spoil disposal and the relative merits of remedial measures to restore mercury contaminated systems need to be addressed.

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APPENDIX 1

The behaviour of methylmercury in sediment samples during storage

Sediment samples spiked with methylmercury chloride were subjected to different methods of storage to assess the effects of freezing, acidification and refrigeration upon methylmercury concentrations in aquatic sediments. The aim was to ascertain which storage procedure best preserved intrinsic methylmercury concentrations.

Experimental design

1 kg of sediment obtained from Breydon Water, was spiked with 5.7 µg of CH₃HgCl made up in RO water and thoroughly mixed. This was calculated to be equivalent to approximately 15 µg kg⁻¹ dry weight of sediment. Spiked sediment (30 g) was placed in each of 30 acid washed polyethylene 125 ml sample bottles. Ten of these bottles were refrigerated, ten were frozen and ten were treated with 1% (v/v) sulphuric acid and refrigerated. The contents of one bottle from each storage method were analysed initially (time 0), after 24 h, 48 h, and subsequently at weekly intervals over a 4 week period. Analysis for methylmercury was by GC-AAS as described in Section 4.6.2.

Results

The storage behaviour of methylmercury over a 30 day period is shown in Figure A1. The percent fluctuations during storage are given in Table A1. It can be seen that the refrigeration of samples with no pretreatment resulted in a reduction in sediment methylmercury concentration by approximately 38% during the first 7 days of storage. From 7 to 30 days the rate of methylmercury loss appeared to level off, with a total loss of 53% by day 30. Sample acidification produced a high degree of fluctuation in the level of methylmercury within the first 7 days of storage, with an initial decrease in concentration over the first 2 days, and an increase of 7% by day 7. Concentration then underwent a gradual decline, with a loss of 8% on day 30. Freezing of the samples seems to give the most constant results, with minimal loss of 2.2% after the 30 day storage period.

Table A1. Percentage fluctuations in methylmercury concentration during storage.

Storage mode	TIME (days)						
	0	1	2	7	15	21	30
Refrigerated	0	-0.7	-4.0	-37.5	51.8	-58.4	-53.1
Acidified	0	-3.7	-3.8	+10.0	-10.4	-14.7	-8.5
Frozen	0	+1.2	+3.6	+7.4	+5.8	-4.8	-2.2

% Losses are depicted by minus signs (-).

% Gains are depicted by plus signs (+).

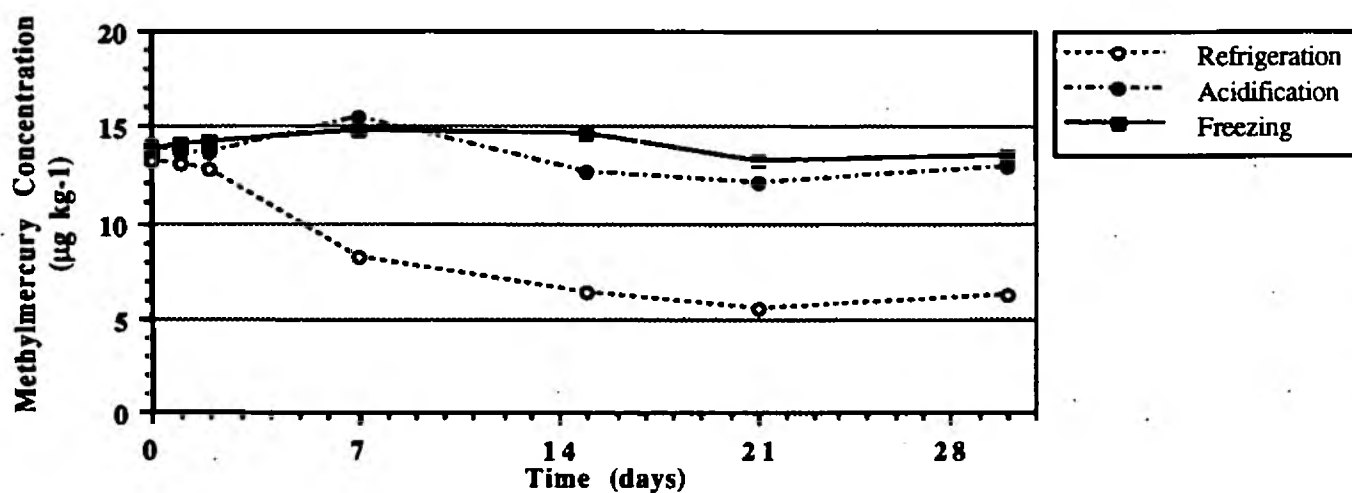
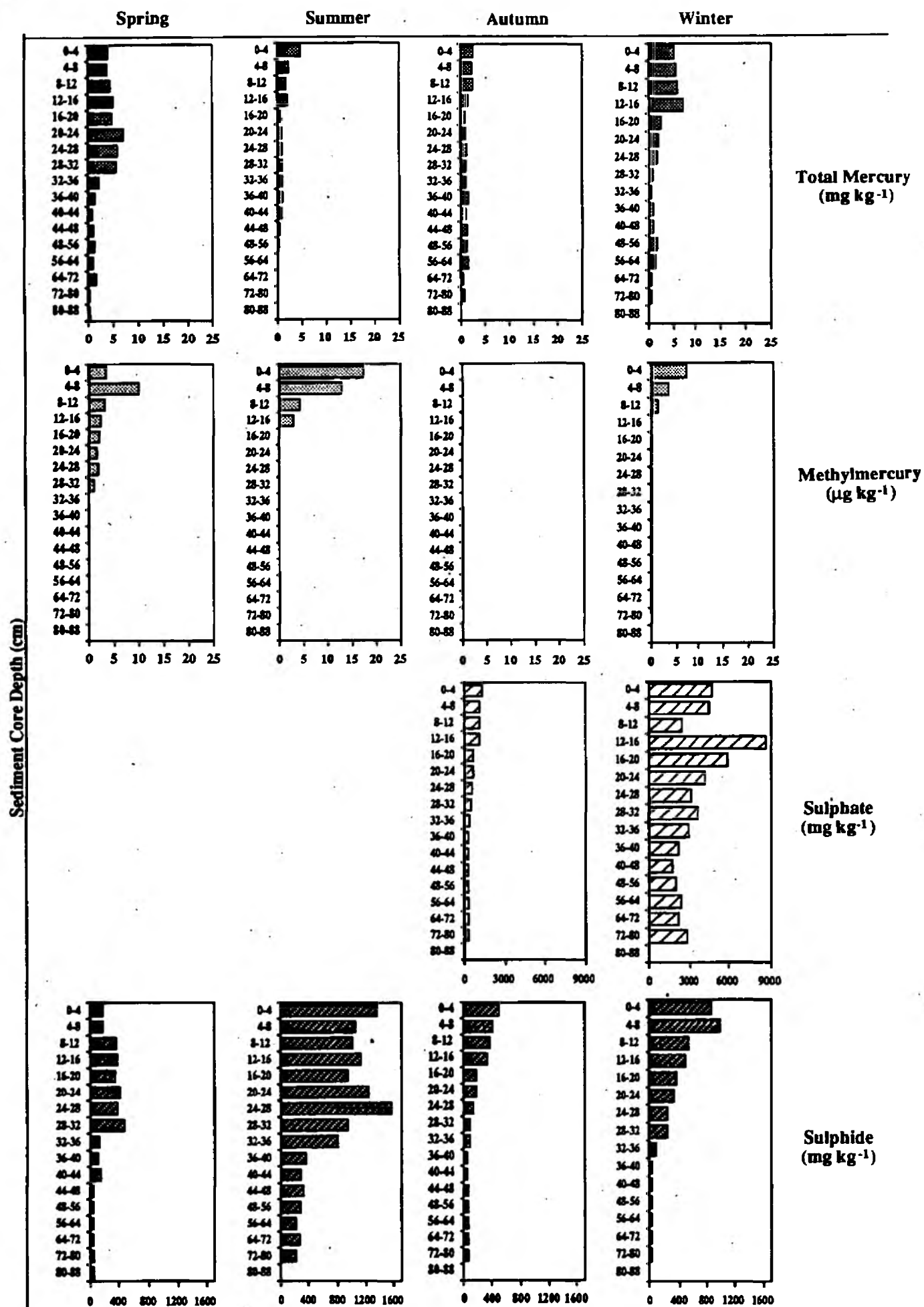


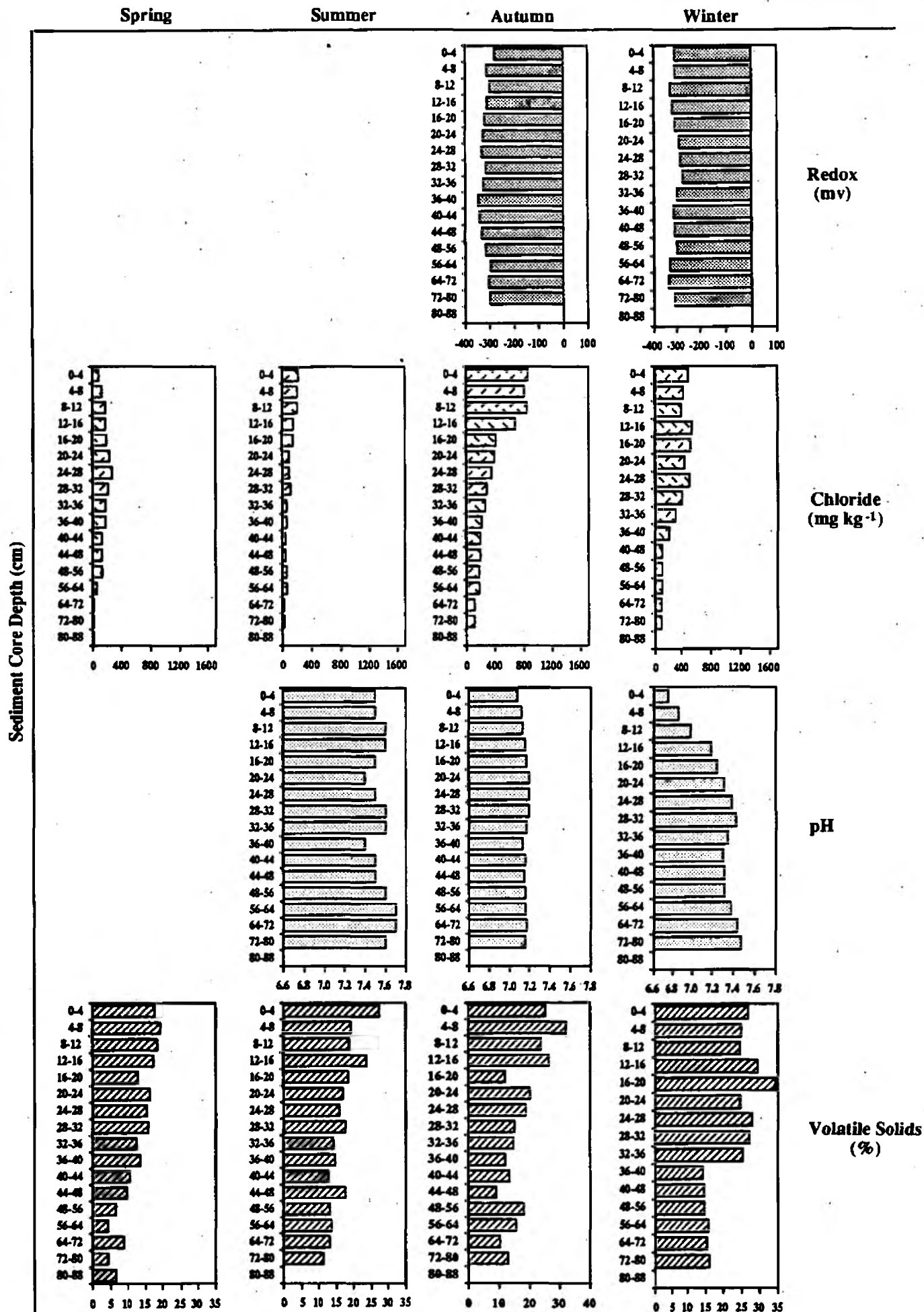
Figure A1. Behaviour of methylmercury in sediment samples during storage.

Conclusion

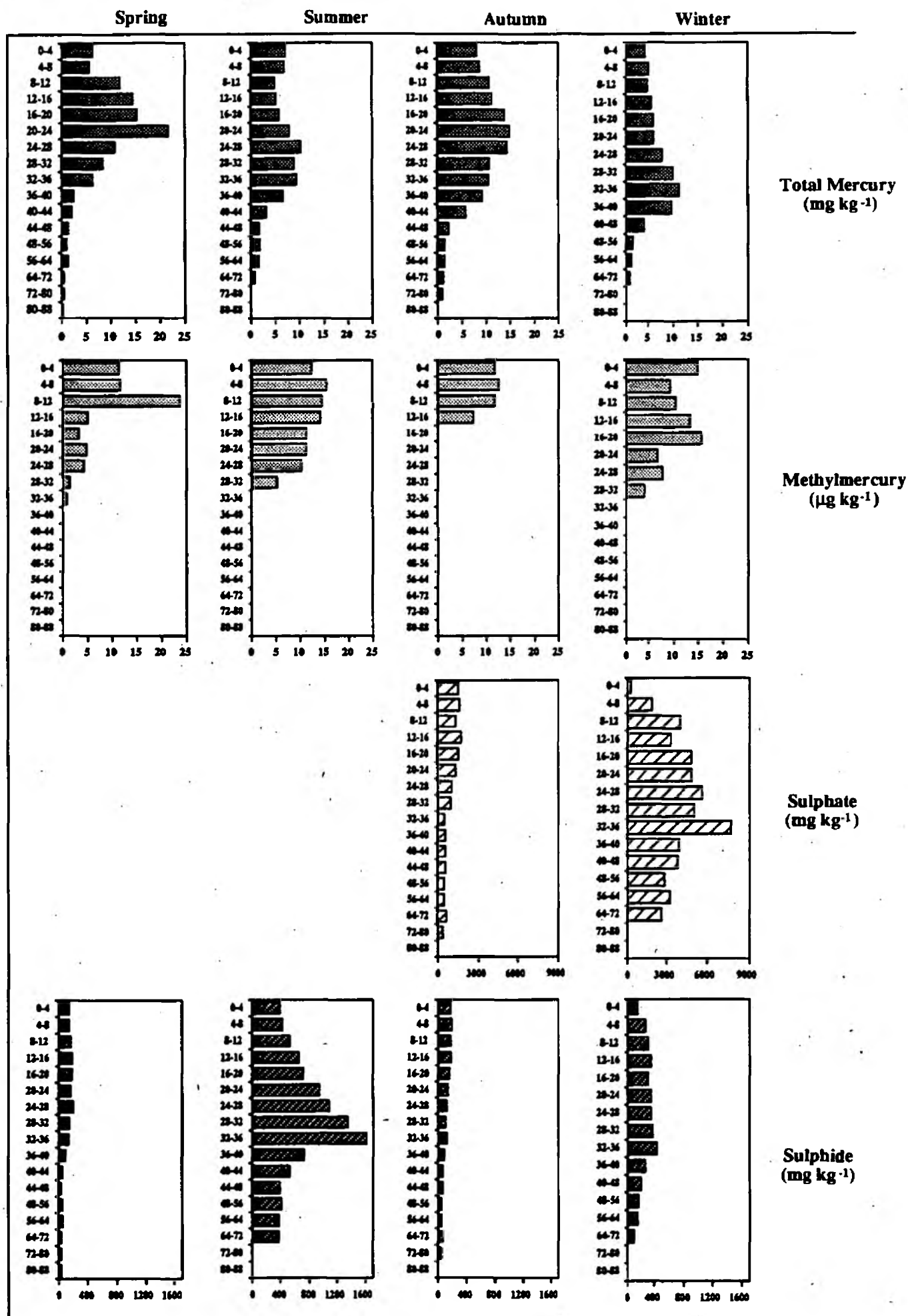
Sediment samples should be frozen as soon as possible after collection to minimize changes in methylmercury concentrations. The refrigeration of samples for methylmercury determination should not be utilized as an intermediate storage method as this can lead to a significant loss of methylmercury from the sample.



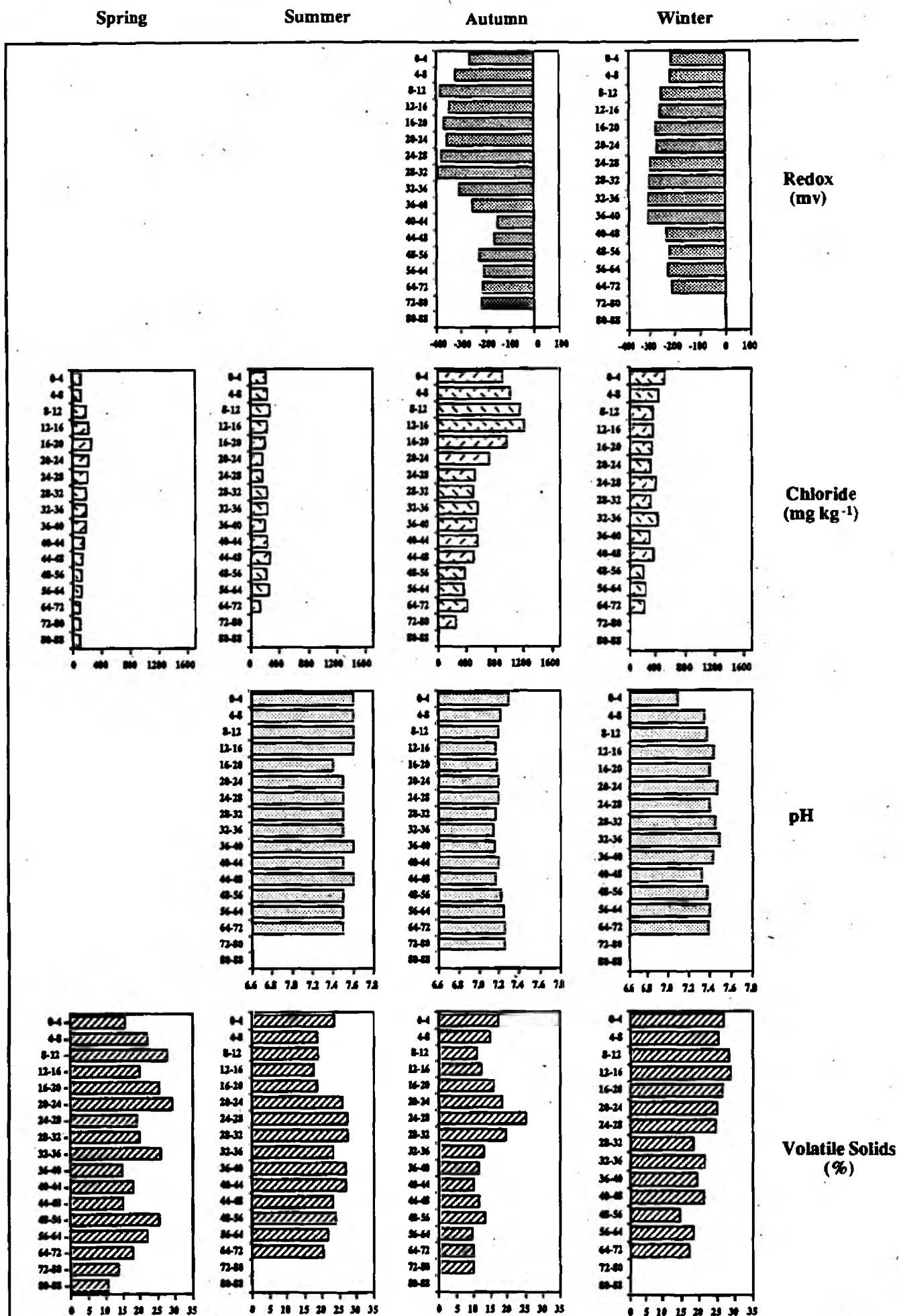
APPENDIX 2 Rockland Broad Seasonal Survey Depth Distribution of Physicochemical Parameters. CORE 1.



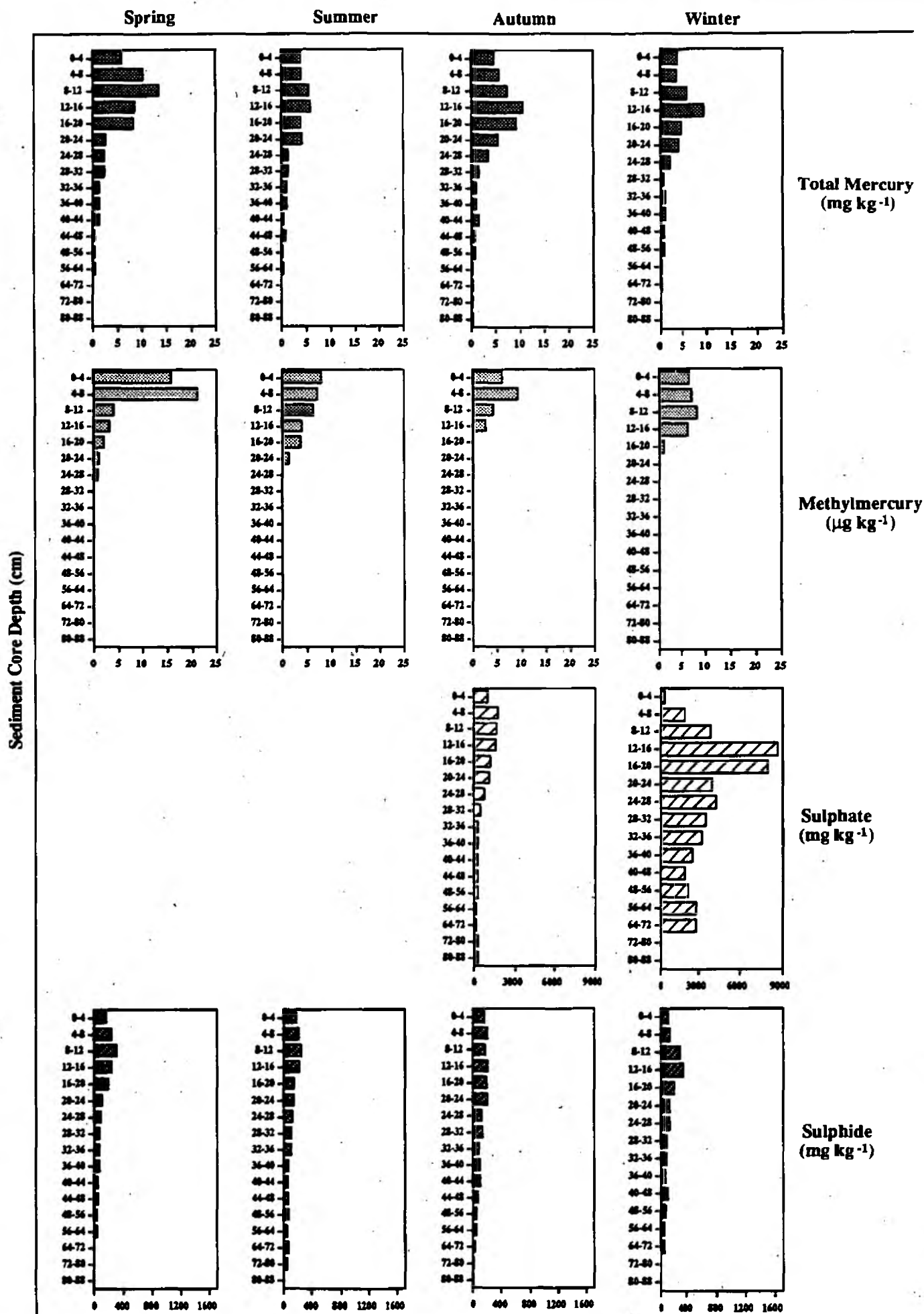
APPENDIX 2 Rockland Broad Seasonal Survey Depth Distribution of Physicochemical Parameters. CORE 1.



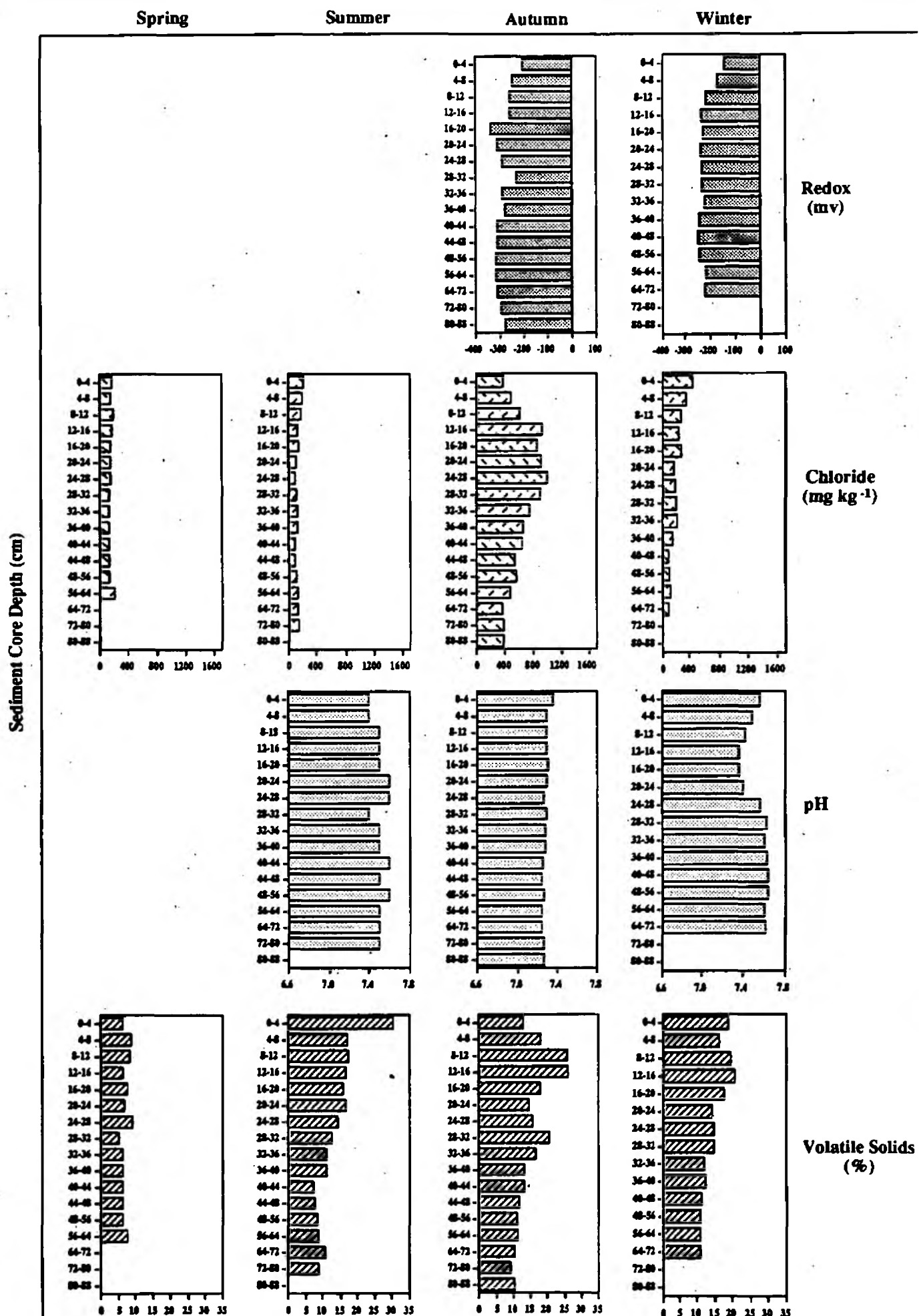
APPENDIX 2 Rockland Broad Seasonal Survey Depth Distribution of Physicochemical Parameters. CORE 2.



APPENDIX 2 Rockland Broad Seasonal Survey Depth Distribution of Physicochemical Parameters. CORE 2.



APPENDIX 2 Rockland Broad Seasonal Survey Depth Distribution of Physicochemical Parameters. CORE 3.



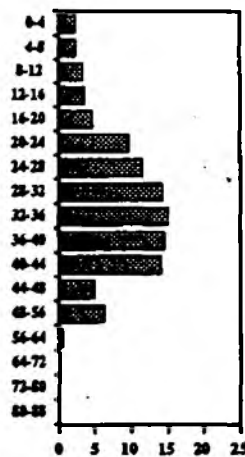
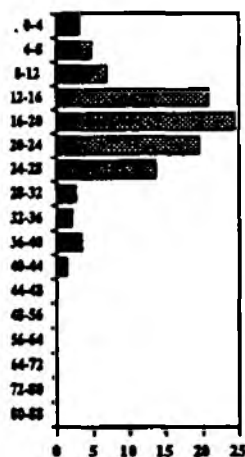
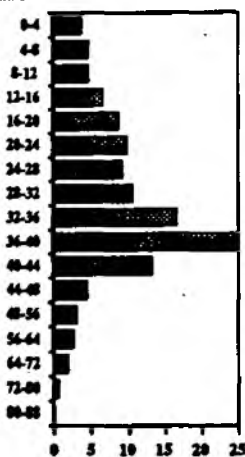
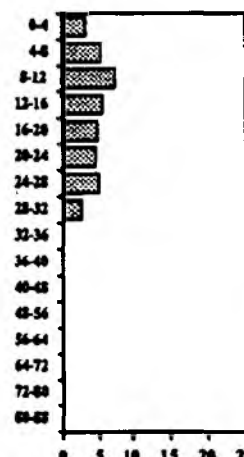
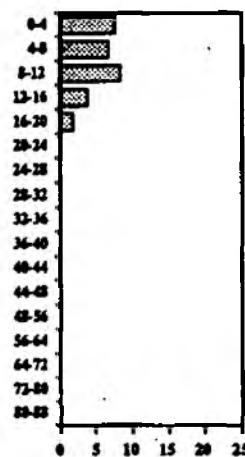
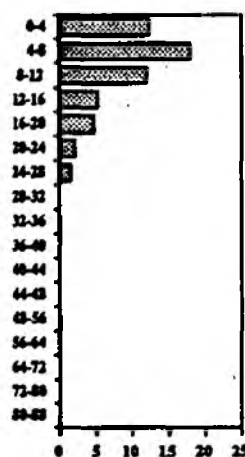
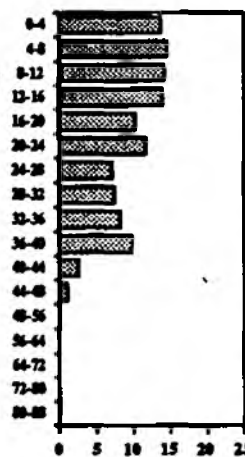
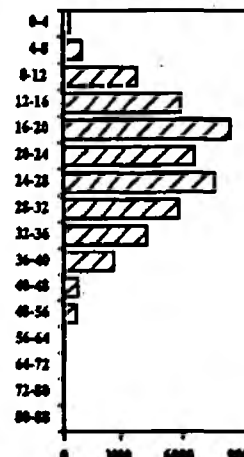
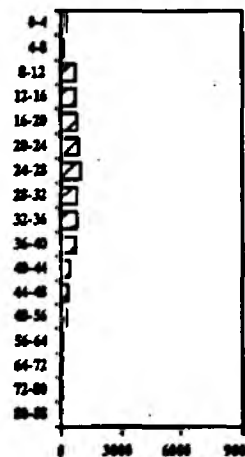
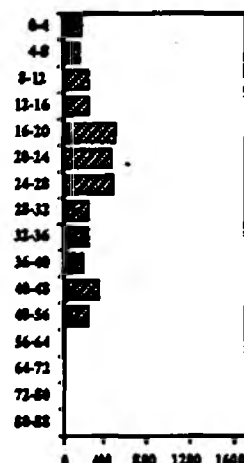
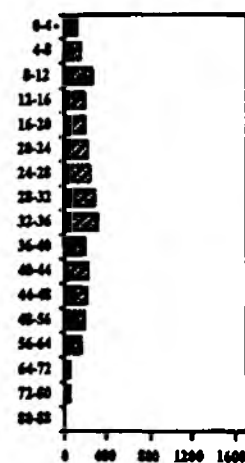
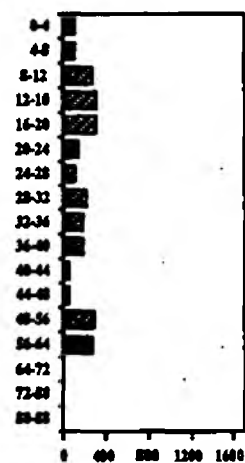
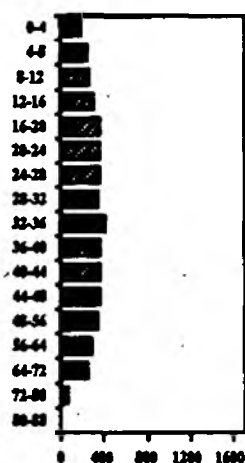
APPENDIX 2 Rockland Broad Seasonal Survey Depth Distribution of Physicochemical Parameters. CORE 3.

Spring

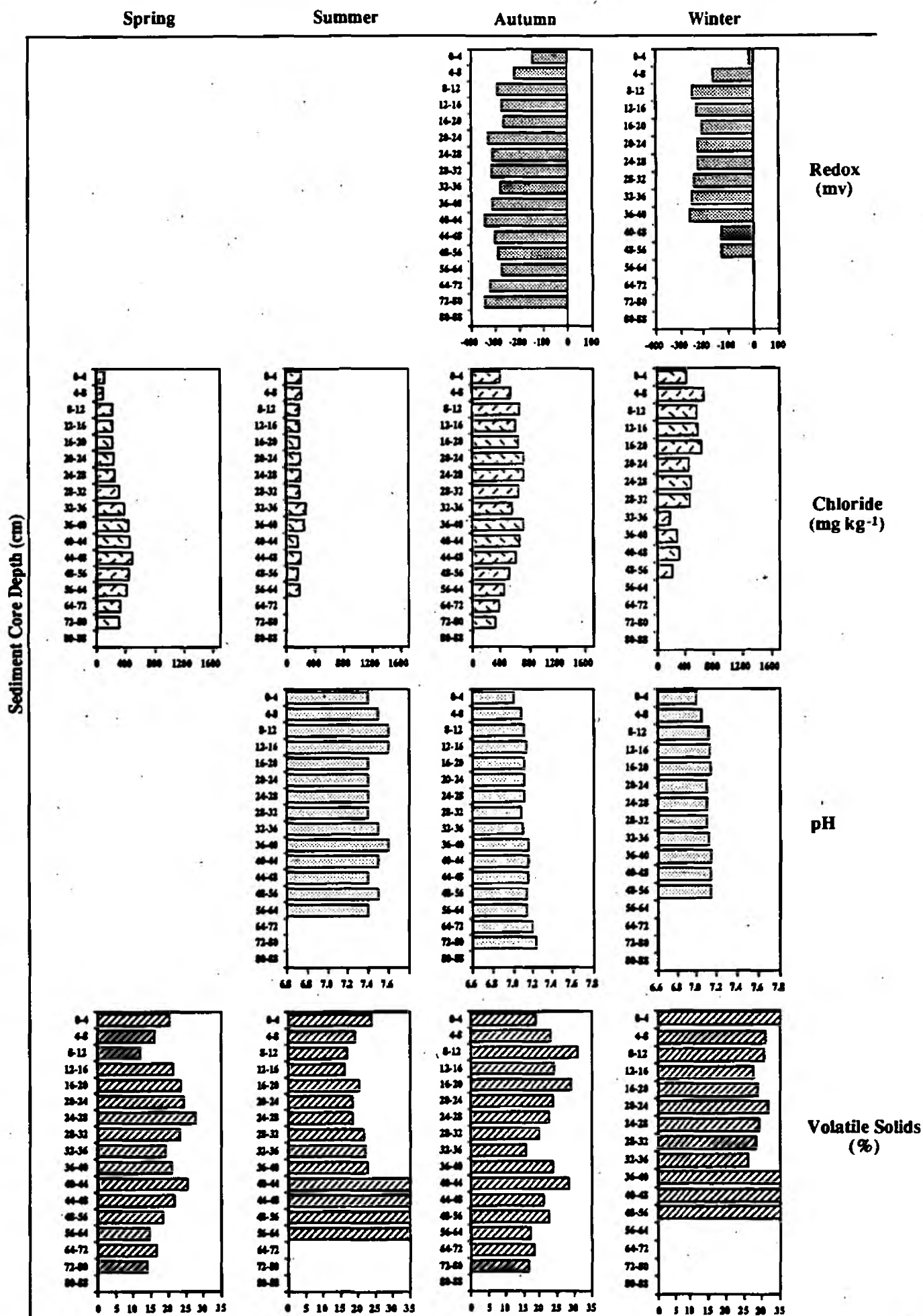
Summer

Autumn

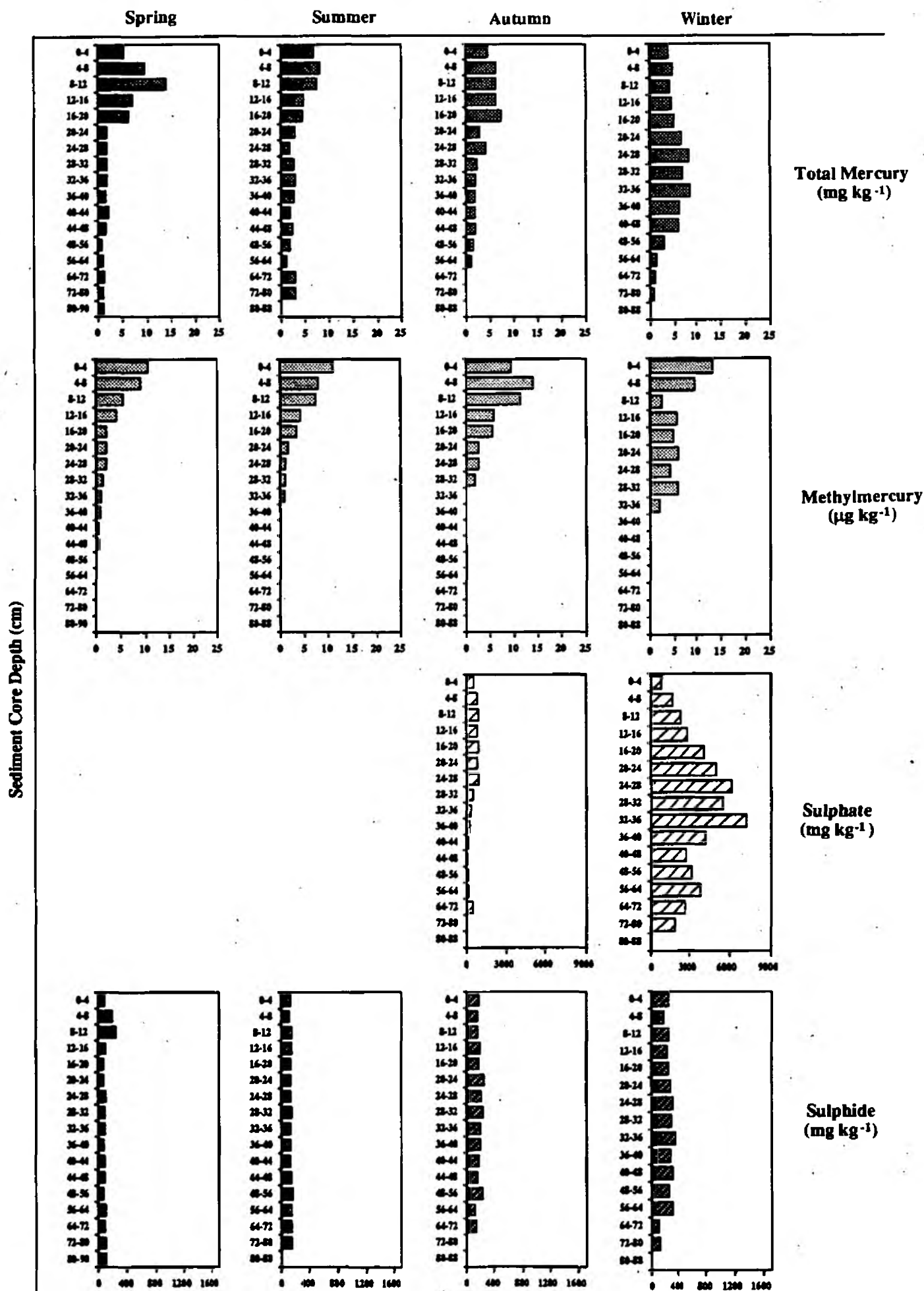
Winter

Total Mercury
(mg kg⁻¹)Methylmercury
(µg kg⁻¹)Sulphate
(mg kg⁻¹)Sulphide
(mg kg⁻¹)

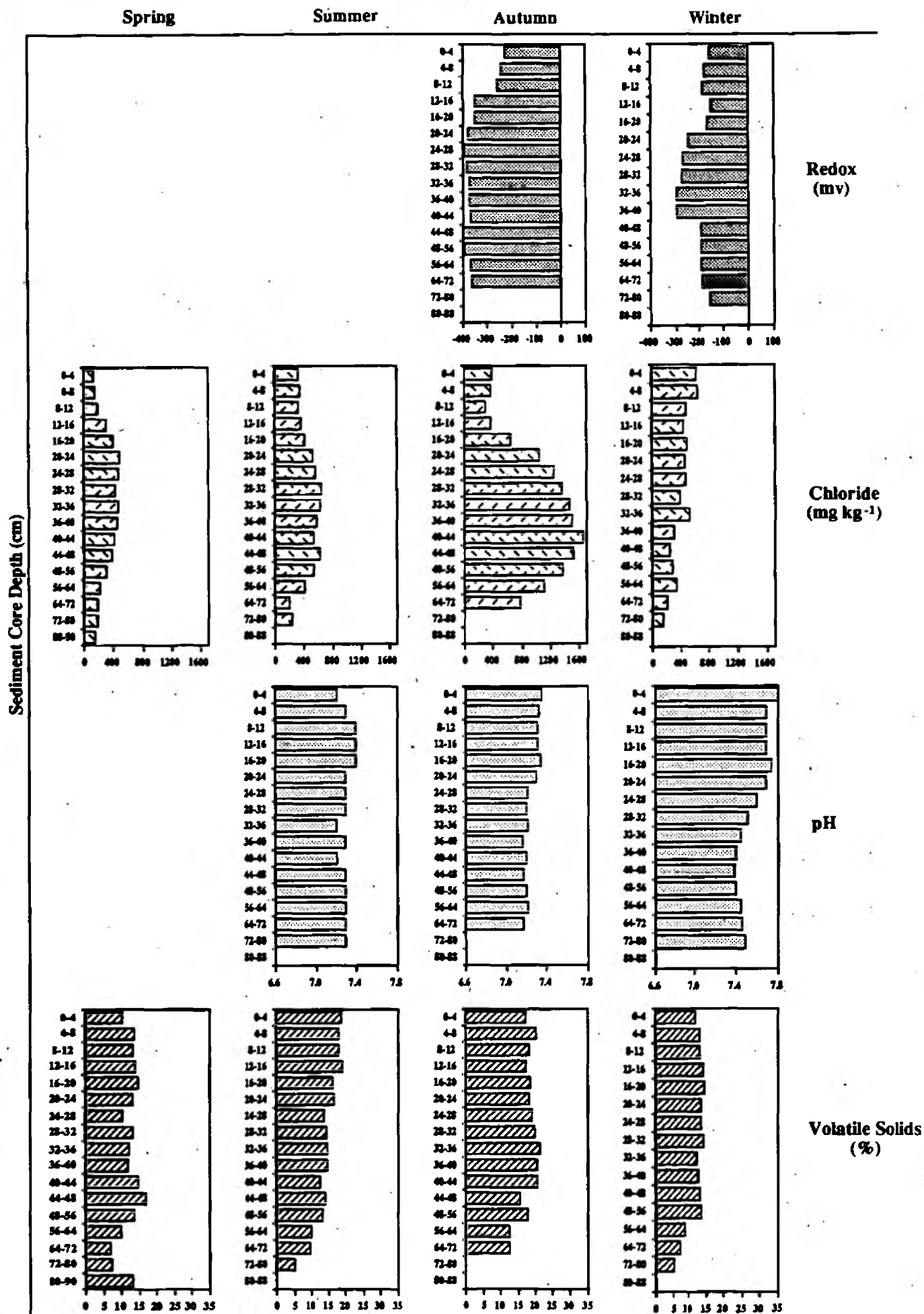
APPENDIX 2 Rockland Broad Seasonal Survey Depth Distribution of Physicochemical Parameters. CORE 5.



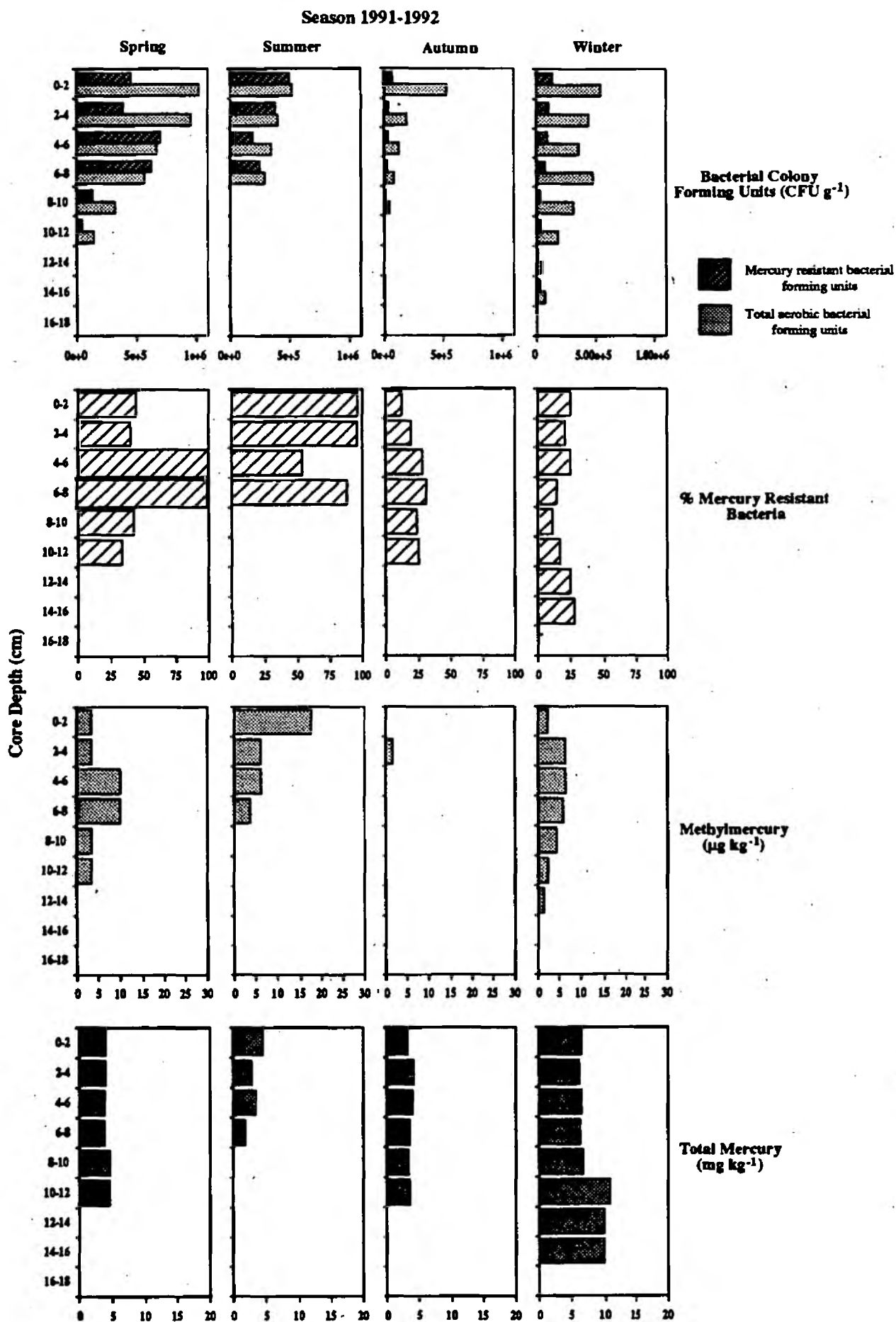
APPENDIX 2 Rockland Broad Seasonal Survey Depth Distribution of Physicochemical Parameters. CORE 5.



APPENDIX 2 Rockland Broad Seasonal Survey Depth Distribution of Physicochemical Parameters. CORE 6.

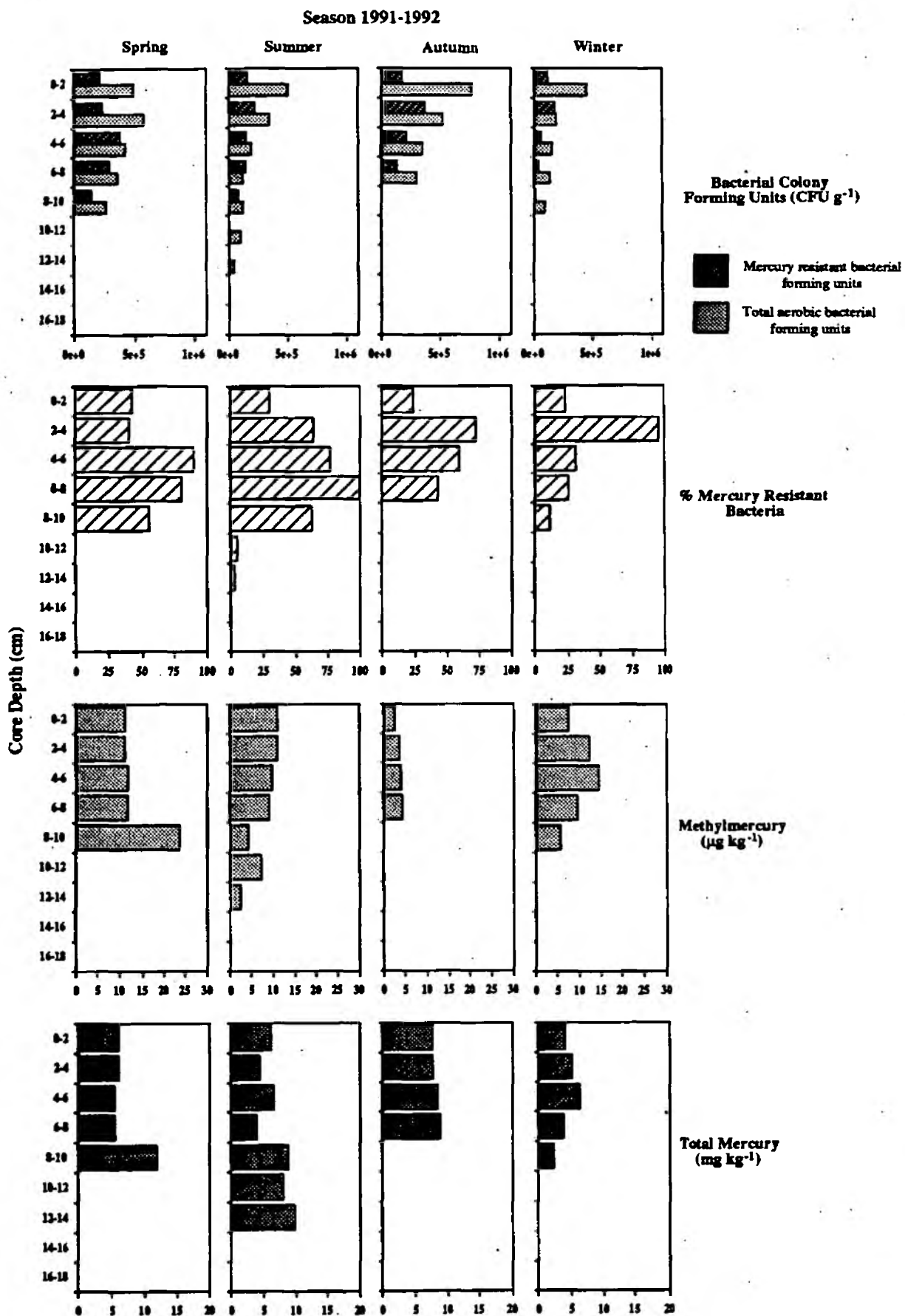


APPENDIX 2 Rockland Broad Seasonal Survey Depth Distribution of Physicochemical Parameters. CORE 6.

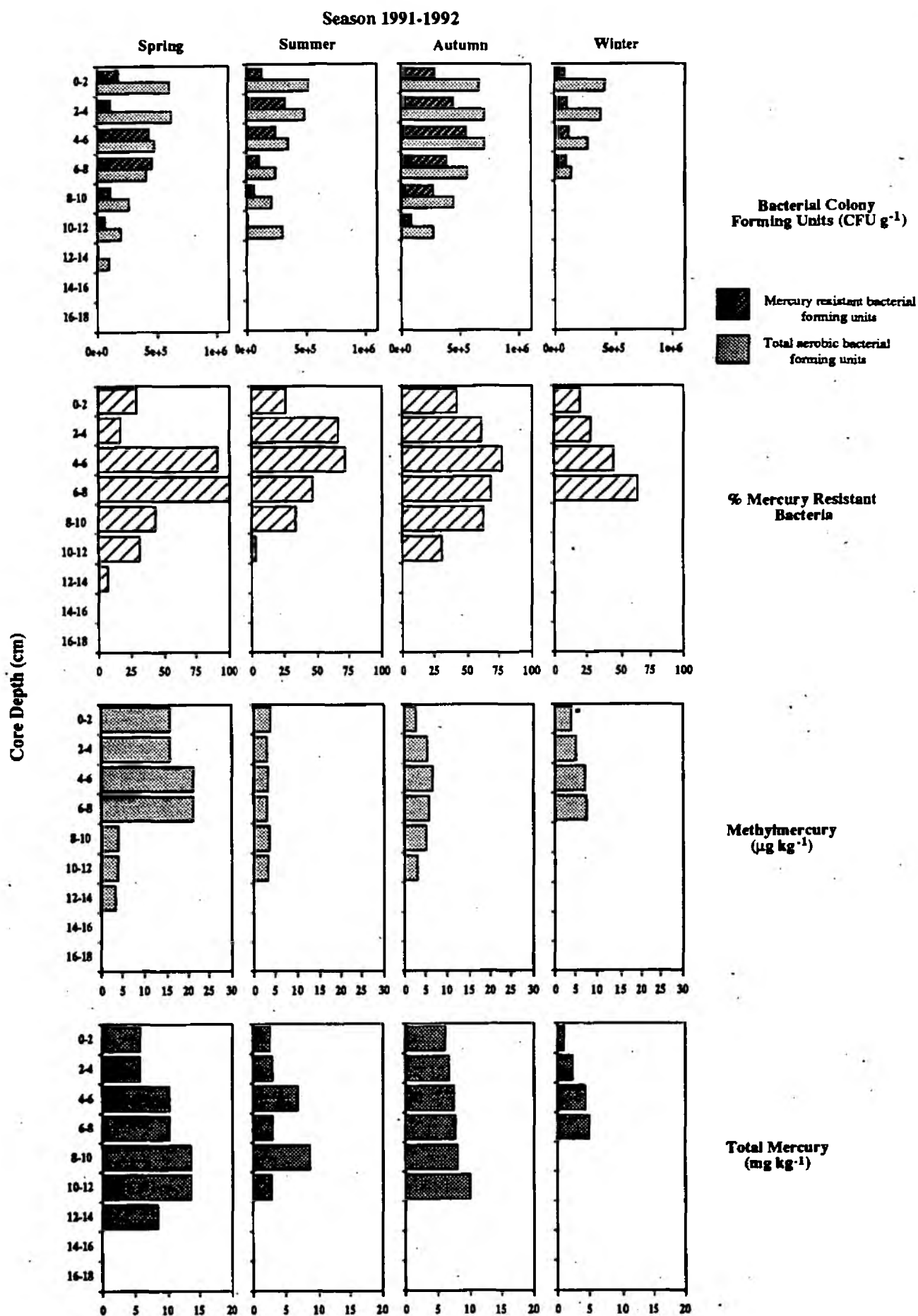


APPENDIX 3 Seasonal variations in mercury resistant bacteria and methylmercury in Rockland Broad sediments.

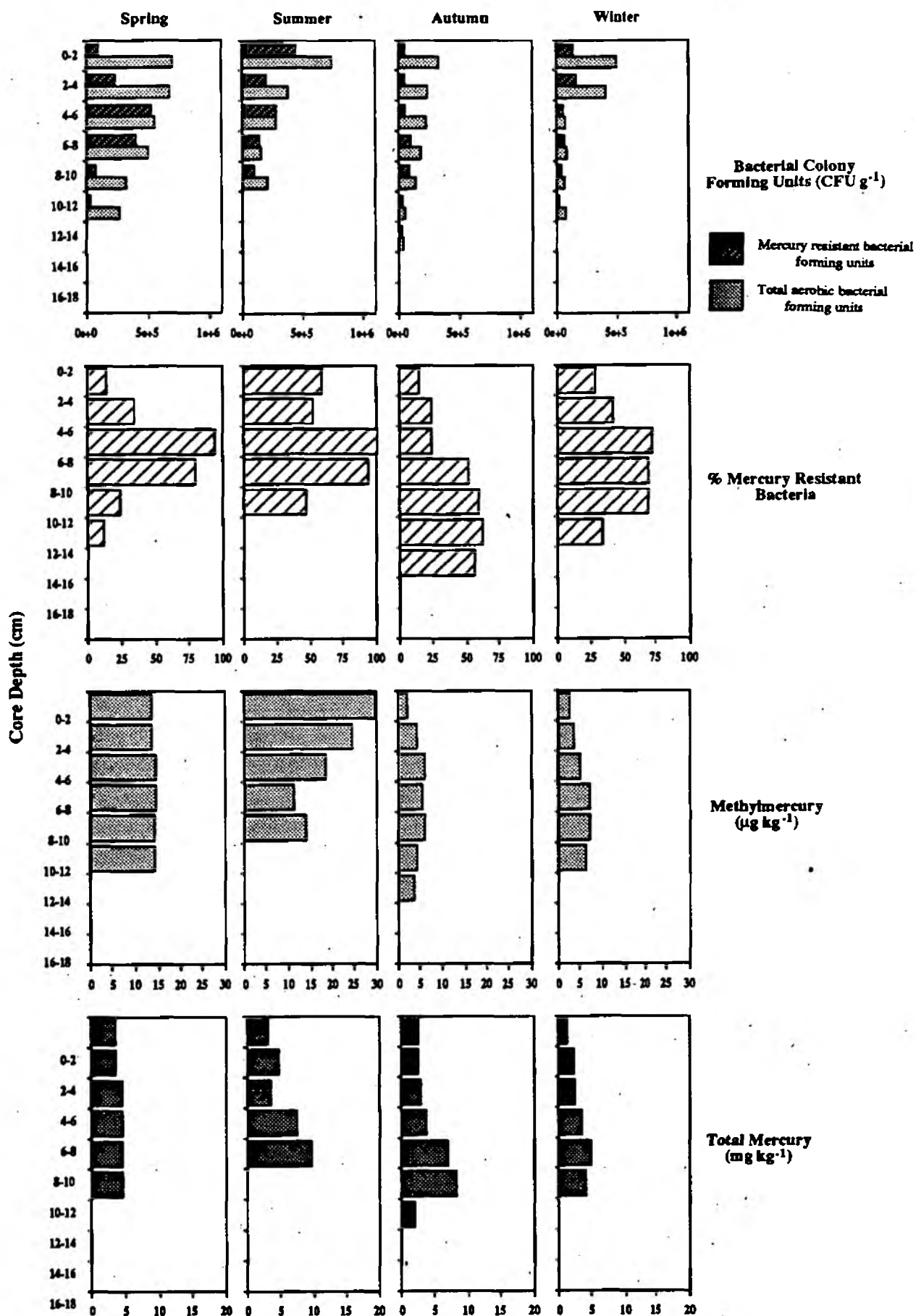
CORE 1.



APPENDIX 3 Seasonal variations in mercury resistant bacteria and methylmercury in Rockland Broad sediments.
CORE 2.

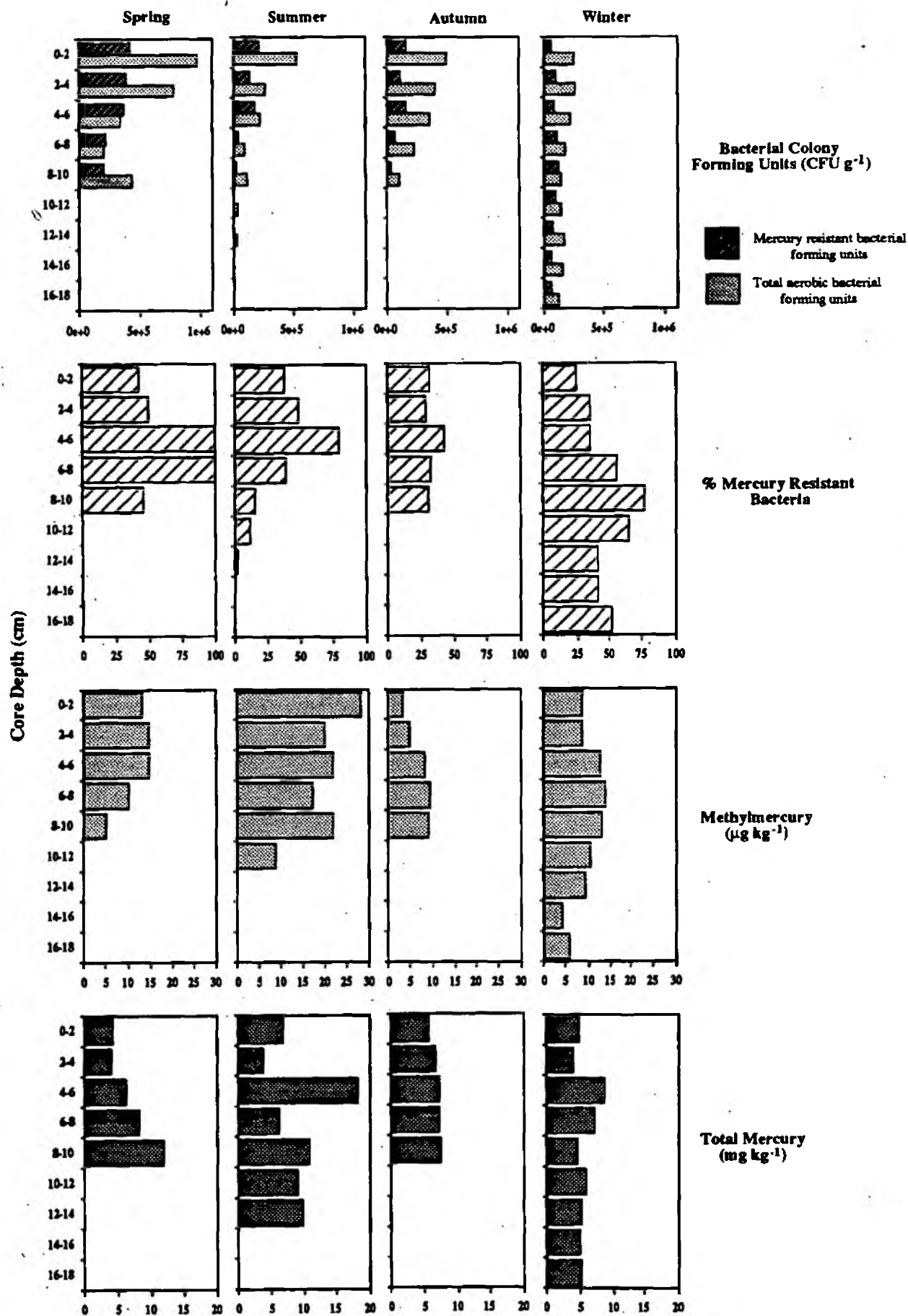


APPENDIX 3 Seasonal variations in mercury resistant bacteria and methylmercury in Rockland Broad sediments.
CORE 3



APPENDIX 3 Seasonal variations in mercury resistant bacteria and methylmercury in Rockland Broad sediments.
CORE 5.

Season 1991-1992



APPENDIX 3 Seasonal variations in mercury resistant bacteria and methylmercury in Rockland Broad sediments. CORE 6.

