# NRA OI 420

Mercury, Methylmercury and Copper in the River Yare, Norfolk

**Report to the National Rivers Authority Anglian Region NRA Contract OI/420/10/A** 

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#### EXECUTIVE SUMMARY

This is the third report submitted by Imperial College of Science, Technology and Medicine, London, to the National Rivers Authority on the mercury, methylmercury and copper contamination in the River Yare, Norfolk. It describes research undertaken since 1992, concerning the magnitude, distribution and bioavailability of sediment bound mercury, methylmercury and copper within the River Yare system. A summary and analysis of all of the data on mercury and methyl mercury collected since 1986 is also presented. Recommendations have been made to assist the NRA in the management of the contaminated reach of the R Yare and the surrounding environments it effects.

Annual monitoring of the R Yare bottom sediments identified Whitlingham STW outfall as the major source of mercury and copper contamination. The contaminated zone stretches from Trowse in the west to Hassingham in the east and includes the intervening broads of Surlingham, Wheatfen and Rockland. Since 1986 the mean mercury concentration within the bottom sediments from Trowse to Cantley has declined from  $5.4 - 2.1 \text{ mg kg}^{-1}$  in 1995. Mean copper concentrations have decreased from  $106.5 - 71.5 \text{ mg kg}^{-1}$  in the same period. The major contributory factor to the improvement in sediment quality has been the reduction in discharge of the metals from the STW. Highly contaminated bottom sediments have gradually become buried by a cleaner overlay of sediments. Bank disturbance and erosion may contribute mercury to the river by the slumping of previously dredged sediments, and further investigation will be required to quantify this. Rockland and Wheatfen Broads sediments acted as sinks for mercury contamination, and are potential sources of mercury to the main river should the deeper sediments within these broads be remobilised.

Methylmercury is a highly toxic form of mercury predominantly synthesised within the bottom sediments by bacteria and probably, to a lesser degree, by humic matter. As a pollutant whose main source was not the STW, it displays a dispersed pollution plume within the bottom sediments which is partly controlled by availability of inorganic mercury and nutrients. Concentrations of methylmercury have fluctuated which may be linked to nutrient cycling within the bottom sediments. However, methylmercury may also be linked to deposition of atmospherically deposited mercury, this requires further investigation.

Mercury within fish from the R. Yare is predominantly in the form of methylmercury (>80%). The contamination of eel and roach flesh with mercury, has declined with the reduction in mercury discharges from the STW. A reduction of more than half from an average of 0.46 mg kg<sup>-1</sup> to 0.21 mg kg<sup>-1</sup> has been observed from 1985-1994. Burial of the mercury contaminated sediments has decreased mercury availability to fish within the river. Correlations between weight and length and mercury burden of the fish were strong as expected by species which bioaccumulate Hg. Female eels accumulated greater burdens of Hg then did males, no differences were observed in Roach. Other rivers within East Anglia, not considered to be mercury contaminated, have eels with similar mercury contamination levels as those reported for the R Yare which may indicate that the bottom sediments are not the only source of mercury to the R Yare fish. This hypothesis is supported by a study of mercury and methylmercury in fish and bottom sediments collected from Ormesby Broad found that while the concentrations of mercury were very low in the sediments the levels in the fish were very similar to those found in fish from the R Yare. Atmospheric deposition of mercury may be another

source. Mercury deposited atmospherically would be more available to the fish within the river then that continually buried deeper within the sediments.

The effects of dredging contaminated bottom sediments on water quality were examined by monitoring a dredging operation at Thorpe St Andrews and by laboratory prediction using elutriate tests. Elevated levels of mercury and copper were found in the water column during and after dredging, but these were not in breach of E.C. regulations. Intrusion of saline water into potential dredge areas and the effects of seasonal changes in physicochemical sediment conditions were also examined. This revealed that while increased salinity and temperature may increase rates of methyl mercury production, this could not be demonstrated with sediments taken from the River Yare. The biggest threat to biota posed by dredging of contaminated sediments is the re-exposure of heavily contaminated material buried at depths of up to 1 m. Experiments found a relation between mercury and iron and total organic carbon within the resuspended sediments suggesting that mercury remobilisation within the river bed sediments may also be effected by factors (such a salinity changes) that destabilise iron oxides and organic matter within the sediments.

The environmental effects of the disposal of dredged sediments on the upland dumpsite at Griffin Lane were examined by using earthworm and plant bioassays and laboratory based sediment drying experiments. The mobilisation potential of copper and mercury was investigated using sequential extraction techniques. Copper was more mobile in the dump site soils then mercury suggesting it is more bioavailable. Analysis of plants across the site found that mercury is primarily concentrated in the roots with little breakthrough into the upper plants. Mercury and copper concentrations in the earthworm bioassay materials were low, suggesting low availability of the metals within the sediments to the environment.

## TABLE OF CONTENTS

LIST OF FIGURES	_ vi
LIST OF TABLES	_ viii
LIST OF APPENDICES	x
GLOSSARY	
1. INTRODUCTION	1
2. OBJECTIVES	
3. MATERIALS AND METHODS	5
3.1 Assessment of the spatial distribution of mercury, methylmercury and copper in t	
River Yare surficial sediments	
3.1.1 Annual monitoring of the River Yare surficial sediments	
3.1.2 Sediment and Water Collection at Ormesby Broad	
3.1.3 Sample collection and processing	7
3.2 Annual monitoring of fish flesh taken from the River Yare	9
3.2.1 Examination of fish flesh collected from Ormesby Broad	10
3.3 Monitoring and laboratory prediction of the effects of dredging River Yare sedim	ents
on water quality	
3.3.1 Survey area and preliminary sampling	
3.3.2 Monitoring of the dredging operation	
3.3.3 Elutriate tests	
3.4 The fate of heavy metals in dredged sediments disposed on an upland landfill	
3.4.1 Experimental design and apparatus	14
3.4.2 Sediment collection and column packing	
3.4.3 Dismantling of columns	
3.5 Assessment of the biological impact of dredged material	_ 18
3.5.1 Heavy metal uptake by the earthworm Eisenia fetida	18
3.5.2 Heavy metal uptake by the plants Urtica dioica (stinging nettle) and Budleja davidii (butte	rfly
bush)	20
3.6 Analytical methods	_ 22
3.6.1 Sample preparation for metal determination	
3.6.2 Total mercury determination	
3.6.3 Total copper, iron and manganese determination	
3.6.4 Organomercury species determination	24

3.6.6 Total organic carbon determination	26
3.6.7 Anion determination	27
3.6.8 Total and volatile solids determination	
3.6.9 pH and redox potential determination	27
3.6.10 Analytical quality and control	27
4. RESULTS	_ 28
4.1 Assessment of the spatial distribution of Hg, MeHg and Cu within the surficial be	d
sediments, 1986-1995	_ 28
4.1.2 Organomercury	33
4.1.3 Copper	36
4.2 The distribution of Hg and Cu within bed sediment cores - 1995	_ 37
4.3 Assessment of mercury and methylmercury in fish flesh from the River Yare, 198	
4.4 Comparison between River Yare and Ormesby Broad bed sediment and fish Hg burden	
4.5 Monitoring and laboratory prediction of the effects of dredging River Yare sedime on water quality	
4.5.1 Sediment type and heavy metal distribution	
4.5.3 Effect of seasonal physicochemical conditions on potential metal remobilisation	
4.5.4 Effect of salinity on potential metal remobilization	
4.5.5 Post-dredging effects on sediment contaminant loadings	
4.6 The fate of heavy metals in dredged sediments disposed on an upland landfill	_ 57
4.6.1 Mercury and copper pathways	58
4.6.2 Redox potential and pH changes	62
4.6.3 Changes in anion concentrations	62
4.6.4 Changes in total solids, volatile solids and total organic carbon content	63
4.7 Assessment of the biological impact of dredged material	_ 64
4.7.1 Heavy metal uptake by the earthworm E. fetida	64
4.7.2 Total and extractable soil metal concentrations	65
4.7.2 Metal uptake by the plants Urtica diocia and Budleja davidii	68
5. DISCUSSION	_ 70
5.1 Assessment of the temporal loadings of mercury, methylmercury and copper in R	iver
Yare bottom sediments, 1986-1995	_ 70
5.1.1 Source and history of mercury inputs	70
5.1.2 Spatial extent of the contamination plume	71

5.1.3 Determination of a background concentration of mercury	73
5.1.4 The magnitude and variation of mercury enrichment within the pollution plume	74
5.1.5 The magnitude and variation of methylmercury within the pollution plume	80
5.1.6 The magnitude and variation of copper enrichment within the pollution plume	83
5.2 Assessment of the contamination of fish flesh from the River Yare by mercury and	
methylmercury, 1986-1994	_ 86
5.2.1 Temporal [Hg] trends in fish from the R. Yare	86
5.2.2 The inter-site study	88
5.2.3 Other Sources of Hg to fish in Ormesby Broad and the R. Yare	90
5.2.4 Comparison with other British Rivers	90
5.3 Dredging and its effects on water quality	_ 92
5.4 The fate of heavy metals in dredged sediments disposed on an upland landiill	_ 95
5.5 Assessment of the biological impact of dredged material	_ 97
5.5.1 A general overview of site conditions	102
6. SUMMARY OF FINDINGS	_ 103
7. CONCLUSIONS	_ 104
8. RECOMMENDATIONS	_ 108
9. REFERENCES	111

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#### LIST OF FIGURES

Figure 1. Map of R. Yare showing locations of sampling points6
Figure 2. Sampling locations at Ormesby Broad8
Figure 3. Location of cores, the dredging operation and water sampling points at Thorpe St. Andrews. 12
Figure 4. Flow diagram of modified elutriate test.   15
Figure 5. Column design for sediment disposal experiments17
Figure 6. Sampling locations of dredge sediment landfill on River Yare21
Figure 7. Spatial distribution of mercury in surficial bed sediments of the R. Yare 19830
Figure 8. The average percentage volatile solids content of surficial bed sediments of the R. Yare for
1986-1995 (bars indicate ranges)32
Figure 9. Spatial distribution of organomercury in surficial bed sediments of the R. Yare 1989 - 1995. 34
Figure 10. Spatial distribution of organomercury as a ratio of total mercury in bed sediments, 1989-
199535
Figure 11. Spatial distribution of copper in surficial bed sediments of the R. Yare 1986 - 199536
Figure 12. Core profiles of anthropogenic Hg and Cu and lithogenic metals at three points in the
contamination plume, 199539
Figure 13. (a). Mercury accumulated in eel sampled from Y - R. Yare and O - Ormesby Broad by sex.
(b). Mercury accumulated in Roach collected from Y - River Yare and O - Ormesby Broad by sex.44
Figure 14. The dredge area showing sediment types46
Figure 15. Depth profiles of Hg and Cu contamination prior to dredging at Thorpe St. Andrews47
Figure 16. Depth profiles of methylmercury at Thorpe St. Andrews prior to dredging48
Figure 17. Field and experimental data for total Hg and Cu concentrations in overlying water during
and after a dredgeing operation51
Figure 18. Field and experimental data for total and dissolved Fe and Mn concentrations in overlying
water during and after a dredging operation52
Figure 19. Experimental and field values for total organic carbon and pH53
Figure 20. Experimental and field values for temperature and dissolved oxygen54
Figure 21. Variations in release of metals from sediments to freshwater during summer and winter for
elutriate tests55
Figure 22. Elutriate test results under fresh and saline water conditions56
Figure 23. Depth profile of Hg and Cu in sediment core 4 taken 3 months after dredging.
Figure 24. Total Hg volatilised from the columns over 70 days58
<b>Figure 25.</b> Depth profiles of Hg concentrations (mg kg <sup>-1</sup> ) with time for the column experiments60
Figure 26. Depth profiles of Cu concentrations (mg kg <sup>-1</sup> ) with time for column experiments61
Figure 27. Change in surface-2.5 cm layer redox potential with time62
<b>Figure 28.</b> Depth profiles of nitrate and sulphate concentrations with time for column experiment63
Figure 29. Metal analysis of plants accross the Griffin Lane landfill66
Figure 30. Transects illustrating location of plume maxima over time73

Figure 31. Average enrichment of Hg over background concentrations, 1986-1995	75
Figure 32. Concentrations of Hg in STW final effluent and bottom sediments, 1976-1994	77
Figure 33. Concentrations of Cu in Whitlingham STW final effluent, 1989-1994.	84
Figure 34. Distance from STW outfall at which maximum spot Cu concentration occurred, 1986-1994.	85
Figure 35. (a). Mercury accumulated in eels from the R. Yare since 1985 and in eel from Ormesby	
Broad. (b). Mercury accumulated in roach from the R. Yare since 1984 and in roach from	
Ormesby Broad	87

Figure 36. Flowchart for the assessment of the biological impact of dredged material. \_\_\_\_\_100

#### LIST OF TABLES

Table 1. River Yare sampling strategy for surficial sediments, 1986-1995.       7
Table 2. The suitability of eels and roach as survey specimens.
Table 3. TimeTable for column dismantling.   18
Table 4. The distribution and weights of E. fetida used for each sample group.       19
Table 5. Digestion matrices for sample digestions.   22
Table 6. Microwave programmes for sample digestions.   22
Table 7. Analytical parameters for organomercury determination by FI-AFS25
Table 8. The reproducibility and recovery of sediment and fish digestions and extractions for the 1994
surveys28
Table 9. Certified and determined concentrations of copper, mercury and methylmercury in sediment and
fish samples for the 1994 surveys28
Table 10. Transects used for averaging sediment Hg data on the R. Yare.       31
<b>Table 11.</b> Pearson's correlation matrix ( $\rho = 0.95$ ) for total mercury concentrations with other parameters
for annual bed sediment surveys, 1986-199531
<b>Table 12.</b> Pearson's correlation matrix ( $\rho$ =0.95) for organomercury concentrations with other
parameters for annual bed sediment surveys, 1987-199533
<b>Table 13.</b> Pearson's correlation matrix ( $\rho$ =0.95) for total copper concentrations with other parameters
for annual bed sediment surveys, 1986-199537
Table 14. Total mercury concentrations in eel, roach and pike fish flesh samples taken from the River
Yare (1971-1994)41
Table 15. Concentrations of THg and MeHg and some physicochemical parameters for bed sediments
and water of the R. Yare and Ormesby Broad in 1994/9542
Table 16. Hg burdens and sample population statistics for eels and roach from the R. Yare and Ormesby
Broad in 1994/9542
Table 17. Total mercury burden in eel and roach muscle tissue taken from the River Yare (1971-1994). 45
Table 18. Physico-chemical parameters and concentrations of metals for bulk sediment and water from
the dredge site (Thorpe St Andrews)49
Table 19. Maximum concentrations of metals in the water column and the enrichment over background
concentrations in the elutriate and field tests (observed) for Thorpe St Andrews50
Table 20. Metal concentrations and physico-chemical parameters for bulk sediment and water for
Rockland Broad elutriate tests56
Table 21. Mean metal concentrations in bulk sediment and clay.     59
<b>Table 22.</b> Total metal concentrations (mean ± standard error) and physico chemical parameters of
contaminated dredge soil and uncontaminated soil64
<b>Table 23.</b> Total metal concentrations (mean ± standard error; range in brackets) of E. fetida and average
weight per worm before and after the bioassay experiment65
Table 24. Worm/soil ratios for concentrations of Hg, Cu, Mn and Fe in E. fetida tissue and soil when
placed in heavy metal contaminated and uncontaminated soil.

Table 25. Average concentrations of	f metals found in soil extracts and di	gestates and U. dioica digestates
from the 7 transect locations.		67

- Table 26. Total metal concentrations (means ± standard error) and physico-chemical parameters of contaminated dredge spoil and uncontaminated soil from which the plant samples were sampled. 69
- Table 27. Total metal concentrations (means  $\pm$  standard error; ranges in brackets) in the leaves of U. diocia and B. davidii collected from the landfill and an adjacent uncontaminated area. \_\_\_\_\_69

Table 28. Statistical appraisal of the Hg and Cu concentration in U. diocia and B. davidii from both contaminated and uncontaminated sites. Significance values attached to the student 'T'-test\_\_\_\_\_69

- Table 29. Mercury loading to Whitlingham STW and thence to the River Yare (data supplied by AWA and NRA). 71
- Table 30. Summary of total mercury concentrations in bottom sediments, 1986-1994. \_\_\_\_\_74 Table 31. Processes contributing to variations in bottom sediment Hg concentrations. \_\_\_\_\_75
- Table 32. Mercury concentrations in river sediments nationally and internationally. 

   Table 33. Summary of methylmercury concentrations in bottom sediments, 1986-1994.
   80
- Table 34. Total and methylmercury concentrations and percentage ratio methyl- to total mercury in some natural sediments. \_81

84

- Table 35. Summary of total copper concentrations in bottom sediments, 1986-1995.
   Table 36. Total mercury concentrations in eel, roach and pike fish flesh samples taken from the River Yare (1971-1994). \_\_\_ 86
- Table 37. Percentage ratio of fish flesh mercury concentration (wet weight) to sediment mercury concentration (dry weight) for the River Yare (1984-1994).
- Table 38. Percentage ratio of fish flesh mercury concentration (wet weight) to sediment mercury concentration (dry weight) for selected river and lake systems. 92
- Table 39. Greater London Council guidelines for contaminated soils suggested ranges of values (mg kg<sup>-</sup> <sup>1</sup> on air dried samples).\_\_\_ 98
- Table 40. Comparison of Hg and Cu concentrations in the contaminated and uncontaminated bioassay soils with concentrations considered phytotoxic and a generalised UK surface soil (mg kg<sup>-1</sup>).  $\_102$

### LIST OF APPENDICES

ppendix 1 Parameters monitored for surficial bed sediments taken from R. Yare, 1986 -1995		
Appendix 2 Concentrations of mercury, copper and organomercury found in cores take	n from Thorpe St.	
Andrews	143	
Appendix 3 Concentrations of metals in dredge spoil extracts and plants	147	
Appendix 4 Fish Surveys of the R. Yare and Ormesby Broad	148	
Appendix 5 Site Licence for operation of Griffin Lane Landfill	152	

## GLOSSARY

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Abiotic	Pertaining to non-living things		
Aerobic	Pertaining to non-living things		
Actobic	Characterised by or occurring in the presence of free oxygen; requiring oxygen for respiration		
Anoxic	The absence of free oxygen, but the existence of inorganic		
Anoan	substances (e.g. sulphate, nitrate) which can provide oxygen to		
	organisms able to break them down		
Bioaccumulate	The ability of a living organism to concentrate and accumulate a		
Divaccumulate	chemical substance from the surrounding environment, as		
	distinct from biomagnification		
Piomognification	Process whereby the concentration of a pollutant within living		
Biomagnification	tissues increases at each link in a food chain		
Biotic	Pertaining to life		
Coprophagy	0		
Coprophagy	A term used to describe the habit of consuming dung. In this report, specifically applied to earthworms ingesting their own		
	dung when no other food is available		
Demethylation	-		
Demethylation	The removal of a methyl group $(CH_3)$ from a compound. This can occur abiotically or biotically in the case of methylmercury		
Fyke net	Also called winged eel basket, is a double-funnelled net		
ryke net	supported by 5-7 circular (or D-shaped) frames. The first funnel		
	has a relatively wide opening and has a square or U-shaped		
	cross-section, while the last or cod-end funnel forms a very		
	narrow slit-like aperture where it opens into the farther chamber		
	from which the eel finds it almost impossible to escape		
Hg	Mercury. Used in the text as a generic abbreviation for		
8	mercury; not intended to indicate any particular valence, species		
	or phase of the element. Similarly used for copper (Cu),		
	manganese (Mn) and iron (Fe)		
MeHg	Methylmercury, CH <sub>3</sub> Hg <sup>+</sup> X <sup>-</sup> . Generic abbreviation for the		
5	covalently bonded methyl group and Hg <sup>2+</sup> ion with a counter		
	ion, most often Cl- or OH-		
Methylation	Addition of a methyl group (CH <sub>3</sub> -) to an element or compound,		
-	often by enzymatic activity for mercury, arsenic and other		
	environmentally relevant metals		
OD	outside diameter		

xi

Oxidation	idation The addition of oxygen to a compound. More generally, an reaction involving the loss of electrons from an atom. It always accompanied by reduction	
Phytotoxic Tox	ic to plants, sometimes also refers to animals	
Reduction Any	process in which an electron is added to an atom or ion.	
	Four common types of reduction are removal o oxygen from a	
	molecule, the liberation of a metal from its compounds, and	
diminution of positive valency of an atom or ion. A occurs with oxidation		
Reducing/oxidising	Used to describe the condition of sediments. A reducing sediment is deficient in free oxygen whilst an oxidising sediment has available free oxygen	
Standard	The electromotive force set up in a solution between two	
redox potential	standard electrodes due to the concentration of oxidising or reducing substances. Aerobic (oxidising) systems are generally considered to be in the range +200 to +600 mV, anaerobic (reducing) systems below -100 mV.	

### **1. INTRODUCTION**

In late 1984 the then Anglian Water Authority analysed roach hearts and livers taken from the R. Yare and found a mean mercury concentration of 0.44 mg kg<sup>-1</sup> (NRA, personal communication). Analysis of bottom sediments close to the Whitlingham sewage treatment works (STW) outfall revealed mercury concentrations of only 0.79 mg kg<sup>-1</sup>, however (Bubb *et al.*, 1991a). A more extensive sediment sampling survey was then considered necessary, but before this was implemented, in late summer 1985, Friends of the Earth (FoE) with the help of local anglers collected fish samples from all the major river valleys in the Norfolk Broads.

'The results of the survey are now history. Eels caught from the Thurne and Waveney were given a clean bill of health; those from the Yare were contaminated with concentrations of mercury in excess of EEC directives.'

'Watchdog anglers in a secret assignment', Eastern Daily Press, 13/2/1986.

So began a highly publicised and occasionally confrontational investigation into the metal pollution in the R. Yare by a number of organisations, including Friends of the Earth, Greenpeace ('Greenpeace tests Yare water', EDP, 2/6/1986) and eventually Imperial College, London, on behalf of Anglian Water and continued for the National Rivers Authority. The initial sample of eels taken by FoE from near Rockland on the R. Yare contained mean mercury (Hg) concentrations of 0.57 mg kg<sup>-1</sup> (wet weight), almost twice the 0.3 mg kg<sup>-1</sup> (wet weight) limit set by the 1984 EEC Directive (Council of European Communities, 1984). It appeared that the Hg contamination affecting the fish was centred on the Whitlingham STW outfall and that the metal contaminated trade effluent was, in turn, coming from a large chemical plant in Norwich.

These discharges were under a consent to discharge agreement, however; from 1964 to 1973 the Norwich City Council consented to the emission of 2000 kg Hg a<sup>-1</sup> to the sewer. The consent was reduced in the light of research published in the mid 1970s that highlighted the potential health effects of Hg and its complexes with alkyl and aromatic groups (Smith and Smith, 1975) and currently stands at 48 kg a<sup>-1</sup>.

The surficial sediment survey conducted by Imperial College in 1986 confirmed that a Hg contamination plume originating at Whitlingham STW outfall stretched 3 km upstream and 12 km downstream. Mercury concentrations ranged from 0.05-32.9 mg kg<sup>-1</sup> (Bubb *et al.*, 1991a).

For the most part sediment in the upper reaches of the river exceeded the Netherlands recommended action level of 10 mg kg<sup>-1</sup> for Hg in sediments (Visser, 1994). Methylmercury (MeHg), a more toxic form of Hg produced by microbial and abiotic activity, was also found in the sediments and gave further cause for concern as it is known to bioaccumulate in fish and other biota and can be biomagnified up foodchains and may be the form in which the contaminated eels accumulate Hg. Copper (Cu) was found to be a major sedimentary co-pollutant with lesser amounts of cadmium, lead and zinc present (Bubb *et al.*, 1991a;b;c).

As part of the initial survey in 1986 a mass-balance was calculated to account for mercury discharged to the river (Imperial College, 1987). It found that 50% of the accountable Hg discharged was deposited within the Broads with the rest deposited in the R. Yare itself. However, this was only 50% of the Hg assumed to have been discharged based on discharge rates supplied by the then Anglian Water Authority. The rest of the mercury is assumed to have been lost by natural processes. Also as part of that survey a finite element model was developed to try to predict mercury deposition within compartments of the R. Yare and to predict the expected bed concentrations in ten years time. The model predicts a broad area of contamination (a 16 km stretch) with levels of mercury decreasing very slowly in the bed sediments (Chow, 1986).

Subsequent to the initial 1986 survey eight further annual surficial sediment surveys have been conducted each summer by Imperial College which have followed the temporal and spatial changes in the Hg, MeHg and Cu contamination. The trends observed and their possible causes are examined in this report. Apart from the annual monitoring of the main river, investigations have been carried out into the contamination of the broads and the behaviour of Hg and MeHg within these low energy systems (Imperial College, 1986; 1990; 1991; 1992). Annual monitoring of eel and roach populations from Rockland Dyke, within the area of highest Hg contamination, have been conducted since 1993 whilst earlier fish surveys have also been pooled and critically examined for trends in contamination in this report.

Comparison has been made between Hg observed in fish from the R. Yare and fish taken from Ormesby Broad, an uncontaminated Broad located to the north of the R. Yare. The role of atmospheric deposition on Hg concentrations observed in the fish and on mercury methylation has been examined and is discussed.

Dredging and subsequent disposal of contaminated sediments has been mooted as a remedial option for many years ('Tons of poison mud: Yare may be dredged', EDP, 4/3/1986) and rumours of expensive remediation by dredging again appeared in 1993

('Yare mercury pollution presents costly problem', EDP, 1/12/1993). Dredging is sometimes required to maintain navigation within the main river channel although deep draught ships seldom enter Norwich port today. In the past two years research conducted by Imperial College has thus concentrated on the possible effects that dredging of Hg and Cu contaminated sediments may have on remediation of the contaminated zone and especially water quality in the light of EEC Dangerous Substances Directive limits of 1  $\mu$ g l<sup>-1</sup> Hg and 26  $\mu$ g l<sup>-1</sup> Cu (Council of European Communities, 1976). Other impacts of dredging, including increases in surficial contaminant loadings brought about by re-exposure of highly contaminated sediments buried at depth and the possible subsequent effects on biota, have been examined. The effects of seasonal changes in redox potential, dissolved oxygen and temperature, and the possible consequences of saline water intrusions within the tidal R. Yare on the release of Hg and Cu from dredged sediments, have also been investigated in the Imperial College laboratories to better understand the potential outcomes of this remediation option.

Linked with the dredging of contaminated sediments is the requirement for its disposal at a suitable site. In the past dredged sediments were often dumped at sea, but with new legislation designed to reduce inputs of priority pollutants to the North Sea by 50-70% by 1995 (based on 1985 levels) this is no longer considered a viable option. Inland disposal thus has to be considered. A site designated and licenced by the Norwich County Council (licence no. NFK/LS/007/0) has been in operation since 1986 at Griffin Lane, Thorpe (grid reference TG 285 081) on which dredgings from the contaminated reach must be placed. However, dredging has not generally been permitted within the contaminated area from Trowse (TG 244 068) to Hassingham (TG 360 045) until the impact of dredging on Hg and Cu contamination has been more thoroughly investigated.

The possible environmental impact of disposal of Hg and Cu contaminated sediments at the Griffin Lane landfill has been investigated. As freshly dredged sediments are exposed to dry, oxic conditions, changes in the mobility of contaminants may be expected; Hg may be volatilised by microbially mediated reactions whilst Hg and Cu may be leached from dumped sediment and transported via run-off or percolation into the surrounding environment. Biotic pathways for these metals may also exist on the landfill via plant and animal uptake. The hypothesis that Hg and Cu may be mobilised and bioconcentrated has been investigated in order to provide data useful to the NRA in developing a management plan for the contaminated sediments.

## 2. OBJECTIVES

- 1. To present the results of the annual monitoring surveys conducted between 1992 and 1995 of bottom sediments of the R. Yare for Hg, MeHg and Cu contamination.
- 2. To collate and summarise all data for the annual sediment surveys carried out by Imperial College on the R. Yare from 1986-1995 and to present an overall view of the trends observed in the behaviour of the Hg and Cu pollutants to date in relation to relevant factors including inputs, hydrology, physicochemistry and anthropogenic effects such as bridge building and dredging.
- 3. To present the results of the annual fish survey of the R. Yare for Hg and MeHg contamination of eel and roach flesh for 1992 to 1994. To determine background levels of Hg in fish by examination of fish from nearby Ormesby Broad.
- 4. To collate and summarise all data available from fish surveys conducted from 1985 to the present and to interpret the trends observed on the basis of changes observed in the contamination of bottom sediments and other relevant factors.
- 5. To assess the effects that dredging of R. Yare Hg and Cu contaminated sediments may have on water quality, and the effects of seasonality and saline water intrusions on water quality at potential dredge sites. Laboratory experiments and field monitoring of a dredging operation at Thorpe St Andrews are reported.
- 6. To assess the potential abiotic and biotic pathways of Hg and Cu from R. Yare dredge spoil dumped on the upland disposal site at Griffin Lane, Norwich, by plant and earthworm bioassays and the use of laboratory based studies of the effects of sediment dessication and oxidation.
- 7. To make recommendations on the basis of the results reported to help the NRA in determining short and long-term management plans for the Hg and Cu contaminated reach of the R. Yare.

### 3. MATERIALS AND METHODS

The River Yare and its main tributaries, the R. Wensum and R. Tas, drain an area of 1415 km<sup>2</sup> of a low-lying plateau in East Anglia (National Rivers Authority, 1994), flowing eastwards into the North Sea at Great Yarmouth (Figure 1).

The shallow bed gradient of approximately 3 cm drop per km and the moderating influence of the Broads give the Yare a stable flow regime with a mean daily flow of 6.74 m<sup>3</sup> s<sup>-1</sup> (NRA). The river is tidal downstream of Norwich with variations in height of up to 1 m, but the saline interface generally occurs at Cantley although it can periodically extend inland as far as Brundall (Figure 1). Conductivity readings in the upstream reach are in the range 540-950  $\mu$ S cm<sup>2</sup> and exceed 21 000  $\mu$ S cm<sup>2</sup> in the estuarine zone. Dissolved oxygen concentrations vary seasonally and the water is generally slightly alkaline (pH 7.1-7.9).

The geology of the surrounding area comprises Cretaceous chalk covered by mixed drift, boulder clays and fluvo-glacial sand and gravel (Yare Catchment Report, 1994). The Broads (Rockland, Wheatfen and Surlingham amongst others) are the result of the excavation by man of the Brushwood Peats in the alluvial plain around 1100-1300 AD. These small water-filled depressions or broads are now rapidly filling with soft uncompacted sediment at a rate of more than 1 cm a<sup>-1</sup> (Garrard, 1984). Today the network of rivers and broads which make up the Norfolk Broads support an extensive tourist industry based on boating and angling.

# 3.1 Assessment of the spatial distribution of mercury, methylmercury and copper in the River Yare surficial sediments

Surveys of the surficial sediments of the R. Yare have been conducted every summer since 1986 with the exception of 1988. The sampling strategies employed have varied slightly, especially since the initial surveys, but changes have not affected the potential for obtaining statistically significant information related to year on year comparisons of metal data from the data base compiled since 1986 (Bubb *et al.*, 1991c, Imperial College, 1992). In 1995, three sediment cores were collected from near the STW, Rockland Broad and Cantley in order to assess current depth profiles of the contamination (Figure 1).

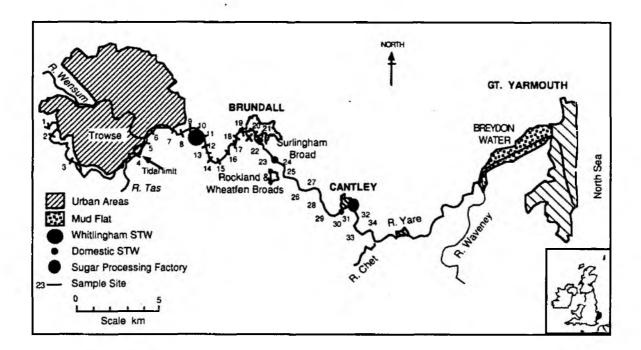


Figure 1. Map of R. Yare showing locations of sampling points.

#### 3.1.1 Annual monitoring of the River Yare surficial sediments

The sampling strategy designed for the annual surveys consisted of a set of transects from which bottom sediment samples were taken. The transect sites were fixed by alignment with distinctive landmarks on each bank and a centrally based buoy. In the initial surveys 5 samples were taken per transect, but this was reduced to 3 per transect (north bank, mid-channel and south bank) for later surveys.

The original bottom sediment survey was conducted in May 1986 and covered a 16 km reach of the R. Yare, from the Norwich New Cut (grid reference TG 254 081) approximately 3.35 km upstream of Whitlingham STW outfall to Rockland Broad (TG 349 045) some 12 km downstream (Table 1). This survey identified the metal contamination zone as being centred on Whitlingham STW outfall, but failed to encapsulate the downstream tailing of contaminants.

The second survey in 1987 was therefore designed to determine the full spatial extent of the metal contamination by including the downstream reach. The survey was from Colney (TG 179 079) at the head of the river to Breydon Water (TG 491 068) at its entry into the North Sea and covered 52 km. One sample was taken at each of transects 1-26, allowing for the determination of upstream background metal concentrations and the re-assessment of the contaminative state of the 1986 survey area. Transects 27-48

were laid at approximately 1 km intervals and 5 sediment samples taken from each transect.

Subsequent surveys have used the transects as defined in 1987, but have generally not gone above transect 4 (Trowse) or beyond transect 34 (above the confluence with the R Chet) as metal concentrations approach background levels in these areas. The 1995 survey encompassed transects 4-34. The sampling strategies employed in each survey are summarised in Table 1.

Year	Dates	Transect nos	Reach (km)	Samples/transect
1986	7-14 May	7-26	16	5
1987	10-24 Oct	1-26	30	1
		27-48	22	5
1989	16-18 July	4-46	40	1
1990	16-19 July	4-30	26	3
1991	3-7 June	4-30	26	3
1992	29 June - 3 July	1-48	52	3
1993	5-7 July	4-34	30	3
1994	19-21 July	4-34	30	3
1 <b>9</b> 95	3-5 July	4-34	30	3

 Table 1.
 River Yare sampling strategy for surficial sediments, 1986-1995.

#### 3.1.2 Sediment and Water Collection at Ormesby Broad

Ormesby Broad is located northeast of Norwich and is a shallow land-locked lake draining into the River Bure (Figure 2). Using a dinghy supplied by the NRA, bed sediments were sampled at 8 locations with an Ekman grab (Figure 2). Sediment samples were treated in the same manner as described for the R. Yare.

Water in the River Yare is monitored monthly by the EA for mercury. However, no mercury data existed for the water in Ormesby Broad, thus water samples from the Broad were collected at the same time as sediment sampling. Water samples were collected immediately prior to sampling of the bottom sediments. Sample collection was done using an acid-washed teflon bailer. Collected water was immediately transferred to acid washed glass bottles and preserved by acidification with Aristar nitric acid. Samples were then placed in a cooler which had not been used previously for transporting Hg contaminated samples for transport to the laboratory.

#### 3.1.3 Sample collection and processing

Bottom sediment samples were obtained with a stainless steel Burge-Ekman grab. Care was taken to minimise contamination by collecting material from the inner part of the

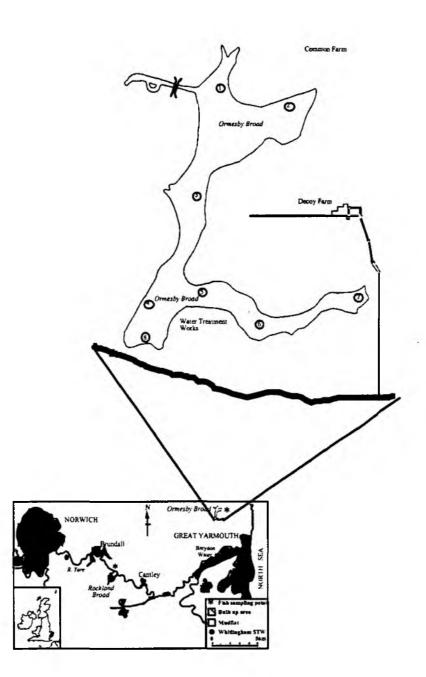


Figure 2. Sampling locations at Ormesby Broad.

sample only. Sediments comprising the top 2 cm of each grab were taken to represent surficial bottom sediments. Samples were placed in air tight 250 ml high density polythene bottles which were filled to the rim to exclude air, preventing sample oxidation. Temperature, redox and pH readings were determined immediately on collection using a portable probe (ELE International, Hemel Hempstead, UK). The sediment appearance and texture were also logged.

In the laboratory the samples were sieved through a 1mm sieve to remove coarse

particles and sub-divided into samples for metal (Hg and Cu), methylmercury and physicochemical analysis. Total metal samples were preserved by the addition of 1% (w/v) HNO<sub>3</sub> (Aristar, BDH) and 0.05%  $K_2Cr_2O_7$  (AnalaR, BDH) according to recommended methods (Comm. Anal. Qual. Control, 1984). Samples for methylmercury analysis were frozen on the day of collection.

#### 3.2 Annual monitoring of fish flesh taken from the River Yare

The monitoring of fish in the R. Yare allows an assessment of the biological availability of Hg contained within the sediment compartment. From 1985-1991 some surveys of fish flesh taken from the river were undertaken, but no clear strategy was developed as to the species sampled, sample size, sample age distribution or the time of year and location of sampling, making interpretation of apparent trends difficult.

**Table 2.**The suitability of eels and roach as survey specimens.

Eels	Roach	
•Abundant and destined for human consumption	•Abundant	
•High fat content (>30%) suitable for MeHg	•Lower fat content allowing comparison with eels	
retention and accumulation	of effect of fat content on MeHg accumulation	
•Carnivorous (food chain biomagnification	•Omnivorous, live in water column, sift large	
possible), forage and live in mud containing Hg	quantities of bottom sediment (to depths of 5 cm)	
and MeHg	containing Hg and MeHg	
•Have long intestines with long digestion times	•Have long intestines for efficient adsorption of	
and consequent implications for intestinal	food and thus Hg and MeHg. Roach are mud	
methylation of mercury	swallowers and process large volumes of sediment	
- <b>z</b> -	which contain the contaminants of interest	

A systematic sampling policy was thus drawn up for the surveys commencing from 1993 to provide a comprehensive data set of both total and methylmercury in fish flesh taken from the river. Eel (*Anguilla anguilla*) and roach (*Rutilus rutilus*) were selected as the most suitable species as they are, amongst other factors, abundant and, in the case of eels, commercially important (Table 2).

Fish growth rate and size may influence body burdens of Hg (Richman *et al.*, 1988; Hakanson, 1984) and so ageing, sex, weighing and sizing of all specimens trapped was included in the sampling protocol. Trapping of survey specimens was undertaken by the NRA over 2 days in July to coincide with the annual surficial sediment survey. Fyke nets (bag nets) were used overnight at Rockland Dyke which is well within the Hg enrichment zone, although it was not possible to identify whether the fish had inhabited the contamination zone for any period of time before trapping.

Representative samples of the population were considered to be achieved with 25 or more specimens per species. The trapped fish were killed and examined fresh for recording weight and length. The NRA then dissected 3 approximately 5 g pieces of axial muscle from each specimen which were deep frozen for transport to Imperial College. Ageing of the fish was also undertaken by the NRA. For roach, ageing was by examination of scales and opercular (gill cover) bones and otoliths were used for eels.

The fish survey for 1994 was undertaken on 13 and 14 July 1994 according to the sampling protocol described above. Data on concentrations of Hg in R. Yare fish for 1991, 1989, 1986, 1985 and 1971 were supplied by the NRA laboratories.

#### 3.2.1 Examination of fish flesh collected from Ormesby Broad

Sampling of fish from Ormesby Broad, was undertaken during a biomanipulation programme in May 1995 by the then National Rivers Authority, now Environment Agency (EA). Roach were caught by electrofishing or gill netting and eels were trapped with fyke nets. The trapped fish were killed and examined fresh for recording weight and length in the biological laboratory of the EA. Dissection of axial muscle from each specimen was undertaken in the laboratory for deep freezing prior to analysis. As with fish collected from the R. Yare ageing and sexing of the fish were conducted by the EA.

# 3.3 Monitoring and laboratory prediction of the effects of dredging River Yare sediments on water quality

Determination of the effects of sediment dredging on river water quality was undertaken by conducting several different simulation elutriate tests on R. Yare sediment and water in the laboratory (Edwards *et al.*, 1995). The likely concentrations of Hg and Cu to be expected in the water column during a real dredging operation were determined and the effects of Fe and Mn and physicochemical parameters such as pH, redox, dissolved oxygen (DO), temperature and total organic carbon (TOC) on the release of Hg and Cu from the sediments were investigated. The effects of seasonality and salinity on heavy metal release were also considered. These results were compared to field monitoring of the water quality near a dredging operation carried out at Thorpe St Andrews next to Norwich New Cut (grid reference TG 254 081) on 11 November 1993.

#### 3.3.1 Survey area and preliminary sampling

A stretch of the R. Yare at Thorpe St Andrews required navigational dredging (Figure 3) and thus a preliminary survey of the proposed dredge area was undertaken to determine the depth and concentrations of Hg and Cu contamination within the bottom sediments. Sediment core samples were taken at 5 locations (Figure 3) using a simple coring device consisting of a 1.8 m long piece of plastic drainpipe (10 cm OD) split over half its length to allow core extrusion. During use the split section was sealed together by tape. The sediment was held in place within the corer by the suction generated by a bung inserted into the lid once the corer was pushed into the sediment. Cores were subdivided into 2.5 cm intervals for the top 10 cm, then at 5 cm intervals to the base of the core. Redox potential, pH and temperature (ELE, Hemel Hempstead) were determined *in situ*. Sediment samples for total metal, methylmercury and other physicochemical parameters were preserved and stored as previously described.

#### 3.3.2 Monitoring of the dredging operation

Dredging was carried out for 8 hours on 11 November 1993 using a grab dredger. Approximately 120 tonnes of dredged sediment was removed and transferred by barge to the Griffin Lane landfill. Water monitoring occurred at 3 sampling stations positioned in mid-channel (Figure 3). Background water samples were collected from each station the day before dredging commenced and then for 50 h from the start of the dredging operation. The samples were collected 1 m below the water surface in acid leached plastic sample containers by Casella sampler and immediately sealed with exclusion of air.

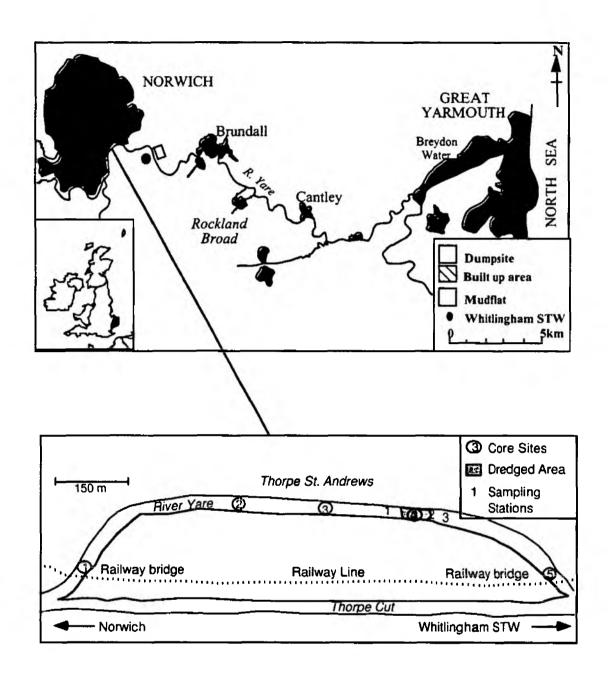


Figure 3. Location of cores, the dredging operation and water sampling points at Thorpe St. Andrews.

Samples for total metal analysis were preserved with 1 % (v/v) HNO<sub>3</sub> (AristaR, BDH, Lutterworth, UK). Dissolved metal samples were syringe filtered through acid leached 0.45 µm pore-size cellulose acetate filter paper (Whatman, Walkerburn, UK) prior to preservation. Filtration and sample blanks were prepared periodically. Total organic carbon (TOC) and methylmercury samples were frozen. Sonde (Grant YSI 3815) automatic samplers positioned 1 m below the water surface were used to record water temperature, DO concentration, pH, conductivity, salinity and turbidity for each sampling interval.

#### 3.3.3 Elutriate tests

Bulk sediment required for elutriate tests was collected from Thorpe St Andrews and Rockland Broad by coring up to a depth of 1 m and immediately placing the sediment in polythene bags with exclusion of headspace air. Overlying water samples were collected in plastic canisters approximately 50 cm below the water surface and all samples were stored at the sampling temperature in the dark.

Elutriate tests were based on a method proposed by the Environmental Laboratory of the U.S. Army Engineer Waterways Experiment Station, Vicksburg, U.S.A. (1985) with some modifications to take account of the requirements of this work; these are incorporated in the method described. Appropriate volumes of sediment and overlying water were thoroughly mixed to give a final sediment/water concentration of 50 g l<sup>-1</sup> on a dry weight basis and placed in a 4 l Pyrex glass cylinder (Radleys, Saffron Walden, UK; 45 cm x 4.4 cm ID). The density of the sediment was pre-determined by oven drying a known volume at 105 °C and weighing the dried sediment.

The slurry was aerated for 1 h to ensure oxidising conditions were present in the supernatant during the subsequent settling phase and to simulate sediment disturbance during a dredging operation. This was done by bubbling air vigorously through a glass tube inserted to the bottom of the cylinder which ensured good agitation of the mixture. The redox potential of the slurry was monitored from time to time to ensure oxidising conditions prevailed. The elutriate systems were maintained at the temperature measured during initial field sampling (an important factor in the seasonal experiments).

The glass tube was removed and quiescent settling allowed to occur. After a short time an interface becomes apparent between the supernatant with low concentration of total suspended solids and the more concentrated settled material. Samples of the supernatant were extracted at various intervals up to a maximum of 48 h after settling had started, instead of the single extraction system used in the Corp of Engineers method. The supernatant was removed at a point midway between the water surface and the interface using plastic tubing attached to a 60 ml plastic syringe, care being taken not to resuspend settled matter. Samples were treated and physicochemical parameters monitored as described for the dredging operation. For experiments involving salinity effects the water was amended with 30 g l<sup>-1</sup> of sodium chloride to give a salinity level equivalent to the maximum level of 30 g solids per kg sea water, measured on 21/2/1993 at Cantley during a saline intrusion (NRA pers. comm., 1993) For experiments involving the effects of seasonality the major differences were found to be temperature and initial redox potential of the sediment. The temperature measured in the field was reproduced in the laboratory and as oxidising conditions are ensured in the aeration phase of the experiment no further changes to the test were made. The elutriate test method is summarised in Figure 4.

#### 3.4 The fate of heavy metals in dredged sediments disposed on an upland landfill

Freshly dredged sediment dumped on an upland disposal site undergoes a number of physical and chemical changes including drying out and oxidation which will affect the behaviour of metals contained within the sediment. In order to determine the pathways for the Hg and Cu contained within R. Yare sediment a time series experiment consisting of columns packed with freshly dredged sediment was used to simulate the effects of exposing this sediment to dry oxic conditions equivalent to those encountered on the landfill.

#### 3.4.1 Experimental design and apparatus

The hypothesis tested in this study was that the major pathways for release of Hg and Cu from freshly dredged and dumped sediment would, in the initial stages, be leaching from the wet sediment and, as drying out occurred, volatilisation of mercury as Hg<sup> $\circ$ </sup> and dimethylmercury would occur. A column was thus designed to contain freshly dredged sediment in a closed system which would enable the monitoring of these two potential pathways as drying out of the sediment occurred over a period of 10 weeks. A total of 12 columns were set up and dismantled at set times over 70 days. Replicate columns were included in the protocol to establish whether trends observed were reproducible. Rockland Broad was chosen as the site for sediment collection as it was known to contain up to 10 mg kg<sup>-1</sup> Hg and Cu at 100 mg kg<sup>-1</sup>.

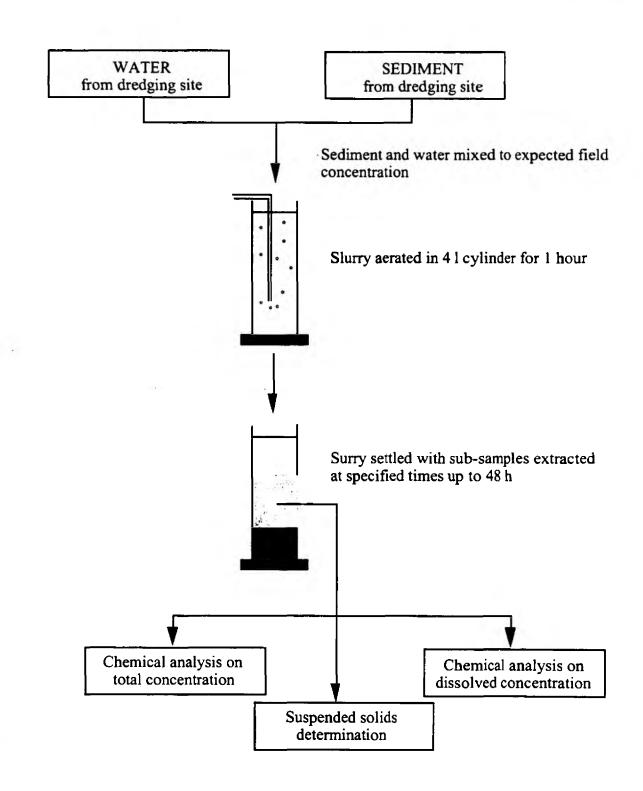


Figure 4. Flow diagram of modified elutriate test.

The columns consisted of clear acrylic 'Perspex' tubes (500 mm long, 150 mm OD, 3 mm wall thickness) (VT plastics, Mitcham, UK) sealed at both ends with 3 mm thickacrylic discs (Figure 5) A hole was drilled into the top disc and into the side of each column to allow air to be pumped over the surface of the dredge spoil to collect any volatilised Hg species (Hg<sup>•</sup> or dimethylmercury) released. The air was pumped into the top of the column after passing through a  $0.2 \mu m$  pore size cellulose nitrate filter

(Whatman, Walkerburn, UK) to exclude bacteria and dreschel bottles containing acidified potassium permanganate solution (to remove any Hg) and a silica gel desiccant to remove water vapour. The air flow rate was not critical, but a steady flow of 1 bubble through the trap solutions every 1 to 2 s was considered to be adequate.

The air left the column via the side port (Figure 5) and was bubbled through 15 ml of Hg trap solution containing 5% 6M HNO<sub>3</sub>, (AnalaR, BDH) 5% 9M H<sub>2</sub>SO<sub>4</sub> (AnalaR, BDH<sub>3</sub> and 15 drops of 1% KMNO<sub>4</sub> (Spectrosol, low in Hg, BDH) in a borosilicate test-tube to oxidise any released Hg species to Hg<sup>2+</sup> (Rapsomanikis, 1989) The air finally entered a second test-tube of Hg trap solution to ensure all Hg was trapped before the air was released back into the laboratory. All the Hg trap solutions were changed each time a column was dismantled and the amounts of Hg released measured. The tubing conducting the air to the columns was of silicone rubber (5 mm bore) and the tubing carrying the air to the Hg trap solutions was Teflon Nalgene 890 (4.8 mm bore) for trace metal analysis. Stoppers for connecting the tubing to the column and test-tubes were silicone rubber. A hole was also drilled in the bottom disc to allow collection of leachate in a 100 ml polypropylene vessel. Gauze was fitted over the opening of the vessel to prevent particulates being collected. The dreschel bottles of silica gel and Hg trap solution were changed daily and weekly, respectively.

#### 3.4.2 Sediment collection and column packing

Sediment was collected from Rockland Broad on 3 May 1994 using the corer previously described (Section 3.3.3) to a depth of approximately 1 m to simulate the likely depth to which a dredging operation would remove sediment. The sediment was stored in polythene bags sealed to exclude air and returned to the laboratory where it was placed in a cold room at  $17 \pm 1$  °C. Within 24 h of collection the sediment sub- samples were thoroughly mixed in a large plastic drum to achieve an homogenous sediment before being packed into columns.

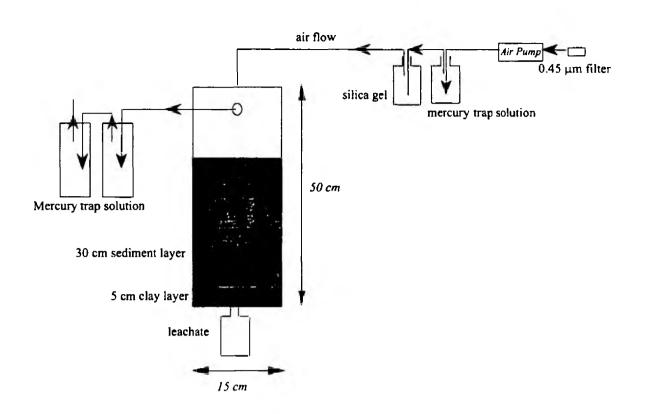


Figure 5. Column design for sediment disposal experiments.

Clay-like material collected from the bank of the R. Yare, mixed with London clay (supplied by Soil Science Section, Civil Engineering Dept, Imperial College), was used to line the bases of the columns to simulate the effect a clay-lined landfill would have on the leaching ability of the metal contaminants. The homogenised sediment was then packed into the columns to a depth of 30 cm. Care was taken to maintain packing consistency between columns and to ensure there were no air pockets present. Once the columns were packed and sealed they were weighed to determine the total mass of sediment used in each column. Columns were then covered in silver foil to prevent any photolytic reactions and placed in a cold room at  $17 \pm 1$  °C. A diumal cycle of 10-12 h fluorescent-tube lighting followed by darkness was maintained throughout the experiment. Sub samples of sediment and clay were taken for analysis of Hg, Cu, Fe and Mn; methylmercury, total organic carbon, anions and total and volatile solids.

#### 3.4.3 Dismantling of columns

The 12 identical columns which were packed and allowed to dry out over a ten week period were dismantled, in some cases with a duplicate, at 8 specified time intervals (Table 3). Each column was extruded by removing the end discs and using an acrylic plunger to maintain the depth profile. Samples were taken at 2.5 cm intervals for the first 10 cm and then at 5 cm intervals for the remainder of the column. As the experiment progressed a lighter surface layer of sediment (approx 1 cm thick) developed on the columns; during later extrusions this was sampled separately to determine the difference between this layer and the remainder of the first 2.5 cm layer. Three sub-samples were taken at each depth and placed in acid washed polypropylene sample bottles. Samples for total metals analysis were preserved with  $1 \% (w/v) \text{ HNO}_3$  (AnalaR, BDH) while MeHg samples were frozen. Volatile solids, total solids, total organic carbon and anion determinations were conducted on a sample stored at 3 °C in a refrigerator.

<b>D</b> .		
Date	Days into experiment	Columns extruded
8 May	0	0
10 May	3	1
13 May	7	2
20 May	14	1
31 May	25	2
9 June	34	1
20 June	45	2
29 June	54	1
15 July	70	2

**Table 3.**Timetable for column dismantling.

#### 3.5 Assessment of the biological impact of dredged material

Dredge spoil dumped on an upland disposal site weathers and after a period of time land plants and animals are able to colonise and inhabit the spoil. This is the case for the sediment dredged from the R. Yare and dumped on the Griffin Lane landfill (on the opposite bank of the river from Whitlingham STW) over a number of years. In order to assess the potential uptake of Hg and Cu in the weathered spoil by resident biota two sets of experiments were conducted. The earthworm *Eisenia fetida* was grown on contaminated dredge spoil in the laboratory while the plant species *Urtica dioica* (stinging nettle) and *Budleja davidii* (butterfly bush) growing on contaminated spoil at the landfill were collected and analysed (Edwards *et al.*, 1996 a).

#### 3.5.1 Heavy metal uptake by the earthworm Eisenia fetida

The earthworm *E. fetida* was used to evaluate the potential availability of Hg and Cu from the sediment disposed at the Griffin Lane landfill as it is has shown a high level of sensitivity as a bioassay animal in its ability to bioaccumulate various heavy metals from a variety of contaminated sources (Rhett *et al.*, 1988). It was also chosen in preference to indigenous species to avoid identification problems. Worms were

purchased from a local angling shop, rinsed to remove any soil adhering to their bodies and placed on wet filter paper for 24 h to purge their gut contents. To avoid coprophagy (ingestion of faeces) the filter paper was changed regularly. The worms were then counted, weighed and divided into 3 groups: a group to inhabit Hg and Cu contaminated weathered dredge spoil; a group to live in uncontaminated soil and a control group of worms which was immediately prepared for metal determination (Table 4).

Table 4.	The distribution and weights of E. fetida used for each sample group	э.

Group	No. of E. fetida	Weight (g)
Contaminated	60	103.2
Uncontaminated	60	92.1
Time zero	27	<b>39.9</b>

The Hg and Cu contaminated dredge spoil was collected from the Griffin Lane landfill on 3 May 1994 in an area where sediment had been dumped from the dredging operation at Thorpe St Andrews (described in Section 3.3) in November 1993. The spoil was collected in a W sampling pattern to a depth of 30 cm (Marquenie and Simmers, 1988) and appeared weathered and dry. Uncontaminated soil was similarly collected from an area adjacent to the landfill.

Approximately 25 kg of the respective soils were prepared by sieving to remove stones and root debris and placed in 0.38 m x 0.33 m x 0.2 m plastic crates. The worms for each soil were introduced on the surface and allowed to burrow at their own pace to determine whether any were dead or unhealthy.

The worms were exposed to the soils for 28 days (Rhett *et al.*, 1988) at a temperature of  $17 \pm 1$  °C. Soil moisture was maintained by addition of known volumes of distilled water and the crates were covered at night to prevent worms attempting to forage on the surface outside of the crates and thus dying. At the end of the 28 d experiment the worms were sorted from the soil, rinsed in distilled water and again left to purge their gut contents before weighing. They were subsequently frozen and prepared for Hg, Cu, Fe and Mn analysis (Bull *et al.*, 1977). The worms within each group were combined into samples of 4 worms to provide sufficient body mass for digestion (Helmke *et al.*, 1979). This yielded 11 samples for the control group, 8 samples for the uncontaminated group and 15 samples of soil were taken for determination of pH, redox potential, total organic carbon and Hg, Cu, Fe and Mn at the start and on completion of the experiment.

# 3.5.2 Heavy metal uptake by the plants *Urtica dioica* (stinging nettle) and *Budleja davidii* (butterfly bush)

Plant growth is lush on the Griffin Lane landfill, but the diversity is limited, possibly to under 10 plant species (a complete survey was not considered possible under the overgrown conditions prevalent on the site), with the majority of the biomass being made up of U. dioica and B. davidii. For this reason and because these 2 species were also available on an adjacent uncontaminated control site a sampling strategy was devised to assess whether plants growing in the weathered dredge spoil accumulated any more Hg and Cu in their leaves than those growing on the uncontaminated site under the prevailing field conditions. The predominant plant species across the landfill was the common nettle U. dioica, making it suitable for comparison of plant metal uptake from the contaminated dredge spoil and uncontaminated river bank soil which makes up the remainder of the site.

Soil and nettles were collected in 2 consecutive years (June 1994 and May 1995). In the first year, 1 site on the dredge heap and 1 site outside the perimeter of the landfill were sampled (starred (\*) on Figure 6).

For the initial study plants growing on the contaminated dredge spoil were collected within a 2 m x 2 m quadrat. Samples were collected so as to be representative of the population and surface trace element contamination was minimised during collection by holding the plant in one plastic-gloved hand and cutting stems at least 10 cm above soil level with stainless steel scissors (Berrow, 1988). Twenty five *U. dioica* plants and four *B. davidii* bushes were sampled for stems and leaves and placed in polythene bags with exclusion of air. A similar protocol was followed for plants sampled from the uncontaminated soil site. Soil samples were collected from each quadrat following a W-shaped transect and analysed *in situ* for pH and redox potential and for total organic carbon and the metals Hg, Cu, Fe and Mn in the laboratory. Iron and Mn are generally critically involved in the binding of other heavy metals (like Hg and Cu) and are non-contaminating and ubiquitous at the sites considered and thus were determined for to provide information on general uptake patterns by the biota on each site.

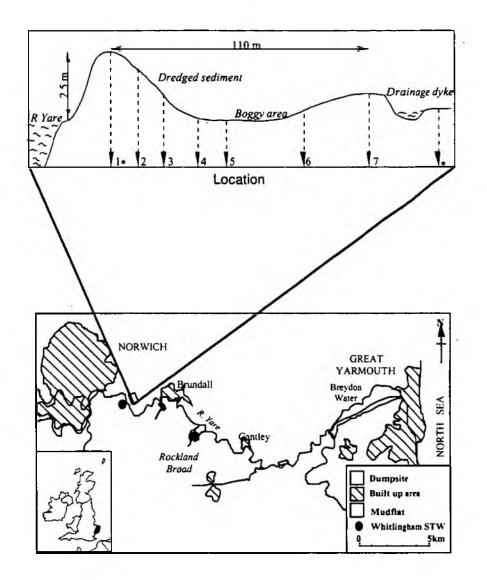


Figure 6. Sampling locations of dredge sediment landfill on River Yare.

In the second year a transect across the dredge disposal site was sampled at 7 locations (Figure 6). Whole plants were removed from the soil by spade and separated into aerial plant and roots with secateurs before being sealed in polythene bags. Soils for sequential extraction were taken from the top 5 cm of the horizon as the nettles were shallow rooted. In the laboratory aerial plants and roots were washed to remove surficial deposits, dried at 40 °C for 48 h and milled to a homogenous powder.

The accumulation of Hg and Cu in the leaves was considered to be of most concern because of the dependence of grazers such as rabbits, voles and various insect species with the resulting potential for bioconcentration of contaminants in the food chain. The plant samples were dried at 40 °C for 4 days and the leaves used for digestion and analysis, the stems were discarded.

#### 3.6 Analytical methods

The following analytical procedures were carried out using chemicals of Analar grade (unless otherwise stated) and Milli-Q water at all times. All of the glassware and plasticware was thoroughly washed and soaked first in 5% Decon 90 solution then rinsed 3 times with distilled water before being soaked in 10% general purpose grade HNO<sub>3</sub> overnight. It was then rinsed again 3 times and left to air dry before use. All volumetric glassware was A-grade and of borosilicate glass.

#### 3.6.1 Sample preparation for metal determination

#### 3.6.1.1 Sediment and water sample preparation

Sediment samples for total metal analysis were thoroughly homogenised and screened through a 2 mm diameter sieve to remove plant debris and stones before weighing (US Geological Survey, 1979; Imperial College, 1987). Before 1992 samples were digested in aqua regia (1:3 HNO<sub>3</sub>:HCl) (BDH, Lutterworth, UK) on a hot plate according to the procedure recommended by Anglian Water Authority (Imperial College, 1987). Since 1992 a Milestone 1200 Mega microwave digester (Milestone, Bergamo, Italy) has been used which utilises a carousel of 10 pressurised digestion bombs.

Table 5.	Digestion	matrices	for sample	digestions.

Sample	Digestion matrix*
Sediment	2 ml HNO <sub>3</sub> 6 ml HCl & 1 ml water
Fish	$2 \text{ ml H}_2\text{O}_2$ 7 ml HNO <sub>3</sub> & 1 ml water
Earthworm	5 ml HNO <sub>3</sub> $0.5$ ml H <sub>2</sub> O <sub>2</sub> & 1 ml water
Plant	5 ml HNO <sub>3</sub> 0.3 ml H <sub>2</sub> O <sub>2</sub> & 1 ml water

	Time (min)			
Power (W)	Sediment	<u> </u>	Earthworms	Plants
250	1	2	2	1
0	1	2	2	2
250	5	2	2	5
0	1	2	2	•
250	-	3	3	•
0	-	2	2	-
400	5	5	5	5
0	2	2	2	-
500	-	5	10	-
650	5	-	-	-
Vent	5	10	15	ç

**Table 6.** Microwave programmes for sample digestions.

In 1992 a subset of samples were prepared using both digestion procedures and the results found to be in good agreement (Imperial College, 1992). The wet weight equivalent of 1 g dry sediment was accurately weighed and digested in duplicate using aqua regia (Table 5) with a microwave protocol recommended by the manufacturers (Table 6). Digested samples were cooled, carefully decanted into 50 ml volumetric flasks and made up to the mark. Digestion blanks and spiked samples were also prepared to monitor possible contamination and loss of Hg from the samples. Water samples were cold digested with a minimum of aqua regia (Aristar, BDH, Lutterworth, UK) to prevent any contamination.

#### 3.6.1.2 Fish, earthworm and plant sample preparation

Digestion procedures for fish, earthworm and plant samples followed those recommended by the microwave manufacturer and are outlined in Table 5 and Table 6. Generally, the equivalent of 0.5-1 g dry weight was accurately weighed and reacted with the digestion matrix for 30 min before the microwave procedure was followed so that possible violent reactions with organic matter would be reduced. Fish and earthworm samples were lightly macerated with a glass rod to aid the digestion procedure. In the case of some eel samples it was necessary to repeat the digestion procedure in Table 6 to ensure complete breakdown of fatty tissue.

#### 3.6.2 Total mercury determination

Total Hg determinations were carried out by cold vapour flow injection using a Perkin-Elmer 5100 PC atomic absorption spectrophotometer (AAS) (Perkin-Elmer, Beaconsfield, UK) linked to an AS-90 autosampler and a FIAS-200 flow injection system. Following the manufacturers recommendations, 10% HCl (Spectrosol, BDH) was used as the carrier solution and 0.2% NaBH<sub>4</sub> (Spectrosol, BDH) in 0.05% NaOH (AnalaR, BDH) as the reductant. The NaBH<sub>4</sub> was made fresh on the day of use and was filtered through a 0.45 µm pore-size cellulose acetate filter (Whatman, Walkerburn, UK) to remove any undissolved reagent. Anti-foaming agent (Dow Corning Silicone DC anti-foaming emulsion) was added to the NaBH<sub>4</sub> to minimise foaming in the chemifold and carry over to the quartz cell. A few drops of 5% (w/v) KMnO<sub>4</sub> (Spectrosol, low in Hg, BDH) were added to standards and samples to prevent rapid reduction and loss of Hg. All standards were made from 1000 mg l<sup>-1</sup> HgNO<sub>3</sub> (Spectrosol, BDH) in 10% HCl. The system was calibrated with standards suitable for the samples being determined. For total Hg in water samples gold amalgamation (Perkin-Elmer Amalgam System) was used to improve sensitivity and reproducibility of detection. Argon (High Purity, BOC, UK) was used as the carrier gas in all cases). All samples, standards and blanks were determined in duplicate. Calibration curves were considered suitable for sample determinations if the linear correlation between absorbance peak height and standard concentration was 0.95-1. For sediments and plants results were quoted as mg kg<sup>-1</sup> dry weight; for fish and earthworm samples as mg kg<sup>-1</sup> wet weight and for water samples as  $\mu g l^{-1}$ .

# 3.6.3 Total copper, iron and manganese determination

Total Cu, Fe and Mn in all samples were determined by acetylene-air flame AAS (Perkin-Elmer 5100PC) attached to an AS-90 autosampler. Manufacturers recommendations were followed and standards were made up in 1% HNO<sub>3</sub> (Spectrosol, BDH) from the respective 1000 mg l<sup>-1</sup> stock solutions (Spectrosol, BDH). On the occasions that samples contained analytes at levels below flame AAS detection limits a graphite furnace AAS (Perkin-Elmer HGA-600) was used.

#### 3.6.4 Organomercury species determination

Two methods for the determination of methylmercury have been used. Prior to 1993 a GC-AAS method was used and is described in detail elsewhere (Imperial College, 1992). Since 1993 a flow injection system coupled to a Hg atomic fluorescence detector has been used. During the 1993 and 1994 survey the two systems were compared for performance and results showed that both systems produce reliable results (Edwards *et al.*, 1996b).

#### 3.6.4.1 Extraction of organomercury species from sediment

The extraction procedure ensured that any organomercury species present in the sample were separated from the inorganic species. The aqueous sodium thiosulphate fraction, into which the organomercury partitions, is subsequently presented to the detector. Approximately 50 g of well homogenised wet sediment was accurately weighed into a 250 ml plastic centrifuge bottle and 5.0 ml of  $0.5M \operatorname{CuSO}_4$  (AnalaR, BDH) and 10 ml of 3M KBr (AnalaR, BDH) in  $1M \operatorname{H}_2\operatorname{SO}_4$  (Aristar, BDH) were added. The mixture was shaken for 1 h on an end-over-end rotary shaker. Five ml of toluene (glass distilled grade, Rathburn, Walkerburn, UK) was added and the mixture was shaken for 24 h and then centrifuged for 10 min at 3000 rpm. An exactly known volume of the toluene layer (3-4 ml) was transferred to a borosilicate sample vial and 1.0 ml of 5% sodium

thiosulphate (AnalaR, BDH) was added. The mixture was shaken for 20 min and then allowed to settle. A 100  $\mu$ l aliquot of the organomercury-containing thiosulphate extract was analysed. Samples spiked with known concentrations of methylmercury were extracted to evaluate the recovery factor used for quantification.

## 3.6.4.2 Extraction of organomercury from fish flesh

The extraction of fish tissue was carried out by a technique originally described by Longbottom *et al*. (1973) but with some modifications. Fish flesh samples provided by the NRA were detached from any bone or skin and accurately weighed (5 g), homogenised and extracted, using 5 ml of 0.5M copper sulphate and 10 ml of 3M acidified potassium bromide, into 10.0 ml of toluene, as described for sediment extraction.. The organomercury was extracted into the aqueous phase by addition of 10 ml of 5% sodium thiosulphate. This layer was removed and 2 ml of HCl (Aristar, BDH) added, allowing back extraction into toluene. This removes many non-polar oily materials initially extracted with the organomercury species, giving a cleaner extract which could finally be partitioned into 1 ml of 5% sodium thiosulphate.

Table 7.         Analytical parameters for organomercury determination
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Parameter/Component	Specification
Injection volume	100 µl
Carrier stream	4 g l <sup>-1</sup> ammonium acetate*
	Flow rate 0.5 ml min <sup>-1</sup>
Oxidising stream	0.25M sulphuric acid, 1.6 g l <sup>-1</sup> copper sulphate 25 g l <sup>-1</sup> potassium peroxodisulphate Flowrate 0.4 ml min <sup>-1</sup> , reaction coil volume 0.5 ml
Reducing stream	15 g l <sup>-1</sup> tin(II)chloride, 48 g l <sup>-1</sup> sodium hydroxide Flowrate 0.5 ml min <sup>-1</sup> , reaction coil volume 0.5 ml
Detector argon flow rates	Drying gas 2 l min <sup>-1</sup> Sheath gas 300 ml min <sup>-1</sup> Carrier gas 300 ml min <sup>-1</sup>

Ar (High Purity, BOC)

# 3.6.4.3 Determination of organomercury species

The organomercury extracts were injected into a flowing carrier stream which was subsequently mixed with a strong oxidising agent within an open reaction coil. The oxidising agent converted any organomercury species present to  $Hg^{2+}$ . Reduction of the mercuric ions was achieved by the addition of an aqueous stream of alkaline stannous chloride. This generated elemental mercury vapour which was separated from the liquid phase by a gas-liquid separator, dried using a permeable tubular membrane (Perma Pure, New Jersey, USA) (Hitchen *et al.*, 1992) and purged through to the atomic

fluorescence detector (10.023 Merlin Detector, PSA, Sevenoaks, UK) for quantitation. The details of the analytical parameters are presented in Table 7. Standards consisting of methylmercury chloride (BDH) in water were made up as required. The limit of detection of the method is 10  $\mu$ g l<sup>-1</sup> which is the equivalent of 0.2  $\mu$ g kg<sup>-1</sup> MeHg in dry sediment (Edwards *et al.*, 1996b).

#### 3.6.5 Sequential soil metal extractions

Two sequential extractions were conducted in triplicate for each of the 7 soil samples collected from the transect to determine bioavailability of the metals. All reagents were of analytical grade or better. Soils were sieved undried through a 3 mm mesh and thoroughly homogenised before weighing and extraction in triplicate. The first extractant consisted of a 0.005 M DTPA (diethylenetriaminepentaacetic acid) + 0.01 M calcium chloride + 0.1 M triethanolamine solution buffered at pH 7.3 (5 ml extractant per g dry soil) as described by Lee *et al.* (1983). The second extraction was performed on the sample remaining after the DTPA extraction and used a cold 10% nitric acid solution at 10 ml extractant per g soil (Jenne, 1968). Separate soil samples were microwave digested in triplicate with *aqua regia* (2 ml HNO3 + 6 ml HCl) for 'total' metal content determinations.

#### 3.6.6 Total organic carbon determination

#### 3.6.6.1 TOC in sediments

Sediment was dried at 60 °C, ground and approximately 0.2 g was accurately weighed. The TOC content was determined by a modified Walkley-Black titration (Gaudette *et al.*, 1974). The results were expressed as %TOC. Standards of potasium hydrogen phthalate (AnalaR, BDH) were run periodically and blanks determined.

#### 3.6.6.2 TOC in waters

A Dohrmann DC80 Carbon Analyser (Pollution and Process Monitoring, Sevenoaks, UK) was used for determination of TOC in water samples. Potassium peroxodisulphate (AnalaR, BDH) was used as the oxidant with an additional UV light source to assist in breakdown of any organic carbon to carbon dioxide. The carbon dioxide generated in the oxidation step was pumped to an infra-red detection cell from which the concentration of organic carbon present was automatically calculated. Potassium hydrogen phthalate (AnalaR, BDH) was used as a standard with a 1 ml sample loop. Samples containing high chloride ion or heavy metal ion concentrations were diluted up to 100 times to prevent interference. Before analysis one drop of concentrated orthophosphoric acid (general purpose reagent, BDH) was added to each sample which

was then purged with oxygen gas to remove any dissolved carbon dioxide or inorganic carbon present.

# 3.6.7 Anion determination

Analysis was undertaken for sulphate, phosphate, nitrate, nitrite and chloride anions using high pressure liquid chromotography (HPLC). Approximately 10 g of wet sediment was accurately weighed for extraction and shaken for 15 min. on an end-overend rotary mixer with 25 ml of water. The resulting supernatant was filtered through a 0.45  $\mu$ m pore-size cellulose nitrate filter (Whatman, Walkerburn, UK). A 100  $\mu$ l sample volume was analysed for anions on a Millipore Corporation HPLC (Massachusetts, USA) using an IC-Pak A anion exchange column with a borate/gluconate eluent, as recommended by the manufacturers (Waters ion chromatography method GABG-101). Mixed standards were made up in accordance with Waters methods and contained Na<sub>2</sub>SO<sub>4</sub>, KH<sub>2</sub>PO<sub>4</sub>, NaNO<sub>3</sub>, NaNO<sub>2</sub> and NaCl (all AnalaR, BDH).

# 3.6.8 Total and volatile solids determination

In each survey, total and volatile solids of sediments were determined using standard methods (APHA 1992). Approximately 10 g of wet sediment was accurately weighed into a pre-weighed crucible and dried at 105 °C to constant weight. The sample was further dried at 500 °C in a muffle furnace for 2 h to determine the volatile solids content which was expressed as a percentage of the dry weight.

# 3.6.9 pH and redox potential determination

The pH of water and sediment samples was measured using a combined pH electrode attached to an ELE portable meter (ELE, Hemel Hempstead, UK). The electrode was calibrated using pH 7.0 and 9.2 buffer solutions. The redox potential of samples was determined using a platinum electrode attached to an ELE meter.

#### 3.6.10 Analytical quality and control

All analytical procedures described were subject to analytical quality control. For metal determinations samples were analysed in duplicate and means determined. If the relative standard deviation (RSD) was greater than 5% samples were re-digested and rerun until this limit were met. Standard and sample blanks were included in all determinations and corrections made to sample determinations when necessary. Standard solutions were treated identically to samples and made up in similar matrices whenever possible.

The reproducibility of the digestion procedures for sediment, fish, earthworms and plants was assessed by undertaking duplicate digestions of 10% of each sample set (Table 8). A sample blank was included with each digestion batch. The percentage recovery of analyte was determined by spiking 5% of samples with a standard metal ion solution. Where certified reference materials were available these were used to check the accuracy and precision of the analytical techniques (Table 9). For sediments the certified river sediment reference material CRM 320 (Community Bureau of Reference, Promochem Ltd, London, UK) was used and for fish samples a certified dogfish muscle reference material (DORM-1, National Research Council, Canada) (Promochem Ltd, London, UK) was employed.

Table 8.	The reproducibility and recovery of sediment and fish digestions and
	extractions for the 1994 surveys.

		Sediment	Fish		
Parameter	Hg	MeHg	Cu	Hg	MeHg
Reproducibility (%)	81.6-99.1	68.8-87.3	96.9-99.5	<b>83.9-96.</b> 1	73.4-90.6
Recovery (%)	91.1 <b>-9</b> 7.2	48-69	88.2-103.3	90.5-102.6	50-65

**Table 9.**Certified and determined concentrations of copper, mercury and<br/>methylmercury in sediment and fish samples for the 1994 surveys.

	Sedi	ment	F	ìish
Parameter	Hg (mg kg <sup>-1</sup> )	Cu (mg kg <sup>-1</sup> )	Hg (mg kg <sup>-1</sup> )	MeHg (mg kg <sup>+1</sup> )
Certified	$1.03 \pm 0.13$	44.1 ± 1.0	0.798 ± 0.074	$0.731 \pm 0.060$
Determined	$1.25 \pm 0.11$	$42.5 \pm 0.3$	0.766 ± 0.043	0.706 ± 0.052

# 4. **RESULTS**

4.1 Assessment of the spatial distribution of Hg, MeHg and Cu within the surficial bed sediments, 1986-1995

The magnitude and distribution of Hg within the R. Yare bed sediments from year to year is represented as transect means in Figure 7. The highest levels were recorded in the initial survey in 1986 with a maximum concentration of 32.9 mg kg<sup>-1</sup> Hg and 14 % of the samples taken exceeding the 10 mg kg<sup>-1</sup> interaction value (Visser, 1994). Mercury enrichment over the background concentration for the river of 0.1-0.2 mg kg<sup>-1</sup> was observed from the start of the survey 3 km upstream (due to tidal reversal) to the end of the survey 12.5 km downstream of the STW outfall. The area of highest concentration occurs 2-6 km downstream of the STW outfall..

Low-level tailing of Hg contamination at the lower end of the 1986 survey reach was confirmed by increasing the range of the 1987 survey to 21 km downstream. A large decrease on 1986 concentrations was recorded with a range of 0.19-15.2 mg kg<sup>-1</sup> Hg. With a few exceptions concentrations approached published background levels of 0.2-0.4 mg kg<sup>-1</sup> in the region of Cantley. In 1989 Hg concentrations were comparable to the 1987 survey and ranged from 0.11-15.9 mg kg<sup>-1</sup> (Figure 7). A further decline to a survey average of 1.28 mg kg<sup>-1</sup> in 1990, was the lowest average concentration recorded for the 9 surveys conducted. From 1990 average bed sediment concentrations fluctuated within a narrow range of 1.33-2.06 mg kg<sup>-1</sup>. Spatially the contamination plume has tended to remain fairly fixed.

Because slight perturbations occur in the data from year to year at each location, the data were divided into 7 transects between Trowse and Cantley (Table 10). The sample locations within each transect were averaged and these average transect values analysed

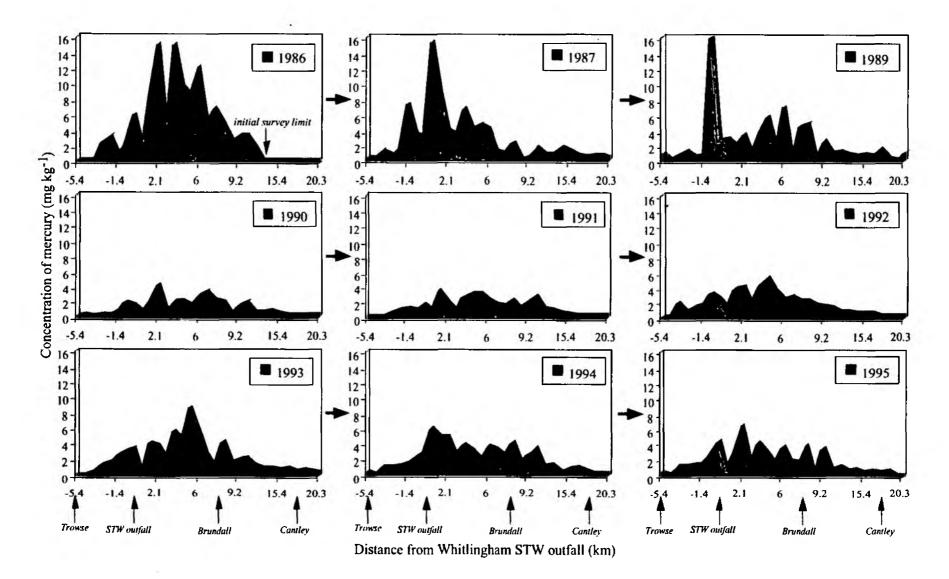


Figure 7. Spatial distribution of merury in surficial bed sediments of the R Yare, 1986-1995

30

to determine if apparant movement in Figure 7 was real or noise in the data. The analysis indicates that by 1990 the levels of Hg in the R. Yare sediments have decreased and remained fairly constant since averaging  $1.8 \text{ mg kg}^{-1}$  Hg.

Transect	Sampling	Average
	Locations	Distance
T1	4-8	-3.92
T2	9-13	0.032
<b>T</b> 3	14-18	3.57
T4	1 <b>9-</b> 22	7.03
T5	23-25	9.54
T5	26-29	13.97
T7	30-35	18.95

**Table 10.**Transects used for averaging sediment Hg data on the R. Yare.

Table 11.	Pearson's correlation matrix ( $\rho = 0.95$ ) for total mercury concentrations
with	o ther parameters for annual bed sediment surveys, 1986-1995.

Year	Distance <sup>1</sup>	%VS	pH	Redox	[Cu]	[MeHg]
1986	-0.02	0.23			0.54*	
1 <b>9</b> 87	-0.33	0.62*			0.77*	-0.05
1989	-0.43*	0.11	0.13			0.29
1990	-0.17	0.38*	-0.05			0.33
1991	-0.36	0.26	-0.06			0.42*
1992	-0.5*	0.38*	-0.56*		0.8*	0.47*
1993	-0.41*	0.24	-0.19	-0.34*	0.82*	0.15
1994	-0.31	0.48*	-0.06	-0.08	0.83*	0.31
1995	-0.22	0.53*	<b>-0</b> .11	-0.05	0.85*	0.41*

Distance from Whitlingham STW outfall

**\*n=33**, α=0.05

no data available where no value is given

As expected for a point source pollution profile, there is a moderately significant negative correlation between Hg concentrations and distance from the STW outfall (Table 11). Copper and Hg bed sediment concentrations are highly correlated (R=0.8) as both contaminants have the same source and behave similarly within the sediment compartment. Although it is clear that total concentrations of Hg within the bed sediments are not the only controlling factor over MeHg production, there has generally been a significant positive correlation between these 2 parameters over the years. In 1992-1994 the fluctuation in correlation between Hg and MeHg concentrations was mirrored by that in the correlation between Hg and %VS, suggesting a possible link between these 2 parameters.

Volatile solids content of the sediment, a surrogate for organic carbon content, has generally been only moderately correlated with Hg concentrations (Table 11), but Figure 8 indicates that average %VS content for the 9 surveys has a similar profile to

that for Hg contamination, with low levels just downstream of the STW outfall and an enriched region further downstream before a decrease to lower levels. This is a reflection of the changing nature of the bed sediments of the river which, in turn, changes the capacity of organic material to bind to it. Sandy and gravely sediments near the outfall bind organic material less than the finer silt further downstream and finally the more clay-like sediments of the lower reach bind the least of all. Whether the correlation between Hg and %VS is due to the presence of organic material or because of the sediment type is difficult to distinguish; it is probably a combination of the two factors reflected in one measured parameter. No significant correlation exists between sediment pH and Hg concentration, probably because the bed sediment pH was generally similar from year to year (range = pH 6-8) and did not differ over the range of the survey area significantly enough for any effect to be observed. Available redox potential data was not sufficient for any firm conclusions to be drawn.

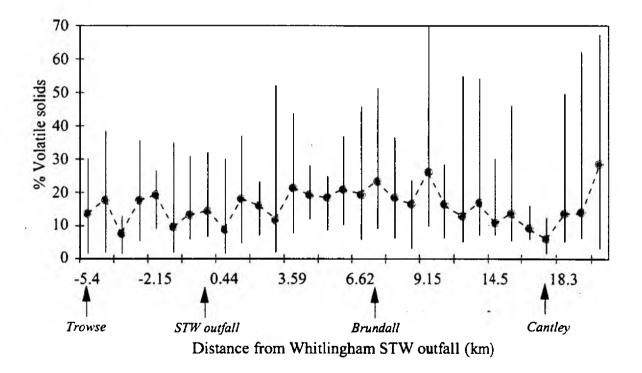


Figure 8. The average percentage volatile solids content of surficial bed sediments of the R. Yare for 1986-1995 (bars indicate ranges).

# 4.1.2 Organomercury

Comprehensive surveys for MeHg were conducted in 1989-1995 and are plotted in Figure 9. Maximum measured concentrations have been in the region of 30  $\mu$ g kg<sup>-1</sup>. Organomercury has always occurred throughout the main contaminated area and is not solely related to Hg concentrations, although a correlation does exist (Table 12). The irregular distribution of MeHg within the bed sediments probably precludes the STW outfall as the main source and implicates in situ production by biotic or abiotic means, using the inorganic Hg as a substrate. When the ratio of MeHg to total Hg is considered for each year (Figure 10) it is apparent that two areas have unusually high MeHg:Hg ratios; at transect 4, 5.4 km upstream of the outfall the ratio is consistently between 4-8% and in the region 12-18 km downstream ratios of 2-6% occur regularly. Within the remainder of the study area the ratio is fairly constant at 0-2%. Reasons for each elevated zone are probably different, the upstream enrichment depending more on conditions created by warmer, shallow, still water allowing light penetration whilst the downstream MeHg enrichment may be due to nutrient enrichment and a warm water input (temperature of discharge effluent 20°C) from a sugar processing plant in the region, creating ideal conditions for microbial methylation of Hg. The downstream area is also within the saline limit of the river thus this may also cause the increase in methylation observed. As the distribution of MeHg is fairly consistent throughout the study reach, correlations with distance from the outfall are generally weakly negative, but fluctuate widely from year to year. Correlation with %VS is apparent at times, but is generally weak (Table 12).

Year	Distance <sup>1</sup>	%VS	pH	Redox	[Hg]	[Cu]
1987	0.35*	-0.08			-0.05	0.03
1989	-0.53*	0.63*	0.00		0.29	
1990	-0.12	0.47*	-0.17		0.33	
1991	-0.44*	0.32	-0.19		0.42*	
1992	-0.17	0.28	-0.25		0.47*	0.33
1993	0.06	<b>-0</b> .16	0.08	-0.16	0.15	0.05
1994	-0.01	0.03	-0.27	-0.09	0.31	0.17

-0.17

0.57\*

0.41 +

0.49

0.07

Table 12. Pearson's correlation matrix ( $\rho$ =0.95) for organomercury concentrations

-0.27<sup>1</sup>Distance from Whitlingham STW outfall

\* n=33, α=0.05

1995

no data available where no value is given

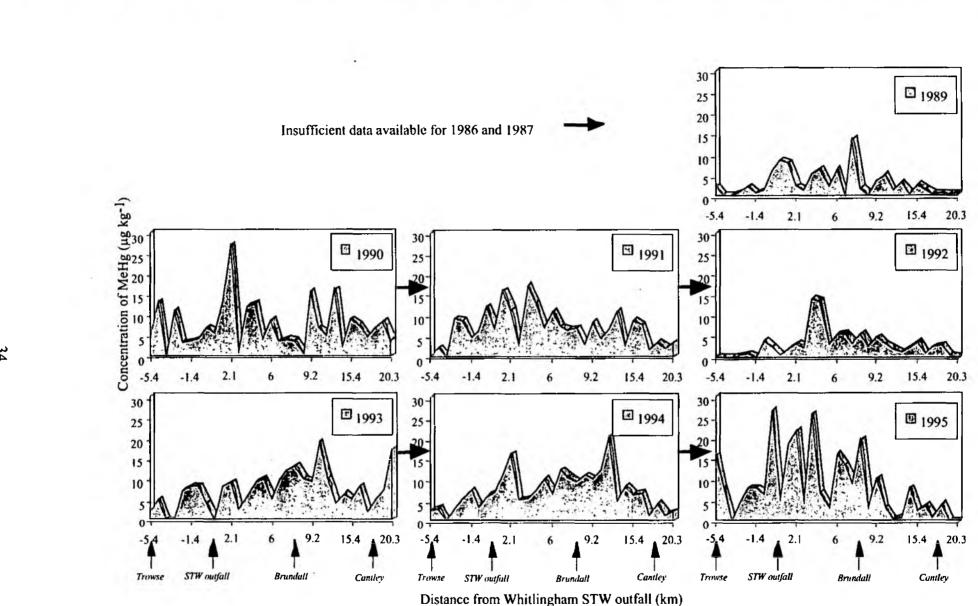


Figure 9. Spatial distribution of organomercury in surficial bed sediments of the R Yare, 1989-1995

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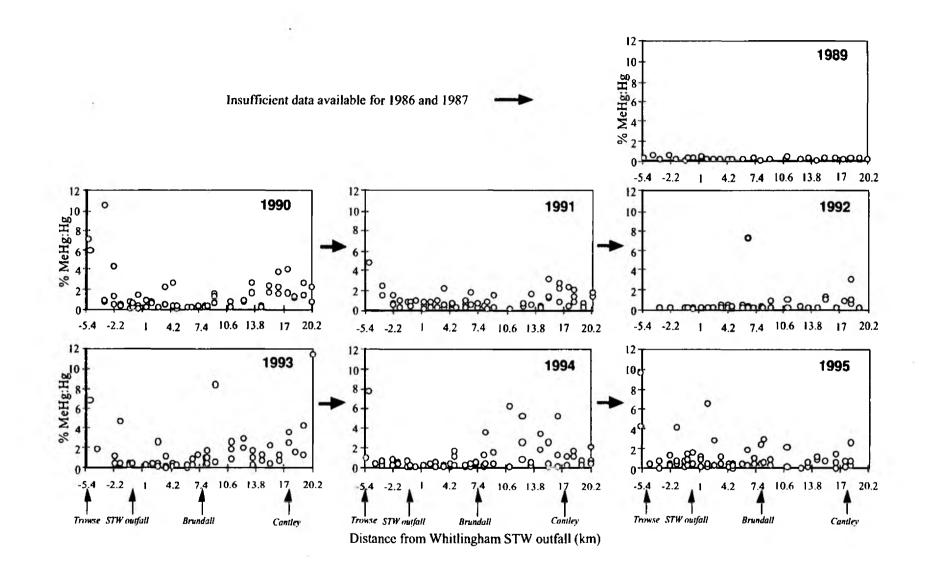
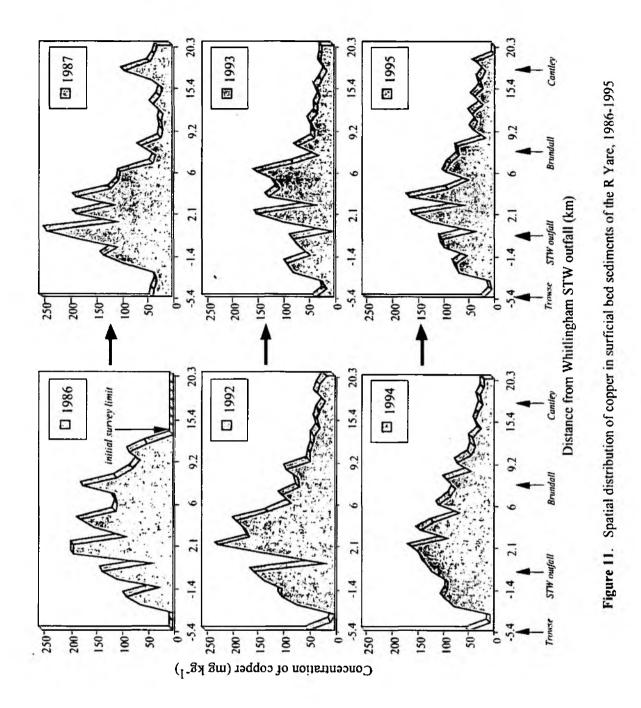


Figure 10. Spatial distribution of organomercury as a ratio of total mercury in surficial bcd sediments of the R Yare, 1989-1995.

35



# 4.1.3 Copper

Six surveys of bed sediment copper concentrations were conducted and the spatial distribution of the contamination plume for each year is plotted in Figure 11. Copper concentrations were highest in 1986 with a maximum spot concentration of 375 mg kg<sup>-1</sup> and a mean for the survey of 106.5 mg kg<sup>-1</sup>. Spatially, the contamination plume was distributed in the same range as that for Hg, but less fluctuation in contamination level within the plume was observed. Downstream tailing of Cu contamination was apparent from approximately 12 km downstream to the end of the survey reach for the 1987

survey and average Cu concentrations declined by 29% to 75.8 mg kg<sup>-1</sup>. In 1992, the next year a survey for Cu was undertaken, concentrations had not changed significantly with an average of 81.5 mg kg<sup>-1</sup>, indicating a clear difference between Cu and Hg which had declined markedly by this point.

The most probable reason was that inputs from Whitlingham STW had declined by more then 100% for Hg, but only by 30% for Cu. This trend has been observed for the 3 most recent surveys in 1993-1995 where no significant further decline in Cu concentrations has been observed over the entire study reach.

**Table 13.** Pearson's correlation matrix ( $\rho$ =0.95) for total copper concentrations with other parameters for annual bed sediment surveys, 1986-1995.

Year	Distance <sup>1</sup>	%VS	pН	Redox	[Hg]	[MeHg]
1986	-0.02	0.49*			0.54*	
1987	-0.2	0.71*			0.77*	0.03
1992	-0.65*	0.21	-0.46*		0.8*	0.33
1993	-0.5*	0.28	-0.21	-0.4	0.82*	0.05
1994	-0.52*	0.62*	0.13	0.16	0.83*	0.17
1995	-0.31	0.72*	-0.13	0.09	0.85*	0.49*

<sup>1</sup>Distance from Whitlingham STW outfall

\*n=33,  $\alpha = 0.05$ 

no data available where no value is given

Comparison of the correlation coefficients for Cu with the other parameters monitored on a year to year basis (Table 13) highlights the point source nature of the pollution profile (Cu v distance) and the link between Hg and Cu as co-pollutants behaving similarly within the sediments (Cu v Hg). There is also an important link between %VS and Cu concentrations as already outlined for Hg. Correlations between pH, redox potential and MeHg were weak or absent.

### 4.2 The distribution of Hg and Cu within bed sediment cores - 1995

The analysis of 3 cores collected in 1995 support the results of the 10 years of surficial bed sediment monitoring. Core C1 was taken close to Whitlingham STW, C2 was collected 8 km downstream in Rockland Broad and C3 was taken 20 km downstream at Cantley. Concentrations of Hg and Cu are lowest at the top of C1 and C2 and highest at the top of C3, reflecting contaminant burial by a cleaner overlay of sediment, accompanied by the continuing expansion of the downstream edge of the contaminant plume. Both these factors are leading to a levelling out of the contaminant plumes, as observed for the spatial surveys over 10 years.

Core 1, taken close to the STW outfall, appears to provide a complete record of the Hg contamination of the R. Yare as there is no reason to believe that the sediment has been disturbed by dredging in this area. Concentrations of Hg increase continually from 4.1 mg kg<sup>-1</sup> at the surface to 20.4 mg kg<sup>-1</sup> at a depth of 35 cm before declining gradually to an apparent background concentration of approximately 0.7 mg kg<sup>-1</sup> at 55 cm which persists to the end of the core at 75 cm (Figure 12). A similar trend was found for Cu, except for the bottom 10 cm of the core where concentrations rose again sharply, suggesting a possible earlier contamination event. In contrast, the lithogenic metals Mg, Al, Ti, Mn and Fe (Figure 12) reflect the 2 sediment types encountered down the core. In the top 45 cm of the core fine river silt, consistent with an area of high deposition, was found. Below this a clay lens and shell hash caused the elevated concentrations of the 5 lithogenic metals observed before concentrations returned to those found for further river silt from 60-75 cm. Normalisation to Al or Li is a common technique that removes the lithogenic overprint from geochemical data. Normalisation of Hg and Cu to Al produced similar profiles to those in Figure 12, further evidence to support the anthropogenic origin of these metals.

Rockland Broad Hg and Cu core profiles (C2) were similar to those for C1 (Figure 12), but the distance from contaminating source (8 km) makes it more difficult to estimate whether the full contamination profile was obtained. It is likely that the sediment deposition rate within the Broad was higher than at the site of Cl as background concentrations of Hg are approached at greater depth (from 70-75 cm downwards). The lithogenic elements all occur within expected concentration ranges for a fine river silt, dropping slightly when the sediment becomes a silt and fine sand mixture at the bottom of the core.

Core 3, taken 20 km downstream of the pollution source, near Cantley, illustrates the continuing movement of bed sediments downstream with the highest Hg and Cu concentrations occurring at the surface and background concentrations occurring below 10-15 cm and for the remainder of the core (Figure 12). One exception is the sudden increase in Cu concentration at 25-30 cm which may be related to the first Cu pollution event suggested by C1 as no corresponding change in Hg concentration is observed. However, the lithogenic metals and redox potential all decrease sharply at this point, suggesting a transition zone in metal adsorption within the sediments at this dept, which may be due to the saltwater / freshwater interface in this region of the river.

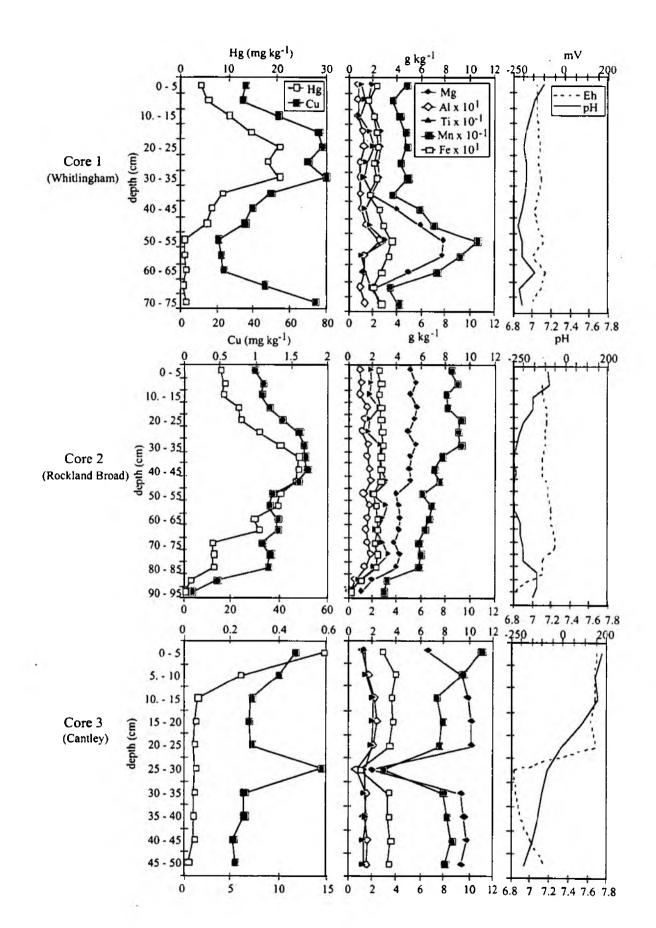


Figure 12. Core profiles of anthropogenic Hg and Cu and lithogenic metals at three points in the contamination plume, 1995.

Knowing that the release of Hg to the river began in 1964 and that background concentrations of Hg begin in C1 at 50-55 cm, it is possible to estimate the average sediment deposition rate in this area of the river over the last 31 years at 1.6-1.8 cm  $a^{-1}$ . Determination of intermediate time periods with this average deposition rate suggest that concentrations of surficial bed sediment Hg in 1986 would have been in the region of 15 mg kg<sup>-1</sup> which is in agreement with concentrations found in the area in the 1986 survey (14.5 mg kg<sup>-1</sup>). This is further supported by core-interpolated Cu concentrations of 75 mg kg<sup>-1</sup> against 51.5 mg kg<sup>-1</sup> for the actual 1986 survey. At Whitlingham, the presence of the clay lense acts as a barrier to downward metal migration through the sediment profile. The fact that mercury in the cores remains low beneath the clay suggests that this sediment was deposited before effluents containing Hg were released from the STW. However, at Whitlingham there is an increase in Cu just beneath the clay. While no clay layer was observed at Cantley, the peak concentrations of Hg and Cu associated with the known discharges from the STW occur within the upper 15 cm of sediment as expected for a lag in contaminant movement downstream. However, at 25-30 cm there is a marked increase in Cu concentration which quickly decreases. If these two increases observed are related, they may indicate an earlier contamination event of very short duration.

# 4.3 Assessment of mercury and methylmercury in fish flesh from the River Yare, 1985-1994

Four surveys of fish flesh were conducted between 1985-1994 and are summarized, along with an early survey from 1971, in Table 14. The bulk of the data is for eel (*Anguilla anguilla*) and roach (*Rutilus rutilus*) flesh although small numbers of pike (*Esox lucius*) have also been sampled. A general decline in total Hg concentrations with time has been observed for all species. Pike sampled in 1986 had the highest mean concentrations of Hg recorded for the R. Yare (0.71 mg kg<sup>-1</sup>), similar to the concentrations found in roach in 1971. However, as pike are at the top of the food chain they are more likely to biomagnify Hg and, as they live to a greater age, accumulate Hg for longer periods of time than roach. The high levels of Hg in roach in 1971 probably reflect the higher concentrations of Hg within the bottom sediments at that time, although data is not available to confirm this.

Since 1991 mean concentrations of Hg in fish flesh have remained relatively constant in the range 0.16-0.22 mg kg<sup>-1</sup> for eels and 0.06-0.17 mg kg<sup>-1</sup> for roach. Maximum Hg contamination levels have dropped slightly in each survey since 1991, 0.63 mg kg<sup>-1</sup> to 0.50 mg kg<sup>-1</sup> for eels and from 0.22 mg kg<sup>-1</sup> to 0.12 mg kg<sup>-1</sup> for roach. The factors controlling the changes in contamination levels are fully discussed in Section 5.

Fish species	Location	Survey date	Sample	Total Hg	(mg kg <sup>-1</sup> )
•		-	size	Mean	Range
Eel	Rockland Dyke	July 1994	51	0.21	0.06-0.50
(Anguilla anguilla)	Rockland Dyke	July 1993	25	0.16	0.06-0.60
	Whitlingham- Langley	June 1991	28	0.18	0.04-0.63
	Rowing club-Langley	Oct 1989	18	0.16	0.01-0.44
	Brundall-Langley	Dec 1985	99	<b>0</b> .46	0.06-1.08
Roach	Rockland Dyke	July 1994	40	0.06	0.028-0.12
(Rutilus rutilus)	Rockland Dyke	July 1993	17	0.17	0.11-0.23
	Whitlingham-Langley	May 1991	17	0.10	0.05-0.22
	Brundall	Dec 1986	9	0.19	0.11-0.47
	Yare (unspecified)	1984	1	0.44	-
	Yare (unspecified)	Jan 1971	13	0.71	not known
Pike	Bramerton Woods	May 1991	2	0.12	0.08-0.16
(Esox lucius)	Brundall	Dec 1986	8	0.71	0.26-0.77
	Coldham Hall-Brundall Gdns	Dec 1985	2	0.28	0.26-0.29

Table 14.	Total mercury concentrations in eel, roach and pike fish flesh samples
	taken from the River Yare (1971-1994).

# 4.4 Comparison between River Yare and Ormesby Broad bed sediment and fish Hg burden

The concentration of mercury observed in water samples collected from the River Yare . and Ormesby Broad was low, hence the need for using the atomic fluorescence method, which has a detection limit of 2 ng  $l^{-1}$  (Edwards *et al..*, 1996 b, c).

In the water samples collected, the Hg concentrations between Ormesby Broad and the R. Yare were found to be similar (Table 15). As Hg is no longer discharged to the R. Yare, the concentrations detected in the water were quite low. No methyl mercury was detected in water samples collected from either location.

Ormesby Broad sediments were composed of an organic mud with a jelly-like texture due to the presence of algae, a product of the eutrophication of the system. The Broad also cuts into chalk with calcite the predominant mineral constituent. Both systems are well buffered with the eutrophication of Ormesby Broad reflected in the elevated concentrations compared to the R. Yare of TOC in the water column and bed sediments (Table 15). The concentration of mercury in the Ormesby Broad sediments was much lower ranging between 0.03 to 0.32 mg kg<sup>-1</sup> Hg. The amount of MeHg in these sediments was also less then 1% of the total Hg measured.

Parameter	R. Yare		Ormesby Broad	
	mean	range	mean	range
THg (mg kg <sup>-1</sup> ) S <sup>*</sup>	2.1	0.04-6.2	0.14	0.03-0.32
	0.05	0.03-0.06	0.04	0.03-0.05
(µg l <sup>⁻1</sup> ) W				
MeHg ( $\mu$ g kg <sup>-1</sup> ) S	7.3	1.0-24	0.6	0.3-2.5
$(\mu g l^{-1})$ W	nd	nd	nd	nd
рН S	7.2	6.9-7.3	6.9	6.7-7.2
· W	7.8	7.6-8.1	7.4	7.1-7.9
TOC (%) S	4	3-6	6	5-9
$(mg l^{-1}) W$	3.1	1.9-4.2	6.8	4.6-11.1

**Table 15.**Concentrations of THg and MeHg and some physicochemical parameters<br/>for bed sediments and water of the R. Yare and Ormesby Broad in 1994/95.

S - bed sediment, W - water

nd - not determined

Table 16.	Hg burdens and sample population statistics for eels and roach from the R.
	Yare and Ormesby Broad in 1994/95.

Parameter		Eel (A. al	nguilla)			Roach (R.	rutilus)	
	Riv	ver Yare	Orme	sby Broad	Riv	er Yare	Ormes	by Broad
	mean	range	mean	range	mean	range	mean	range
THg ( $\mu$ g kg <sup>-1</sup> ) M <sup>+</sup>	255	57-501	104	14.7-285	55.1	27.9-121	54.3	19.4-99.3
Accum. Hg (µg)	31.77	3.95-102.01	30.75	3.86-131.2	7.9	3.03-19.34	2.85	0.56-7.1
MeHg (µg kg <sup>-1</sup> ) M <sup>+</sup>	223	57-426	84.3	11.3-232	47.5	25.0-108	43.6	17.6-81.9
Accum. MeHg (µg)	28.06	3.48-97.44	25.10	2.97-115	<b>6</b> .78	2.52-18.28	2.28	0.51-5.97
MeHg:THg M <sup>+</sup>	88	70-104	82	71-92	86	70-105	81	71-93
Length (cm)	40.1	24.7-65.5	52.5	35.0-77.0	19.2	16.0-23.0	14.8	12.0-19.8
Weight (g)	127.7	30.7-539.3	310.5	74.6-1000.8	139.7	73.0-223.9	51.1	22.4-128.0
Age (y)	12.8	6-21	13.6	8-18	5	4-6	3.5	3-5
Sample size	51		51		40		49	

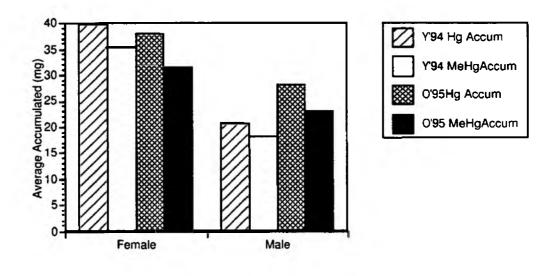
<sup>\*</sup>M - muscle tissue,

Concentrations of total Hg (THg) and MeHg in the bed sediments of the R. Yare were, approximately 15 times higher than in Ormesby Broad in 1994/95. This difference was not reflected in variations in roach muscle THg concentrations from the two sites as mean concentrations (55  $\mu$ g kg<sup>-1</sup>) and ranges were approximately the same (Table 16). However, in terms of total accumulated mercury, large differences are observed between these two populations. Roach from the River Yare have a total average body burden of mercury of 7.9  $\mu$ g Hg, 2 times greater then the body burden (2.8  $\mu$ g Hg) observed in roach collected from Ormesby Broad, this is because roach collected from the R. Yare were almost 3 times heavier then those from Ormesby Broad. Within the eel populations, the concentration of Hg found in muscle from eels collected from the R. Yare was, on average, 2.5 times higer than similar samples from Ormesby Broad

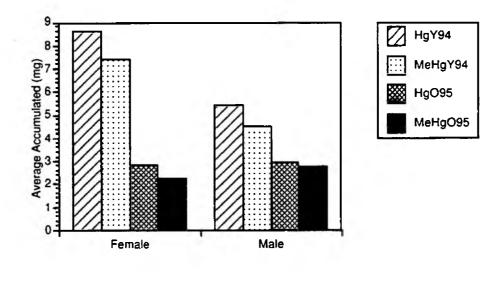
(Table 16). The amount of accumulated Hg within the eels however, was similar, with eels from the Yare having an average body burden of 28  $\mu$ g Hg and those from the broad having 25  $\mu$ g mercury.

Means testing using a Kruskall-Wallis (Systat for Macintosh, SPSS, Chicago, Illinois) analysis showed no difference between mercury burdens in these two fish populations. However, the equivalency of body burden between the two eel populations is due to the larger size of the eels at Ormesby Broad. Also note that Hg was primarily in the form of methyl mercury in both roach and eel regardless of sampling location. The MeHg:THg ratio was consistently high across sites and species at an average of 81-88 % per population sampled.

Correlation matrices calculated using Systat found strong significant correlations between accumulated THg and MeHg with the length (0.7) and weight (0.8) of eels for both the R. Yare and Ormesby Broad populations. A weaker correlation (0.4) was found to exist between age and accumulated Hg. For roach, the relations between Hg. accumulated and size parameters were slightly different with length and weight correlations of 0.7 in the Yare and 0.9 in Ormesby Broad. The relation with age, though was very different between the two populations, roach from Ormesby Broad had a correlation of 0.8 between age and accumulated Hg species and those from the Yare were not correlated at all (0.03). Differences were also noted between accumulated loads in male and female populations of fish from both locations (Figure 13). These data show that the female eels have higher mercury body burdens then do the males, especially those collected from the R. Yare. With roach however no difference was found between Hg accumulated by females and males from Ormesby Broad while females from the Yare were again elevated compared to the males. The differences observed with respect to sex and age of the roach populations may be reflecting differences in source of Hg to these fish.



(a)



(b)

Figure 13. (a). Mercury accumulated in eel sampled from Y - R. Yare and O - Ormesby Broad by sex. (b). Mercury accumulated in Roach collected from Y - River Yare and O - Ormesby Broad by sex.

Concentration data from four surveys of fish flesh conducted between 1985-1993 along with the 1994 survey data were averaged and the body burden of Hg in the fish estimated (Table 17). A general decline in total Hg burdens with time has been observed for both species. The high levels of Hg in roach in 1971 probably reflect the higher concentrations of Hg within the bed sediments at that time, although data is not available to confirm this. Since 1991 concentrations of mean THg in muscle tissue have remained relatively constant in the range 160-250  $\mu$ g kg<sup>-1</sup> for eels and 60-170  $\mu$ g kg<sup>-1</sup> for roach. Maximum THg contamination levels have dropped slightly in each survey since 1991 from 630  $\mu$ g kg<sup>-1</sup> to 500  $\mu$ g kg<sup>-1</sup> for eels and from 220  $\mu$ g kg<sup>-1</sup> to 120  $\mu$ g kg<sup>-1</sup> for roach. MeHg concentrations were always within 80-90 % of the THg concentrations for both species and are not presented in detail.

Fish species	Survey date	Sample	Total Hg (µg kg <sup>-1</sup> )		
		size	Mean	Range	
Eel	Dec 1985	99	462	61-1080	
(A. anguilla)	Oct 1989	18	164	14-443	
	June 1991	28	181	42-635	
	July 1993	25	166	67-604	
	July 1994	51	255	57-501	
Roach	Jan 1971	13	713	not known	
(R. rutilus)	Dec 1986	9	197	114-477	
	May 1991	17	106	57-226	
	July 1993	17	171	110-233	
	July 1994	40	55.1	28-121	

Table 17.	Total mercury burden in eel and roach muscle tissue taken from the River
	Yare (1971-1994).

# 4.5 Monitoring and laboratory prediction of the effects of dredging River Yare sediments on water quality

The impact of dredging on water quality is of concern on the R. Yare because the sediments are contaminated with Hg and Cu, which when exposed to or suspended in the water column, may pose a threat to resident biota or lead to further methylation of Hg with other knock-on effects Laboratory predictions of the likely results of sediment disturbance on water quality were carried out using an elutriate test. The effects of salinity and changes in other physicochemical parameters from season to season were also predicted in the laboratory. The water quality at a dredging operation at Thorpe St Andrews was monitored and the results compared to the laboratory predictions.

# 4.5.1 Sediment type and heavy metal distribution

The sediment at Thorpe St Andrews is predominantly soft river silt, easily penetrated to depths of up to 1 m with a pole. The highest sedimentation of river silt tended to be near the southern bank (Figure 14). Sediments near the northern bank were stoney and gravelly with large lumps of chalk in areas and could only be penetrated to 20-30 cm. Water depths varied (1-3 m) with the shallowest water near the most silted southern bank, restricting boat movements during low tides.

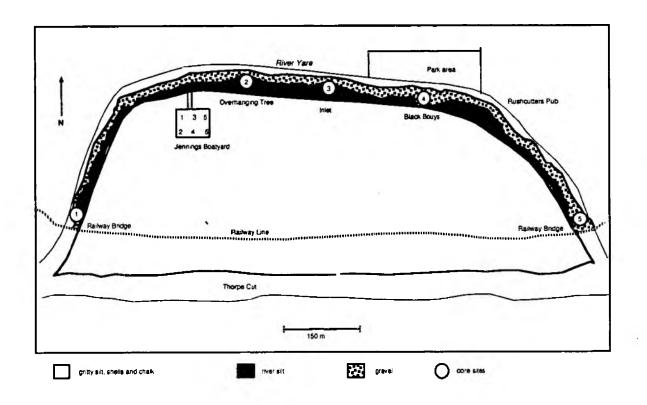


Figure 14. The dredge area showing sediment types.

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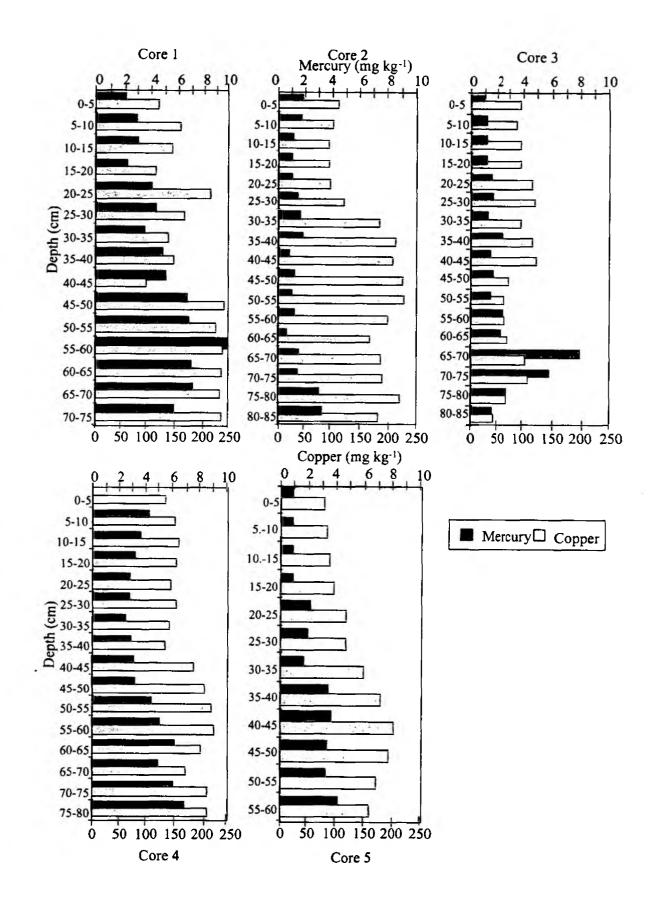
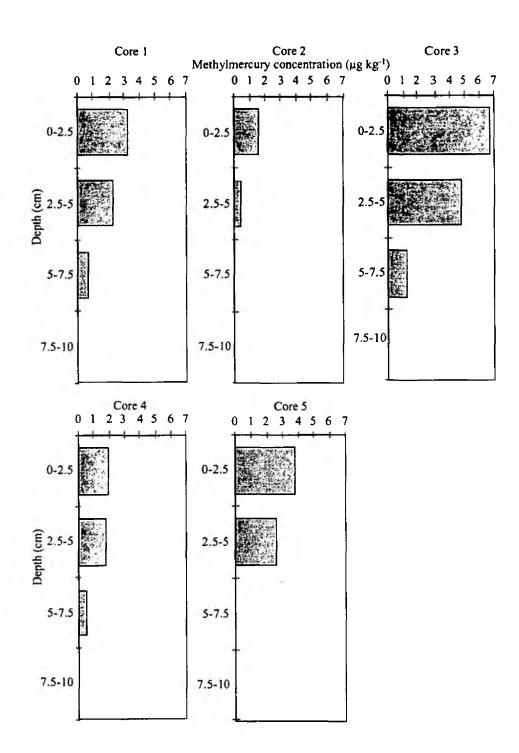


Figure 15. Depth profiles of Hg and Cu contamination prior to dredging at Thorpe St. Andrews.





The preliminary survey of the bottom sediments before dredging revealed subsurface enrichment of Hg and Cu with peak loadings of 9.9 mg kg<sup>-1</sup> and 250 mg kg<sup>-1</sup> respectively occurring at depths in excess of 50 cm (Figure 15). Overall concentrations tended to decrease in the direction of Trowse, with increased distance from Whitlingham STW. The top 40 cm of each core contained Hg in the range 1-4.5 mg kg<sup>-1</sup>. Methylmercury was detectable in all the bottom samples (2-7  $\mu$ g kg<sup>-1</sup> to a maximum depth of 7.5 cm (Figure 16). Copper contamination followed the trends observed for Hg with highest concentrations in cores closest to Whitlingham STW (250 mg kg<sup>-1</sup>). The copper distribution with depth was less variable than observed for Hg with concentrations in the range 100-250 mg kg<sup>-1</sup> through the entire core (Appendix 5 contains the full data set). The sediments were anoxic; the redox potential of the surface layers was -50 mV which decreased to -200 mV at depth. Sediment pH remained constant with depth and was in the region of pH 7. Silts within the surveyed area were therefore perceived as having similar phyliscochemical characteristics. On the basis of these findings it was recommended to the dredging authority that sediment be dredged to a depth of at least 1 m to ensure that the bulk of the metal contamination was removed.

# 4.5.2 Comparison of water quality predicted by elutriate tests and observed during dredging

The sediment and water samples used for the elutriate experiments were taken from the dredge site prior to dredging. Analysis of the bulk samples (Table 18) indicated that the sediment compartment acted as the major sink for the contaminant metals. Various physico-chemical parameters were also recorded and taken to represent background or undisturbed levels. For comparison of the effects of seasonal change on water quality some parameters were recorded in the following summer as well as before the dredging operation (winter).

Parameter		Thorpe St A	ndrews
Metals		Sediment (mg kg <sup>-1</sup> )	Water (µg 1 <sup>-1</sup> )
Mercury		5.24	0.05
Copper		189.6	<b>2</b> .1
Iron		24730	706
Manganese		628.2	151
Temperature (*(	C) winter	7.8	9.4
summer	-	21.0	22.5
pН	winter	7.11	7.92
summer		7.14	7.68
Redox (mV)	winter	-209	+207
summer		-168	+292
% Total solids		25.1	
TOC (g kg <sup>-1</sup> /mg	<b>χ 1</b> <sup>-1</sup> )	74.0	3
Chloride (mg 1	<sup>[</sup> )		199
$DO(mg l^{-1})$	winter		10.6
summer			9.1

Table 18.	Physico-chemical parameters and concentrations of metals for bull	s
	sediment and water from the dredge site (Thorpe St Andrews).	

The dredging operation caused up to 7-fold enrichments of total Hg and Cu in the water column (Table 19), but for a relatively short period of time compared to Fe and Mn which displayed lower more persistent enrichments. Peak concentrations of metals within the water column occurred within 12 h of dredging and in the case of Mn was observed during the dredging operation, reflecting its relatively high mobility. These field results are compared with elutriate test data in Figures 17 and 18. The field results presented are for Station 2, but similar results were obtained for the other stations. The elutriate data is an average of 3 settling experiments as results were consistent (student 'T'-tests p=0.15). It should be noted that elutriate test data equates to the first 48 h after dredging activities ceased (from time = 8 h) and not the onset of dredging.

**Table 19.** Maximum concentrations of metals in the water column and the enrichment over background concentrations in the elutriate and field tests (observed) for Thorpe St Andrews.

Metal fraction	Experimental Observed Fold of Enrichn over backgrou			
	(µg l <sup>-1</sup> )	(µg l <sup>-1</sup> )	Experimental	Observed
Total Hg	0.57	0.34	11	7
Total Cu	12.5	7.3	6	4
Dissolved Fe	983	712	1.8	1.3
Total Fe	1338	1007	1.8	1.4
Dissolved Mn	200	222	1.6	1.6
Total Mn	253	292	1. <b>6</b>	2

The elutriate test simulations successfully predicted the metal concentrations observed in the field monitoring exercise for Hg and Cu to within a maximum factor of 2.3 times the field concentration. In the majority of cases the factor was between 1 and 2, suggesting that even at moderately low Hg and Cu concentrations in the overlying water, the elutriate test provides a sensitive prediction of water quality. Iron and Mn concentrations were accurately predicted by the simulation to within a maximum factor of 1.5 with most predictions lying in the range 0.9-1.2. In all cases, except for Mn, the laboratoty experiments predicted maximum metal concentrations higher than those observed in the field (Table 19).

The elutriate tests predicted that Hg and Cu concentrations in the water column should peak within 7 h of cessation of dredging and approach background concentrations 48 h after dredging. This was observed for the field water samples and suggests that Hg and Cu were at least partially associated with Fe which displayed a similar water column profile. Regression analysis at 95% confidence limits indicated the strongest metalmetal correlation was between Hg and Fe in the overlying water ( $r^2=0.63$ ) with Cu and Fe concentrations less strong but still significantly correlated ( $r^2=0.52$ ). The majority of both Fe and Mn was soluble (<0.45  $\mu$ m) rather than particulate associated with 85% dissolved Mn and 70% dissolved Fe in both the elutriate tests and field monitoring.

Dredging appeared to have less pronounced effects on water physico-chemistry. An exception was that for TOC concentrations (Figure 19) which displayed a 4-fold increase above the  $T_0$  concentration of 3 mg l<sup>-1</sup> during the dredging operation before dropping rapidly once dredging had stopped.

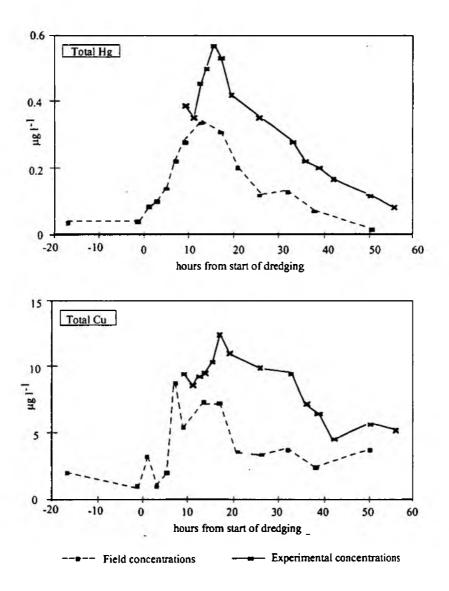


Figure 17. Field and experimental data for total Hg and Cu concentrations in overlying water during and after a dredgeing operation.

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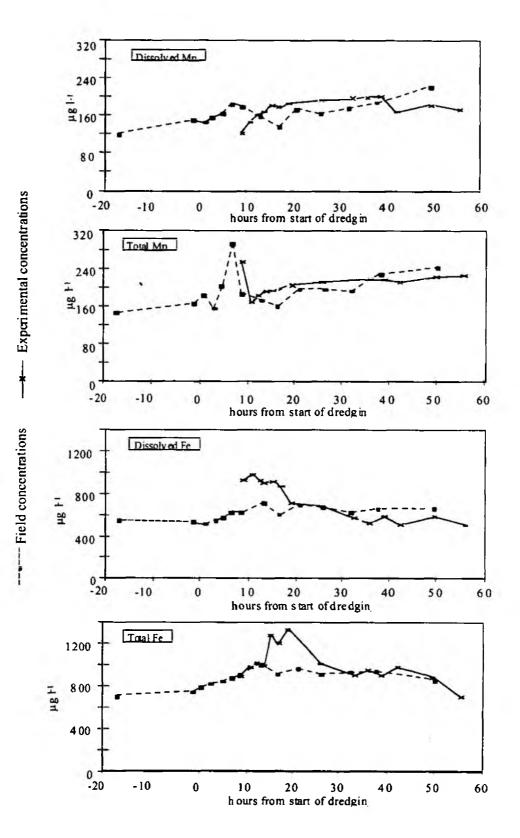


Figure 18. Field and experimental data for total and dissolved Fe and Mn concentrations in overlying water during and after a dredging operation.

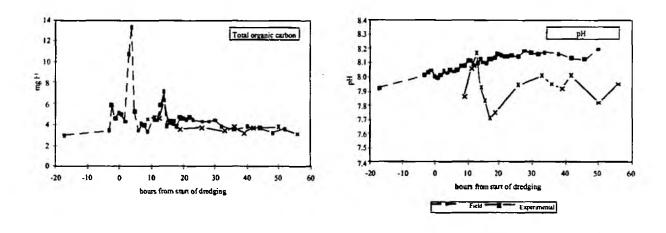
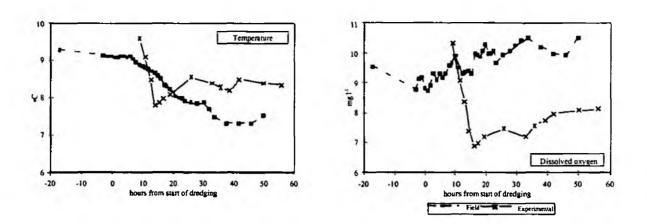
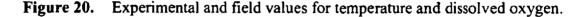


Figure 19. Experimental and field values for total organic carbon and pH.

A second peak was evident at time 12-14 h which coincided with the maximum release of Hg, Cu and Fe to the overlying water, before returning to the background concentration. In the elutriate tests TOC was significantly correlated with Hg ( $r^{2}=0.65$ ), but not with Cu ( $r^{2}=0.4$ ) which indicates the existence of strong organic-Hg complexation in the water column.

The predicted and observed values for pH, DO, temperature and TOC are compared in Figure 18 and 19. Although the pH was generally 0.1 pH units lower in the elutriate tests than that observed in the field (pH 8-8.1), the simulation did predict a fairly constant pH which was confirmed during the dredging operation. Dredging therefore had no effect on surface water pH in the R. Yare system. Values for DO were predicted to show a steady decline from 10 mg l<sup>-1</sup> 1 h after settling had begun to 7 mg l<sup>-1</sup> at 8 h, however a slight recovery to 8.5 mg l<sup>-1</sup> was predicted after 48 h. This was not seen in the field. Since DO concentration depends on temperature the continuous drop in temperature observed in the field (from 9.4 to 7.2 °C over 50 h) could have affected the water DO concentration profile observed. The diffusion of oxygen into the elutriate system does not simulate field conditions very closely as there is not a continuous supply of fresh water flowing through the simulation as occurs in the field. Conductivity values were predicted to fluctuate slightly around 0.85 mS cm<sup>-2</sup> which was observed in the field. Dredging thus had little impact on DO concentrations or conductivity of the River Yare water.





# 4.5.3 Effect of seasonal physicochemical conditions on potential metal remobilisation

Elutriate tests on sediment taken from the dredge site during the summer months were used to compare the likely remobilisations of metals under two extreme seasonal conditions. Initial metal concentrations within the sediment and water column were similar to those found during the winter months. The most important physico-chemical changes were a 40 mV increase in sediment redox potential and a 13 °C increase in sediment and water temperature in the summer months (Table 17). Neither of these changes produced significantly different results for the release of metals (all 'T'-tests p>0.05) from those presented for the elutriate tests conducted under winter conditions (Figure 21).

# 4.5.4 Effect of salinity on potential metal remobilization

Rockland Broad sediment was used to conduct elutriate tests with and without the addition of sodium chloride to determine the effect of a saline water intrusion on metal remobilisation during a dredging operation. The dredging site described at Thorpe St Andrews was not considered realistic for simulations of this type as saline intrusions do not occur in that area. Bulk sediment and water parameters used in the Rockland Broad elutriate tests are given in Table 20.

Mercury contamination of this sediment was twice as high (9.8 mg kg<sup>-1</sup>) as that observed at the dredge site whilst the Cu concentration was lower (86 mg kg<sup>-1</sup>). Total concentrations of Hg, Fe and Mn obtained in the overlying fresh water and more saline water are presented in Figure 22 and indicate that metal release was not significantly

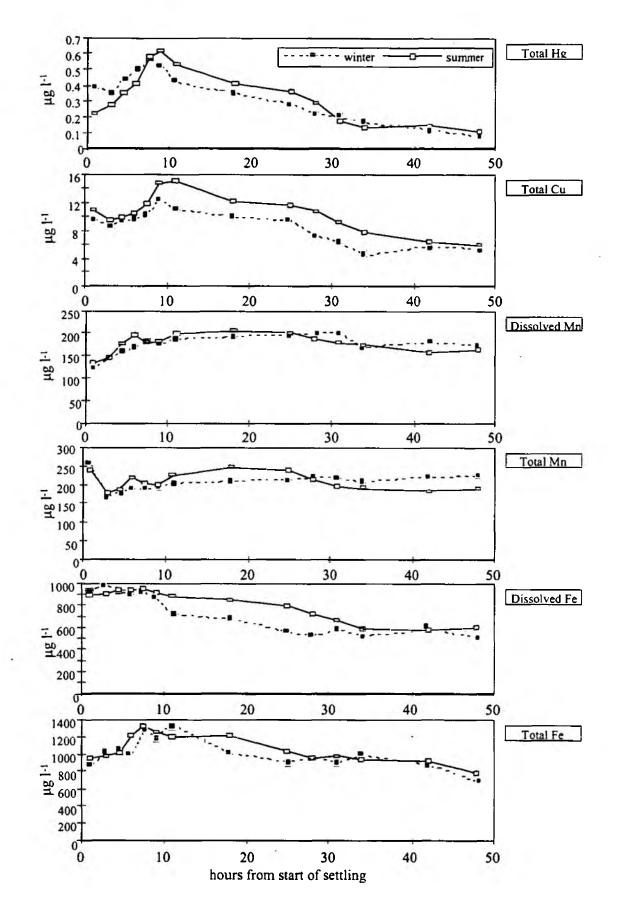
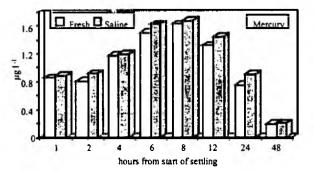


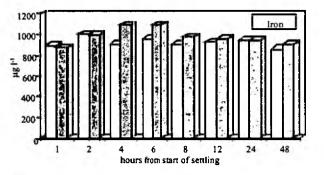
Figure 21. Variations in release of metals from sediments to freshwater during summer and winter for elutriate tests.

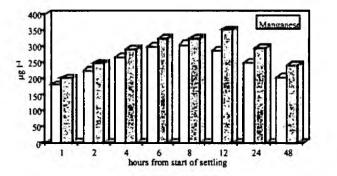
Table 20.

Metal concentrations and physico-chemical parameters for bulk sediment and water for Rockland Broad elutriate tests.

Parameter	Rockland Br	oad
Metals	Sediment (mg kg <sup>-1</sup> )	Water (µg l⁻¹)
Mercury	9.81	0.05
Соррег	86.2	2.0
Iron	27847	720
Manganese	606.1	115
Temperature ('C)	8.1	8.7
pH	6.47	7.55
Redox (mV)	-226	+225
% Total solids	21.6	
TOC $(g kg^{-1}/mg l^{-1})$	101.1	10
Chloride (mg l <sup>-1</sup> )		234
$DO(mgl^{-1})$		10.8





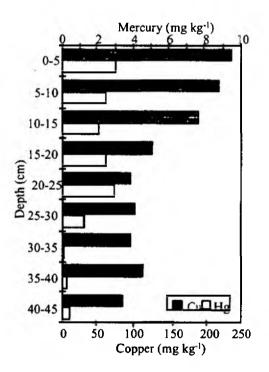


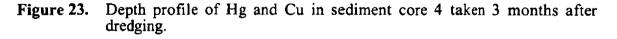
Elutriate test results under fresh and saline water conditions. Figure 22.

different (student 'T'-test p=0.09) in the two experiments, but concentrations always tended to be slightly higher under simulated saline conditions. Copper concentrations in the overlying water did not exceed 5 µg l-1 and changes in concentration observed were not sufficient to provide statistically significant data.

#### 4.5.5 Post-dredging effects on sediment contaminant loadings

Grab samples of bottom sediment taken 3 months after the dredging operation indicated a two-fold increase in Hg and Cu concentrations in the top 2 cm of sediment within a 50 m radius of the dredged area. The average surficial concentration of Hg before dredging was 0.9 mg kg<sup>-1</sup> which increased to 2.2 mg kg<sup>-1</sup> while surficial Cu concentrations nearly doubled from an average of 112 mg kg<sup>-1</sup> to 198 mg kg<sup>-1</sup>. These increases were probably caused by the overlaying of more highly contaminated sediment dredged up from depth. This view is supported by a core taken from the dredged site (Figure 23) which exhibits high concentrations of Hg in the upper layers, decreasing down the core which is the reverse contamination profile to that obtained during the preliminary survey of the area. This increase in surficial Hg and Cu concentrations may have implications for the long term effects of dredging operations on metal availability.





#### 4.6 The fate of heavy metals in dredged sediments disposed on an upland landfill

The removal of sediment from its wet, anoxic environment to the oxic, drier conditions created in the laboratory to imitate the prevailing conditions on an upland disposal site caused a number of physicochemical changes. As the 70 d period of the experiment progressed the top 0.5-1 cm of the sediment changed from the initial dark brown-black

colour to a lighter brown colour and took on a drier crumbly appearance. This was accompanied by an increase in redox potential. Leaching of water through the sediment and clay layers and into the collection bottles at the base of the columns occurred to varying degrees with some columns yielding no leachate and the 54 day column leaching 123 ml. In some cases water also settled on the surface of the sediment. As a result of the bottom leaching and evaporation of water from the sediment surface due to air being pumped over the surface, the sediment throughout the column became more compact and drier. These general observational trends were reflected in changes in Hg volatilised from the sediment surface, increases in redox potential, a shift towards a more alkaline pH and increases in sulphate and nitrate concentrations, all of which are presented in the following sections.

#### 4.6.1 Mercury and copper pathways

The major pathways considered for Hg and Cu from the sediment were leaching in the aqueous phase and movement through the sediment of any mobile species. In the case of Hg voltilisation of Hg<sup>0</sup>, methyl- and dimethylmercury were considered possible. The results indicate that there were no pathways which could be considered significant for Hg or Cu from the bulk sediment over the 70 day period. However, of the minor changes observed the volatilisation of Hg was the most important, although this only represented approximately 0.0005% of the mercury in the sediment core. Volatile Hg species released from the sediment were trapped and measured on a regular basis (Figure 24). Over 70 days 1.56  $\mu$ g Hg was released from a surface area of 1.63 x 10<sup>-2</sup> m<sup>2</sup>.

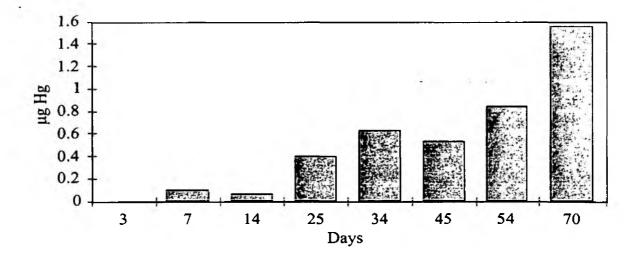


Figure 24. Total Hg volatilised from the columns over 70 days.

Changes in metal concentration within the sediment of each column were minimal. Comparison between the initial bulk metal concentrations of the sediment when collected (Table 21) and those obtained for Hg and Cu during the experiment (Figure 25 and 26) indicate that the variations observed with time were not significantly different from natural variations which could be expected within the sediment.

Metal (mg kg <sup>-1</sup> )	Sediment	Clay
Hg	7.70 ± 1.2	<b>0.41 ± 0.06</b>
Cu	$102.4 \pm 14$	$18.8\pm3.1$
Mn	937.6 ± 105	614.8 ± 155.2
Fe	29281 ± 3485	<b>26189 ± 7235</b>

Table 21.	Mean metal concentrations in bulk sediment and clay.
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An increased loss in volatile Hg species with time from the surface of the sediment is not reflected in a drop in Hg concentration at the sediment surface, but this is because the loss to volatilisation as a percentage of the total amount of Hg in a column was only approximately  $1.05 \times 10^{-5}$  %. The concentrations of both total Fe and Mn remained constant throughout the sediment profiles with time (Appendix 7 contains all data recorded).

The leachate collected from each of the columns was analysed for Hg but none was detected (detection limit 0.1  $\mu$ g l<sup>-1</sup>) suggesting that either the clay layer had trapped any Hg leached in the pore water or there was no Hg in the pore water. As no significant increase in the clay layer Hg content was observed with time, it is likely that little Hg was leached in the pore water. The movement of soluble Hg species through the sediment profile was not thus not considered to be a major pathway under the conditions and over the time period studied. The sediment was also analysed for organomercury, but none was detected at greater than 0.2  $\mu$ g.kg<sup>-1</sup>.

59

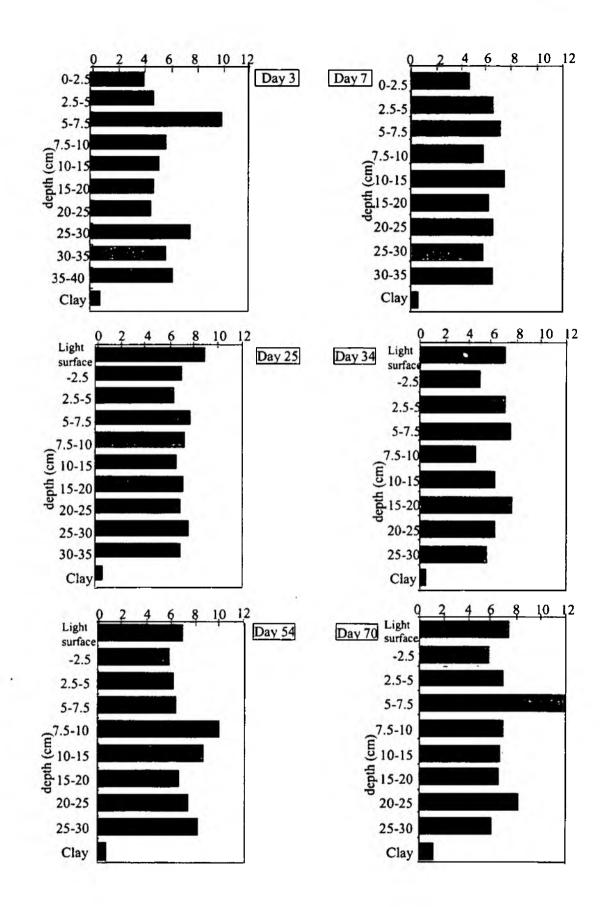


Figure 25. Depth profiles of Hg concentrations (mg  $kg^{-1}$ ) with time for the column experiments.

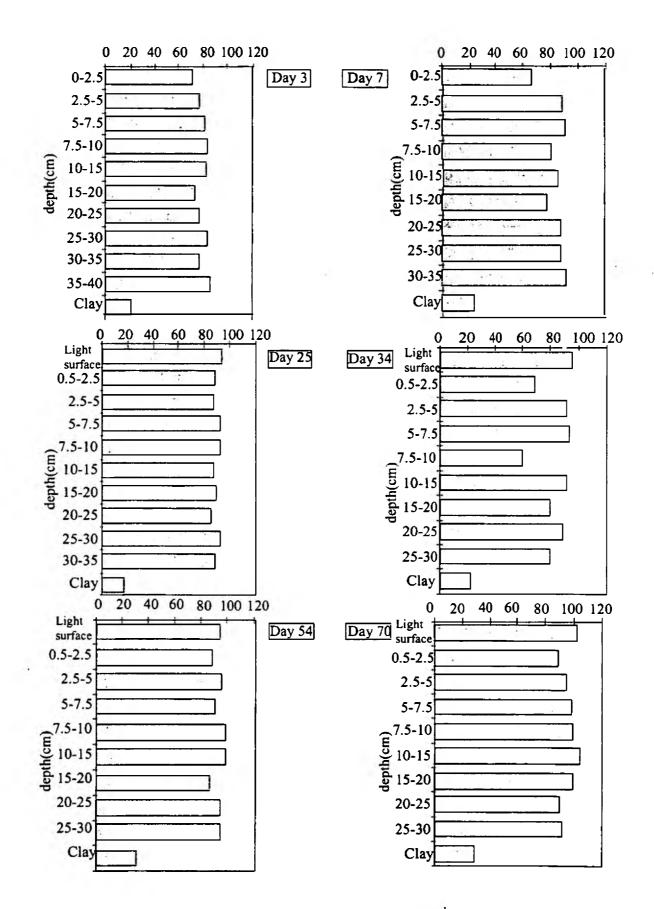


Figure 26. Depth profiles of Cu concentrations (mg  $kg^{-1}$ ) with time for column experiments.

### 4.6.2 Redox potential and pH changes

A general increase in sediment redox potential was observed with time, especially within the surface to 2.5 cm interval (Figure 27) which experienced the highest oxygen penetration. Initially conditions were strongly anoxic (-225 mV) and within the first 7 days a rapid increase to 20 mV was observed. During the remaining 9 weeks of the experiment fluctuations between 50-100 mV were recorded with a final redox potential of 150mV, thus approaching oxic conditions. Column profiles indicated more anoxic conditions with depth, but as time progressed these more negative redox potentials also moved into the moderately anoxic zone. The clay layer was generally less anoxic than the sediment directly above it, reflecting the low mobility of compounds bringing about reducing conditions from the sediment to the clay.

The pH of the sediment remained relatively constant with time in the range pH 6-7, however the lighter surface layer was generally slightly above neutral pH and ranged from pH 7.5-8 after the first 7 days of the experiment. Drying out of the surface layer did thus not promote acidification.

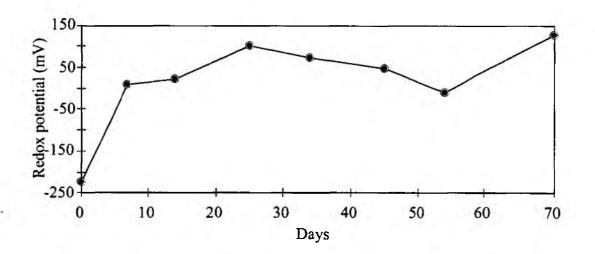


Figure 27. Change in surface-2.5 cm layer redox potential with time.

#### 4.6.3 Changes in anion concentrations

Chloride, nitrite, nitrate, sulphate and phosphate were analysed for, but only sulphate and nitrate concentrations changed significantly with time. The increases observed generally reflected the increases in redox potential. Thus surface sediments which were becoming less anoxic displayed the largest increases in nitrate and sulphate concentrations with time (Figure 28). The sulphate concentration in the surface to 2.5 cm interval of sediment was 1232 mg kg<sup>-1</sup> on day 3 and increased to 1504 mg kg<sup>-1</sup> by day 70 while nitrate concentrations increased from 14-36 mg kg<sup>-1</sup> over the same period. However, these changes appeared to not be large enough to cause mobilisation of Hg or Cu to a measurable extent.

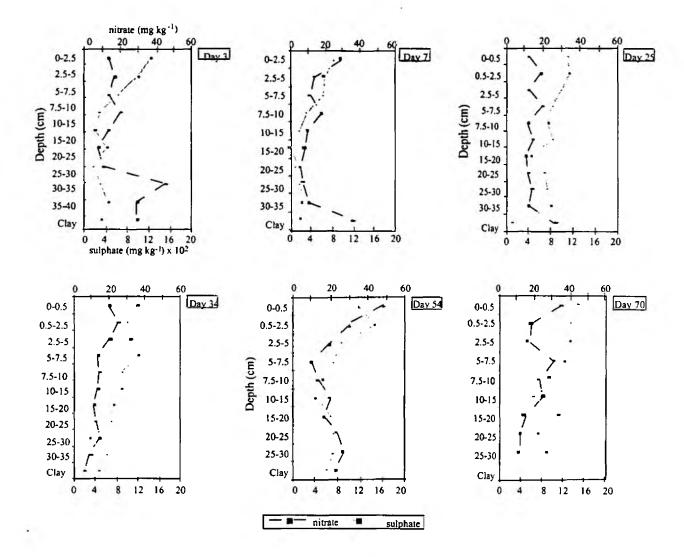


Figure 28. Depth profiles of nitrate and sulphate concentrations with time for column experiment.

### 4.6.4 Changes in total solids, volatile solids and total organic carbon content

Sediments dried out relatively slowly under the laboratory regime of 17 °C and pumped air so that the moisture content of the sediment decreased by approximately 2.5% over the 10 week period with more drying out occurring at the sediment surface than lower down the columns. The volatile solids content remained relatively constant at approximately 16%. Total organic carbon levels were in the range 4-8% without any trends over time being apparent (Appendix 7).

63

### 4.7 Assessment of the biological impact of dredged material

An assessment of the potential availability of Hg and Cu in dredge spoil to earthworms and plants was carried out by growing earthworms on contaminted dredge spoil in the laboratory and by collection and analysis of plants growing on a landfill.

### 4.7.1 Heavy metal uptake by the earthworm *E. fetida*

The earthworm *E. fetida* was grown on Hg and Cu contaminated weathered dredge spoil from the Griffin Lane landfill or uncontaminated soil collected from an adjacent field for 28 d under controlled laboratory conditions. A group of worms  $(T_0)$  was also analysed immediately, without being exposed to either soil.

Table 22.	Total metal concentrations (mean $\pm$ standard error) and physico chemical
1	parameters of contaminated dredge soil and uncontaminated soil.

	Total metal concentration (mg kg <sup>-1</sup> )*					g <sup>-1</sup> )*	
<b>C</b> 7	Redox	pН	TOC	Hg	Cu	Mn	Fe
Soil	(mV)		%				
Uncontaminated	380	7.0	2.31	0.069±0.013	5.2±0.10	560±0.2	10186±121
Contaminated	244	6.9	3.12	2.84±0.27	82±0.4	323±5	14630±632

\*n = 5 samples

The contaminated dredge spoil contained approximately 40 times more Hg and 15 times more Cu than the uncontaminated soil (Table 22), but this was not reflected in the metal concentrations found in the earthworm tissue after exposure to the respective soils (Table 23). Although the average Hg concentration in earthworms living in the contaminated soil was greater than for worms living in uncontaminated soil (Table 23), as a proportion of the spoil Hg concentration it comprised only 2%. Earthworms that lived on the uncontaminated soil had body burdens of Hg of 50% as a proportion of Hg in the soil. Similar earthworm:soil ratios are presented in Table 24 for all the metals determined.

The average concentration of Cu in the worms grown on contaminated soil and in the control group was greater than in the uncontaminated group (Table 23), but the worm:soil ratio for the worms grown in contaminated sediment is low, suggesting low Cu availability. The concentration of both Mn and Fe is higher in the worms grown on uncontaminated soil, as are the worm:soil ratios, suggesting lower availability of these metals in the contaminated soil.

**Table 23.** Total metal concentrations (mean  $\pm$  standard error; range in brackets) of *E*. *fetida* and average weight per worm before and after the bioassay experiment.

	Sample	Average	weight (g)	Average	metal conc	entration (mg	g kg <sup>-1</sup> )
Group	size	Before	After	Hg	Cu	Mn	Fe
Control	40	1.30±0.36	-	0.012±0.004	1.7±0.3	1.5±0.7	57±16
				(0.0017 - 0.015)	(1.2-2.2)	(0.7-2.5)	(35-79)
Uncontaminated	30	1.54	1.07±0.27	0.035±0.005	1.2±0.2	8.8±2.6	207±45
			(0.58-1.68)	(0.029 - 0.039)	(0.9-1.4)	(5.5-12.6)	(155-273)
Contaminated	60	1.72	1.07±0.23	0.056±0.012	3.2±0.3	2.6±0.7	152±32
			(0.55-1.57)	(0.034-0.069)	(2.8-3.7)	(1.4-3.6)	(104-186)

**Table 24.** Worm/soil ratios for concentrations of Hg, Cu, Mn and Fe in *E. fetida* tissue and soil when placed in heavy metal contaminated and uncontaminated soil.

Metal	Contaminated	Uncontaminated
Hg	0.02	0.5
Cu	0.04	0.2
Mn	0.008	0.02
Fe	0.01	0.02

No earthworm fatalities were observed, although the average weight per earthworm fell in both test groups during the 28 d duration of the experiment. In the contaminated group the average weight fell by 0.65 g and in the uncontaminated group by 0.47 g. The loss of weight may have been due to the nutritional requirements of the worms not being met.

### 4.7.2 Total and extractable soil metal concentrations

The differences in the physicochemical parameters of the contaminated spoil and uncontaminated soil will determine the degree of adsorption, precipitation and solubility of the metals within the soil structure. This in turn will affect the mobilisation of the metal and hence availability. Soil total metal concentations across the transect could be divided into two groups, according to their source. The geochemical metals (Fe, Mn and K) occurred within the range of expected background concentrations, but did display a trend with the topography of the transect (Figure 29). Generally, the higher the elevation of the sampling location, the lower was the geochemical metal content of the soil. This may have been brought about by the runoff of soluble Fe and Mn oxyhydroxides to the lower sampling locations on the dredge spoil heap (locations 3, 4 and 5).

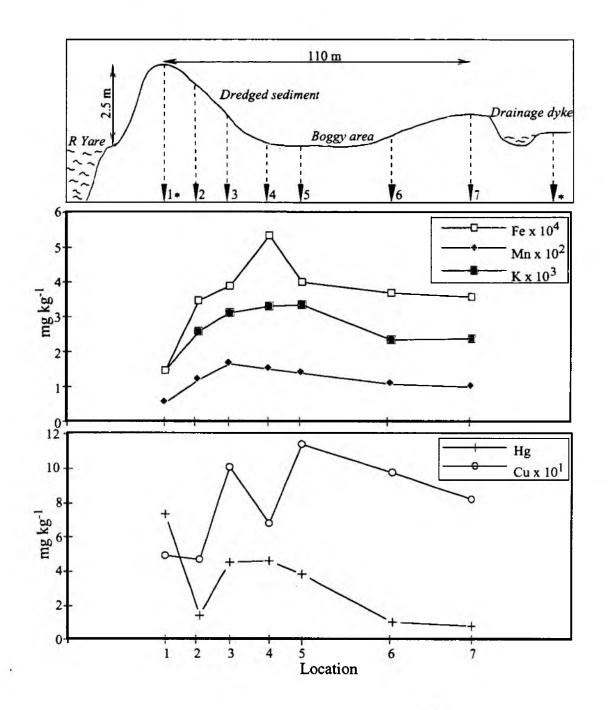


Figure 29. Metal analysis of plants accross the Griffin Lane landfill.

Mercury, one of the two metals of anthropogenic source investigated, was most similarly distributed to the geochemical metals, except for at location 1 where the highest Hg concentration for the transect occurred (Figure 29 and Table 24). This distribution probably reflects a combination of the different sediment disposal episodes which have each introduced distinct concentrations of the pollutants, and the subsequent upland environmental factors, including runoff, which have affected the distribution of Hg in the disposed sediment. It is known that soils sampled at locations 1 and 2 were dredged and dumped in November 1993 and that the remainder of the spoil heap (up to location 4) is made up of dredgings from before 1992. The soil from locations 6 and 7

66

	Soil	sequential	extractio	ns and dige				digestion	s
Metal/	DTPA	dilA¶	Total <sup>*</sup>	%DTPA <sup>†</sup>	%dilA <sup>†</sup>	Plant	Root	BAC	<sup>‡</sup> x 10 <sup>3</sup>
location		(mg kg <sup>-1</sup>	)			(mg	kg <sup>-1</sup> )	Plant	Root
Fe		x 10 <sup>4</sup>	$x \overline{10^4}$						
1	198	0.538	1,47	1.35	36.6	95.0	73.9	6.5	5.0
2	330	1.40	2.59	1.27	54.2	101	202	3.9	7.8
3	211	1.32	3.13	0.67	42.2	38.1	62.2	1.2	2.0
4	386	1.54	3.31	1.17	46.7	73.4	151	2.2	4.6
5	646	1.57	3.36	1.93	46.9	7.51	143	0.2	4.3
6	392	1.22	2.33	1.69	52.6	56.0	526	2.4	22.6
7	400	1.09	2.40	1.67	45.5	90.8	612	3.8	25.5
Mn									
1	9.51	124	148	6.4	84.1	25.0	13.1	169	89
	25.0	330	346	7.2	95.4	25.9	22.1	75	64
2 3	16.7	254	386	4.3	65.8	26.3	15.5	68	40
4	35.9	455	532	6.7	85.5	24.2	21.0	45	40
5	28.3	335	400	7.1	83.7	22.7	25.3	57	63
6	14.9	305	369	4.0	82.8	23.8	27.6	65	75
7	18.2	304	<u>359</u>	5.1	84.7	25.6	29.9	71	83
K			x 10 <sup>3</sup>			x 10 <sup>4</sup>	x 10 <sup>3</sup>		
1	62.9	150	0.559	11.3	26.8	0.884	3.86	15800	6890
2	173	361	1.21	14.3	30.0	1.27	4.17	10570	3460
3	288	459	1.64	17.6	28.1	1.60	10.4	9760	6350
4	78.6	314	1.52	5.2	20.6	1.33	8.36	8740	5490
5	15.6	180	1.39	1.1	13.0	0.970	7.15	7000	5160
6	197	505	1.07	18.5	47.4	1.40	8.04	13180	7540
7	142	330	0.992	14.3	33.2	1.25	7.00	12560	7060
Cu							······		
1	15.2	30.4	49.7	30.6	61.3	13.2	12.2	265	246
2	9.76	29.8	46.8	20.9	63.6	9.81	14.2	210	303
3	30.5	59.4	101	30.2	58.7	7.27	9.45	72	93
4	17.8	39.2	68.3	26.1	57.4	15.3	14.2	225	208
5 6	33.2	67.6	114	29.1	59.3	8.75	8.58	77	75
6	20.5	60.2	97.5	21.0	61.7	15.3	12.8	157	131
7	21.2	52.6	81.8	25.9	64.3	15.2	14.4	186	176
Hg			<b></b>					_	
1	-	2.43	7.32		33.2	0.066	0.164	9	22
2	-	0.54	1.45	-	37.1	0.025	0.133	17	92
2 3 4	•	1.59	4.57	-	34.7	0.034	0.159	7	35
4	-	2.46	4.64	-	53.1	0.105	0.165	23	36
5 6	-	2.61	3.81	-	68.5	0.043	0.287	11	75
6	-	0.552	1.01	-	54.6	0.028 -		28	137
7	-	0.422	<u>0.841</u>	•	49.5	0.224	0.087	267	104

Average concentrations of metals found in soil extracts and digestates and Table 25. U. dioica digestates from the 7 transect locations.

dilute Acid (10% nitric acid) extract Aqua regia digestion Extract as percentage of total metal in soil

<sup>‡</sup>Biological absorption coefficient

has been on the site for an unknown length of time. Copper was present in contaminating concentrations, but was erratically distributed across the transect in the fairly narrow range of 40-120 mg kg<sup>-1</sup>. The highest concentration of Cu occurred at location 5 which was topographically the lowest point on the transect. This location is

also a very boggy, organic rich region on the landfill where mobile Cu would accumulate.

Other physicochemical parameters monitored indicated uniformally slightly alkaline and oxic soil across the transect (pH 7.2-7.6 and Eh +181 to +270 mV) and a total organic carbon content of 5-6%, except for locations 1 and 4 where 2.8% and 3.8% TOC was found. The ranges of these parameters were small and probably did not cause any observable differences in the extractability of metals or their uptake by plants from location to location.

The bioavailability of the metals was determined by sequential DTPA and cold 10% nitric acid (dilute acid) extractions and there were marked differences between extractabilities of the metals of geochemical and anthropogenic source. The DTPA extractable Fe and Mn concentrations were low and in the ranges 0.7-2 % and 4-7 % of the respective total metals present. As for all metals determined, a higher percentage of the total Fe and Mn were extracted with 10% nitric acid than with DTPA, but similar trends to those for DTPA were apparent across the transect (Table 25). In contrast, the anthropogenic Cu was bioavailable right across the transect as 20-30% was DTPA extractable and 57-64% dilute acid extractable. Mercury was not extracted by DTPA, but the dilute acid extracted approximately 35% of the total Hg from the dredge spoil heap (locations 1-3) and 50-68% from the more mature dredge spoil (locations 4-7).

The redox potential can affect the oxidation state of both Hg and Cu directly or the nature of their associations with components in the soil. The contamimated soil had a lower redox potential than the uncontaminated soil but a larger percentage of organic matter (Table 26). The pH of both soils was approximately neutral.

### 4.7.2 Metal uptake by the plants Urtica diocia and Budleja davidii

The plant species *U. diocia* and *B. davidii* grow in abundance on the site where the river dredgings were dumped. Leaf samples were collected from the site and from an adjacent field and analysed for the metals Hg, Cu, Mn and Fe. The locations used for soil collection in the earthworm experiment were the same for the plant bioassay samples, providing an opportunuty to compare potential uptakes by different biota. The plants collected for analysis showed no obvious external signs of metabolic disorders resulting from micronutrient excesses or deficiencies. Table 27 indicates the metal concentrations in both *U. diocia* and *B. davidii* collected from contaminated and uncontaminated sites.

68

Table 26.Total metal concentrations (means  $\pm$  standard error) and physico-chemical<br/>parameters of contaminated dredge spoil and uncontaminated soil from<br/>which the plant samples were sampled.

· · · · · · · · · · · · · · · · · · ·	Redox	pН	TOC	Total r	netal concent	entration (mg	kg-1)
Soil	(mV)		(%)	Hg	Cu	Mn	Fe
Uncontaminated	380	7.0	2.3	0.069±0.013	5.2±0.1	560±0.2	10186±121
Contaminated	244	<b>6.9</b>	3.1	2.840±0.270	82±0.4	323±5	14630±632

**Table 27.** Total metal concentrations (means  $\pm$  standard error; ranges in brackets) in the leaves of *U. diocia* and *B. davidii* collected from the landfill and an adjacent uncontaminated area.

		A	verage metal con	ncentration (mg kg	g <sup>-1</sup> )
Sample	Sample size	Hg	Hg Cu		Fe
Uncontaminated	5	0.060±0.026	21.7±4.3	16±10.6	243±23
U. diocia		(0.0013-0.093)	(16.5-26.5)	(7-33)	(222-281)
Contaminated	24	0.066±0.032	12.83±4.36	3±2.9	198±37
U. diocia		(0.010-0.140)	(7.0-22.5)	(0-11)	(85-269)
Uncontaminated	5	0.071±0.010	16.6±2.2	1.4±1.1	204±31
B. davidii		(0.055-0.084)	(14.0-19.5)	(0-3)	(159-232)
Contaminated	14	0.075±0.055	17.3±5.5	1.7±2.6	1 <b>74</b> ±22
B. davidii		(0.051-0.100)	(9.0-26.0)	(0-8)	(134-220)

The Hg concentrations in U. diocia and B. davidii from both the contaminated and uncontaminated sites are comparable. A statistical unpaired 'T'-test (Table 28) suggests no significant difference exists between the Hg concentrations in either U. diocia or B. davidii leaves when collected from the two sites, indicating that Hg accumulation by the two plant species from the contaminated site was no greater than from the uncontaminated area.

**Table 28.** Statistical appraisal of the Hg and Cu concentration in *U. diocia* and *B. davidii* from both contaminated and uncontaminated sites. Significance values attached to the student 'T'-test

Species	Hg	Cu	-
U. diocia	0.56	0.0003	_
B. davidii	0.5	0.79	

A significance value p>0.05 indicates that both sets of data could have come from the same population and are not significantly different).

A comparison of Cu accumulation in *B. davidii* from the two sites also indicates that there was no significant difference in Cu concentration in the leaves of the plants, but for *U. diocia* there was significantly more Cu in the leaves of the plants collected from the uncontaminated site than from the dredge disposal site. This supports the earthworm bioassay results that Hg and Cu in the weathered dredge spoil do not pose a serious contamination threat to the species studied under the condition prevailing on the site. It is possible that the most of the Hg and Cu contained within the dredge soil are in a form unavailable to the plants and earthworms which could explain the similarity in the concentrations of the metals found, especially in the plant leaves. However, as the plant species growing on the landfill are not considered standard bioassay plants, it is difficult to assess the overall bioavailability of the metals to these plants.

### 5. DISCUSSION

### 5.1 Assessment of the temporal loadings of mercury, methylmercury and copper in River Yare bottom sediments, 1986-1995

### 5.1.1 Source and history of mercury inputs

The nine annual surveys of the R. Yare bottom sediments carried out by Imperial College from 1986-1995 have revealed a number of trends in the loading of Hg to the river. From the initial 1986 survey it was apparent that the spatial distribution of the contaminants depended on the morphology and bottom sediment types of the river, but that generally there was a downstream profile equivalent to a point source pollution plume. The point source was identified as Whitlingham STW outfall and this has continued to be the major source of heavy metals to the bottom sediments up to the present time. Investigations into the behaviour of Hg in the sewage treatment process at Whitlingham STW indicated removal of approximately 62% of the Hg input could be expected (Goldstone et al., 1990). On this basis the load of Hg released to the river from the STW for the period 1964-1995 has been calculated as approximately 5000 kg (Table 29) with the major contamination occurring prior to 1973. Prior to the establishment of the Water Authorities by the 1973 Water Act the Norwich County Council were responsible for granting discharge licences; a limit of 2000 kg Hg a<sup>-1</sup> was set on the main chemical factory responsible for Hg inputs. Since the introduction of the Control of Pollution Act in 1974, the commissioning of a new treatment works at Whitlingham in 1989 and stricter controls on the load of Hg into the sewage works, inputs of Hg to the river have declined to less than 25 kg a-1. (Anglian Water, 1994).

Period	Load received (kg y <sup>-1</sup> )	Total received (kg)
1964-1972	896	8068
1973-1984	variable	4909
1985-1986	< 30	50
1987-1995	< 25	170
Total received		
		13197
Total released		5015*

**Table 29.**Mercury loading to Whitlingham STW and thence to the River Yare (data<br/>supplied by AWA and NRA).

\*Assuming mean Hg removal efficiency at Whitlingham STW of 62 %

At present the STW is consented to release a final effluent with a maximum concentration of 7  $\mu$ g l<sup>-1</sup> Hg (Whitlingham STW consent of 30/1/1990, reference AW4TF1789B). This is equivalent to a maximum legal release of 0.464 kg Hg per day under dry flow conditions (66250 m<sup>3</sup> effluent per day) or approximately 170 kg Hg a<sup>-1</sup>.

### 5.1.2 Spatial extent of the contamination plume

In 1986 the Hg contamination plume emanating from Whitlingham STW outfall was apparent along the full length of the survey (17 km) from Trowse in the west to Hassingham in the east. The complete river survey in 1987 from Colney in the west, to Breydon Water in the east, confirmed that the plume extended upstream of the STW outfall due to tidal reversal and downstream as far as Hassingham, beyond which lowlevel tailing down to Breydon Water occurred. Downstream transport and dispersion of Hg-containing sediments by fluvial sediment transport has played an important role in the position of the contamination plume. In 1986 it was apparent that the heaviest loadings of Hg to the sediment did not occur at the STW outfall, but 4-6 km downstream (Figure 6). This was partly because the sediment in the vicinity of the outfall is gravely or sandy and thus the Hg did not adsorb strongly onto these sediments. Silty sediments occurred in the most contaminated region. Thus the regions with the highest concentrations of Hg were found to be areas where sediment deposition actively occurs in the river. There has been little downstream movement of the contamination, due first to the strong attraction between Hg and the organic-rich bed sediments and secondly to the slow movement of sediment within this specific reach of the river. The large drop in sediment concentration observed after 1989 reflects the corresponding decrease in Hg discharges from the STW. Since that time, when discharges had declined to <1  $\mu$ g l<sup>-1</sup>, the maximum Hg concentration observed in the sediments has remained fairly fixed (Figure 30). Examination of average river transects further illustrates the stability of the peak postion suggesting that downstream movement is dependent upon movement of bed-load and that with the low flow regime of the R. Yare this is a very slow process. The siltation rate in the river is fairly high, thus the highest concentrations of Hg and Cu now occur below the surface of the bottom sediments.

As the sewage effluent quality improved, cleaner sediment material transported into the contaminated zone was probably less contaminated with Hg. This cleaner sediment overlaid and mixed with the more contaminated older sediments and a dilution effect was created. Cores taken from within the contaminated area clearly show the most contaminated sediments are buried at depths of up to 50 cm with cleaner sediments in the surficial regions (Figure 11, Core 1). This overlaying of the contaminated sediments by cleaner sediments is further supported by the analysis of cores taken at Rockland Broad in 1990, 1992 (Imperial College, 1992) and 1995. In 1995 the highest concentrations of Hg were observed at core depths between 40 and 58 cm, whereas in 1992 the Hg maxima was closer to the surface between 12 and 25 cm and in 1990 the maxima occured between 8 to 18 cm below the sediment surface.

Surveys of Rockland, Wheatfen, Strumpshaw and Surlingham Broads conducted between 1986-1992 indicate that the Broads have formed a significant sink for mercury contaminated sediments accounting for fully 50% of the Hg bound within the river sediments (Imperial College, 1992). Thus remobilisation of contaminated sediments from the Broads, either through mud-pumping, storm surges or dredging could prove to be a source of moving a contaminant plume downstream or re-exposing contaminated sediment and providing a fresh source of Hg to biota.

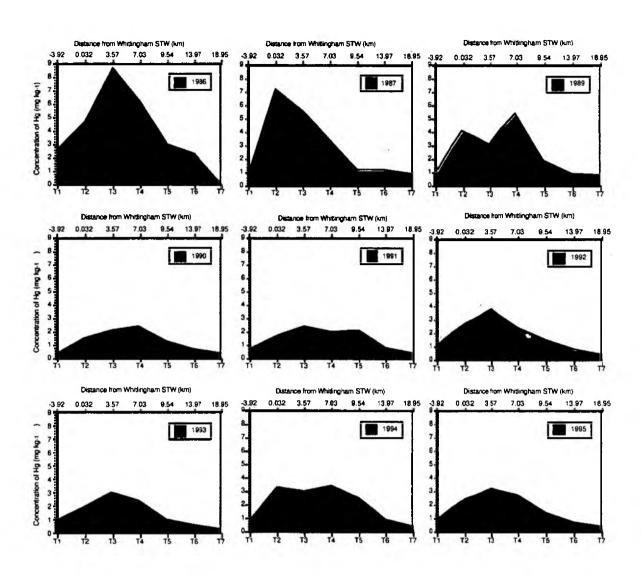


Figure 30. Transects illustrating location of plume maxima over time.

### 5.1.3 Determination of a background concentration of mercury

The determination of a background concentration of Hg within the R. Yare system enables a quantitative assessment of the magnitude of Hg enrichment within the polluted area. Morphologically similar sediments to those encountered within the contaminated area were obtained from the lower study reach (Reedham to Breydon Water) which is considered to be outside the contaminated zone. The average Hg concentration was 0.4 mg kg<sup>-1</sup> which is higher than the 0.19 mg kg<sup>-1</sup> calculated as the mean global sediment concentration (Marowski and Wedepohl, 1971) but agrees with the average shale concentration of 0.4 mg kg<sup>-1</sup> (Forstner and Wittmann, 1979). This suggests some contamination of the lower reach sediments may have occurred, but for comparison purposes the internal background concentration was considered most suitable. Mercury concentrations in the upper catchment area of the R. Yare are generally  $<0.1 \text{ mg kg}^{-1}$ , but the sediments are sandy or gravelly, precluding comparison with the silts and clay deposits of the contaminated zone.

# 5.1.4 The magnitude and variation of mercury enrichment within the pollution plume

In 1986 bottom sediment Hg concentrations were in the range of 0.05-32.9 mg kg<sup>-1</sup> with an average concentration of 5.35 mg kg<sup>-1</sup> or an average enrichment of 13.4 over the background concentration of 0.4 mg kg<sup>-1</sup> (Table 29). From 1986 the mean Hg concentration declined every year to 1.28 mg kg<sup>-1</sup> in 1990, a 4-fold decrease in mean enrichment in 4 years (Figure 31). From 1990 to 1995 the mean concentration fluctuated between 1.28-2.06 mg kg<sup>-1</sup>, an average enrichment of 3.2-5.2, indicating little improvement in the contamination levels for these 6 years.

Table 30.	Summary of total mercury concentrations in bottom sediments, 1986-
	1994.

Year	No of samples	Total merce	Total mercury (mg kg <sup>-1</sup> )		
		Mean†	Range <sup>‡</sup>		
1986	197	5.35	0.05-32.9	13.4	
1987	103	2.98	0.19-15.2	7.5	
1989	40	2.47	0.11- 15.9	6.2	
1990	66	1.28	0.01-4.68	3.2	
1 <b>99</b> 1	78	1.33	0.02-4.59	3.3	
1992	115	1.78	0.01-6.89	4.5	
1993	114	1.40	0.03-8.67	3.5	
1 <b>994</b>	69	2.06	0.04-6.13	5.2	
1995	73	1.90	0.08- 6.60	4.8	

†Mean of transects 4-34 except 1986 (7-26). Full data set in Appendix 2

‡Range of full survey

\*No of times background of 0.4 mg kg<sup>-1</sup> Hg is exceeded by mean concentration

The processes which could potentially have contributed to the variations in concentrations of Hg in the R. Yare bottom sediments seen from 1986-1995 are outlined in Table 30. On a national scale the R. Yare is one of the most Hg contaminated rivers (Table 31), but alongside rivers receiving Hg inputs from mercury processing plants and gold mining, especially in South America, the contamination appears less considerable.

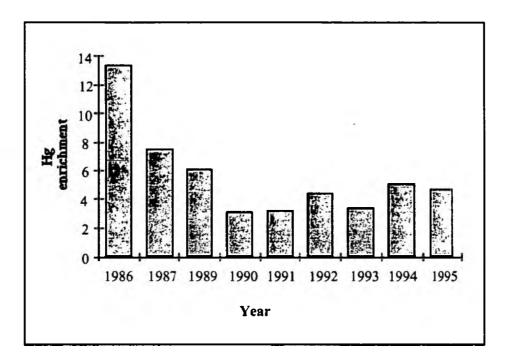


Figure 31. Average enrichment of Hg over background concentrations, 1986-1995.

Table 31.	<ul> <li>Processes contributing to va</li> </ul>	riations in bottom se	ediment Hg concentrations.
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Decreased loadings	Increased loadings
•Decreased Hg inputs	•Increased Hg inputs
•Downstream transport and dispersion of	•Re-exposure of buried contaminated sediment by
particulate bound Hg by sediment transport	dredging activity or boat movements
•Burial of contaminated sediment by less	•Bioturbation of contaminated sediments buried at
contaminated fresh sediment	depth by various organisms
•Remobilization of bound Hg due to	•Increased river flow rates caused by storm events
physicochemical changes or microbial	or unusually high rainfall leading to scouring of
activity leading to Hg solubilization or	bottom sediments and re-exposure of
volatilization	contaminants
•Uptake by biota	

Inputs of Hg to the river from Whitlingham STW declined sharply from 1976-1980 and this was reflected in a sharp drop in average bottom sediment Hg concentrations 10 years later, from 1986-1990 (Figure 32). Effluent Hg concentrations have subsequently declined still further to approximately 0.1  $\mu$ g l<sup>-1</sup> by 1994, but since 1990 mean sediment concentrations have plateaued out in the range 1.3-2.1 mg kg<sup>-1</sup> with no significant improvement in sediment quality evident. Assuming maximum sediment concentrations of 30 mg kg<sup>-1</sup> and a 97% reduction in Hg inputs, current surface deposits should contain 0.9 mg kg<sup>-1</sup>. In reality the maximum spot sample in 1995 contained nearly 7 times this level (6.6 mg kg<sup>-1</sup>). This suggests that the decrease in Hg inputs played the predominant

role in the initial decreases observed in bottom sediment Hg, but that subsequently other mechanisms became more important in controlling the presence of Hg within the bottom sediments.

Location	River	[Hg] (mg kg <sup>-1</sup> )	Reference
Britain	Brett	0.24-0.59	Barak and Mason (1989)
	Carron estuary	2.49	Craig and Moreton (1983)
	Clyde	0.4-4.4	Bartlett, et al. (1978)
	Dart	0.01-0.55	Dept. Environ. (1976)
	Dart `	0.11-1.72	Craig and Moreton (1986)
	Dee	0.02-1.3	Dept. Environ. (1976)
	Liffey estuary	0.14-4.61	Jones and Jordan (1979)
	Mersey	0.40-6.0	Dept. Environ. (1976)
	Plym estuary	0.018-2.61	Millward and Herbert (1981)
	Plym estuary	0.08-0.44	Craig and Moreton (1986)
	Swansea estuary	0.02-1.6	Dept. Environ. (1976)
	Teign	0.09-0.34	Craig and Moreton (1986)
	Thames	1.0-3.3	Lindberg et al. (1975)
Continental	de Waal (Rhine)	5.2 (1958)	Japenga et al. (1990)
Europe		6.3 (1970)	
		6.5 (1972)	
		1.2 (1981)	
	Rhine	1.2-23.3	de Groot et al. (1971)
	Danube	0.09-0.86	Kozlova et al. (1986)
USA	Mississippi	0.07-1.10	Andren (1973)
	St Louis	5-5070	Glass et al. (1990)
	Berrys Creek*	9-452	Berman and Bartha (1986)
	Brunswick estuary*	1-27	Winger et al. (1993)
Canada	Lake Tadenac	0-0.3	Wren & MacCrimmon (1986)
	Wabigoon River	0.1-7.8	Armstrong & Hamilton (1973)
Australia	Lerderberg*	0.03-130	Bycroft et al. (1982)
Brazil	Madeira River†	50-280	Pfeiffer et al. (1989)
	Mutum Parana†	210-19800	Pfeiffer et al. (1989)
	Paraiba do Sul†	300-550	Pfeiffer et al. (1989)
	Muriaé†	90-650	Pfeiffer et al. (1989)
	Paraibuna†	300-900	Pfeiffer et al. (1989)
Venezuela	Roscio district†	0.12-129	Shrestha & de Quilarque (1989)

Table 32.	Mercury	concentrations in	ı river	sediments	nationally	v and interr	nationally.
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\* Mercury processing plants, † Gold extraction using mercury

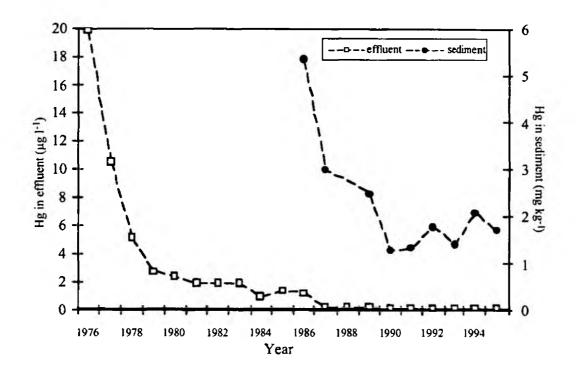


Figure 32. Concentrations of Hg in STW final effluent and bottom sediments, 1976-1994.

As the sewage effluent quality improved newer sediment material transported into the contaminated zone could be expected to be less contaminated with Hg. This cleaner sediment overlayed and mixed with the more contaminated older sediments and a dilution effect was created. Cores taken from within the contaminated area clearly show the most contaminated sediments are buried at depths of up to 20 cm with cleaner sediments in the surficial regions. Thus sediment transport not only affected the position of the most contaminated area but also contributed to the absolute decline in Hg concentrations.

The changes in Hg concentrations observed in bottom sediments since 1986 are also dependent on changes in sediment and water chemistry which affect the mobility and availability of Hg. Salinity levels within the R. Yare vary with tidal conditions and although the saline limit generally occurs at Cantley, occasional intrusions further upstream into the Hg contaminated area do occur (NRA data, 1993). Release of trace metals from estuarine sediments has been interpreted as due to oxidation processes and intensive breakdown of organic matter (both mediated by micro-organisms, Prause *et al.*, 1985) whereafter the released metals become complexed with chloride and/or ligands from the decomposing organic matter in the water. In this way the uptake by or precipitation on suspended matter may be inhibited. It has also been suggested that the major cations, magnesium and calcium, are co-adsorbed and that competition from these species for adsorption sites increases with increasing salinity (Millward and

Moore, 1982). Mercury mobilised under such conditions would thus be likely to be permanently lost from the sediment sink, but the slow dissipation of Hg from R. Yare sediments by this process is likely to be masked by processes with larger short-term impacts. As saline intrusions to the contaminated area are intermittent and variable in magnitude the extent of re-mobilisation caused is also difficult to estimate.

Increases in acidity of sediments and water are known to cause substantial increases in dissolved metal concentrations and the acceleration of Hg methylation in sediments (Fagerström and Jernelöv, 1972). The R. Yare is, however, a well buffered, slightly alkaline system due partly to the presence of a calcareous bedrock. The measurements of water and sediment pH have varied within the range 6.9-8.0 for the duration of the river surveys suggesting a stable system not likely to be conducive to Hg remobilisation.

Changes in naturally dissolved organic matter such as humic material and amino acids may also play a role in metal remobilisation. Increases in dissolved organic carbon can lead to elevated concentrations of Hg in the water column (Mierle and Ingram, 1991). This is discussed in more detail for the R. Yare in the section on the effects of dredging on water quality. Synthetic chelators such as nitrolotriacetic acid (NTA) which are released in sewage effluent may have a more significant impact on Hg mobility (Salomons and van Pagee, 1981) by actively desorbing it from the sediment and by negatively effecting the natural adsorption processes it undergoes when discharged in effluent containing NTA. There is no evidence to support the role of any synthetic complexing agents in Hg re-mobilisation within the R. Yare.

Seasonal changes in redox potential of R. Yare bottom sediments have been observed, but changes of approximately 30 mV were not sufficient to change the sediments from reducing to oxidising conditions nor were these changes for sustained periods of time. Only under extreme conditions such as dredging will redox conditions suitable for metal re-mobilisation arise. Other minor routes for Hg loss from sediments are volatilisation as Hg<sup>0</sup> or dimethylmercury as a result of microbial activity (Bothner *et al.*, 1980) and uptake by biota (0.2% of total load, Kudo *et al.*, 1978), but these most be considered as minimal when compared to sediment transport and burial over a 9 year period.

Bioturbation, or the stirring and mixing of sediments by the burrowing and feeding of benthic organisms, may contribute to the re-exposure and mobilisation of contaminated sediments buried at depth (Reynoldson, 1987). Krantzberg *et al.* (1985) demonstrated increased oxygen penetration, enhanced microbial activity, changes in pH and alteration of particle and pore sizes of sediments caused by benthic macro-invertebrates such as

78

oligochaete worms and bivalve molluscs. This may result in the redistribution of physicochemical forms and promote the flux of nutrients and pollutants to the water column. Increased release of methylmercury in the presence of benthic invertebrates has been reported (Jernelöv, 1970) whilst other trace constituents behave in a similar fashion (Wood, 1975; Karickoff and Morris, 1985). Most bio-turbation is confined to depths of 0-20 cm (Petr, 1977) but as large amounts of mussel and snail shell debris are routinely encountered on the annual sediment surveys, bioturbation may represent a continual low-level turnover of contaminated bottom sediments to surface sediments.

Another and possibly more important source of the periodic increases observed is bank erosion and slumping of sediments into the river which may contain elevated levels of mercury deposited in pre-1986 dredging events. Along the River Yare from Cantley to Whitlingham the banks show evidence of having been built up artificially. Dredged sediments have historically been used to build up the banks for flood defence purposes. It is likely that Hg contaminated material has been used. Subsequent erosion of these banks could provide a steady but low level source of Hg back to the river. Storms which cause rapid erosion, may again be the source of episodic increase of Hg observed in bottom sediments. This potential source of Hg back to the river, was not commisioned in this study and should be looked at in the future.

From the information collected over the nine years of bottom sediment surveys the most important controlling factors for the nature and behaviour of the Hg contamination have been:

- i. Decreased inputs led to decreased bottom sediment loadings within 10 years
- ii. The dominant fate of Hg contaminated sediments has been burial at depth by a cleaner overlay of sediment, as evidenced by cores taken at Thorpe St Andrews (this report) and in the main river (Imperial College, 1992)
- iii. Fluvial transport of contaminated sediments is less dominant than sediment burial, but is of concern due to the Broads acting as sediment traps and the need to dredge the Broads periodically.
- iv. Disturbances of contaminated sediments either by storm surges or anthropogenic activity may cause sporadic increases in bottom sediment Hg concentrations
- v. Changes in the contamination profile brought about by biota and other natural processes such as saline intrusions and bottom scouring due to increased flow rates are continuous, but mostly low-level in comparison to bank erosion and anthropogenic influences

## 5.1.5 The magnitude and variation of methylmercury within the pollution plume

The occurrence of methylmercury (MeHg) within the R. Yare bottom sediments is probably a result of methylation of inorganic Hg by both biotic and abiotic pathways. The concentrations measured within the sediments reflect the net production of MeHg as both methylation and demethylation mechanisms exist. Investigations by Imperial College have focussed on biotic pathways by examining the influences of microbial populations and factors which affect their performance within the methylationdemethylation cycle including pH, redox potential, DO, temperature and sulphide concentrations and have already been comprehensively reviewed (Imperial College, 1992). The occurrence of MeHg in the main river surveys and some of the possible abiotic pathways for methylation are discussed here.

Methylmercury concentrations within bottom sediments of the R. Yare are, spatially, highly variable, contrasting with the more predictable total Hg profiles (Figures 7 & 9). A pollution plume centred on Whitlingham STW is thus not as evident for MeHg as it is for Hg, suggesting that total Hg is not the most important factor in dictating MeHg levels in bottom sediments. On closer inspection, however, a plume profile is evident; it is the areas of unexpectedly high MeHg concentrations around Trowse and Cantley, which is better illustrated by plotting MeHg as a percentage of total Hg, which masks the profiles. In most surveys the maximum MeHg concentration corresponds with the region of highest Hg contamination 2-6 km downstream of the STW outfall and this is supported by moderately significant correlations between MeHg and total Hg concentrations. Since 1986 the mean concentration of MeHg has ranged between 1.8 and 7.9  $\mu$ g kg<sup>-1</sup> (Table 33).

Table 33.Summary of methylmercury concentrations in bottom sediments, 1986-<br/>1994.

Year	No of samples	Methylmero	ury (µg kg <sup>-1</sup> )
		Meant	Ranget
1986	10	5.3	0.7-13.2
<b>19</b> 87	24	1.8	0.5-6.4
1989	46	3.3	0.3-13.7
1990	69	7.7	0.7-29.5
1991	71	7.3	0.1-22.2
1992	58	3.6	0.1-21.8
1993	64	7.9	1.0-23.1
1994	69	7.3	1.0-24.4

†Mean of transects 4-34, except 1986 & 1987 which were preliminary studies in which a limited number of samples were analysed from the contaminated reach ‡Range of full survey Although the overall average concentration of MeHg for this period has been 5.5  $\mu$ g kg<sup>-1</sup> in some locations the MeHg concentration has appeared to be increasing with time indicating that either Hg available for methylation has increased. Thus while the total concentration of Hg is decreasing within the sediments, bioavailable mercury has remained constant or increased.

River or location	[MeHg]	[Hg]	% MeHg:Hg	Reference
	(µg kg <sup>-1</sup> )	(mg kg <sup>-1</sup> )		
Freshwater				
Southern Indian Lake, MB	0-18	0.03-0.12	0-1.5	Ramlal et al. (1987)
Quabbin Reservoir, MA	0.02-0.86	0.009-0.045	0.05-16.3	Gilmour & Henry (1991)
Wachusetts Reservoir, MA	<0.01-0.4	0.020-0.060	<0.02-1.1	Gilmour & Henry (1991)
Vernon Lake, ON	0-0.2	0.017-0.052	0-5.3	Gilmour & Henry (1991)
Harp Lake, ON	0-0.8	0.001-0.007	0-12.3	Gilmour & Henry (1991)
Deep Creek Lake, MD	0-0.25	0.017-0.055	0-0.92	Gilmour & Henry (1991)
Estuarine/marine				
San Fransisco Bay	0.01-0.14	0.19	0.01-0.21	Olson & Cooper (1974)
R Carron, UK	<0.5-50.2	1.0-3.95	<0.04-2.6	Craig & Moreton (1983)
Mersey Estuary, UK	<0.3-7.8	<0.05-5.3	<0.05-0.81	Bartlett & Craig (1981)
R Clyde, UK	<0.3-44	<0.3-4.9	<0.1-1.02	Bartlett & Craig (1981)

Table 34.	Total and methylmercury concentrations and percentage ratio methyl- to
	total mercury in some natural sediments.

All other conditions being equal total Hg concentrations would dictate MeHg concentrations (Rudd *et al.*, 1983; Parks *et al.*, 1984), however, in the environment MeHg concentrations, due to their predominantly biological nature of origin (Compeau and Bartha, 1985) are significantly influenced by factors such as temperature and bacterial populations that have little or no effect on Hg concentrations. The result of this is that total and methylmercury concentrations may show very poor correlations in the field. The varying abilities of particular environments to methylate Hg is often compared quantitatively by citing the precentage ratio of MeHg to total Hg present. These ratios are highly variable, with values up to 58% in some anaerobic waters (Parks *et al.*, 1989) and up to 16% in certain sediments (Table 34). Sediment ratios, as observed for the majority of the R. Yare sediments, are more usually less than 1% (Jernelöv and Asell, 1975; Bartlett and Craig, 1981). Elevated MeHg to total Hg ratios evident at Trowse and Cantley illustrate this variability. At Trowse it is possible that both abiotic MeHg production play a significant role in causing elevated

MeHg loadings. Abiotic methylation has been proposed as an important mechanism in the presence of methyltin compounds (by methyl group transfer) and humic substances (Weber, 1993). Methyltin compounds (mono- di- and trimethyltin) occur in water, biota and the sediments of many aquatic environments because of their use in antifouling paints in the past, but humic matter is the most likely environmental methylating agent for several reasons. Its concentration in waters and sediments is high. It is associated with the solubility and thus mobility of Hg in freshwater, probably by complexation. In addition, several model studies have demonstrated that humic matter effectively methylated Hg(II) forming MeHg (Nagase *et al.*, 1982; Weber *et al.*, 1985).

Correlations, more significant in some years than others, have been established between %VS, the surrogate for organic material content, and MeHg concentrations for the R. Yare sediments. The difficulty in knowing whether this is due directly to methylation by humic material or because of stimulation of microbial methylation in the presence of humic material is illustrated by a study of Jackson (1988) who investigated the problem of why fish in newly formed reservoirs contain high concentrations of Hg.

Increased Hg concentrations correlated with increased terrestrial organic matter from the submerged forest land. Jackson attributed increased MeHg formation in sediments primarily to stimulation of microbial activity by the organic matter and simultaneous oxygen depletion. However Weber (1993) argues that Hg(II) solubilisation by terrestrial humic matter and its ability to methylate Hg(II) may contribute to increased methylation of Hg(II) in sediments.

The %VS content at Trowse is high, but not particularly elevated over other regions of the river. However, other factors such as the still shallow water in this area allow facile temperature rises and the penetration of light, both implicated in increased MeHg production (Summers and Silver, 1972; Callister and Winfrey,1986). Other low energy areas such as the broads behave similarly. At the other extreme Parks and Hamilton (1987) predicted high river flows would also increase MeHg production by oxidation of anaerobic sulphide and subsequent release of Hg(II). At Cantley physicochemical conditions are not generally different from the remainder of the river in that region, but the presence of a sugar beet processing plant which discharges cooling water at 25 °C (NRA, pers. comm.) and possibly some nutrients, could create ideal conditions for microbial increases and possible elevated MeHg production.

Additionally it was noted during sampling at Cantley in July 1995, that adjacent to the processing plant on the eastern side there is a large storage area of coal. The average concentration of mercury in coals ranges between 12  $\mu$ g kg<sup>-1</sup> to 46,000  $\mu$ g kg<sup>-1</sup>

82

concentrations as high as 300,000  $\mu$ g kg<sup>-1</sup> are not unknown (Hem, 1970). Atmospherically deposited mercury may be more readily available for methylation then mercury sorbed to sedimentary particles. At Cantley, atmospherically derived Hg from the combustion of coal cannot be ignored.

Furthermore, Cantley occurs in upstream section of tidally induced salinity fluxes. While the toe of the saline wedge may occur further upstream, this is a zone of freshwater/saltwater mixing with waters alternating between salinity extremes. While the literature suggests that microbial methylation rates are suppressed by saline water little is known as regards the impact of alternating saline and freshwater conditions on either microbial or inorganic methylation. However, provided the current conditions within the region of Cantley are condusive to methylation and a continual source of available Hg elevated MeHg could be expected within this region of the river.

Methylation does not necessarily have to occur within the river sediment or water column, but can also occur at the STW itself, either by microbial or abiotic means, leading to discharge of Hg as MeHg into the river. In a study of the behaviour of Hg during sewage treatment at Whitlingham STW (Goldstone *et al.*, 1990) less than 0.5% of the total Hg present was converted to MeHg during treatment and small concentrations (<10-20 ng l<sup>-1</sup>) was detected sporadically in the final effluent (0.91  $\mu$ g l<sup>-1</sup> total Hg), most having presumably been removed with the settleable sludge. In 1994 the total Hg concentrations in the final effluent are so low as to make the detection of MeHg virtually impossible. Thus, this mode of introduction of MeHg to the river may have been important when effluent Hg levels were very high, but it makes a very minor contribution today.

# 5.1.6 The magnitude and variation of copper enrichment within the pollution plume

Copper, as a co-pollutant with Hg from Whitlingham STW outfall, has displayed broadly similar behaviour and trends within the bottom sediments to those already discussed for Hg; burial has been the dominant process with some fluvial movement. Inputs to the river have decreased 5-fold since 1989 to approximately 6  $\mu$ g l<sup>-1</sup> in the final effluent in 1994 and 1995 (Anglian Water data, Figure 33, 1995 not shown), but with a consent of 300  $\mu$ g l<sup>-1</sup> (NRA consent for Whitlingham STW, 1990) there is still a legal possibility of approximately 7200 kg of Cu being discharged into the river every year under dry flow conditions. Current discharges of Cu to the river are in the order of 145 kg a<sup>-1</sup>.

A background concentration of Cu within the R. Yare bottom sediments was determined as 20.9 mg kg<sup>-1</sup> (n=64) from the average concentration of Cu within the study reach below Cantley to Breydon Water (transects 35-48) for the 1992 and 1993 river surveys. This is lower than the average shale standard of 45 mg kg<sup>-1</sup> (Förstner and Wittmann, 1979) and is in the lower range of 20-80 mg kg<sup>-1</sup> reported for lacustrine deposits (Wedepohl, 1978).

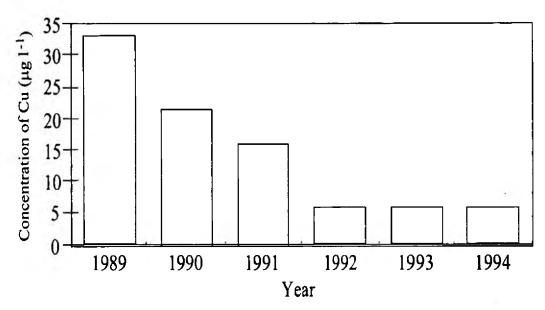


Figure 33. Average concentration of Cu in final effluent discharged from Whitlingham STW, 1989-1994.

Table 35.	Summary of total copper concentrations in botto	om sediments, 1986-1995.

Year	Year No of samples		Total copper (mg kg <sup>-1</sup> )		
	-	Mean†	Range <sup>‡</sup>		
1986	197	106.5	5.0-375.0	5.1	
1987	103	75.8	2.2-239.6	3.6	
1992	115	81.5	2.1-290.5	3.9	
1 <b>993</b>	114	59.8	4.2-214.8	2.9	
1 <b>994</b>	69	71.5	5.8-192.9	3.4	
1995	74	59.1	4.9-164.2	2.8	

†Mean of transects 4-34 except 1986 (7-26). Full data set in Appendix 2, ‡Range of full survey

\*No of times background of 20.9 mg kg<sup>-1</sup> Cu is exceeded by mean concentration

Discharges of Cu have declined more recently than those for Hg and this is reflected in a more constant persistence of Cu within the bottom sediments (Table 35). The average enrichment of Cu within the contaminated reach has not declined substantially below the 1987 level of 3.6 to date. From 1986 to 1994 the average bottom sediment Cu concentration declined by 33% whilst Hg concentrations fell by 61% in the corresponding period. An improvement in the current effluent quality for Cu is not expected as the sources are diverse and mostly domestic in nature. However, if sediment Cu concentrations mirror the 10 year lag time observed for Hg after improvements in effluent quality, improvements in sediment quality for Cu may not be observed for a number of years yet.

The extent of the contamination plume is similar to that for Hg, stretching from Trowse in the west to approximately Hassingham in the east with the most contaminated area located 2-6 km downstream of the STW outfall. As with Hg the position of the plume has not shown much downstream movement with the highest concentration of Cu occurring within 3.5 km of the STW (Figure 34).

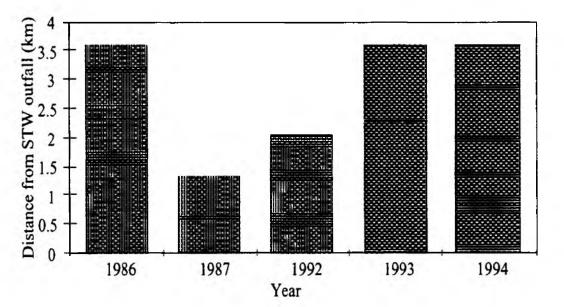


Figure 34. Distance from STW outfall at which maximum spot Cu concentration occurred, 1986-1994.

The more fixed nature of the contamination plume is further evidenced by the relatively low concentrations of Cu found in Surlingham and Rockland Broads which are approximately 5 km and 7 km downstream respectively. In 1986 cores taken in these broads had Cu concentrations in the range 14.4-177 mg kg<sup>-1</sup>, a maximum enrichment of 8.5 over the background concentration. Mercury concentrations were in the range 0.3-22.4 mg kg<sup>-1</sup> with a maximum enrichment of 56 times background. In 1994 bulk sediment taken to a depth of 1 m in Rockland Broad had a mean Hg concentration of 7.7 mg kg<sup>-1</sup> and a Cu concentration of 102.4 mg kg<sup>-1</sup>, enrichments of 19 and 5 times background respectively. These broads would thus not be expected to act as a source of Cu to the main river, as appears to be the case for Hg.

## 5.2 Assessment of the contamination of fish flesh from the River Yare by mercury and methylmercury, 1986-1994

Surveys of fish flesh from within the Hg contaminated reach have been conducted on a rigourous basis since 1993, using roach (*Rutilus rutilus*) and eel (*Anguilla anguilla*) as sample species. Prior to 1993 a number of surveys were conducted on eel, roach and northern pike (*Esox lucius*). Sampling for these surveys was less exacting and in some cases sampling numbers were too small to be considered representative. However, data from before 1990 still gives an indication of the extent of Hg contamination when sediment Hg concentrations were at their highest. A summary of the surveys undertaken is given in Table 36.

Fish species	Location	Survey date	Sample	Total H	Total Hg (mg kg <sup>-1</sup> )	
			size	Mean	Range	
Eel	Rockland Dyke	July 1994	51	0.21	0.06-0.50	
(Anguilla anguilla)	Rockland Dyke	July 1993	25	0.16	0.06-0.60	
	Whitlingham- Langley	June 1991	28	0.18	0.04-0.63	
	Rowing club-Langley	Oct 1989	18	0.16	0.01-0.44	
	Brundall-Langley	Dec 1985	99	0.46	0.06-1.08	
Roach	Rockland Dyke	July 1994	40	0.06	0.028-0.12	
(Rutilus rutilus)	Rockiand Dyke	July 1993	17	0.17	0.11-0.23	
	Whitlingham-Langley	May 1991	17	0.10	0.05-0.22	
	Brundall	Dec 1986	9	0.19	0.11-0.47	
	Yare (unspecified)	1984	1	0.44	-	
	Yare (unspecified)	Jan 1971	13	0.71	not known	
Pike	Bramerton Woods	May 1991	2	0.12	0.08-0.16	
(Esox lucius)	Brundall	Dec 1986	8	0.71	0.26-0.77	
	Coldham Hall-Brundall Gdns	Dec 1985	2	0.28	0.26-0.29	

**Table 36.** Total mercury concentrations in eel, roach and pike fish flesh samples taken from the River Yare (1971-1994).

### 5.2.1 Temporal [Hg] trends in fish from the R. Yare

The most important environmental factor effecting Hg concentrations in eel flesh from the R. Yare appears to be the total availability of Hg in the system. An examination of sediment and fish data collected since 1986 found that as average bottom sediment concentrations have declined so have average eel flesh Hg concentrations. Regression analysis of these two factors gives a correlation coefficient of 0.95 (n=5,  $r^2=0.9$ , F value = 26.9, p<0.05). There therefore seems to be a strong link between bottom sediment Hg concentrations and eel flesh Hg concentrations on the R. Yare, but this relation is not that straightforward. This is shown by examination of the average Hg burden of eels surveyed since 1985 which shows that since the source of the Hg was stopped the overall burden of Hg in these fish quickly dropped to levels similar to those observed in eel from Ormesby Broad (Figure 35). What this means is that the decrease of Hg in eels from the Yare is related to availability of Hg in the system rather then amount of Hg.

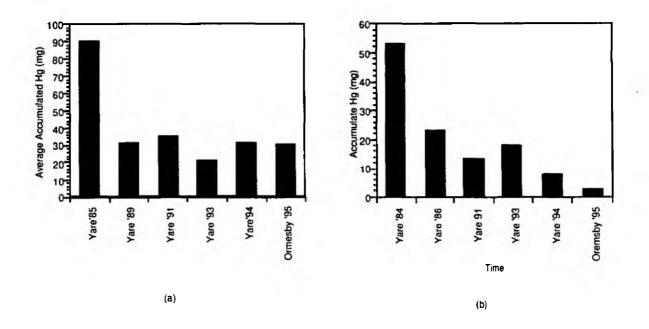


Figure 35. (a). Mercury accumulated in eels from the R. Yare since 1985 and in eel from Ormesby Broad. (b). Mercury accumulated in roach from the R. Yare since 1984 and in roach from Ormesby Broad.

As eels are predatory, the sharp decrease is probably due to the immediate response of the plankton population to the improved water quality of the system. An intermediate stage in the Hg pathway from sediment to fish such as zooplankton or phytoplankton may be invoked for example (Nishimura and Kumagi, 1983) where the plankton feed on Hg contaminated particulate matter suspended from the river bed by water flow. The Hg contaminated plankton is then swallowed by the fish. Mason *et al.* (1995) believe that phytoplankton initiate the enrichment of MeHg from the water by accumulating MeHg in their cytoplasm. This leads to greater trophic transfer of MeHg to zooplankton during grazing. This ultimately leads to MeHg concentrations in fish being determined by water chemistry which controls MeHg speciation and uptake at the bottom of the foodchain. Whatever the true pathway is, it depends initially on THg concentrations within the bottom sediment.

### 5.2.2 The inter-site study

Fish were collected from Ormesby Broad in order to determine how far the fish from the R. Yare needed to drop in Hg burden in order to reach background. In this case, background is defined as the concentration of Hg found in fish from an uncontaminated area within the same region. The background concentrations of Hg in fish at Ormesby Broad were much higher then expected considering that no contamination was found in the sediments. In the UK, a sediment concentration of <1.0 mg kg<sup>-1</sup> Hg is considered to be not contaminated (Greater London Council Guidelines), the average concentration of Hg in the sediment of Ormesby Broad was 10 time less and in a range expected for sediments derived from carbonate rocks (Dooley, 1992).

Accumulation patterns of Hg in fish are dependent on a variety of interconnecting variables. Even if the availability of Hg from food and water is similar for different species, the uptake rates and total body burdens may vary with rate of ingestion, voidance time, assimilation of food and the ability to assimilate Hg from the food sources and water column. The type of food eaten, the organisms' membrane permeabilities and species specific metabolic differences may also play an important role in influencing body burdens. In addition, sex, breeding status and growth dilution of the contaminant must be considered (Richman *et al.*, 1988; Håkanson, 1984). Badsha and Goldspink (1988) demonstrated that the main factors affecting uptake and accumulation of contaminants were locality, species, sex, age and state of gonadal maturation, as well as environmental factors.

In the inter-site study the most important factor affecting eel muscle tissue THg concentrations was locality and the major difference between the localities was the bed sediment THg concentrations. Eels reflect this difference more readily than roach because they burrow in bottom sediments and predate on various organisms including polychaetes, decapods, gastropods and fish (Moriarty, 1978) and may be expected to both bioaccumulate Hg from the water column and sediment and biomagnify Hg from contaminated food. However, biomagnification can be more apparent than real (DeFreitas *et al.*, 1974) as predators at the top of the food chain are generally longer lived and have different metabolic and growth rates compared to their shorter lived, faster growing prey. The mean age of eels in the 1994 R. Yare and Ormesby surveys was 13 y whilst roach averaged 4-5 y. Eels probably also accumulate more Hg than roach as they are solely predatory, whilst roach are omnivorous. Predators such as eels will generally be exposed to Hg for a longer period of time, and therefore, even in the absence of trophic transfer would accumulate more Hg. However, field studies indicate that predatory fish will contain more Hg regardless of age. In the 1994 R. Yare eel

survey the correlation between age and flesh Hg content was low, suggesting that whilst age is an important factor, its use as a pointer to bed sediment THg concentrations is complicated by other species-dependent parameters. Wren *et al.* (1986) observed that the average Hg concentration of a 3 year old pike (*Esox lucius*) was 1.0 mg kg<sup>-1</sup> compared with 0.34 mg kg<sup>-1</sup> for yellow perch of the same age from the same lake.

Eel length was correlated with Hg flesh concentrations for both locations in the intersite comparison. As shown by Håkanson (1984), the relationship between fish length and metal concentration is dependent on the organ studied as each chemical form of Hg targets a particular body organ. A positive length/metal concentration correlation will be obtained when the metal target is the dependent factor in the relationship. Fish flesh was the main target of organomercurials, as was observed in the eel surveys, where approximately 85% of Hg was present as organomercury, regardless of site. A positive relationship between length and Hg in flesh is possible even at relatively uncontaminated sites such as Ormesby Broad because of the long half-life of organic Hg in fish flesh (Brooks and Ramsey, 1974).

Roach muscle tissue concentrations of Hg have generally mirrored those observed for eel although the data sets are smaller and thus less representative. The slow decline in body burden of roach since the initial study of the R. Yare in 1985 suggests that Hg is less available to eel in this system. Since the Hg burden in the eel has been constant and at background since 1988 while for roach it has has a gradual decrease this certainly seems to be the case. The study suggests that for monitoring long term effects of Hg discharges to a river system similar the the Yare that roach are an excellent indicator.

Human Hg poisoning by consumption of fish from the R. Yare is very unlikely. Eels are an important food source in continental Europe, but are less important locally. The suggested tolerable weekly intake of Hg for humans is 300  $\mu$ g of which no more than 200  $\mu$ g should be present as MeHg (FAO/WHO, 1973). This would require the consumption of more than 160 g of eel muscle tissue (approximately 1.5 eels) every day from the R. Yare at mean 1994 contamination levels before the tolerable Hg intake would be exceeded in a given week. The US EPA (1984) recommended a more conservative average daily intake (ADI) of 20  $\mu$ g Hg day<sup>-1</sup>, which was then recommended as an AIS (maximum dose tolerable for subchronic exposure) for alkylmercury and mixed inorganic and alkylmercury. This ADI would still require average consumption of approximately 100 g of eel muscle tissue a day over a sustained period of time before poisoning occurred. The lowest reported oral lethal dose (LD<sub>10</sub>)

in humans for MeHgCl is 5 mg kg<sup>-1</sup> which for a human of 70 kg would require the consumption of 1960 kg or over 15 000 R. Yare eels at one sitting.

### 5.2.3 Other Sources of Hg to fish in Ormesby Broad and the R. Yare

Eels and Roach from Ormesby Broad contained higher amounts of Hg than would have been predicted from the R. Yare data alone. One of the possible reasons for this is that there is probably a further Hg source to the fish at both sites which has not been considered and this source could be the major Hg source to roach as the muscle tissue Hg concentrations from roach in the R. Yare did not appear to reflect bed sediment THg concentrations. As roach THg concentrations were similar for both sites it is also possible that this source of Hg is the same. The only possible source in this case, as the two sites are 25 km apart, is atmospheric Hg deposition. Sorenson et al. (1994) and Glass et al. (1990) have reported small, but continuous inputs of atmospheric Hg to remote lakes in the USA, mostly dominated by the amount of precipitation in the region. In Sweden Håkanson et al. (1990) have established definitive links between atmospheric Hg deposition and fish contamination. Very little data is available on Hg fluxes in the UK, although Airey (1982) provides figures for Hg in air, snow and rainwater in central England. As the prevailing winds in East Anglia are from the east where the industrialised regions of England are centred, it is possible that similar levels of atmospheric Hg deposition occur over the area investigated, but further work is required before a definitive link can be established.

The average concentration of THg in eel flesh has fluctuated in the range 0.16-0.21 mg kg<sup>-1</sup> since 1989. In lake systems where Hg concentrations in fish have increased the principal controlling factor proposed has been water pH. As waters become more acidic due to acid rain, Hg increasingly partitions into the water column, MeHg production may be stimulated, demethylation rates decrease and fish gills become more permeable to MeHg (Haines *et al.*, 1992). The R. Yare is a well buffered slightly alkaline system with a water pH in the range 7.6-8.1 and thus increased acidity is unlikely to have played a major role in the fluctuations in eel flesh Hg concentrations observed.

### 5.2.4 Comparison with other British Rivers

Mercury concentrations in eel and roach muscle tissue from the R. Yare are similar to those reported for other British rivers. This includes rivers whose bed sediments are not considered to be polluted by Hg, such as the R Chelmer and R Brett in eastern England (Table 37). MAFF (1973) reported a mean eel muscle tissue concentration of 0.16 mg

kg<sup>-1</sup> Hg for the UK, while Mason (1987) found Hg concentrations in the range 0.09-0.66 (mean 0.31) mg kg<sup>-1</sup> in eel muscle tissue from East Anglian sites. Rickard and Dulley (1983) recorded a range of 0.07-0.68 mg kg<sup>-1</sup> Hg in eels from the tidal R Thames. This suggests that either the Hg contained within the R. Yare bottom sediments is relatively unavailable to the eels in comparison to other less Hg contaminated British rivers.

A consideration of the percentage ratio of  $[Hg]_{fish flesh}$  :  $[Hg]_{sediment}$  suggests that the availability of the Hg in the bottom sediments of the R. Yare to the fish, and probably other aquatic biota, is low relative to other river systems and Ormesby Broad (Tables 37 and 38). For eels in the R. Yare this percentage ratio has fluctuated in the range 6.5-14% whilst in the three uncontaminted East Anglia sites ratios of 70-260% were found. A related study on Hg in water and invertebrates from the R Brett and R 30) found water concentrations of < 0.1 µg 1<sup>-1</sup> while invertebrates had body burdens in the range 0.025-1.103 mg kg<sup>-1</sup> Hg. Water samples from the R. Yare had comparable Hg concentrations (mean=0.05 µg 1<sup>-1</sup>) with these unpolluted East Anglian rivers.

Table 37.Percentage ratio of fish flesh mercury concentration (wet weight) to<br/>sediment mercury concentration (dry weight) for the River Yare (1984-<br/>1994).

Fish species	Year	Year Mean total Hg (mg kg <sup>-1</sup> )		% Ratio
-		Sediment	Fish	fish:sediment
Eel	1994	2.05	0.21	10
(Anguilla anguilla)	1993	1.40	0.16	11
	1991	1.33	0.18	14
	1989	2.47	0.16	6.5
	<u>1985</u>	5.35*	0.46	8.6
Roach	1994	2.05	0.06	2.9
(Rutilus rutilus)	1993	1.40	0.17	12
	1991	1.33	0.10	7.5
	1986	5.35	0.19	3.6
	1984	5.35*	0.44	8.2
	1971	-	0.71	-
Pike	1991	1.33	0.12	9
(Esox lucius)	1986	5.35	0.71	13
. ,	1985	5.35*	0.28	-5.2

\*approximated to closest chronologically available sediment survey

**Table 38.** Percentage ratio of fish flesh mercury concentration (wet weight) to sediment mercury concentration (dry weight) for selected river and lake systems.

Fish species	Location	Mean total H Sediment	Ig (mg kg <sup>-1</sup> ) Fish	% Ratio fish:sediment	Reference
Eel	R Brett, 1	0.15	0.21	140	Barak & Mason
(Anguilla anguilla)	UK* 2	0.20	0.21	110	(1989; 1990)
	R Chelmer, 1	0.14	0.37	260	
	UK 2	0.33	0.31	90	
Roach	R Brett 1	0.15	0.12	80	Barak & Mason
(Rutilus rutilus)		20.20	0.09	50	(1989; 1990)
	R Chelmer 1	0.14	0.18	130	
		20.33	0.13	40	
Pike	Tadenac Lake	0.14	0.86	600	Wren & MacCrimmon
(Esox lucius)	Tadenac Bay	0.07	0.38	500	(1986)
Crayfish	Lake	3.0	10.0	330	Armstrong & Hamilton
	Ontario				(1973)
Blackfish	Lerderberg R,	0.15	0.085	60	Bycroft et al. (1982)
		1.75	0.64	40	
Brown Trout	Australia	0.15	0.18	120	Bycroft et al. (1982)
(Salmo trutta)		0.75	0.35	50	-

\*Two sites, above and below a town, were sampled for sediment and fish on each river

### 5.3 Dredging and its effects on water quality

Elutriate tests have previously been validated as a method for predicting metal release to the overlying waters following sediment disturbance by dredging (Ludwig *et al.*, 1989). By making minor modifications to the test procedure it has been possible to use the test to accurately predict water quality for Hg, Cu, Mn and Fe in the River Yare over an extended period of time. The method predicted water quality for the 4 metals to within a factor of 1-1.5 times that observed in the field in most cases. This factor rose to a maximum of 2.3 for the low concentration contaminants, Hg and Cu, where small differences between predicted and observed values led to relatively large ratios. All predictions were within 1 order of magnitude of field values.

Results obtained for metals released in the elutriate tests for the dredge site were generally conservative, i.e. they predicted concentrations higher than those observed in the field, as has been previously reported (Ludwig *et al.*, 1989; Palermo and Thackston, 1988b). Conservative elutriate data for Hg at 2 sites was reported by Ludwig *et al.* where field water concentrations were 0.1  $\mu$ g l<sup>-1</sup> and predicted concentrations varied between 0.5-100  $\mu$ g l<sup>-1</sup> (between 1 and 3 orders of magnitude). The variable success of the simulation for Hg in these cases is not clear, but is possibly due to the low concentrations encountered in the sediment. The River Yare is a more contaminated system, allowing Hg concentrations to be predicted to within a smaller range of error.

92

Dredging caused a sizeable short-term release of Hg and Cu into surrounding water which declined to background concentrations within 48 h. The strongest correlation of the release of these metals was with the TOC concentration profile. Increases in concentrations of dissolved organic carbon (DOC) have previously been correlated to increases in water Hg concentrations in river systems (Mierle and Ingram, 1991). Comparison of the time at which peak TOC concentrations were observed in the simulations and the field (Figure 19) with the peak Hg and Cu concentrations (Figure 15) suggest that these metals are largely associated with the organic fraction probably comprising humic and fulvic acids. Lindberg *et al.*. (1975, 1977) demonstrated similar behaviour for Hg and DOC in a dredging operation in which Hg had a peak concentration of 5 times the background concentration in the water column 3 h after sediment disturbance, decreasing within 4.5 h to a steady state value.

Saline water did not appear to have an important effect on concentrations of Hg or Cu released to the overlying water during sediment disturbance. This is probably due to the stability of the metal complexes already present in the sediment and the relatively short contact time of the metal contaminants with the saline water before settling out occurs. In the field, effects of saline water intrusions on the concentration of Hg in the water column differ widely and appear to be governed by the amount of suspended matter in the saline water and not by the salinity directly (Lindberg et al., 1975). Increased salinity does, however, cause a decrease in the Hg complexing ability of fulvic acid, but organic-Hg complexes already formed under low salinity conditions in the sediment appear to be little affected by later influxes of seawater (Xu and Allard, 1991). Similar results have been reported for organic-Cu complexes (Förstner et al., 1989). Experiments conducted at Imperial College on Hg desorption from R. Yare sediments under varying salinities suggests that Hg is strongly sorbed R. Yare sediments and not affected by salinity changes (Priaulx, 1996). Thus, over the short timespan that Hg and Cu concentrations increase in the water after dredging little mobilization is likely to occur from organic-Hg or organic-Cu complexes due to increases in salinity.

The long term effect of increased salinity levels on biotic Cu uptake by *Hediste* diversicolor was also found to be negligible in the range 7.6-30.5 ppt Cl (Ozoh, 1991). This infers that no adverse effects to water column total Hg or Cu will occur if dredging of contamianted fresh water sediment occurs during periods of saline water intrusion.

As the water pH remained fairly constant during and after the dredging operation it is assumed that pH in the range of 7.9-8.1 did not play a significant role in the release profiles observed for Hg and the other metals. Hannan and Thompson (1977) concluded from elutriate tests conducted with radio-labelled <sup>203</sup>Hg that water in the pH

range 7.5-8.1 was not an important mobilisation factor in various sediments and soils. Under the slightly alkaline and oxidising (pH 8.0, 250 mV) water column conditions prevailing at the River Yare dredge site, Hg has been shown by Gambrell *et al.* (1980) to be mostly bound to the high molecular weight organic fraction (humics) and to the reducible fraction containing Fe and Mn oxides with low levels of dissolved Hg (0.05%). Moderately acid reduced (pH 5.0, -150 mV) and weakly alkaline oxidised (pH 8.0, 500 mV) conditions, however, enhanced soluble levels of Hg (Gambrell *et al.*, 1980). Duarte *et al.* (1991) also found a 7-fold decrease in Hg desorption from sediments in the pH range from 5 to 8 while Mosello *et al.* (1989) reported substantial improvements in water quality for trace metal concentrations on elevating the pH of lake water from pH 6 to 6.5. This implies that the slightly alkaline and oxidised conditions in the River Yare water may minimize metal desorption during sediment disturbance. The calcareous nature of the sediments in the River Yare also provide a highly buffered system which is unlikely to suffer from the radical decreases in pH required to induce elevated releases of Hg and Cu from the sediments upon dredging.

Variations in oxygen availability can also stimulate metal desorption from sediments (Wang *et al.*, 1985) but although water DO concentrations did change during dredging this did not correlate with the release of Hg or Cu into the water. This was probably because extreme decreases in DO concentrations are required to produce significant increases in Hg and Cu water concentrations. Increased Hg release from sediment as DO was depleted from 4 to  $0 \ \mu g \ ml^{-1}$  was reported by Wang *et al.* (1989). The release of Hg under these conditions can be partially attributed to the dissolution of Fe and Mn oxides and hydroxides with which it is associated. In the River Yare DO concentrations remained comparatively high (9-10 mg l<sup>-1</sup>) suggesting an oxygen rich environment which would not bring about metal desorption from particulates.

The release of Mn from the sediment compartment, which occurred much more rapidly than for Fe, probably reflects differences in their geo-chemical partitioning (Osaki *et al.*, 1990a,b). Manganese and Fe are redox sensitive metals, which effects their mobilisation potential. Manganese oxides are reduced to form soluble Mn<sup>+2</sup> in much more oxic conditions then for iron oxides (McBride, 1994). Sequential extraction methods are useful for determining metal mobility in a sediment. Sequential extraction studies on the River Yare (Bubb and Lester, 1994) have shown that Mn in the sediment compartment is primarily associated with exchangeable (20%) and carbonate (40-50%) forms and is therefore relatively receptive to changes in the physicochemical environment. Iron is primarily present in the form of oxides and thus less mobile then is Mn. The release of Hg and Cu to the water column coincided with elevated Fe and TOC levels in the water. Mercury and Cu readily partition to organic matter and oxides,

sequential extraction experiments investigating heavy metal partitioning within sediments generally find that these metals are in the organic or oxide fractions (Santschi, P. *et al.*, 1990; Skowronek, F. *et al.*, 1994; Zwolsman, J.G. *et al.*, 1993). Thus the destablisation of oxides and organic matter in sediments and their release to the water column could be considered to be major factors controlling Hg and Cu release from contaminated sediment in the River Yare system.

Mercury and Cu concentrations in the overlying water did not breach designated E.C limits of 1  $\mu$ g l<sup>-1</sup> total Hg and 28  $\mu$ g l<sup>-1</sup> total Cu as respective annual averages (Environmental Standards for List I, II Substances, 1992) at the dredge site where maximum bulk sediment concentrations were 5.2 mg Hg kg<sup>-1</sup> and 190 mg Cu kg<sup>-1</sup>. Using the equation of Ludwig *et al.* (1989) to calculate 90% confidence limits for upper bound concentrations of contaminants from elutriate data results for the dredge site, Hg concentrations can be expected to not exceed 0.8  $\mu$ g l<sup>-1</sup> while Cu will not exceed 18  $\mu$ g l<sup>-1</sup>, Fe 3780  $\mu$ g l<sup>-1</sup> and Mn 360  $\mu$ g l<sup>-1</sup> and then only for a short period of time.

Despite the apparent low release to the water column of metals, elevated Hg and Cu loadings were detected in bottom sediments in the vicinity of the dredge site 3 months after sediment removal. The total amount of Hg removed in the 120 tonnes of sediment dredged was 0.63 kg. Considering the approximate volume of water to be affected by dredging as 1350 ML and the peak Hg concentration observed in the water as 0.34  $\mu$ g l<sup>-</sup> the maximum amount of Hg present in the water column was 0.46 g. This indicates that at peak loadings, 0.07% of the Hg removed was present in the water column. Similarly for Cu, 22.75 kg was removed with a maximum of 9.8 g (0.04%) suspended in the water column. This data suggests that the two-fold increases in bottom Hg and Cu concentrations observed 3 months after dredging could not be have been caused by the settling out of contaminated suspended solids, but as data collected for the water column was taken at a depth of 1 m below the surface, no account was taken of suspended sediment movement at the sediment-water interface where suspended solids concentrations will be far higher and where settling will also occur more rapidly. Turbidity monitored at various depths during the dredging indicated that there were higher suspended solids loadings close to the river bed which probably caused the increases in bottom sediment Hg and Cu concentrations observed.

### 5.4 The fate of heavy metals in dredged sediments disposed on an upland landfill

The column experiments conducted to determine the effects of a dry oxic environment on Hg and Cu contained within the sediments suggested that very little Hg was in a mobile form over the 10 week period of the experiment. This may have been due to a number of factors. It has been established that all sediments or synthetic scavengers containing sulphur possess high affinity for Hg compounds (Reimers *et al.*, 1975). The greatest uptake of Hg under test conditions was by organic mercaptans followed by sulphide-containing materials, but when high free-sulphide ligand concentrations occurred, inorganic Hg formed soluble polysulphide complexes. However, the occurence of reducible iron in sediments usually prevents the formation of enhanced sulphide levels. Although total concentrations of sulphur have yet to be determined within R. Yare sediments used in the disposal experiments it was clear that sulphate concentrations increased through the course of the experiment, suggesting the presence of a more reduced form of sulphur such as sulphide may be present in large quantities. This may partly explain the low Hg and Cu mobility observed, but more work on the mineralogy of the sediments has to be conducted to confirm this.

The presence of high levels of chloride is also known to effect the binding of Hg to sediments. Partition coefficients for mercury between suspended matter and water have been reported to be in the order of  $10^5$ . Adsorption is considered to be the main process for the enrichment of Hg in suspended sediments (Reimers and Krenkel, 1974). The chemical form of its dissolved, inorganic species determines the degree of association of suspended material and residence time of Hg in natural waters. The chloride ligand concentration , e.g. at the mineral-water interface, influences the adsorptive capacities of Hg because of the formation of chloro-mercurial complexes. The adsorptive capacity of sediments decreases in the order Hg(OH)Cl>Hg(OH)\_2>HgCl\_3'>HgCl\_4^2->HgCl<sub>2</sub> (Liu Ching-I and Tan Hongxiao, 1985). At chloride concentrations <  $10^{-4}$  M (approximately 60 mg kg<sup>-1</sup>) humic matter, MnO<sub>2</sub> and illite have a considerable adsorption capacity for Hg.

At a chlorinity of 0.56 M characteristic of seawater (in which mercuric chlorocomplexes predominate) only the organic matter retains its adsorption capacity for Hg. Chloride concentrations within the sediments used in the R. Yare experiments were in the range where strong adsorption by humic matter as well as Fe and Mn oxides could be expected.

Sequential chemical extraction experiments carried out on contaminated and natural sediments indicate that most of the particulate Hg found in aquatic environments is associated with humic materials soluble in KOH, and with organics and sulphides oxidisable with 30% hydrogen peroxide. Crecelius *et al.* (1975) found that more than 82% of the Hg in oxic sediments was leachable with hydrogen peroxide and assumed that this Hg was bound to organic matter rather than to authigenic sulphides.

Insignificant levels of Hg were found to be water soluble and exchangeable or associated with carbonates and oxides even in highly polluted sediments (Peng An and Wang Zijian, 1985). These results appear to support the findings of the column experiments that little leaching of Hg or Cu from the disposed sediments may be expected. However, if the pH of the dried sediments was found to drop over a number of years leaching of metals may occur. Mineralogical data will give an indication of the likely buffering capacity of the sediment from the amount of carbonates and bicarbonates found.

Likewise, laboratory prediction of volatilisation of Hg from dredged sediment dumped at an upland site on was found to be very low and is related to the factors already discussed for leaching. The possibility of run-off from the site carrying contaminants into the surrounding environment has not been excluded, but better management of the landfill, as recommended in this report, will reduce the risk of this occurring.

#### 5.5 Assessment of the biological impact of dredged material

Definition of what constitutes a risk to the surrounding environment is difficult and often rather arbitrary. An example of this is the Greater London Council guideline for contaminated soils (Table 38). Five classes of contamination have been defined, ranging from 'not contaminated' to 'very heavily contaminated', without reference to the significance of these classes to human, or any other, risk. The definition of each class is solely dependent on the total concentration of the contaminant of concern. Values which make up the boundaries of these classes are presumably based on toxicity data, but it is not clear what relationship exists between the classes and toxicity. As toxicity is crucially dependent on the form in which the metal occurs (MeHg $^{+}X^{-}$  versus HgS for instance) and the availability of this form to humans, animals or plants within the contaminated matrix, setting of boundaries of this type can be misleading and often irrelevant to the question of what threat is posed by the presence of such contaminants. It is likely that the toxicity data used in construction of Table 38 was for one of the more toxic free forms of the metal or compound and thus presents an over-cautious estimate of the risks involved; not an unreasonable approach, but possibly misleading and potentially the cause of the expenditure of much time and money in a clean-up operation where a more exact understanding of the risks involved may have proven more cost-effective.

The concentrations of Hg in the sediments of the River Yare range between 0.1 to 6.8 mg kg<sup>-1</sup> for 1995. Using the Table 38, the river sediments range between not contaminated to contaminated. The Dutch Government guidelines suggest clean-up target values for Hg of 0.3 mg kg<sup>-1</sup> and intervention values of 10 mg kg<sup>-1</sup>. Thus while

the river bottom sediments, are for the most part contaminated with Hg, its concentration remains below action trigger values, therefore disposal of dredging of this shallow sediment (less then 3 cm) is of lower environmental risk. On the landfill Hg concentrations in the soils ranged between 1.2 and 9.7 mg kg<sup>-1</sup> again indicating contaminated soil using the Greater London Council guidelines, but, only just below the intervention value suggested by the Dutch guidelines. The copper concentrations observed in the bottom sediments of the River Yare ranged between 4.9 and 321 mg kg<sup>-</sup> <sup>1</sup> for 1995, again indicating sediments ranging from not contaminated to contaminated by the Council guidelines. The Dutch guidelines suggest clean-up target values of 36 mg kg<sup>-1</sup> Cu in soil and intervention value of 190 mg kg<sup>-1</sup> indicating that within some sections of the River Yare localised hot spots of Cu may exist that need closer scrutiny and that dredging of these sediments may cause a problem for disposal of the dredged material. Within the landfill sediments the concentrations of Cu observed range between 50 and 115 mg kg<sup>-1</sup> Cu indicating that the landfill sediment is only slightly contaminated according to the Greater London Council Guidelines and well below the action limit according to Dutch guidelines.

Table 39.	Greater London Council guidelines for contaminated soils - suggested
	ranges of values (mg kg <sup>-1</sup> on air dried samples).

Element	Not contaminated	Slightly contaminated	Contaminated	Heavily contaminated	Very heavily contaminated
Hg	0-1	1-3	3-10	10-50	>50
Cu	0-100	100-200	200-500	500-2500	>2500

An alternative to this 'total contaminant' approach is the use of bioassays (defined as 'any test in which organisms are used to detect or measure the presence or effect of one or more substances or conditions' EPA, 1973) to determine the proportion of total contaminant which is assimilated from the matrix by test animals or plants. This, under the right conditions, allows a more accurate assessment of the potential threat of contamination to both plants and animals, and by further extrapolation, to humans.

Ahlf and Munawar (1988) have proposed a number of stages in the biological evaluation of the impact of dredged material (Figure 36). Each step further down the flow chart represents as increase in time and expenditure, accompanied by a more realistic assessment of the likely impact of any contaminants contained within the dredge material. Dotted lines indicate that a risk assessment may be made after any of the 3 test stages, but that different assessments are possible for the same dredge material, depending on the test conducted. In the work reported for the Griffin Lane

landfill the solid sediment phase has been assessed by long term bioaccumulation experiments in both the field and laboratory.

The earthworm bioassay indicated that after 28 days of exposure to the contaminated dredge soil earthworms contained 4.6 times more Hg than they did at the start of the experiment. Earthworms grown on the uncontaminated soil increased their Hg body burdens 3-fold in the same period. Further analysis of the data indicated that worms grown on the uncontaminated soil had Hg body burdens equivalent to 50% of the total Hg in the soil whilst worms from the contaminated soil had taken up only 2% of the total Hg in their soil. These data suggest that Hg in the contaminated soil was not in an easily assimilated form for the earthworms, but that they were still able to accumulate it to a certain extent.

The word 'accumulation' is used in different senses by different authors. According to Van Hook (1970), accumulation occurs when the ratio of the concentration of metal in the tissue over the concentration in the environment exceeds 1.0. This is disputed by Hartenstein *et al.* (1980) who point out that anomolously high levels of metals may be present in the environment which could not exist chemically or physically within a living organism. Accumulation is perhaps thus best described as when animals exposed to a single level of metal in the environment over a period of time show increasingly high levels in the tissues or, for a given time, the animal's tissue shows increasing levels related to the concentations in the environment.

According to this definition both the worms grown on the contaminated and uncontaminated soils have accumulated Hg. Whether the accumulations observed are significant is a more complex issue. *E. fetida* has been extensively used in bioaccumulation experiments, but no species of earthworm is considered a standard laboratory test material.

Dredged sediment often has higher silt and organic matter contents than the corresponding soils. This results in lower bioavailabilities of the contaminants. In the long run the organic matter will be partly decomposed with a corresponding increase in bioavailability. Soil pH is a very important factor in controlling mobility and availability of heavy metals. Dredged materials with a high sulphide content and with a relatively low calcium carbonate level turn acid during conversion of the wet soil from anaerobic to aerobic conditions. Dredged materials with high calcium carbonate levels remain neutral. Fortunately, this appears to be the case for the R. Yare sediments.

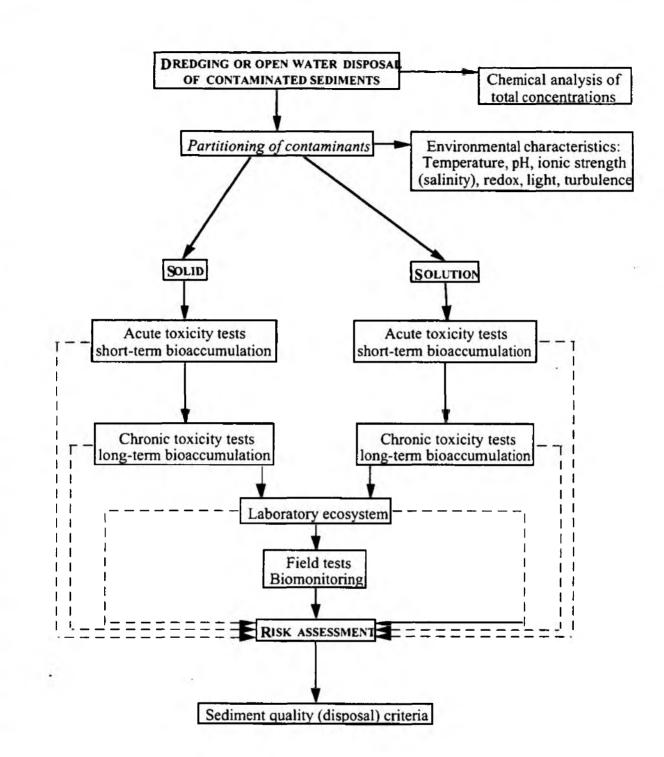


Figure 36. Flowchart for the assessment of the biological impact of dredged material.

In all soils losses of soluble calcium salts gradually lead to decalcification of the soils and thus to lower pH. These processes may be accelerated under wet conditions. Other soil factors such as soil salinity and redox conditions may affect heavy metal bioavailability in dredged materials. These conditions are subject to large variations in sediments dredged from brackish or saline waterways, and in partly dewatered soil profiles repectively. It is therefore probable that the relatively small accumulation of Hg and Cu by the earthworms from the contaminated soil is a fairly accurate reflection of the stability of the soil (which was on the landfill for approximately 7 months when it was used in the bioassay) and the Hg and Cu complexes within it.

Factors controlling availability of contaminants to plants, on the other hand, are the nature and properties of the contaminant, of the soil and the plant species whilst predominant soil factors are texture, concentration and nature of organic matter and pH. High pH, high clay and organic matter contents reduce the plant availability of most metals.

Plants differ in their ability to accumulate heavy metals. Some metals (Cu, Fe, Mn, Mo and Zn) are essental to plant life, but the non-essential elements can also be accumulated and can interact with the essential elements in their biochemical functioning. Monocotyledonous plant species accumulate less metals than dicotyledons (Cottenie, 1981), but differences between species, varieties and subspecies may mask this. Moreover, growth condition, nutrient status, temperature and transpiration rate determine growth rate and element uptake. The organs of the plant also differ in their ability to accumulate metals: for most plant species seeds and fruits accumulate less metal than leaves and roots. Green plant leaves accumulate more heavy metals than other plant organs (van Driel and Nijssen, 1988) Simulations of processes in the rooting medium responsible for the flow rate of metals into the roots by chemical extraction procedures have been attempted. Promising results have been obtained with the chelating extractants EDTA (Lakanen and Erviö, 1971) and DTPA (Lindsey and Norvell, 1978), and with neutral salt extractants based on CaCl<sub>2</sub> (Saurbeck and Stypereck., 1985) and NaNO<sub>3</sub>, but the soil-plant system is apparently too complex to be simulated by a chemical extractant. The neutral salt extractants mentioned give better results than the total metal contents of the soil in indicating differences in mobility and bioavailability of heavy metals.

Considering these observations in conjunction with the results obtained for the plant bioassay experiments at the Griffin Lane landfill makes it clear that no simple conclusion may be drawn. Neither plant species examined is a standard laboratory material, nor were the plants grown under laboratory conditions. No attempt can thus be made at making a definitive statement about the ability of either species to bioaccumulate Hg or Cu. However, the results obtained do give a snap-shot impression of the conditions experienced by plants actually growing on the contaminated soil and the amount of Hg and Cu contained within their leaves as a result of this. T-tests indicated that there was no significant difference between the

concentrations of Hg in leaves of either species from both uncontaminated and contaminated sites. Buddleia leaves contained significantly more Cu on the uncontaminated site. Thus, either both species do not accumulate Hg in their leaves, no matter what the substrate, or the Hg is in a form unavailable to the plants. No conclusion can be drawn from the data available, nor from the scarce information in the literature. However, on a purely quantitative level the concentrations of Hg and Cu found in the leaves of both species gives no cause for concern to the surrounding environment. Concentrations of Hg and Cu considered to be phytotoxic (Table 40) were not observed in the contaminated dredge soil.

**Table 40.** Comparison of Hg and Cu concentrations in the contaminated and uncontaminated bioassay soils with concentrations considered phytotoxic and a generalised UK surface soil (mg kg<sup>-1</sup>).

Metal	Contaminated bioassay soil	Phytotoxic concentration <sup>†</sup>	Uncontaminated bioassay soil	Generalised soil <sup>†</sup>
Нg	2.85	5	0.069	0.01-0.09
Cu	82	100	5.2	11-323

<sup>†</sup>Pendias, 1992

#### 5.5.1 A general overview of site conditions

The Griffin Lane Landfill is not at present in operation and in the past the site has not been operated to the terms of the license issued by Norfolk County Council as Waste Regualtion Authority (now the responsibility of the Environment Agency) nor are the present license conditions stipulated seen as the most appropriate. There is a need to review the license in terms of the future proposed use of the site. This is particularly important in the light of recent changes in the legislation which may nullify the use of the site for the disposal of sediments with Hg above certain levels as these sediments may in future be classified as "Special Waste".

The prevailing situation on the utilised area of the site may be summarised as consisting of a steeply banked area of deposited dredged sediment (approximately 2-3 m high) within a couple of metres of the river bank which then slopes away on the landward side of the dump where the dredge spoil has been allowed to flow unimpeded until it stopped. All of this is totally overgrown by buddleia bushes and nettles which reach more than 6 feet tall in the summer months, making foot access to even the newest areas of sediment disposal extremely difficult. These conditions are in apparent breach of a number of the conditions of the current enforceable licence (reproduced in Appendix 10).

The major concern when designating a site such as this must be the minimisation of the potential contamination of the surrounding environment with any form of Hg or Cu contained within dredged sediments disposed there. One of the issues which has been raised is the presence of a clay-lining, natural or otherwise, to the site which would reduce the potential for contamination of groundwater by Hg or Cu leached from the disposed dredge spoil. The understanding is that no such lining exists and was not, in any event, stipulated in the schedule of conditions of the present licence (Appendix 10) when it was issued some years ago. However, preliminary findings of research shows little potential of Hg contamination to ground water.

### 6. SUMMARY OF FINDINGS

Analysis of sediment data collected between 1986 and 1995 finds that:

- 1. Tighter emission controls imposed on Whitlingham STW have been the major contributor to the decline in bottom sediment loadings of Hg and Cu. The decline in sediment loadings did not occur immediately stricter standards were imposed, but with a time-lag of approximately 10 years for Hg and over an as yet undetermined period for Cu and was also dependent on the remaining processes outlined below.
- 2. The predominant fate of Hg and Cu contaminated suspended sediments has been deposition followed by burial. This was in competition with fluvial transport which varies depending on climatic conditions. The fate of soluble or non-particle associated Hg and Cu was also controlled by the variation in bottom sediment types which is reflected in the position of the region of highest contamination up to 9 km downstream of the STW outfall. Fluvial transport and sediment reworking is the main mode of downstream movement of mercury contamination and is very slow..
- 3. Anthropogenic disturbance of bottom sediments by dredging and other civil engineering works can cause sporadic increases in Hg concentrations, due to reexposure of heavily contaminated sediments normally buried at depth.

- 4. Methylmercury concentrations within the bottom sediments were not dependent on total mercury concentrations alone, but showed some correlation with %VS and also probably depended on other combinations of physicochemical parameters such as light penetration, temperature and water flow rate at Trowse and possible nutrient availability and temperature at Cantley due to the presence of a sugar processing plant. Atmospheric deposition of Hg may be an important contibutor of mercury for methylation, especially at Cantley.
- 5. The body burdens in eel from the R. Yare have reached levels similar to those observed in eel from pristene or non-contaminated water bodies. Roach however are still decreasing and have not yet reached background levels.
- 6. Fish, both eel and roach collected from Ormesby Broad have higher then expected body burdens of Hg, suggesting that a diffuse source such as precipitation may be important in East Anglia.
- 7. Mercury in contaminated dredge spoil has both limity mobility and bioavailability in the soils as evidenced by laboratory and field study.
- 8. Dredging may cause buried mercury to be brought near the surface thereby increasing its bioavailability. Furthermore such sediment disturbance may cause local increases in the total Hg concentration in the water column due to suspended load.

## 7. CONCLUSIONS

Annual monitoring of the spatial distribution of mercury, copper and methylmercury within the R. Yare bottom sediments, 1986-1994

The data collected from nine years of monitoring the Hg and Cu pollution of the R. Yare bottom sediments have been used to demonstrate that:

1. Virtually all of the Hg and Cu was discharged to the river in the final effluent from Whitlingham STW before 1980. This is evidenced by a characteristic point source pollution plume within the bottom sediments centred on the STW for both metals.

- 2. The main area of contamination is from Trowse (TG 244 058) to Hassingham (TG 360 045) or from approximately 5.1 km upstream (transect 4) to 13.5 km downstream (transect 27) of the STW outfall. The highest concentrations of contaminants within this area have always occurred within 8 km downstream of the STW outfall.
- 3. The level of Hg contamination in surface sediment declined most rapidly from 1986-1990. In this period the mean Hg concentration within the bottom sediments for the survey reach from Trowse to the confluence of the R Chet (transects 4-34) declined from 5.35 mg kg<sup>-1</sup> to 1.28 mg kg<sup>-1</sup>, a 4.2-fold decrease. From 1990 to 1994 the mean concentration did not decline further, fluctuating in the range 1.28-2.06 mg kg<sup>-1</sup>.
- 4. Copper concentrations did not decline markedly, dropping from an average of 106.5 mg kg<sup>-1</sup> to 81.5 mg kg<sup>1</sup> by 1992, only a 1.3-fold decrease. This is largely a consequence of continued emissions from Whitlingham STW. Since 1992 the mean concentration has been in the range 59.1-71.5 mg kg<sup>-1</sup>.
- 5. Methylmercury concentrations were generally independent of total Hg concentrations, the concentrations were generally low in 1989 (mean concentration 3.3 µg kg<sup>-1</sup>) and 1992 (3.6 µg kg<sup>-1</sup>) and higher in the intervening years 1990-1991 and 1993-1994 (range of means 7.3-7.9 µg kg<sup>-1</sup>). Overall methyl mercury makes up less then 1% of the total mercury concentration in the sediments.
- 6. The deposition and consequent burial of Hg and Cu contaminated suspended sediment particles has created a large sink of these metals within the bottom sediments of the main river, as evidenced by core profiles with Hg concentrations exceeding 10 mg kg<sup>-1</sup> and Cu concentrations of 250 mg kg<sup>-1</sup> at depths of up to 1 m.

#### Annual monitoring of mercury contamination of R. Yare fish flesh

 Eel and roach flesh contamination by Hg has declined as Hg emissions to the river and thus contamination of the bottom sediments has declined. From 1985-1994 average total Hg concentrations in eel flesh have declined by more than half from 0.46 mg kg<sup>-1</sup> to 0.21 mg kg<sup>-1</sup>. Approximately 80-90 % of the total Hg present was in the form of MeHg.

- 2. Eel (A. anguilla) muscle tissue THg was the better accumulator of Hg both between a contaminated and an uncontaminated site. Roach (R. rutilus) muscle however, was a better monitor for Hg temporally as the THg burdens decreased gradually with time in a trend similar to that observed for the river bed sediments. The reasons for these species differences lie in their different behaviours, age spans, feeding habits and lipid contents.
- 3. Decreased discharges of Hg to the R. Yare led to an immediate response in the eel population with a decreased Hg body burdens similar to that observed in uncontaminated systems within 1 year. Mercury concentrations in fish from Ormesby Broad were significantly higher then expected for an uncontaminated system.
- 4. It is likely that most of the Hg available to fish is contained within the water column. This Hg may originate partly from the contaminated bottom sediments, but is possibly mostly from atmospheric deposition. This could account for the similarity in Hg contamination levels of eels and roach taken from rivers in East Anglia with little or no Hg contamination of bottom sediments (R Chelmer and R Brett). The importance of atmospheric deposition of Hg in East Anglia is currently poorly understood, but is likely to contribute to fish Hg body burdens.

## Monitoring and labratory simulation of the effects of dredging on R. Yare water quality

- Small dredging operations, such as the one monitored at Thorpe St Andrews, cause localised increases in sediment loadings to the water column. This was accompanied by elevated concentrations of Hg and Cu which were largely associated with organic matter and particles > 0.45 µm in size.
- 2. Laboratory based elutriate tests for studying the effects of sediment disturbance on water quality successfully predicted that concentrations of total Hg and total Cu observed in the field dredging would not exceed 0.6 µg l<sup>-1</sup> or 13 µg l<sup>-1</sup> respectively. These concentrations were within the E.C. regulation limits of 1 µg l<sup>-1</sup> for Hg and 26 µg l<sup>-1</sup> for Cu as annual averages and thus did not pose an immediate threat to water quality.
- 3. Elutriate tests on the effect of saline water intrusion to potential dredge sites indicated that local water quality would not be more severely affected by

dredging than under freshwater conditions. Seasonal variations (between summer and winter) in redox potential and temperature were also found to not markedly effect the release of Hg or Cu from bottom sediments to the water column.

4. The dredging of Hg and Cu contaminated sediments once buried at depths of up to 1 m leads to a limited re-deposition of contaminated sediments as a thin surfacial layer on the bottom sediments with accompanying changes in physicochemical conditions which may lead to increased availability of Hg and Cu.

# The fate of heavy metals in dredged sediments disposed on an upland disposal site

- 1. During the 10 week period of the experiment the most important pathway for Hg from the dredged material was volatilisation. However, this pathway made an insignificant change to Hg concentrations within the disposed sediment.
- 2. Mercury and Cu were not leached from the sediment to an appreciable extent. Leached water contained undetectable amounts of the two metals. A clay layer, introduced to test its effectivity in preventing contaminants leaching from the sediment, also did not experience any increased levels of Cu or Hg from the dredge material.
- 3. The stability of the contaminants within the dredged material is probably due to the apparent high buffering capacity of the sediments and the presence of humic material which binds the metals.
- 4. The stability within the sediment assumes that the nature and use of the sediment remains unchanged. Should these conditions change after a number of years, i.e. land-use change then mobilisation of the contaminants may be enhanced, however this requires further study.

#### Assessment of the biological impact of dredge material

- 1. As the results of a preliminary study no biomagnification of Hg or Cu was found in the earthworm *Eisenia fetida*.
- 3. The plants *Urtica diocia* (stinging nettle) and *Budleja davidii* (butterfly bush) grow naturally on the contaminated dredge soil and were healthy and vigorous.

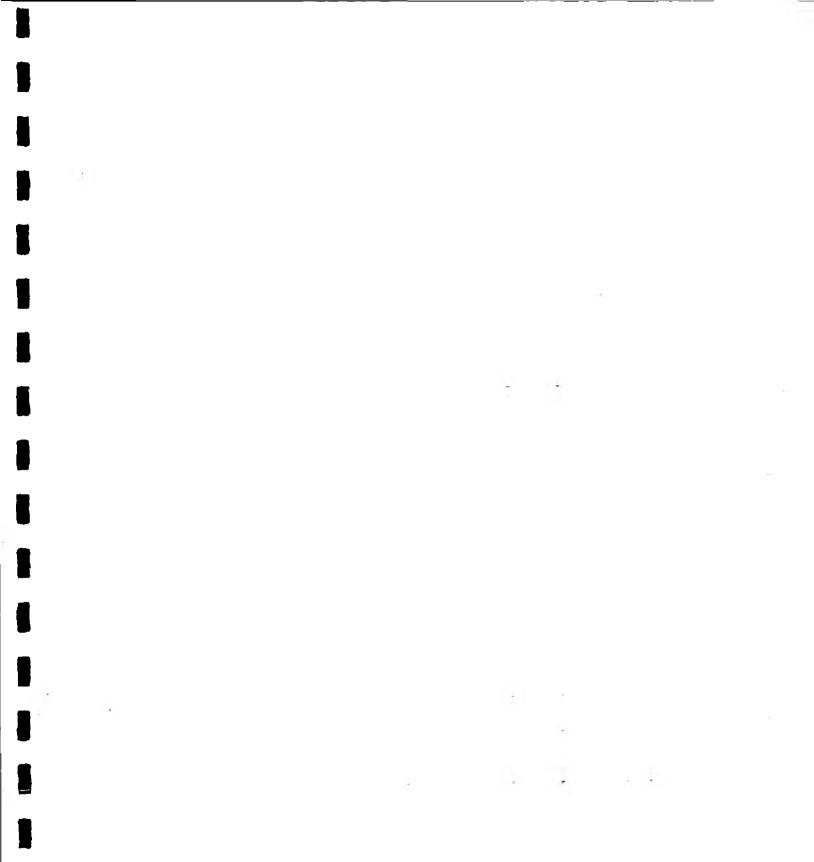
4. Mercury was accumulated in the roots of *Urtica diocia* but its overall bioavailability was low.

### 8. RECOMMENDATIONS

The critical analyses of data collected by Imperial College on the contamination of R. Yare bottom sediments by Hg, MeHg and Cu and contamination of fish by Hg and MeHg from 1985-1995, combined with research on the effects of sediment disturbance by dredging on water quality and the effects of disposal of contaminated dredged sediments on the Griffin Lane landfill, allows a number of recommendations to be made on the short- and long-term management of the contaminated reach of the R. Yare and its associated broads:

- 1. Emissions of Hg and Cu to the river from Whitlingham STW have had the largest impact on bottom sediment contamination and must continue to be strictly monitored by the NRA. Mercury discharges are now tightly controlled but further tightening of the consent for Cu discharges would ensure that recent improvements are maintained.
- 2. Sediment disturbance within the contaminated reach should be minimised. Dredging should only be permitted when absolutely essential and then under strict supervision of the Environment Agency. The option of complete removal of the contaminated sediments is not cost effective nor can the resultant effects on the system be predicted with any certainty. Dredging activity should still be considered with circumspection in the future because of the large sink of Hg and Cu buried at depth within the bottom sediments. General caution with minimal further anthropogenic intervention will allow a natural equilibrium of low contamination levels to develop within the system. However, any marked changes in factors such as pH, flow rate and salinity would require re-assessment of these recommendations at the appropriate time.
- 3. The long-term threat that the Hg contamination holds for the river system, including biota, is relatively small, provided there is minimal anthropogenic disturbance. It is evident from analysis of the data collected for the annual surveys that it is necessary to monitor the sediments and fish into the forseeable future. Discussions should be held now to determine the most suitable course of action in this regard.

- 4. It has become apparent that Hg contained within the bottom sediments of the R Yare is probably not the only, and possibly not the main, source of Hg to eels and roach. Data on atmospheric concentrations of Hg in the R. Yare region are required to establish whether this is a potential source. This may require the establishment of a further study on atmospheric Hg emissions if no database presently exists.
- 5. A decision must be taken as to the viability of the Griffin Lane landfill in the light of changes in legislation for East Anglia and the likely disposal requirements from dedging within the contaminated reach. The current license should be reviewed in the light of these changes before the site is reopened.
- 6. The existing site needs to be landscaped to bring it into accord with its existing license.
- 7. While the indications are that there is minimal risk to ground water and biota from the use of the dredge site, further investigation is needed to determine the most cost-effective way to dispose of the mercury contaminated sediments. If the site is deemed suitable for future disposal of dredged contaminated sediments a revised licence should be issued to the operators which should include the following:
  - i. The site must be completely re-landscaped with the laying down of a clay base is recommended to prevent downward leaching of the metals which may occur if the site is abandoned and land-use permitted to change. The site should be sectioned into bunded areas for dumping of sediments on a suitable rotational basis. Run-off should be controlled by ditches.
  - ii. Once suitable drying out of sediments has occurred a capping layer should be considered because of erosional and volatile losses. Suitable capping layer materials should be specified. Plant growth on the site should be controlled, but not prevented. Planting of suitable grasses for binding the soil to prevent soil erosion should be considered.
  - iv. A dated record of the volume of sediments dumped with an indication of where the sediments were removed from must be kept (as much for the operator's benefit as for the regulatory body').
  - v. Other minor regulations such as restricted access to the site, fencing and identification of the site as such should be enforced.



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## **APPENDIX 1**

Parameters monitored for surficial bed sediments taken from the R Yare, 1986-1995

1986 5	Survey	·			Hg C	ONCEN	TRATION	(mg kg <sup>-1</sup> )		
	Distance*			Sample	•					Standard
Transect	(km)	i	ü	üi	iv	v	Maximum	Minimum	Average	deviation
7	-3.35	2.79	2.09	2.36	1.83	2.11	2.79	1.83	2.24	0.36
	-3.32	1.36	2.25	2.61	1.62	1.95	2.61	1.36	1.96	0.50
8	-2.15	3.53	1.48	4.06	3.24	2.23	4.06	1.48	2.91	1.04
	-2.12	2.90	2.49	3.17	2.56	3.73	3.73	2.49	2.97	0.51
9	-1.41	0.16	0.57	0.26	0.21	2.49	2.49	0.16	0.74	0.99
	-1.38	0.20	0.37	1.26	1.82	0.73	1.82	0.20	0.88	0.67
10	-0.41	0.98	2.56	ns	2.84	1.58	2.84	0.98	1.99	0.86
	-0.38	2.96	3.76	5.78	6.04	3.77	6.04	2.96	4.46	1.37
11	-0.22	2.36	4.21	2.84	17.20	2.20	17.20	2.20	5.76	6.44
	-0.19	5.53	2.17	ns	16.20	3.24	16.20	2.17	6.79	6.43
12	0.44	2.60	1.76	1.06	0.94	0.05	2.60	0.05	1.28	0.96
	0.47	2.34	2.11	1.38	0.30	0.31	2.34	0.30	1.29	0.96
13	1.32	7.63	7.56	12.00	13.50	2.62	13.50	2.62	8.66	4.28
	1.35	20.00	23.80	12. <b>9</b> 0	13.70	1.92	23.80	1.92	14.46	8.34
14	2.05	2.52	6.79	29.20	27.90	7.84	29.20	2.52	14.85	12.67
	2.08	1.51	2.07	19.60	10.20	11.10	19.60	1.51	8.90	7.45
15	2.78	0.15	1.44	1.85	6.49	7.41	7.41	0.15	3.47	3.26
	2.81	0.03	0.54	6.76	2.86	6.71	6.76	0.03	3.38	3.24
16	3.59	15.20	11.90	1 <b>9</b> .80	19.20	8.59	19.80	8.59	14.94	4.78
	3.62	3.64	2.06	12.90	17.10	8.19	17.10	2.06	8.78	6.29
17	4.42	1.89	5.02	12.10	19.40	9.42	19.40	1.89	9.57	6.76
	4.45	2.98	12.60	15.60	10.30	2.25	15.60	2.25	8.75	5.91
18	4.91	4.14	18.30	6.02	7.18	5.74	18.30	4.14	8.28	5.71
	4.94	8.85	6.27	6.30	4.58	0.67	8.85	0.67	5.33	3.02
19	6.03	9.40	32.90	6.45	10.70	0.40	32.90	0.40	11.97	12.36
	<b>6</b> .06	2.56	0.86	6.67	4.74	3.88	6.67	0.86	3.74	2.20
20	6.62	3.30	7.66	9.25	3.89	1.38	9.25	1.38	5.10	3.25
	6.65	3.55	6.36	4,77	4.15	3.88	6.36	3.55	4.54	1.11
21	7.31	6.18	8.41	8.74	8.86	0.35	8.86	0.35	6.51	3.61
	7.34	7.49	7.53	0.38	0.54	15.00	15.00	0.38	6.19	6.06
22	8.18	5.27	6.73	0.98	5.33	4.58	6.73	0.98	4.58	2.16
	8.21	9.69	2.06	1.65	6.10	12.30	12.30	1.65	6.36	4.67
23	8.36	0.96	1.80	5.25	1.90	1.95	5.25	0.96	2.37	1.66
	8.39	14.00	2.56	4.84	4.29	1.04	14.00	1.04	5.35	5.06
24	9.15	6.31	1.89	2.63	1.39	2.85	6.31	1.39	3.01	1.93
	9.18	0.54	3.33	ns	0.28	0.79	3.33	0.28	1.24	1.41
25	11.10	2.67	0.28	7.47	1.96	3.14	7.47	0.28	3.10	2.67
	11.13	3.01	0.18	1.23	3.08	4.85	4.85	0.18	2.47	1.81
26	12.53	1.17	0.32	4.19	1.75	0.86	4.19	0.32	1.66	1.51
	12.56	0.84	2.53	3.64	4.46	2.20	4.46	0.84	2.73	1.39

## 1. Total mercury concentrations

\*Distance from Whitlingham STW, negative values indicate upstream, positive values downstream ns=no sample

1987 5	Survey			<b>6</b> . 1	н	CONCE	NTRATION (mg	kg <sup>-T</sup> )		
Transect	Distance* (lon)	i	ü	Sample	iv	v	Maximum	Minimum	Average	Standard deviation
		0.09			-	·				GC TRUE
1 2 3	-17.4 -15.6	0.09 0.04					0.09 0.04	0.09	0.09 0.04	
3	-11.6	0.05					0.05	0.05	0.05	
4	-5.1	0.19					0 19	0.19	0.19	
5	-4.85	0.19 0.25					0.19 0.25	0.19 0.25	0.25	
6	-5.1 -4.85 -4.15	1.22					1.22	1.22	0.25	
6 7	-3.35	0.48					0.48	5.42	0.48	
8	-2.15	1.58					1.58	0.48 1.58	1.58	
9	-1.41	7.16					7.16	7.16	7.16	
io	_A 41	110					7.10	7.10	1.10	
11	-0.41 -0.22 0.44	3.29					3.29	3.29	3.29	
12	0.44	2.91					2.27	2.91	2.91	
13	1 32	15 20					2.91 15.20 8.72 3.73	4.71	15 20	
14	2.05	977					13.20	13.20	15.20 8.72	
15	1.32 2.05 2.78	15.20 8.72 3.73					8.72	15.20 8.72 3.73 3.04	8.72	
15	2.10	3.73					3.73	3.75	3.73	
10	3.59 4.42	3.04 6.55					3.04	3.04	3.04	
19	4.42	0.33					6.55	6.55	6.55	
14 15 16 17 18 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39	4.91	75								
17	6.03	3.88					3.88	3.88	3.88	
20	6.62	4.52					4.52 3.92	4.52	4.52 3.92	
21	7.31 8.18	3.92					3.92	3.92	3.92	
22	8.18	1.12					1.12	1.12	1.12	
23	8.36 9.15	0.91 2.25					1.12 0.91	1.12 0.91 2.25	1.12 0.91 2.25 0.10	
24	9.15	2.25					2.25 0.10	2.25	2.25	
25	11.1 12.53	0.10					0.10	0.10	0.10	
26	12.53	0.32 0.31					0.32	0.32	0.32	
27	13.5	0.31	0.18	2.17	0.30	5.14	5.14 2.02	0.18	1.62 0.84	2.13
28	14,5 15,4	2.02 0.43	TLS.	ns	0.21	0.28	2.02	0.21	0.84	1.03
29	15.4	0.43	0.55	ns	0.64	1.66	1.66	0.43	0.82	0.57
30	16.6	0.13	1.05	1.17	4.03	1.94	4.03	0.13	1.66	1.47
31	17.6	1.54		0.79	0.96		154	0.79	1.10	0.39
32	18.3	1.22	ns 0,77	1.00	0.40	ns 0.34	1.54 1.22 0.56	0.14	0.75	0.38
33	103	0.45		0.26	0.56	0.15	0.56	0.34 0.15	0.36	0.18
34	19.3 20.3	1 34	лз 0.37	ns	ns	0.26	1.34	0.14	0.50	0.59
35	21.6	1.34 0.51	0.24	0.27	1.21	0.98	1 71	0.26 0.24	0.66 0.64 0.30	
ž	22.5	0.53	0.27	ns	ns	0.11	1.21 0.53	0.11	0.04	0.43 0.21
37	21.6 22.5 23.4	0.54	0.18	ns	ns	0.74	0.74	0.11	0.30	0.21
29	23.4	1.50	0.10		0.11	0.11	1.50	0.18 0.09	0.49 0.45	0.28 0.70
30	24.4 25.4	0.36	0.09 0.42	пs 0.03			1.50	0.09	0.45	0.70
37	26.4		0.42		0.21	0.18	0.42	0.03	0.24	0.15
40 41	20.4	0.63 0.47	0.33	0.27	0.12	0.07 2.38	0.63 2.38	0.07 0.21	0.28 0.90	0.22
41 42	21.4		រាន	0.54	0.21	2.58	4.58	0.21	0.90	1.00
4/	28.4	ns	ns	ns	0.81	0.32	0.81	0.32	0.57	0.35
43 44	29.4	0.07	0.52 0.07	0.63	0.45	0.63	0.63	0.07	0.46	0.23
44	30.4	0.07	0.07	0.48	0.36	្រាន	0.48	0.07	0.25 0.19	0.21
45	31.1 32.5	0.13	0.19	ns	0.41	0.01	0.41	0.01	0.19	0.17
46	32.5	0.17					0.17	0.17	0.17	
47	33.5	0.17					0.17	0.17	0.17 0.05	
48	34.5	0.05					0.05	0.05	0.05	
1989 5	Survey				н	g CONCE	NTRATION (mg	kg <sup>-1</sup> )		
<b>T</b>	Distance*			Sample		-				Standard
Transect	(km) -17,4	i	ji .	<u>iii</u>	iv	v	Maximum	Minimum	Average	deviation
1 2 3	-17.4	ាន កន								
3	+11.6	ns								
4	-51	0.87					0.87	0.87	0.87	
3	-4.85	ns.					0.07	0.01	0.07	
6	-4.15	0.62					0.62	0.62	0.62	
6 7	-4.85 -4.15 -3.35	0.02				1.14	1.14	1.14	1.14	
é	-2.15		0.38			4.14	0.38	0.38	0.38	
8 9	-2.15 -1.41		0.38		0.99		0.38	0.38	0.58	0.55
10	-0.41		15.91		0.99			V.21	0.00	0.55
	-0.41		2.59				15.91 2.59	15.91	15.91	
11	41.77									

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1989 5	Survey			_	Н	CONCE!	TRATION (mg	kg <sup>-1</sup> )		
Transect	Distance*	1	ii	Sample iii	iv	v	Maximum	Minimum	Average	Standard deviation
1	-17,4	ns.								<u>ut : 10</u> 1101
2	-15.6	ns								
2 3 4	+11.6	ns								
4	-5.1	0.87					0.87	0.87	0.87	
5 6 7 8	-5.1 -4.85	ns.								
6	-4.15	0.62					0.62	0.62	0.62	
7	-3.35					1.14	1.14	1.14	1.14	
8	-2.15		0.38				0.38	0.38	0.38	
9 10 11 12 13 14 15 16	-1.41		0.21		0.99		0.99	0.21 15.91 2.59 2.63 1.75 3.32 1.20	0.60	0.55
10	-0.41		15.91				15.91 2.59 2.63	15.91		
ii	-0.22		2.59				2.59	2.59	15.91 2.59 2.63 1.75 3.32 1.20 3.82 5.57	
12	0.44	2.63	•,				2 63	2.63	2.63	
13	1.32 2.05	2.00	1.75				1.75	175	1 75	
14	2.05					3.32	1.75 3.32	3 37	3 32	
15	2 78	1.20				0.00	1.20	1 20	1.20	
16	2.78 3.59	1.20				3.82	1,20 3.82	3.93	2.20	
17	4.42					5.57	5.57	3.82 5.57	5.02	
10	4.91					1.49	1.49	1.49	1.49	
10	4.91					6.89		6.89		
19	6.03 6.62					0.89	6.89	0.89	6.89	
20	0.02	<b>N</b> 3								
21	7.31 8.18	4.36					4.36	4.36	4.36	
22	8.18					4.71	4.71	4.71	4.71	
23	8,36	ns								
24	9.15					2.53	2.53	2.53	2.53	
25	11.1	1.08					1.08	1.08	1.08	
26	11.1 12.53					1.21	1.21	1.21	1.21	
27	13.5					0.80	0.80	0.80	0.80	
28	14.5				0.67		0.67	0.67	0.67	
29	15.4 16.6					0.88	0.88	0.88	0.88	
10	16.6	0.59					0.59	0.59	0.59	
31	17.6	0.97				1.84	1.84	0.97	1.41	0.62
32	18.3	•				0.22	0.22	0.22	0.22	0.04
33	19.3					0.11	0.11	0.11	0.11	
17 18 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 7 38 39 40	20.3	1.00				v. 11	1.00	1.00	1.00	
25	20.5	1.00				0.80	0.80	0.60	0.80	
30	21.6	0.34				0.00	0.34	0.34	0.34	
30	22.5 23.4 24,4	0.12					0.12	0.12	0.12	
3/	23.4						0.37	0.12		
38	24,4	0.37							0.37	
39	25.4	0.09					0.09	0.09	0.09	
40	26.4 27.4	ស								
4]	27.4	រាន								
42	28.4				0.64		0.64	0.64	0.64	
43	29.4					0.45	0.45	0.45	0.45	
44	30.4					0.46	0.46	0.46	0.46	
45 46	31.1 32.5					0.32	0.32	0.32	0.32	
46	32.5	រាវ								

<b>199</b> 0 (	Survey			I	Ig CONCENT	RATION (mg k	g <sup>-1</sup> )	
_	Distance*	_	Sample					Standard
Transect	<u>(km)</u>	<u>i</u>		<u>v</u>	Maximum	Minimum	Average	deviation
4	-5.1	0.13			0.13	0.13	0.13	
5	-4.85	0.21			0.21	0.21	0.21	
6	-4.15	ns						
7	-3.35	0.24	0.57	0.44	0.57	0.24	0.42	0.17
8	-2.15	0.56	0.19	0.11	0.56	0.11	0.29	0.24
9	-1.41	1.16	ns	0.50	1.1 <del>6</del>	0.50	0.83	0.47
10	-0.41	0.75	4.28	0.96	4.28	0.75	2.00	1.98
11	-0.22	1.58	2.07	1.23	2.07	1.23	1.63	0.42
12	0.44	0.23	0.69	1.20	1.20	0.23	0.71	0.49
13	1.32	2.34	រាន	2.23	2.34	2.23	2.29	0.08
14	2.05	3.92	4.68	ns	4.68	3.92	4.30	0.54
15	2.78	0.92	ពន	0.89	0.92	0.89	0.91	0.02
16	3.59	0.47	3.55	2.35	3.55	0.47	2.12	1.55
17	4.42	2.16	0.82	3.31	3.31	0.82	2.10	1.25
18	4.91	0.98	0.96	2.64	2.64	0.96	1.53	0.96
19	6.03	ns	ns	2.83	2.83	2.83	2.83	
20	6.62	ns	ns	3.39	3.39	3.39	3.39	
21	7.31	2.78	ns	1.59	2.78	1.59	2.19	0.84
22	8.18	2.45	ns	1.34	2.45	1.34	1.90	0.78
23	8.36	0.31	<b>TI S</b>	0.47	0.47	0.31	0.39	<b>J</b> .11
24	9.15	1.38	1.27	1.87	1.87	1.27	1.51	0.32
25	11.3	2.77	лs	1.12	2.77	1.12	1.95	1.17
26	12.53	0.50	0.82	ns	0.82	0.50	0.66	0.23
27	13.5	0.62	ns	0.85	0.85	0.62	0.74	0.16
28	14.5	0.85	ns	0.86	0.86	0.85	0.86	0.01
29	15.4	0.50	0.52	ns.	0.52	0.50	0.51	0.01
30	16.6	0.60	0.58	0.03	0.60	0.03	0.40	0.32
31	17.6	0.01	лз	0.56	0.56	0.01	0.29	0.39
32	18.3	0.38	<b>ns</b>	0.43	0.43	0.38	0.41	0.04
33	19.3	0.38	ກຣ	0.50	0.50	0.38	0.44	0.08
34	20.3	0.42	រាន	0.19	0.42	0.19	0.31	0.16

\*Distance from Whitlingham STW, negative values indicate upstream, positive values downstream ns=no sample, blank spaces indicate no sampling was attempted i.e. transects 4-6 were sampled once only

1991 5	Survey				Ig CONCENT	RATION (mg k	g <sup>-1</sup> )	
Transect	Distance* (km)	i	Sample iii	v	Maximum	Minimum	Average	Standard deviation
4	-5.1	0.02			0.02	0.02	0.02	deviation
5	-4.85	0.02			0.02	0.02	0.02	
6	-4.15	0.05 ns			0.05	0.05	0.05	
7	-3.35	0.49	0.61	0.88	0.88	0.49	0.66	0.20
8	-2.15	1.37	0.01	1.07	1.37	0.49		
<b>9</b>	-1.41	1.37	0.85	0.55			1.05	0.33
					1.81	0.55	1.07	0.66
10	-0.41	1.31	1.01	0.68	1.31	0.68	1.00	0.32
11	-0.22	1.35	2.51	1.37	2.51	1.35	1.74	0.66
12	0.44	0.36	0.62	1.82	1.82	0.36	0.93	0.78
13	1.32	3.55	4.28	2.73	4.28	2.73	3.52	0.78
14	2.05	2.09	3.04	0.77	3.04	0.77	1.97	1.14
15	2.78	0.27	0.74	1.55	1.55	0.27	0.85	0.65
16	3.59	0.94	3.61	3.25	3.61	0.94	2.60	1.45
17	4.42	4.59	2.60	2.40	4.59	2.40	3.20	1.21
18	4.91	1.58	3.65	4.42	- 4.42	1.58-	3.22	1.47
19	6.03	1.55	3.27	1.78	3.27	1.55	2.20	0.93
20	6.62	0.65	2.72	1.69	2.72	0.65	1.69	1.04
21	7.31	2.37	0.83	1.70	2.37	0.83	1.63	0.77
22	8.18	2.11	1.85	2.75	2.75	1.85	2.24	0.46
23	8.36	0.46	ns	1.94	1.94	0.46	1.20	1.05
24	9.15	0.46	រាន	3.80	3.80	0.46	2.13	2.36
25	11.1	2.64	ns	2.83	2.83	2.64	2.74	0.13
26	12.53	0.99	ns	1.35	1.35	0.99	1.17	0.25
27	13.5	0.96	ns	1.04	1.04	0.96	1.00	0.06
28	14.5	0.51	ns	0.68	0.68	0.51	0.60	0.12
29	15.4	0.39	0.64	0.39	0.64	0.39	0.47	0.14
30	16.6	0.45	0.29	0.49	0.49	0.29	0.41	0.11
31	17.6	0.50	0.12	0.29	0.50	0.12	0.30	0.19
32	18.3	0.36	0.25	0.18	0.36	0.18	0.26	0.09
33	19.3	0.33	ns	0.45	0.45	0.33	0.39	0.08
34	20.3	0.14	ns	0.29	0.29	0.14	0.22	0.11

\*Distance from Whitlingham STW, negative values indicate upstream, positive values downstream ns=no sample, blank spaces indicate no sampling was attempted i.e. transects 4-6 were sampled once only

Structure		0.03	90.06		0.87 0.24	1.37 0.20																												0.39 0.01			
Hg CONCENTRATION (mg kg' <sup>1</sup> )	Minum Average	0.03	0.06	3	0.14	1.16	1.83	25		990	651	0.3A	3.76	4.36	1.57	1.91	1.1	191	145	0.45	0,42	16.0		0.0	0.32	17.0	0.78	90.0	0.14	0,11	01.0	190	0.10	0.38	8.8	10.0	1
He CONCENT	Maximum	0.03	90:0		101	1.56	1.63	5.29	120	6.89	6.15	4.79	471	6.19	8.5	523	d :	140	1.76	201	206	10	1.27	121	0.92	10.0		0.69	0.27	0.46	() () ()		6.0	0.40	800	20.0	C.1.D
	٨				1.03	36	1.83	576	25	0.66	6.15	4.79	3.76	619	121	16	16.7	35	12	10	0.42	22.0	50	5	0.92	50	010	90.0	0.27	110		0.23	0.10	0.38	3.0	120	1
Semule	iii				0.88	1.38	10	1.52		6.89	1.59	10	1.2	8	8	151	8	00	22	0.45	53	2	240	0.35	0.74	17.0	0.28	0.07	0.14	940	01.0	51.0	2	2	55	0.07	C.10
	i	0.03	90'0	2	50	1.16	2	3.8	5	3.85	3	¥.0	4.71	4.78	8	ว		2.4	1.65	1.1	80	20	2	0.30	0.32	25.0	0.33	0.69	0.18	65.0		40.0	6.93	0.40	80.0	700	C.4.0
urvey Distance	(km)	15.6	5.1	18.85	335	-215	141-	15.0	777	3	2.05	2.78	65	4.42	16.4	6.03	20.0		8.8	9.15		507	45	15.4	16.6	0.7	20	20.3	21.6	522	444	25.4	26.4	27.4	4.00	29.4	
1992 Survey	Transect	1414	) <b>1</b>	•	0r-	80	0	2:		10	14	51	9			6.6	2	10	12	2	21	96		29	9	25	18	A	35	85	10	30	40	4	41	54	1

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Turne         Turne <th< th=""><th>Av Ar av 6 - av 6</th><th></th><th></th><th></th><th>D-, A.,</th><th></th><th>Part and</th></th<>	Av Ar av 6 - av 6				D-, A.,		Part and
4.1       4.1         4.1       4	2844 2844 2852 2854 2852 2852 2852 2852				Minimum	Avenac	deviation
	AAEGG-999-222844888515295282828282828282828282828282828282828	~			0.08	100	
#15       #16       #	4 ú ý ÷ é é é é é é é é é é é é é é é é é é			0.03	0.03	0.03	
		0		0.29	0.29	0.29	
	4		1.25	1.27	0.68	1.12	0 24
	1-9-9-9-1-2-2-8-8-8-9-9-1-9-9-1-9-9-1-9-9-1-9-9-1-9-9-9-9		0.86	191	0.86	1 36	0 38
	2999 2999 2999 2999 2999 2999 2999 299		100	12 6			
	200-1022884488851122123228282828282828282828282828282828						
	249-229292929292929292929292929292929292				120	0.7	1
	22222222222222222222222222222222222222		505	3.15	c.c.0	05.2	111
	282844666258821252332866666684888558866666666666666666666666		2				
	22222222222222222222222222222222222222		0.55	4.09	cc.0	7.67	1.81
	22222222222222222222222222222222222222		3.71	3.71	3.71	3.71	
4443         4443 <t< td=""><td>22222222222222222222222222222222222222</td><td></td><td>1.93</td><td>1.93</td><td>0.12</td><td>1.21</td><td>0.91</td></t<>	22222222222222222222222222222222222222		1.93	1.93	0.12	1.21	0.91
<pre>44 44 45 45 45 45 45 45 45 45</pre>	4498851989519999999999999999999999999999		2	5.64	1.26	3.94	2.19
99       99         91       92         92       92	98897888888888888888888888888888888888		3.19	4.38	4	3.35	1.48
	999 299 299 299 299 299 299 299 299 299		2.51	8.67	2.51	02.5	3.44
	288 288 288 288 288 288 288 288 288 288		265	573	296	0.4	218
				05 0	Sa I	5	
	200 200 200 200 200 200 200 200 200 200						
	225 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2						2
	225 225 225 225 225 225 225 225 225 225		77.4	11.4	7.1	26.7	2
	121 121 122 122 122 122 122 122 122 122		0.83	1.48	0.8.0	17.1	0.33
	112 122 122 122 122 122 122 122 122 122		0.10	1.80	0.10	8	06:0
1253       0.03	125 25 25 25 25 25 25 25 25 25 25 25 25 2		2.05	2.05	8.0	151	0.63
113       0.23       0.33	11 22 22 22 22 22 22 22 22 22 22 22 22 2		1.28	1.28	27.0	0.95	0.47
1111       0.05       0.05       0.05       0.05         1111       0.05       0.05       0.05       0.05       0.05         1111       0.05       0.05       0.05       0.05       0.05       0.05         1111       0.05       0.05       0.05       0.05       0.05       0.05       0.05         1111       0.05       0.05       0.05       0.05       0.05       0.05       0.05         1111       0.05       0.05       0.05       0.05       0.05       0.05       0.05         1111       0.05       0	287 287 287 287 287 287 287 287 287 287		0.83	0.83	20	0.67	0.32
155       050       050       050       050         156       050       050       050       050       050         156       050       050       050       050       050       050         156       050       0	1284 1285 1285 1285 1285 1285 1285 1285 1285		0.15	0.81	0.15	0.59	0.47
155       0.05       0.15       0.25         17.5       0.25       0.25       0.25       0.25         17.5       0.25       0.25       0.25       0.25         17.5       0.25       0.25       0.25       0.25         17.5       0.25       0.26       0.26       0.26       0.27         17.5       0.25       0.16       0.26       0.26       0.27         17.5       0.26       0.16       0.26       0.26       0.27         17.5       0.26       0.16       0.26       0.26       0.27         17.5       0.26       0.26       0.26       0.26       0.27         17.5       0.26       0.26       0.26       0.26       0.27         17.5       0.26       0.26       0.26       0.26       0.27         17.5       0.27       0.28       0.26       0.26       0.27         17.5       0.27       0.28       0.26       0.26       0.27         17.5       0.27       0.28       0.26       0.27       0.27         17.5       0.27       0.28       0.26       0.27       0.27         17.5       0.27	1995 1995 1995 1995 1995 1995 1995 1995		0.63	0.65	0.59	0.63	0.03
175       0.5       0.5       0.5         176       0.5       0.5       0.5       0.5         176       0.5       0.5       0.5       0.5         176       0.5       0.5       0.5       0.5         176       0.5       0.5       0.5       0.5       0.5         176       0.5       0.5       0.5       0.5       0.5       0.5         176       0.5       0.5       0.5       0.5       0.5       0.5       0.5         176       0.5       0	17.5 28.5 29.5 29.5 29.5 29.5 29.5 29.5 29.5 29		0.72	0.72	0.08	0.42	55.0
111       0.00       0.01	11 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2		110	0.49	0.08	0.20	500
101       101       101       101         101       101       101       101       101         101       101       101       101       101         101       101       101       101       101       101         101       101       101       101       101       101       101         101       101       101       101       101       101       101       101         101       101       101       101       101       101       101       101       101         101       1	19 20 20 20 20 20 20 20 20 20 20 20 20 20		0.33	0.59	0.13	0.41	0.23
3215       3215       3215       3215         3215       3215			040	040	0.76	20	10
316       0.01       0.02         311       0.05       0.01       0.02         312       0.05       0.01       0.02         312       0.05       0.01       0.02         312       0.05       0.01       0.02         312       0.05       0.01       0.02         312       0.05       0.01       0.02         312       0.05       0.01       0.02         312       0.05       0.01       0.02         014       0.05       0.01       0.02         020       0.01       0.02       0.02         021       0.02       0.03       0.03         022       0.03       0.03       0.03         023       0.02       0.03       0.03         024       0.03       0.03       0.03         023       0.03       0.03       0.03         024       0.03       0.03       0.03         023       0.03       0.03       0.03         024       0.03       0.03       0.03         025       0.03       0.03       0.03         023       0.03       0.03       0.03 </td <td>11.00 20 20 20 20 20 20 20 20 20 20 20 20 2</td> <td></td> <td></td> <td></td> <td>110</td> <td>0.74</td> <td>010</td>	11.00 20 20 20 20 20 20 20 20 20 20 20 20 2				110	0.74	010
222       224       0.39       0.16       0.31         224       0.3       0.16       0.3       0.16       0.3         224       0.3       0.16       0.3       0.16       0.3         224       0.3       0.16       0.3       0.16       0.3         224       0.3       0.16       0.19       0.3       0.16       0.3         224       0.3       0.16       0.13       0.16       0.3       0.16       0.3         224       0.3       0.16       0.13       0.16       0.13       0.16       0.16         224       0.3       0.16       0.13       0.16       0.16       0.16       0.16         224       0.20       0.16       0.13       0.13       0.14       0.16       0.16         224       0.20       0.16       0.16       0.16       0.16       0.16       0.16         224       0.20       0.21       0.23       0.23       0.24       0.26       0.16       0.16       0.16         225       0.22       0.23       0.23       0.24       0.26       0.16       0.16       0.16       0.16       0.16       0.16	11 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8		1.48	0.4t		12	110
234     234     234     234       234     234     234     235       234     235     235     235       234     235     235     235       234     235     235     235       235     235     235     235       235     235     235     235       235     235     235     235       235     235     235     235       235     235     235     235       235     235     235     235       235     235     235     235       236     237     235     235       237     238     237     235       238     237     233     245       237     238     237     235       238     237     237     237       248     237     237     237       259     238     237     237       250     238     237     237       251     237     237     237       252     237     237     237       253     237     237     237       254     238     237     237       255     237     237	12888888 12888888 1288888888 12888888888					140	24.0
224 224 224 2255 225	222 222 222 222 222 222 222 222 222 22				110		12
224 224 225 226 226 226 226 226 226 226 226 226	11 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8		1				
224 0.03 234 0.05 234 0.05 234 0.05 234 0.05 234 0.05 234 0.05 234 0.05 234 0.05 234 0.05 234 0.05 232 0.05 232 0.05 0.24 0.05 0.25 0.25 0.25 0.27 0.28 0.29 0.2	222 238 238 238 238 257 257 257 257 257 257 257 257 257 257		21.0	0.19		0.10	70.0
23.4         0.1 <td>205 4 4 4 4 205 4 4 4 4 31.1</td> <td></td> <td></td> <td>200</td> <td>3.5</td> <td></td> <td>01.0</td>	205 4 4 4 4 205 4 4 4 4 31.1			200	3.5		01.0
0.09 0.15 0.16 0.10 0.10 0.15 0.15 0.15 0.15 0.10 0.10			0.13	16.0	0.10	17-0	11.0
009 015 045 045 045 046 019 019 019 019 019 019 019 010 021 011 021 010 021 010 021 010 010			8	C9.0	000	4.0	0.47
0.41 0.19 0.23 0.24 0.19 0.19 0.19 0.26 0.23 0.27 0.27 0.20 0.22 0.20 0.22 0.20 0.20			0.45	0.45	600	0.29	0.19
0.10 0.23 0.27 0.27 0.10 0.26 0.08 0.32 0.32 0.08 0.27 0.20 0.24 0.27 0.08 0.20 0.24 0.27 0.08 0.20 0.20 0.20 0.20			0.32	0.41	0.19	0.33	0.11
0.26 0.08 0.32 0.32 0.08 0.27 0.20 0.24 0.27 0.20 0.24 0.20 0.24 0.27 0.20 0.24 0.20			0.27	0.27	0.10	0.22	60.0
0.27 0.20 0.24 0.27 0.20 0.20 0.24 0.20 0.20 0.24 0.24 0.24			0.32	0.32	0.08	0.25	0.12
0.20 0.20 0.20 0.20 0.20 0.24 0.24 0.24			4C 0	1.77	0.0	0.25	200
0.24 0.24 0.24				0.20	0.00	0.20	
L7:0 L7:0				10.0	20.0	90.04	
		1 4		174	20.0	40.0	

1994 S	Survey		<b>F</b> 1	-	Hg CONCENTI	RATION (mg k	g <sup>-1</sup> )	
Transect	Distance* (km)	i	Sample iii	v	Maximum	Minimum	Average	Standard deviation
4	-5.1	0.3			0.3	0.3	0.3	
5	-4.85	0.0			0.0	0.0	0.0	
6	-4.15	0.9			0.9	0.9	0.0	
7	-3.35	0.6	1.0	0.9	1.0	0.6	0.8	0.2
8	-2.15	1.1	1.0	1.4	1.4	1.0	1.2	0.2
9	-1.41	1.1	ns	2.0	2.0	1.0	1.2	0.6
10	-0.41	0.6	ns	3.4	3.4	0.6	2.0	2.0
n	-0.22	2.3	3.5	ns	3.5	2.3	2.9	0.8
12	0.44	5.9	ns	ពន	5.9	5.9	5.9	0.0
13	1.32	3.6	4.6	5.7	5.7	3.6	4.6	1.1
14	2.05	ns	-7.0 D1	4.7	4.7	4.7	4.7	1.1
15	2.78	ns	1.1	3.9	3.9	1.1	2.5	2.0
16	3.59	5.3	3.3	2.9	5.3	2.9	3.8	1.3
17	4.42	3.0	4.7	1.4	4.7	1.4	3.0	1.5
18	4.91	4.1	1.2	0.4	4.1	0.4	1.9	1.7
19	6.03	3.3	ns	3.9	3.9	3.3	3.6	0.4
20	6.62	2.0	ns	4.3	4.3	2.0	3.2	1.6
21	7.31	3.0	ns	1.5	3.0	1.5	2.3	1.0
22	8.18	6.1	1.3	5.0	6.1	1.3	4.1	2.5
23	8.36	0.3	រន	2.7	2.7	0.3	1.5	1.7
24	9.15	4.8	ns	0.4	4.8	0.4	2.6	3.2
25	11.1	0.2	ns	6.5	6.5	0.2	3.3	4.5
26	12.53	0.5	0.8	2.1	2.1	0.5	1.1	0.9
27	13.5	1.6	ns	1.1	1.6	1.1	1.3	0.3
28	14.5	0.5	ns	0.2	0.5	0.2	0.4	0.3
29	15.4	0.6	1.4	0.3	1.4	0.3	0.4	0.6
30	16.6	0.2	1.9	0.7	1.9	0.2	0.8	0.8
31	17.6	0.4	1.7 DS	0.7	0.4	0.2	0.9	0.9
32	18.3	0.4	113 115	0.2	0.4	0.2	0.3	0.2
33	19.3	0.4	0.3	0.4	0.4	0.2	0.3	0.1
34	20.3	0.2	0.3	0.3	0.3	0.2	0.3	0.1

\*Distance from Whitlingham STW, negative values indicate upstream, positive values downstream ns=no sample, blank spaces indicate no sampling was attempted i.e. transects 4-6 and 47-49 were sampled once only

1995 S				]	H <sub>g</sub> CONCENTI	RATION (mg k	g <sup>-1</sup> )	
	Distance*		Sample					Standard
Transect	(km)	i	<b>i</b> ii	<b>v</b>	Maximum	Minimum	Average	<u>deviation</u>
4	-5.1	0.4			0.4	0.4	0.4	
5	-4.85	0.}			0.1	0.1	0.1	
6	-4.15	0.9			0.9	0.9	0.9	
7	-3.35	0.5	1.1	1.2	1.2	0.5	0.9	0.4
8	-2.15	1.5	1.2	0.9	1.5	0.9	1.2	0.3
9	-1.41	0.1	2.6	1.4	2.6	0.1	1.3	1.3
10	-0.41	0.8	1.5	5.2	5.2	0.8	2.5	2.4
11	-0.22	6.6	3.3	2.8	6.6	2.8	4.2	2.1
12	0.44	1.5	0.3	ាះ	1.5	0.3	0.9	0.8
13	1.32	4.0	3.2	0.9	4.0	0.9	2.7	1.6
14	2.05	0.5	5.9	2.7	5.9	0.5	3.0	2.6
15	2.78	0.2	1.0	3.5	3.5	0.2	1.6	1.7
16	3.59	3.8	4.8	3.7	4.8	3.7	4.1	0.6
17	4.42	2.7	4.0	1.3	4.0	1.3	2.7	1.3
18	4.91	1.7	1.7	0.3	1.7	0.3	1.2	0.8
19	6.03	6.5	1.4	2.5	6.5	1.4	3.4	2.7
20	6.62	1.9	1.3	1.8	1.9	1.3	1.7	0.3
21	7.31	1.8	2.3	0.7	2.3	0.7	1.6	0.8
22	8.18	4.0	0.6	6.8	6.8	0.6	3.8	3.1
23	8.36	0.2	D\$	0.3	0.3	0.2	0.2	0.1
24	9.15	5.9	<b>D</b> \$	0.6	5.9	0.6	3.3	3.8
25	11.1	0.3	ns	0.9	0.9	0.3	0.6	0.5
26	12.53	0.5	ns.	1.8	1.8	0.5	1.1	0.9
27	13.5	0.7	ពន	0.2	0.7	0.2	0.4	0.4
28	14.5	0.4	ns	1.0	1.0	0.4	0.7	0.4
29	15.4	0.2	DS	0.4	0.4	0.2	0.3	0.1
30	16.6	0.4	0.5	0.7	0.7	0.4	0.5	0.1
31	17.6	0.6	0.2	0.1	0.6	0.1	0.3	0.2
32	18.3	0.8	0.3	0.3	0.8	0.3	0.5	0.3

 32
 18.3
 0.8
 0.3
 0.3
 0.8
 0.3

 \*Distance from Whitlingham STW, negative values indicate upstream, positive values downstream

 ns=no sample, blank spaces indicate no sampling was attempted i.e. transects 4-6 were sampled once only

#### 2. **Total copper concentrations**

986 Surve	y		Cu CONCENTRATION (mg kg <sup>-1</sup> )							
-	Distance*		Sample							Standard
Transect	(km)	. i	ii	រ៉េរ	iv	v	Maximum	Minimum	Average	deviation
7	-3.35 -3.32	32	41.1 75.8	54.8 98.3	81.3	64.7 36.7	81.3 98.3	32 36.7	54.8 68.8	19.4
8	-3.32	80.8	75.8	98.3	52.6	36.7	98.3	36.7	68.8	24.3
0	-2.15 -2.12	87.8	83.3	94.2	93.2	105	105	83.3	92.7	8.2
9	-2.12	93.3	88.3	96.3	53.6	101	101	53.6	86.5	19.0
y	-1.41	5	11.4	13.1	61.4	74.2	74.2	5	33.0	32.2
10	-1.38 -0.41	10	6.2	61.3	46.9	27.3	61.3	6.2	30.3	23.7
10		41.6	ns 97.4	115 248	104	53.5	104	41.6	66.4	33.1
••	-0.38	58.8	97.4	248	87.5	167	248	58.8	131.7 145.7	76.2
11	-0.22	97.5	155	243	76.2	157	243	76.2	145.7	64.9
	-0.19	164	124	ns	59.6	<u>ns</u>	164	59.6	115.9	52.7
12	0.44	52.3	32.2	25.7	11.2	46.4	52.3	11.2	33.6	16.4
	0.47	125	71.8	40.9	9.11	10.7	125	9.11	51.5	48.4
13	1.32	122	141	178	304	36.3	304	36.3	156.3	97.6
	1.35	189	220	270	325	109	325	109	222.6	81.8
14	2.05	64.3	150	135	196	ns.	196	64.3	136.3	\$4.6
	2.08	67.5	<b>N</b> 5	211	325	364	364	67.5	136.3 241.9	133.1
15	2.78	10.4	24.8	31.9	181	230	230	10.4	95.6	102.1
_	2.81	6.82	13.6	122	20.4	246	246	6.82	81.8	103.2
16	3.59	375	73.5	39	125	228	375	39	168.1	135.9
	3.62	71.9	65.8	210	143	181	210	65.8	134.3	64.4
17	4.42	69	188	236	ns	237	210 237	69	182.5 176.4	79.0
	4.45	107	226	148	238	163	238	107	176.4	\$4.9
18	4.91	107	107	124	118	130	130	107	117.2	10.2
	4,94	180	176	73.6	73.2	15.1	180	15.1	103.6	72.0
19	6.03	208	153	18.4	27.3	133	208	18.4	103.6 107.9	82.4
	6.06	152	36.1	ns	95.3	118	152	36.1	100.4	48.8
20	6.62	82.4	132 79.2	289	112	37.2	289	37.2	130.5	95.5
	6.65	60.5	79.2	103	146	85.8	146	60.5	94.9	32.4
21	7.31	107	171	ns	262	207	262	107	186.8	65.0
	7.34	129	147	142	139	244	244	129	160.2	47.3
22	8.18	179	154	42	120	160	179	42	131.0	\$4.1
	8.21	98.1	67.3	40.7	112	103	112	40.7	84.2	29.6
23	8.36	41.B	58.2	118	68.7	11.5	118 .	11.5	59.6	39.1
	8.39	82.3	86.7	158	87.5	35.5	158	35.5	90.0	43.8
24	9.15	70.2	60.7	102	25.2	53.1	102	25.2	62.2	27.8
	9.18	36.8	78.1	ກຣ	105	29.6	105	29.6	62.4	35.6
25	11.10	62.2	23.8	177	103	39.4	177	23.8	81.1	55.8 61.4
	11.13	03	20.2	160	104	63.3	160	20.2	85.5	51.7
26	12.53	30.1	21.8	119	37.8	19	119	10	45.5	41.7
	12.56	23	66.8	52.8	49.6	54.3	66.8	19 23	49.3	16.1

1987 Survey Distance*		Cu CONCENTRATION (mg kg <sup>-1</sup> ) Sample								<b>6</b>
Transect	<u>(km)</u>	i	ii	jii	iv	v	Maximum	Minimum	Average	Standar deviatio
1	-17.4	2.2 6.9					2.2	2.2 6.9	2.2 6.9	
2	-15.6	0.9					6.9	6.9	6.9	
3	-11.6	11.9					11.9	11.9	11.9	
2 3 4 5 6 7 8 9	-5.1	35.8					35.8	35.B	35.8	
Ş	-4.85	35.4					35.4 26.7	35.4	35.4	
0	-4.15	26.7					26.7	26.7	26.7	
1	-3.35	31.3					31.3	31.3	31.3	
8	-2.15	93.9					93.9	93.9	93.9	
9	-1.41	130.8					130.8	130.8	130.8	
10 11 12 13	-0.41	ns								
11	-0.22	103.B					103.8	103.8	103.8	
12	0.44	180.9					180.9	180.9	180.9	
13	1.32	239.6					239.6	239.6	239.6	
14 15	2.05 2.78	104.2		100			104.2	104.2	104.2	
15	2.78	185.0					185.0	185.0	185.0	
16 17 18 19 20 21 22 23 24 25 26 27 28	3.59 4.42	111.0					111.0	111.0	111.0	
17	4.42	185.0					185.0	185.0	185.0	
18	4.91	ns 117.5								
19	6.03	117.5					117.5	117.5	117.5	
20	6.62	100.9					100.9	100.9	100.9	
21	7.31	100.2					100.2	100.2	100.2	
22	8.18	37.7					37.7	37.7	37.7	
23	8.36	29.2					29.2	29.2	29.2	
24	6.62 7.31 8.18 8.36 9.15	59.8					59.8 21.7 17.4	59.8 21.7	59.8	
25	11.1	21.7					21.7	21.7	21.7	
26	12.53	17.4					17.4	17.4	17.4	
27	13.5	20.8	18.5	76.3	42.2	30.6	76.3	18.5	37.7	23.5
28	14.5	41.1	ns -	DS	13.8	12.7	41.1	12.7	22.5	16.1
29	15.4	12.4	16.1	<b>n.s</b>	13.5	30.0	30.0	12.4	18.0	8.1
30	16.6	24.3	24.0	41.7	91.3	18.9	91.3	18.9	40.0	29.9
31	17.6	69.6	ns	150.8	54.1	D5	150.8	54.1	91.5	51.9
32	18.3	46.9	135	44.0	29.6	48.1	48.1	29.6	42.2 32.7	8.5
33	19.3	29.2	<b>D5</b>	\$4.5	33.0	13.9	54.5	13.9	32.7	16.7
34	20.3	38.3	29.8	<b>N</b> 4	ភន	15.8	38.3	15.B	28.0	11.4
29 30 31 32 33 34 35 36 37 38 39 40	21.6 22.5	19.8	17.3	10.3	20.6	<b>D4</b>	20.6 33.9	10.3	17.0	4.7
36	22.5	33.9	7.3	<b>D.S</b>	25	10.9	33.9	7.3	17.4	14.4
37	23.4	19.6	52.2	25	<b>D.5</b>	16.5	52.2 15.0	16.5	29.4	19.8
38	24.4	14.2	6.3	15.0	8.3	15.0	15.0	16.5 6.3	11.8	4.1
20	25.4	9.6	11.5	20.2	8.4	14.3	20.2	8.4	12.8	4.7
<b>4</b> 0	26.4	18.1	5.2	9.4	10.4	5.7	18.1	5.2	9.8	5.2
41	27.4	41.4	23.0	ns.	27.2	50.3	50.3	23.0	35.5	12.6
42	28.4	19.3	ns	ns	25.1	43.6	43.6	19.3	29.3	12.7
43	29.4	3.9	17.1	45.1	57.2	40.2	57.2	3.9	32.7	21.7
	30.4	17.1	9.5	22.3	11.6		22.3	9.5	15.1	5.8
44 45	31.1	14.0	16.5	25.6	13.9	16.0	25.6	13.9	17.2	4.8
46	32.5	14.9	10.0	2.0	10.9	10.0	14.9	14.9	14.9	4.6
47	33.5	18.6					18.6	18.6	18.6	
48	34.5	_ 31.6					31.6	31.6	31.6	

\*Distance from Whitlingham STW, negative values indicate upstream, positive values downstream ns=no sample, blank spaces indicate no sampling was sitempted i.e. transects 2-6 and 46-49 were sampled once only

1992 5	Survey				C1 CONCENT	RATION (mg kg	*)	
<b>T</b>	Distance*		Sample				· .	Standard
Transect	<u>(len)</u>		111	v	Maximum	Minimum	Avenage	deviation
23	-15.6	235						
4	-11.6 -5.1	50.3			<b>*</b> •••			
	-3.1	50.3 7.1			50.3	50.3	50.3	
5 6	-4.85				7.1	2.1	7.1	
7		37.5		~ ~	A( A			
	-3.35		84.1	96.9	96.9	37.5	72.8	31.3
8	-2.15	100.2	102.0	107.0	107.0	100.2	103.1	3.5
9	-1.41	П <b>5</b>	75	103.5	103.5	103.5	103.5	
10	-0.41	94.7	130.3	177.6	177.6	94.7	134.2	41.6
11	-0.22	104.4	155.6	210.6	210.6	104.4	156.9	53.1
12	0.44	<u>ns</u>	23.6	14.1	23.6	14.1	18.9	6.7
13	1.32	137.3	205.2	34.1	205.2	34.1	125.5	86.2
14	2.05	715	161.4	290.5	290.5	161.4	226.0	91.3
15	2.78	39.1	239.5	218.4	239.5	39.1	165.7	110.1
16	3.59	193.6	165.6	165.6	193.6	165.6	174.9	16.2
17	4.42	199.5	168.5	207.5	207.5	168.5	191.8	20.6
18	4.91	195.4	90.0	102.0	195.4	90.0	129.1	57.7
19	6.03	101.8	71.1	84.5	101.8	71.1	85.8	15.4
20	6.62	112.2	96.7	97.1	112.2	96.7	102.0	6.8
21	7.31	95.6	41.9	67.5	95.6	41.9	68.3	26.9
22	8.18	86.3	45.3	84.4	86.3	45.3	72.0	23.1
22 23	8,36	60.8	149.7	72.2	149.7	60.8	94.2	48.4
24 25	9.15	58.3	37.0	46.1	58.3	37.0	47.1	10.7
25	11.1	65.B	39.9	30.1	65.8	30.1	45.3	18.4
26 27	12.53	30.2	52.9	38.8	52.9	30.2	40.6	11.5
27	13.5	50.0	35.8	30.5	50.0	30.5	38.8	10.1
28	14.5	48.2	25.4	15.8	48.2	15.8	29.8	16.6
29	15.4	19.9	47.5	35.5	47.5	19.9	34.3	13.8
30	16.6	19.7	27.9	40.6	40.6	19.7	29.4	10.5
31	17.6	18.5	19.4	14.4	19.4	14.4	17.4	2.7
32	18.3	29.8	33.7	36.0	36.0	29.8	33.2	3.1
33	19.3	27.3	32.5	31.6	32.5	27.3	30.5	2.8
34	20.3	17.2	13.0	21.2	21.2	13.0	17.1	4.1
35	21.6	36.8	31.7	34.4	36.8	31.7	34.3	2.6
36	22.5	35.0	19.1	16.4	35.0	16.4	23.5	10.1
37	23.4	20.5	16.7	19.1	20.5	16.7	18.8	1.9
38	24.4	25.7	17.9	13.6	25.7	13.6	19.1	6.1
39	25.4	10.1	8.6	8.2	10.1	8.2	9.0	1.0
40	26.4	31.9		11.3	31.9	11.3	21.6	1.0
41	27.4	25.1	ns	11.3	25.1	22.0		
41	28.4		ns	22.0			23.6	2.2
	28.4	9.5	ns	29.2	29.2	9.5	19.4	13.9
43		18.0	12.1	19.9	19.9	12.1	16.7	4.1
44	30.4	27.2	12.6	14.0	27.2	12.6	17.9	8.1
45	31.1	17.6	2.1	21.0	21.0	2.1	13.6	10.1
46	32.5	23.9			23.9	23.9	23.9	
47	33.5	15.5			15.5	15.5	15.5	
48	34.5	16.0			16.0	16.0	16.0	
49	35.5	40.6			40.6	40.6	40.6	

1993 9	Survey				Cu CONCEN	TRATION (mg k	g <sup>-1</sup> )	
	Distance*		Sample			-		Standard
Transect	<u>(km)</u>	i	iii	<u>v</u>	Maximum	Minimum	Average	deviation
4	-5.1	35.2			35.2 14.6	35.2 14.6	35.2	
5	-4.85	14.6			14.6	14.6	14.6	
6	-4.15	22.1			22.1	22.1	22.1 78.3	
7	-3.35	30.0	114.0	<b>9</b> 0.9	114.0	30.0	78.3	43.4
8	-2.15	82.7	110.4	83.8	110.4	82.7	92.3	15.7
9	-1.41	10.2	25.9	<del>9</del> 9.0	<b>99</b> .0	10.2	45.0	47.4
10	-0.41	34.5	99.0	ns.	99.0	34.5	66.8	45.6
11	-0.22	43.4	138.0	60.2	138.0	43.4	80.5	50.5
12	0.44	ns	ns.	<b>D</b> .5	0.0	0.0		
13	1.32	123.0	154.2	29.0	154.2	29.0	102.1	65.2
14	2.05	ns	ns.	150.5	150.5	150.5	150.5	
15	2.78	4.2	23.6	83.0	\$3.0	4.2	36.9	41.1
16	3.59	45.6	117.9	214.8	214.8	45.6	126.1	84.9
iž	4.42	63.3	118.8	134.3	134.3	63.3	105.5	37.3
18	4.91	93.2	105.0	157.6	157.6	93.2	118.6	34.3
19	6.03	157.6	ns.	145.8	157.6	145.8	151.7	8.3
20	6.62	64.6	78.0	95.2	95.2	64.6	79.3	15.3
	7.31	34.8	53.1	14.2	53.1	14.2	34.0	19.5
21	8.18	83.7	45.2	14.2 88.6	88.6	45.2	72.5	
22	8.36	40.0			40.0	33.4	36.5	23.8
23 24			36.2	33.4				3.3
24	9.15	56.5	38.5	18.8	\$6.5	18.8	37.9	18.9
25 26	11.1	, 42.7	40.6	55.0	55.0	40.6	46.1	7.8
26	12.53	19.4	30.0	47.6	47.6	19.4	32.3	14.2
27	13.5	20.0	41.0	38.0	41.0	20.0	33.0	11.4
28	14.5	35.4	<b>D3</b>	14.6	35.4	14.6	25.0	14.7
29	15.4	37.0	26.1	31.3	37.0	26.1	31.5	5.5
30	16.6	17.5	17.4	37.0	37.0	17.4	24.0	11.3
31	17.6	22.4	6.4	10.1	22.4	6.4	13.0	8.4
32	18.3	26.6	27.4	23.0	27.4	23.0	25.7	2.3
33	19.3	T15	22.0	22.0	22.0	22.0	22.0	
34	20.3	16.9	23.0	27.8	27.8	16.9	22.6	5.5
35	21.6	25	ករ	23.0	23.0	23.0	23.0	
36	22.5	ns	14.3	26.4	26.4	14.3	20.4	8.6
36 37	23.4	29.0	16.4	ns	29.0	16.4	22.7	8.9
38	24.4	ns	26.7	18.5	26.7	18.5	22.6	5.8
39	25.4	20.8	16.4	17.5	20.8	16.4	18.2	2.3
40	26.4	11.7	11.0	17.7	17.7	11.0	13.5	3.7
41	27.4	TS	15.2	19.5	19.5	15.2	17.4	3.0
42	28.4	12.9	13.1	26.7	26.7	12.9	17.6	7.9
	28.4	29.8	8.4	25.0	29.8	8,4	21.1	11.2
43						11.0	16.8	
44	30.4	11.0	14.2	25.3	25.3			7.5
45	31.1	22.0	9.4	28.5	28.5	9.4	20.0	9.7
46	32.5	25.0			25.0	25.0	25.0	
47	33.5	19.2			19.2	19.2	19.2	
48	34.5	22.0			22.0	22.0	22.0	

1994 §	Survey			Cu	CONCENTI	RATION (mg	kg <sup>-1</sup> )	
	Distance*		Sample				U ·	Standard
Transect	(km)	<u>i</u>	iii	v	Maximum	Minimum	Average	deviation
4	-5.1	47.4			47.4	47.4	47.4	
5	-4.85	5.8			5.8	5.8	5.8	
6	-4.15	5.8			5.8	5.8	5.8	
7	-3.35	34.3	103.5	<b>9</b> 3.0	103.5	34.3	76.9	37.3
8	-2.15	91.1	90.9	111.2	111.2	90.9	97.7	11.7
9	-1.4]	89.2	<b>T</b> 15	87.1	89.2	87.1	88.2	1.5
10	-0.41	24.3	<b>D</b> 5	152.3	152.3	24.3	88.3	90.5
11	-0.22	111.6	129.7	<b>715</b>	129.7	111.6	120.7	12.8
12	0.44	131.8	0.5	TLS.	131.8	131.8	131.8	-2
13	1.32	98.3	161.9	163.6	163.6	98.3	141.3	37.2
14	2.05	ns	ns	161.4	161.4	161.4	161.4	
15	2.78	715	30.3	146.8	146.8	30.3	88.6	82.4
16	3.59	192.9	113.1	126.6	192.9	113.1	144.2	42.7
17	4.42	136.8	171.8	47.6	171.8	47.6	118.7	64.0
18	4.91	131.2	48.1	17.4	131.2	17.4	65.6	58.9
19	6.03	113.1	ns	98.6	113.1	98.6	105.9	10.3
20	6.62	65.2	ns	101.8	101.8	65.2	83.5	25.9
21	7.31	88.5	ns	60.1	88.5	60.1	74.3	20.1
22	8.18	121.1	38.7	114.2	121.1	38.7	91.3	45.7
23	8.36	17.8	ns	72.0	72.0	17.8	44.9	38.3
24	9.15	104.3	ns	34.3	104.3	34.3	69.3	49.5
25	11.1	16.0	лз	69.8	69.8	16.0	42.9	38.0
26	12.53	23.3	29.3	61.4	61.4	23.3	38.0	20.5
27	13.5	50.2	ns	31.1	50.2	31.1	40.7	13.5
28	14.5	30.8	ns	17.9	30.8	17.9	24.4	9.1
29	15.4	34.6	45.2	20.4	45.2	20.4	33.4	12.4
30	16.6	17.7	42.8	28.7	42.8	17.7	29.7	12.6
31	17.6	32.3	ns	12.5	32.3	12.5	22.4	14.0
32	18.3	35.1	ns	22.1	35.1	22.1	28.6	9.2
33	19.3	26.7	14.8	19.4	26.7	14.8	20.3	6.0
34	20.3	20.2	11.3	28.2	28.2	11.3	19.9	8.5

•Distance from Whitlingham STW, negative values indicate upstream, positive values downstream ns=no sample, blank spaces indicate no sampling was attempted i.e. transects 4-6 were sampled once only

1995 §	Survey		•	Cī	CONCENT	RATION (mg	kg <sup>-1</sup> )	
Transect	Distance* (km)	i	Sample iii	v	Maximum	Minimum	Average	Standard deviation
4	-5.1	21.6			21.6	21.6	21.6	_
5	-4.85	4.9			4.9	4.9	4.9	
6	-4.15	8.7			8.7	8.7	8.7	
7	-3.35	26.6	91.0	80.3	91.0	26.6	66.0	34.5
8	-2.15	76.0	79.9	66.4	79.9	66.4	74.1	7.0
9	-1.41	7.0	86.2	68.6	86.2	7.0	53.9	41.6
10	-0.41	43.8	92.2	153.7	153.7	43.8	96.6	55.1
11	-0.22	111.0	115.7	72.2	115.7	72.2	99.6	23.8
12	0.44	62.9	10.2	กร	62.9	10.2	36.5	37.3
13	1.32	146.5	181.6	37.9	181.6	37.9	122.0	74.9
14	2.05	34.3	321.4	115.3	321.4	34.3	157.0	148.0
15	2.78	10.3	23.3	140.2	140.2	10.3	57.9	71.5
16	3.59	175.9	199.2	117.6	199.2	117.6	164.2	42.0
17	4.42	111.5	121.4	29.3	121.4	29.3	87.4	50.6
18	4.91	51.1	77.1	19.2	77.1	19.2	49.1	29.0
19	6.03	149.6	61.9	71.1	149.6	61.9	94.2	48.2
20	6.62	80.3	88.7	86.8	88.7	80.3	85.2	4.4
21	7.31	85.3	37.8	79.2	85.3	37.8	67.4	25.8
22	8.18	82.3	30.7	91.6	91.6	30.7	68.2	32.8
23	8.36	12.7	ns	19.6	19.6	12.7	16.1	4.8
24	9.15	62.8	01	19.8	62.8	19.8	41.3	30.4
25	11.1	14.5	ns	51.5	51.5	14.5	33.0	26.1
26	12.53	30.2	ns	57.7	57.7	30.2	44.0	19.4
27	13.5	31.5	ns	14.0	31.5	14.0	22.8	12.4
28	14.5	22.2	n's	54.2	54.2	22.2	38.2	22.6
29	15.4	19.4	ns	26.6	26.6	19.4	23.0	5.1
30	16.6	18.8	28.2	33.4	33.4	18.8	26.8	7.4
31	17.6	32.1	10.5	9.3	32.1	9.3	17.3	12.9
32	18.3	34.4	23.8	49.8	49.8	23.8	36.0	13.1

\*Distance from Whitlingham STW, negative values indicate upstream, positive values downstream namo sample, blank spaces indicate no sampling was attempted i.e. transects 4-6 were sampled once only

## 3. Organomercury concentrations

1

1986	Survey	MeH	g CONC	ENTRAT	ΠΟΝ (μ	g kg <sup>-1</sup> )		
	Distance*	Sample						
Transect	<u>(</u> km)	i	ü	iü	iv	v		
7	-3.32			0.7				
10	-0.38			13.2				
13	1.35		8.2					
14	2.08			3.8				
15	2.81			7.0				
16	3.62			10.6	+			
17	4.45				0.7			
19	6.03		5.0					
21	7.31				3.2			
26	12.53			4.0				

\*Distance from Whitlingham STW, negative values indicate upstream, positive values downstream

1987	Survey	MeHg	CONC	ENTRA	ΓΙΟΝ (μ	g kg <sup>-1</sup> )
	Distance*			Sample		
Transect	(km)	i	ü	iii	iv	v
6	-4.15	0.7				
7	-3.35	1.6				
8	-2.15	<0.5				
9	-1.41	1.0				
11	-0.22	<0.5				
13	1.32	<0.5				
14	2.05	1.6				
16	3.59	1.6				
17	4.42	<0.5				
19	<b>6</b> .03	1.4				
20	6.62	1.8				
21	7.31	1.1				
22	8.18	0.6				
23	8.36	<0.5				
24	9.15	<0.5				
25	11.1	<0.5				
28	14.5				1.2	
29	15.4					<0.5
31	17.6	6.4				
33	19.3					<0.5
35	21.6					<0.5
40	26.4					<0.5
41	27.4					<0.5 <sup>a</sup>
43	29.4				1.1	

\*Distance from Whitlingham STW, negative values indicate upstream, positive values downstream

<b>198</b> 9 (	Survey Distance*			Sample	MeHg	CONC	ENTRATION	(µg kg <sup>-1</sup> )		Standard
Transect	<b>(k</b> m)	i	ü	üi	iv	v	Maximum	Minimum	Average	deviatior
1	-17.4									
2	-15.6									
3	-11.6									
4	-5.1	2.2					2.2	2.2	2.2	
5	-4.85	0.1					0.1	0.1	0.1	
6	-4.15	3.4					3.4	3.4	3.4	
7	-3.35					0.9	0.9	0.9	0.9	
8	-2.15		2.2				2.2	2.2	2.2	
9	-1.41		0.3		1.4		1.4	0.3	0.8	0.7
10	-0.41		1.4				1.4	1.4	1.4	
11	-0.22	•	5.9				5.9	5.9	5.9	
12	0.44	8.3					8.3	8.3	8.3	
13	1.32		7.7				7.7	7.7	7.7	
14	2.05					2.2	2.2	2.2	2.2	
15	2.78	1.6				9.2	9.2	1.6	5.4	5.4
16	3.59					5.1	5.1	5.1	5.1	
17	4.42					6.4	6.4	6.4	6.4	
18	4.91					2.3	2.3	2.3	2.3	
19	6.03					6.5	6.5	6.5	6.5	
20	6.62		2.8				2.8	2.8	2.8	
21	7.31	13.7				2.4	13.7	2.4	8.0	8.0
22	8.18					1.9	1.9	1.9	1.9	
23	8.36	1.3					1.3	1.3	1.3	
24	9.15					3.5	3.5	3.5	3.5	
25	11.1	5.0				0.0	5.0	5.0	5.0	
26	12.53	5.0				1.2	1.2	1.2	1.2	
27	13.5					3.1	<b>3</b> .1	3.1	3.1	
28	14.5				0.3	2.1	0.3	0.3	0.3	
29	15.4				0.0	2.7	2.7	2.7	2.7	
30	16.6	1.3				2.7	1.3	1.3	1.3	
31	17.6	1.5				0.3	1.5	0.3	0.8	0.8
32	17.8	1.4				0.5	0.6	0.5	0.6	<b>Q</b> .0
33	18.3					0.0	0.3	0.3	0.3	
33 34	20.3	0.7				0.5	0.3	0.3	0.3 0.7	
		0.7				0.7	0.7	0.7	0.7	
35	21.6	0.4				0.7	0.7	0.7	0.7	
36	22.5		1.	-			0.4			
37	23.4	0.3						0.3	0.3 0.1	
38	24.4	0.1					0.1	0.1		
39	25.4	1.7					1.7	1.7	1.7	
40	26.4	ns								
41	27.4	ns			<u> </u>	<u>^</u>	<b>^</b>	<b>^</b>		
42	28.4				0.5	0.5	0.5	0.5	<b>.</b>	
43	29.4					0.1	0.1	0.1	0.1	
44	30.4	0.3					0.3	0.3	0.3	
45	31.1					0.8	0.8	0.8	0.8	
46	32.5	0.3					0.3	0.3	0.3	
47	33.5	ns								

\*Distance from Whitlingham STW, negative values indicate upstream, positive values downstream ns=no sample, blank spaces indicate no sampling was attempted

1990 5	Survey			M	eHg CONCEN"	TRATION (µg	kg <sup>-1</sup> )	
Transect	Distance* (km)	i	Sample iii	v	Maximum	Minimum	Average	Standard deviation
4	-5.1	9.2			9.2	9.2	9.2	
5	-4.85	0.7			0.7	0.7	0.7	
6	-4.15	ns			•	•	0.1	
7	-3.35	25.3	4.1	3.5	25.3	3.5	10.9	12.4
8	-2.15	2.7	2.4	4.7	4.7	2.4	3.3	1.3
9	-1.41	5.7	ns	1.6	5.7	1.6	3.6	2.9
10	-0.41	5.6	1.1	6.4	6.4	1.1	4.4	2.9
11	-0.22	2.2	12.1	6.7	12.1	2.2	7.0	5.0
12	0.44	0.7	រាន	16.8	16.8	0.7	8.8	11.4
13	1.32	20.9	ns	5.9	20.9	5.9	13.4	10.6
14	2.05	29.5	24.7	ns	29.5	24.7	27.1	3.3
15	2.78	2.6	ns	0.7	2.6	0.7	1.7	1.3
16	3.59	10.4	15.0	11.6	15.0	10.4	12.3	2.4
17	4.42	5.5	22.0	10.9	22.0	5.5	12.8	8.4
18	4.91	3.4	0.7	8.0	8.0	0.7	4.0	3.7
19	6.03	10.6	ns	6.7	10.6	6.7	8.6	2.8
20	6.62	ns	3.6	ns	3.6	3.6	3.6	
21	7.31	2.9	ns	5.2	5.2	2.9	4.0	1.6
22	8.18	7.4	ns	3.6	7.4	3.6	5.5	2.7
23	8.36	0.7	<b>ns</b>	1.7	1.7	0.7	1.2	0.7
24	9.15	20.5	16.0	10.4	20.5	10.4	15.7	5.1
25	11.1	6.2	រារ	7.3	7.3	6.2	6.8	0.7
26	12.53	3.4	7.3	ns	7.3	3.4	5.3	2.8
27	13.5	10.0	ກຣ	22.2	22.2	10.0	16.1	8.6
28	14.5	3.2	ns	1.4	3.2	1.4	2.3	1.3
29	15.4	12.0	8.8	5.9	12.0	5.9	8.9	3.1
30	16.6	9.0	12.6	1.1	12.6	1.1	7.6	5.9
31	17.6	0.7	ns	9.2	9.2	0.7	4.9	6.0
32	18.3	4.5	9.5	5.7	9.5	4.5	6.5	2.6
33	19.3	10.1	ns	6.8	10.1	6.8	8.4	2.3
34	20.3	3.2	ns	4.2	4.2	3.2	3.7	0.7

•Distance from Whitlingham STW, negative values indicate upstream, positive values downstream ns=no sample, blank spaces indicate no sampling was attempted

1991 S	-			М	eHg CONCEN	TRATION (µg	kg <sup>-1</sup> )	
Transect	Distance* (km)	:	Sample iii	v	Maximum	Minimum	Average	Standard deviation
		1	111	<u> </u>	WiaXimum	Multinom	Average	deviation
4	-5.1	ns				• •	• •	
5	-4.85	2.4			2.4	2.4	2.4	
6	-4.15	ns						
7	-3.35	ns	15.0	13.2	15.0	13.2	14.1	1.3
8	-2.15	9.5	10.4	6.5	10.4	6.5	8.8	2.0
9	-1.41	6.0	7.8	<b>ns</b>	7.8	6.0	6.9	1.3
10	-0.41	10. <b>9</b>	8.7	ns	10.9	8.7	9.8	1.6
11	-0.22	10.6	19.4	6.7	19.4	6.7	12.2	6.5
12	0.44	3.5	ns	16.4	16.4	3.5	10.0	9.1
13	1.32	19.7	6.3	22.2	22.2	6.3	16.1	8.6
14	2.05	15.5	12.0	6.2	15.5	6.2	11.2	4.7
15	2.78	2.6	2.5	4.0	4.0	2.5	3.0	0.8
16	3.59	20.9	11.2	20.1	20.9	11.2	17.4	5.4
17	4.42	8.0	15.1	16.2	16.2	8.0	13.1	4,4
18	4.91	5.6	2.6	13.1	13.1	2.6	7.1	5.4
19	6.03	8.7	8.9	15.5	15.5	8.7	11.0	3.8
20	6.62	12.0	ns	9.6	12.0	9.6	10.8	1.7
21	7.31	8.4	ns	10.8	10.8	8.4	9.6	1.7
22	8.18	9.4	ns	11.8	11.8	9.4	10.6	1.7
23	8.36	3.5	ns	2.4	3.5	2.4	3.0	0.8
24	9.15	6.7	ns	9.9	9.9	6.7	8.3	2.2
25	11.1	4.4	ns	4,4	4.4	4.4	4.4	0.0
26	12.53	4.5	ns	9.1	9.1	4.5	6.8	3.3
27	13.5	5.4	ns	16.6	16.6	5.4	11.0	8.0
28	14.5	2.3	ns	2.7	2.7	2.3	2.5	0.3
29	15.4	5.0	8.5	12.2	12.2	5.0	8.6	3.6
30	16.6	12.4	6.2	4.1	12.4	4.1	7.5	4.3
31	17.6	2.3	2.8	ns.	2.8	2.3	2.5	0.3
32	18.3	2.9	5.1	2.5	5.1	2.5	3.5	1.4
33	19.3	2.4	ns	1.6	2.4	1.6	2.0	0.5
33	20.3	1.9	ns	5.2	5.2	1.9	3.5	2.3

\*Distance from Whitlingham STW, negative values indicate upstream, positive values downstream ns=no sample, blank spaces indicate no sampling was attempted i.e. transects 4-6 were sampled once only

1992 \$	Survey			M	He CONCEN	TRATION (µg	kg <sup>-1</sup> )	
	Distance*		Sample					Standard
Transect	(km)	<u>i</u>	iii	<u>v</u>	Maximum	Minimum	Average	deviation
4	+5.1	ns						
5	-4.85	TI S						
6	-4.15	ns						
7	-3.35	0.4	ns	ns	0.4	0.4	0.4	
8	-2.15	ns	ns	0.9	0.9	0.9	0.9	
9	-1.41	ns	ns	ពរ				
10	-0.41	2.5	5.4	ករ	5.4	2.5	3.9	2.0
11	-0.22	1.5	4.7	1.6	4.7	1.5	2.6	1.8
12	0.44	ns	0.7	0.3	0.7	0.3	0.5	0.3
13	1.32	2.3	2.9	1.0	2.9	1.0	2.1	1.0
14	2.05	<b>ms</b>	1.7	5.1	5.1	1.7	3.4	2.4
15	2.78	ns	0.8	3.6	3.6	0.8	2.2	2.0
16	3.59	11.8	21.8	8.5	21.8	8.5	14.0	7.0
17	4.42	D1	19.6	7.2	19.6	7.2	13.4	8.7
18	4.91	2.8	1.9	4.6	4.6	1.9	3.1	1.4
19	6.03	11.2	1.9	2.9	11.2	1.9	5.3	5.1
20	6.62	2.5	9.0	5.8	9.0	2.5	5.8	3.2
21	7.31	3.6	ns.	3.1	3.6	3.1	3.4	0.3
22	8.18	10.0	2.8	4.7	10.0	2.8	5.8	3.8
23	8.36	1.3	3.0	3.3	3.3	1.3	2.5	1.1
24	9.15	4.5	4.2	5.4	5.4	4.2	4.7	0.6
25	11.1	3.7	1.6	4.2	4.2	1.6	3.1	1.4
26	12.53	ns	1.6	2.4	2.4	1.6	2.0	0.6
27	13.5	1.2	ກຣ	ns	1.2	1.2	1.2	0.0
28	14.5	2.2	1.2	ns	2.2	1.2	1.7	0.7
29	15.4	3.9	3.6	ns	3.9	3.6	3.8	0.2
30	16.6	0.8	0.6	ns	0.8	0.6	0.7	0.1
31	17.6	2.6	ns.	ns	2.6	2.6	2.6	0.1
32	18.3	3.1	3.4	1.7	3.4	1.7	2.0	0.9
33	19.3	0.5	D.4 DS	ns	0.5	0.5	0.5	0.9

\*Distance from Whitlingham STW, negative values indicate upstream, positive values downstream

ns=no sample, blank spaces indicate no sampling was attempted i.e. transects 2-6 were sampled once only, sites below transect 33 were below the detection limit

1993 8	Survey			N	leHg CONCEN	IRATION (ug	kg <sup>-1</sup> }	
Transect	Distance* (km)	i	Sample iii	v	Maximum	Minimum	Average	Standard deviation
4	-5.1	រាទ						
5	-4.85	2			2	2	2	
6	-4.15	5			2 5	5	2 5	
7	-3.35	ns	лs	ns		-	-	
8	-2.15	7	6	9	9	6	7	2
9	-1.41	6	ns	11	11	6	9	4
10	-0.41	3	12	3	12	3	6	5
11	-0.22	4	ns	ns	4	4	4	-
12	0.44	ns	ns	ns				
13	1.32	7	8	ns	8	7	8	1
14	2.05	ns	4	14	14	4	9	7
15	2.78	3	3	រាន	3	3	3	Ó
16	3.59	13	3	3	13	3	6	6
17	4.42	5	16	5	16	5	9	
18	4.91	ពន	14	7	14	7	11	6 5 2
19	6.03	3	រាទ	6	6	3	5	2
20	6.62	4	ns	17	17	4	11	9
21	7.31	12	ns	រាន	12	12	12	
22	8.18	16	11	11	16	11	13	3
23	8.36	10	7	13	13	7	10	3
24	9.15	11	រាន	8	11	8	10	2
25	11.1	18	23	16	23	16	19	4
26	12.53	10	17	ns	17	10	14	5
27	13.5	4	7	2	7	2	4	3
28	14.5	10	ns	1	10	1	6	6
29	15.4	14	ns	2	14	2	8	6
30	16.6	13	1	9	13	1	8	3 6 6 2
31	17.6	0	2	4	4	0	2	2
32	18.3	ns	ns	5	5	5	5	_
33	19.3	4	11	5	11	4	7	4
34	20.3	17	រាន	ns	17	17	17	
35	21.6	13	រាន	1	13	1	7	8
36	22.5	ns	ns	5	5	5	5	

•Distance from Whitlingham STW, negative values indicate upstream, positive values downstream ns=no sample, blank spaces indicate no sampling was attempted i e. transects 4-6 once only, sites below transect 36 contained concentrations below the detection limit

1994	Survey			М	eHg CONCEN	TRATION (µg	kg <sup>-1</sup> )	
Transect	Distance* (km)	i	Sample iii	v	Maximum	Minimum	Average	Standard deviation
4	-5.1	2.7			2.7	2.7	2.7	de ristion
5	-4.85	3.1			3.1	3.1	3.1	
6	-4.15	4			4.0	4.0	4.0	
7	-3.35	3.6	2.2	6.2	6.2	2.2	4.0	2.0
8	-2.15	4.9	8.3	3	8.3	3.0	5.4	2.7
9	-1.41	6.2	ns	8.3	8.3	6.2	7.3	1.5
10	-0.41	4.1	05	2.8	4.1	2.8	3.5	0.9
11	-0.22	4	7.3	53	7.3	4.0	5.7	2.3
12	0.44	6.6	D'S	03	6.6	6.6	6.6	
13	1.32	7.9	11.2	14.3	14.3	7.9	11.1	3.2
14	2.05	ns	ns	16.2	16.2	16.2	16.2	
15	2.78	ns	6.4	3.3	6.4	3.3	4.9	2.2
16	3.59	9.7	2.5	4.0	9.7	2.5	5.4	3.8
17	4.42	4.9	10	6.7	10.0	4.9	7.2	2.6
18	4.91	8.3	18.5	4.1	18.5	4.1	10.3	7.4
19	6.03	3.2	ns	9.6	9.6	3.2	6.4	4.5
20	6.62	3.1	ns	21.1	21.1	3.1	12.1	12.7
2]	7.31	11.4	ns	9.4	11.4	9.4	10.4	1.4
22	8.18	10.3	15.6	14	15.6	10.3	13.3	2.7
23	8.36	12.2	מ	9.6	12.2	9.6	10.9	1.8
24	9.15	14.1	រាន	5.7	14.1	5.7	9.9	5.9
25	11.1	10.6	16.5	9.9	16.5	9.9	12.3	3.6
26	12.53	24.4	19.2	17.7	24.4	17.7	20.4	3.5
27	13.5	3.3	ns	6.1	6.1	3.3	4.7	2.0
28	14.5	8.5	ns	7.9	8.5	7.9	8.2	0.4
29	15.4	14.6	2.2	1.3	14.6	1.3	6.0	7.4
30	16.6	9.3	1.5	8.1	9.3	1.5	6.3	4.2
31	17.6	1.1	ns	1.7	1.7	1.1	1.4	0.4
32	18.3	4.2	л. Л.S	3.8	4.2	3.8	4.0	0.4
33	19.3	2.0	1.0	4.5	4.5	1.0	2.5	1.8
34	20.3	1.2	ns	1.6	1.6	1.2	1.4	0.3

\*Distance from Whitlingham STW, negative values indicate upstream, positive values downstream ns=no sample, blank spaces indicate no sampling was attempted i.e. transects 4-6 were sampled once only

1995	Survey			М	eHg CONCEN	TRATION (Hg	kg <sup>-1</sup> )	
	Distance*		Sample		•	1.11	•	Standard
Transect	(km)	i	iii	v	Maximum	Minimum	Average	deviation
4	-5.1	15.6			15.6	15.6	15.6	
5	-4.85	7.7			7.7	7.7	7.7	
6	-4.15	3.8			3.8	3.8	3.8	
7	-3.35	0.0	0.6	8.1	8.1	0.0	2.9	4.5
8	-2.15	5.6	15.6	2.0	15.6	2.0	<b>7</b> .7	7.1
9	-].4]	3.3	10.4	8.6	10.4	3.3	7.4	3.7
10	-0.41	3.4	9.8	4.8	9.8	3.4	6.0	3.4
11	-0.22	14.1	27.4	38.4	38.4	14.1	26.6	12.2
12	0.44	- 5.5	4.4	D.S	5.5 -	4.4 -	4.9	0.7
13	1.32	23.6	3.3	7.6	23.6	3.3	11.5	10.7
14	2.05	34.2	23.3	7.8	34.2	7.8	21.8	13.3
15	2.78	4.7	2.6	6.5	6.5	2.6	4.6	2.0
16	3.59	13.7	24.5	39.2	39.2	13.7	25.8	12.8
17	4.42	2.3	15.7	1.6	15.7	1.6	6.5	8.0
18	4.91	0.6	7.8	0.8	7.8	0.6	3.1	4.1
19	6.03	31.2	6.9	9.8	31.2	6.9	15.9	13.3
20	6.62	115	23.1	3.4	23.1	3.4	13.2	13.9
21	7.31	16.2	6.9	3.4	16.2	3.4	8.8	6.6
22	8.18	17.1	15.0	26.4	26.4	15.0	19.5	6.1
23	8.36	4.8	ns	1.7	4.8	1.7	3.3	2.1
24	9.15	15.6	ns	4.9	15.6	4.9	10.2	7.5
25	11.1	5.2	ns	0.8	5.2	0.8	3.0	3.1
26	12.53	0.0	ns	0.4	0.4	0.0	0.2	0.2
27	13.5	0.8	ns.	1.0	1.0	0.8	0.9	0.1
28	14.5	3.5	ns	11.4	11.4	3.5	7.4	5.6
29	15.4	1.6	กร	2.8	2.8	1.6	2.2	0.8
30	16.6	0.2	7.0	3.6	7.0	0.2	3.6	3.4
31	17.6	0.4	1.5	0.8	1.5	0.4	0.9	0.5
32	18.3	2.0	7,7	2.0	7.7	2.0	3.9	3.3

\*Distance from Whitlingham STW, negative values indicate upstream, positive values downstream ns=no sample, blank spaces indicate no sampling was attempted i.e. transects 4-6 were sampled once only

# . Percentage volatile solids content

	Distance*				% VOL	ATILE	SOLIDS			
Site	<u>(km)</u>	1986	1987	<u>1</u> 989	<u>1990</u>	1991	1992	1993	1994	1995
4	-5.1		10.5	1.5	17.8	1.7	30.0	18.6	14.2	13.3
5	-4.85		16.6	20.6	23.3	38.3	3.9	17.9	2.0	4.1
6	-4.15		5.4				11.3	12.6	1.5	3.4
<b>7</b> i	-3.35	7.2	5.4		27.4	35.7	7.1	7.2	6.2	9.3
7ii		10.9								
7iii		17.2			22.4	29.6	23.1	22.4	25.0	21.2
7iv		18.8								
7v		12.9		18.9	22.6	27.7	28.4	20.9	20.2	20.1
<b>8</b> i	-2.15	9.3	15.9		20.3	20.5	19.9	19.4	24.2	25.1
8ii		23.2		18.9						
8iii		22.4			20.6	21.9	17.6	22.4	18.5	20.4
8iv		16.5								
8v		20.1			20.8	26.5	13.0	10.5	23.1	16.6
<b>9</b> i	-1.41	1.9	16.8		17.4	20.1		3.8	20.6	2.9
9ii		4.9		1.8						
9iii		1.9		1		34.7	1	4.2		16.2
9iv		1.9		5.1						
9v		9.4			8.8	19.5	15.7	13.4	15.9	10.1
10i	-0.41	6.1			11.5	30.8	8.8	7.5	10.9	8.7
10ii		13.7		7.2						
10iii					13.3	24.1	14.3	15		18.3
10iv		11.1								
10v		27.4			14.2	6.4	16.9	13.1	17.7	23.7
11i	-0.22	9.9	10.3		22.4	21.6	7.8	17.8	22.9	12.6
<b>1</b> 1ii		15.2		17.3						
11iii		23.7			26.6	31.9	11.8	20.2	16.8	26.5
Hiv		7.2								
11v		11.7			19.8	10.5	6.6	7.0		16.6
12i	0.44	4.6		19.4	5.1	3.6			15.8	9.9
12ii		2.5	15.8							
12iii		3.6			10.3	4.6	6.8			3.3
12iv		2.9								212
12v		1.4			30.0	18.0	11.7			
13i	1.32	21.7	17.9		21.6	24.3	21.0	20.9	36.8	25.3
13ii		12.9		17.6			5. C.			
13iii		16.7				20.9	15.5	-19.5	17.0	24.4
13iv		18.9								
13v		6.3			24.5	27.7	4.6	5.3	17.4	12.6
14i	2.05	7.9	19.6		18.6	19.0				27.1
14ii		13.0								
14iii		17.3			23.2	23.2	7.3			22.9
14iv		15.8								<del>т</del> )
14v		21.1		11.8		9.4	17.4	21.8	20.4	23.0
15i	2.78	2.1	19.8	4.5	6.7	3.2	3.9	49.8		3.7
15ii		2.7								
<b>15</b> iii		1.9				11.4	4.2	51.9	8.9	9.4
15iv		13.7								
15v		18.4		9.8	3.1		15.5	12.5	22,4	16.2
16i	3.59	34.2	17.9		25.9	15.3	21.2	17.9		27.1
16ii		13.6							<b>.</b> .	
<b>16</b> iii		7.8			24.9	25.5	19.3	43.6	35.7	24.9
16iv		22.3								
16v		20.3		14.1	28.1	37.2	20:1	17.0	20.2	25.5

4.

	Distance*			-			SOLIDS			
Site	<u>(km)</u>		1987	<u>1989</u>	<b>19</b> 90	1991	1992	1993	1994	1995
17i	4,42	11.9			28.2	21.6	12.6	18.5	24.4	26.4
17ü		22.2								
l7iii		<b>20.6</b>			25.5	20.4	15.9	19.1	21.1	24.5
7iv		13.5								
17v		23.5		16.5	21.9	23.9	21.6	18.3	13.5	19.7
18i	4.91	12.7			14.1	18.7	22.8	19.8	16.8	14.5
8ii		24.7							-0.0	
8iii		10.3			15.9	16.5	13.2	16.0	15.3	18.0
18iv		19.5								
18v		18.4		11.5	24.8	16.5	13.9	16.7	8.6	4.5
19i	6.03	22.9	14.4		18.4	15.9	23.3	18.5	19.2	25.0
19ü		17.4	-				-0.0	10.0		
9iii		37.0				34.7	19.5			17.4
l9iv		16.4				<b>Q</b>				
19v		18.2		20.9	13.1	30.6	10.5	31.7	23.5	14.1
20i	6.62	13.9	16.9		20.1	19.3	37.8	45.7	20.5	22.6
.0ii	0.02	17.2	10.7	16.4	20.1	17.5	27.0	43.7	20.5	22.0
Oiii		25.2		10		21.4	17.7	16.8		23.6
0iv		18.3				£1.4	· · · · ·	10.0		20.0
20v		10.9			17.2	20.7	5.8	17.0	20.4	19.1
21i	7.31	17.8	17.4	19.2	19.5	42.7	18.7	9.3	17.8	23.6
21ü	,	22.5	17.4	17.2	17.5	72.1	10.7	3.5	17.0	25.0
21iii		23.1				22.8	11	51.2		16.0
liv		23.1				22.0	4.1	51.2		10.0
21v		22.7		49.6	18.8	18.8	16.3		16.1	18.8
2i	8.18	20.0	19.8	49.0	19.7	20.9	14.5	14.5	14.3	10.0
2ii	0.10	18.2	19.0		17.7	20.9	14.0	14,5	14.5	17.4
2iii		14.3				16.3	12.4	6.3	144	11.7
2111 2iv		22				10.5	12.4	0.5	14.4	11.7
2v		22.2		22.0	<b>9</b> .1	6.4	36.4	20.2	28.1	24.5
23i	8.36	23.7	<b>8</b> .0	6.1	9.1 9.4	17.7	14.9	13.6		24.5
3ii	8.50	15.8	0.0	0.1	7.4	17.7	14.7	13.0	8.4	9.2
3iii		21.3					14.5	20.1		
3iv		22.9					14.5	20.1		
3v		17.3				11.0	15.0	3.2	17.6	10.2
24i	9.15	19.4	17.7		19.5	34.2	15.0 14.2	12.7		10.3
241 241i	9.10	21.7	17.7		19.5	54.2	14.2	12.7	21.4	20.8
411 4111		15.6			21.4		700	107		
4111 4iv		15.0 39.0			∡1.4		70.0	18.7		
41v 24v		39.0 15.7		17.7	15.3	17.7	9.8	10.0	24.0	10 4
25i	11.1	10.2	6.5	9.6	15.5 24.7	17.7			34.9	12.6
251 2511	11.1	10.2	0.5	9.0	24.1	13.1	10.6	10.7	9.9	6.4
2511 25111		20.6					11.4			
.5111 25iv		20.0 28.5					11.4	15.1		
51v 25v		28.5 16.8			12.2	12.2	8.7	167	16.2	10 1
26i	17 62		<b>6</b> 1 <sup>3</sup>		12.2	13.2		15.7	16.2	18.1
	12.53	10.8	5.1		11.9	17.7	10.3	9.7	7.5	10.4
26ii		15.2			11.5		16.0	07	10.0	
6iii		15.6			11.5		16.8	8.7	10.9	
6iv		6.6		74		E10	o ^	10 4		
26v	12.5	9.2	~ 1	7.6	11.4	54.9	8.2	12.4	16	19.1
27i	13.5		7.1		11.4	30.9	7.3	8.1	13	13.5
7iii			13.8				<b>54</b> .0	13.4		
27v			12.4	10.4	11.3	9.7	<b>9</b> .1	12.2	9.8	8.5
28i	14.5		29.9		8.4	12.0	12.8	14.5	12	8.4
28iii							8.3			
28v			8.0		10.9	10.1	8.0	7.2	8.4	21.7
29i	15.4		7.8		10.3	12.0	5.7	8.5	12.3	6.2

	Distance*				% VOI		SOLIDS			
Site	(km)	1986	1987	1989	1990	1991	1992	1993	1994	1995
<b>2</b> 9iii	(1411)				11.1	13.1	46.1	9.0	23.8	
29v			10.6	15.8	8.2	9.8	10.6	9.4	9.5	6.9
30i	16.6		6.9	8.3	11.3	6.5	8.3	7.7	8.9	10.5
30iii	10.0		10.6	0.0	9.2	13.8	8.5	7.8	15.8	11.0
30v			10.0		6.7	7.1	6	10.2	8.2	12.1
30v 31i	176		10.2	4.8	8.5	1.9	5.7	<b>5</b> .0	8.2 10.4	12.1
31iii	17.6			4.0	<b>6</b> .2	6		2.5	10.4	3.8
			5.8		7.7		1.6		2.8	7.5
31v 32i	10.2		10.5			11.7	7.3	3.1	9.2	11.1
	18.3		10.5		6.2	7.3	7.7	8.4	9.2	17.3
32iii			14.5	0 1	6.0	9.1	31.6	49.7	67	<b>7.8</b>
32v	10.2		6.8	8.1	5.2	7.7	7.8	5.4	6.7	7.0
33i	19.3		8.6		8.1	7.9	7.5	16.8	19.1	
33iii			6.5				62	6.8	10.8	
33v			8.3	9.8	7.6	14.9	9.3	7.7	6.5	
34i	20.3		10.3	9.5	11.4	43.7	3.1	21.1	20.8	
34iii							67.3	61.5	16.2	
34v		•	6.5		11.9	3.8	48.2	37.5	14.2	
35i	21.6		5.4				46.4	9.7		
35iii			5.4				49.4	44.9		
35v			12.6	5.4			15.9	8.9		
36i	22.5		6.9	6.1			10.4	12.3		
36iii							8.6	45.7		
36v			4.2				∈ <b>19.4</b>	12.2		
37i	23.4		33.3	9.1			10.2	12		
37iii							6.3	7.0		
37v			3.3				8.9			
<b>38</b> i	24.4		11.2	9.7			1.9			
<b>3</b> 8iii							5.7	4.8		
38v			15.9				7.2	7.9		
39i	25.4		5.2	27.9			7.6	44.3		
<b>39ii</b> i			81.3				47.6	<b>5</b> 0.3		
39v			8.5				16.4	8.2		
40i	26.4		11.4				22.6	7.4		
40iii			4.3					57.2		
40v			4.8				5.6	5.4		
41i	27.4		10.0				11.4	••••		
<b>41</b> iii			9.1					43.5		
41v			11.2				10.8	7.3		
42i	28.4		11.5				3.7	7.4		
42iii	<b>4</b> 0.7		÷				0.1	65.8		
42m 42v			9.8	10.7			10.7	9.9		
42v 43i	29.4		6.0	10.7			45.8	12.3		
43i	<u> </u>		7.1				<b>57.1</b>	2.8		
43m 43v			9.1	22.6			7.8	8.8		
43v 44i	20.4		9.1 6.1	10.9			11.3	6.7		
	30.4			10.7			95.7	5.9		
44iii			6.8				<b>16.4</b>	5.9 9.8		
44v	71.1		Q _			-	15.9	9.8 8.4		
45i	31.1		8.6				15.9 72.9	6.4 56.4		
45iii			7.8	47						
45v	20 E		5.8	6.7			14.4	8.8 6 1		
46	32.5		8.9	7.4			5.7	6.1		
47	33.5		8.6				5.0	9.5		
48	34.5		5.1				8.8	11.3		
49	35.5						1.2	9.2		

\*Distance from Whitlingham STW, negative values indicate upstream, positive values downstream

5. pH

	<b>D</b>		_				-			-				
Silet	Distance* (km)	1989	1990	ा <del>हो।</del> 1991	1992	1993		Sitet	Distance* (km)	1989	1990	pH 1991	1992	1993
4	+5.1		7.9	7.6		7	-	26v		7.8		7.5	7.3	7.2
5	-4.85		7.6	7.8		7.3		27i	13.5			7.5	7	7.5
6	-4.15				7.2	7.4		27111					•	7.5
<b>7</b> i	-3.35		7.3	7.5	7.2	7.4		27v		7.7		7.5	7.6	7.3
700			7.4	7.6	7.2	7.4		<b>28</b> i	14.5			7,7	7.1	7.3
7v			7.2	7.5	6.9	6.9		<b>28</b> iii	1-2			•••	7.4	
<b>8</b> i	-2.15		7.1	7.4	6.5	6.7		28v (iv)		7.7		7.3	7.1	7.8
8iii (ii)	2.10	6.9	7.2	7.4	7.2	6.9		29i	15.4	1.1		7.3	7	7
8v		0.9	6.9	7.4	7.1	6.7		<b>29</b> iii	10.4		7.9	7.3	7.5	7.3
9i	-1.41		7	7.4	7.4	7.9		29v		75	75	7.8	7.3	7.1
9iii (ii)	-1.41	7.3	,	7.3		7.8			16.6	7.7	15		7.4	75
		7.3	7.1					30i	1 <del>5</del> .6	1.7		7.4		
9v (iv)	0.41	1.5	7.1	7.4	6.9	7.4		30iii			7.3	7.6	7.4	75
10i	-0.41	20	* •	7.4	7	75		30v				7.2	7.2	7
10iii (ii)		7.6	7.2	7.4	7	7.3		31i	17.6	7.7	75	7.5	7.4	7
10v			7	7.5	7.1	7.1		<b>31</b> iii			-	8	7,4	
111	-0.22		7.4	7.6	7.4	7.8		31v			8	7.8	7.2	7.6
11iii (ii)		7.6	7.1	7.5	7.1	7.6		32i	18.3		7.8	7.4	7.1	7
11v	_	_	_	7.3	7.1	7.7		<b>32</b> iii			75	7.5		
12i	0.44	7.1	7.4	7.1				32v		7.6	7,4	7.6		7.1
12iii				7.3				33i	19.3		7.6	7.4	7.5	7.2
12v			7.1	7.4				33iii					7.2	7,5
13i	1.32		7	7.2	7.4	7.4		33v		7.4	7.3	7.5	7.1	7.1
13iii (ii)		7.6		7.6	6.9	7.2		<b>34</b> i	20.3	7.2	6.8	7.3	7.4	7.2
13v			7.4	7.2	7.2	7.4		34iii					7.5	
14i	2.05		7.1	7.2				34 v			7.6	7.4	7.5	
14111			7.2	7.3	7.4			35i	21.6					7.2
14v		7.5		6.9	6.8	5.7		<b>35</b> iii						
15i	2.78	7.3	7.1	7.2	7.3	5.6		35v		7.4			7.6	7.5
15iii				7.4	7.3	6		<b>36</b> i	22.5	7.2			6.9	7.5
150		7.4	7,4	7.4	7	6		<b>36</b> iii	*****				7.3	
16i	3.59	1.4	7	7.5	7.1	7		36v					7.3	7.1
1611	2.29		7.3	7.3	7	7.1		37i	23.4	7.2				
		7.4			ź				43.4	1.1			7.2	7.1
16v		7.4	7.3	7.5		6.8		37iii					7.6	7.3
17i	4.42		7.1	7.3	6.7	7.1		37v	• • •	• •			7.6	
17iii		• •	7.2	7.4	7.2	6.7		381	24.4	7.3			6.6	
175		7.1	7.3	7.1	6.9	7.1		38iii					7.1	7.3
18i	4. <del>9</del> 1		7.8	7.4	6.9	7.1		385		_			7	7.3
18iii			7.5	7.3	7.2	7.2		39i	25.4	7.4			7.2	
18v		7.7	7.6	7.4	7.3	7.5		39iii						
19;	6.03		7.3	7.4	7.1	7.1		39						7.1
1911				7.4				40 i	26.4				7.2	6.9
19		7.6	7.6	7.3	7.3	7.7		40iji						+
20i	6.62		7.7	7.6	7.1	7.3		40 v					7.3	6.8
20iii (ii)				7.4	7.2	7.4		41i	27.4				7.1	
2011 (11)			7.7	7.3	7.2	7		<b>4</b> 1iii	£ 7				•••	
21i	7.31		7.7	7.4	6.9	7.3		41v						
2111	1.51		• • •	7.3	7.3	*		421	28.4				7.6	7
			7.4	7.3	7.3	7.6			20.4				1.0	
21v (vi)	810		7.3			7.4		42iii 42v						67
22i	8.16		د.،	7.5	7.4				20.4				7.4	6.7
22iii				7.5	7.5	7,4		43i	29.4				7.4	6.8
22v	0.44	<b>.</b>	7.3	7.5	7.4	7.2		<b>43</b> iii						7.2
23i	8.36	7.5	7.5	7.8	7.2	7.6		<b>4</b> 3v						6.1
<b>23</b> iii	<i>x</i>				7.6	7.6		<b>4</b> 4i	30.4				6.7	
23	_		7.3	7.5	7.2	7.6		<b>4</b> 4iii						
24i	9.15		7.2	7.6	7.1	7.2		<b>4</b> 4 v						6.4
24iii			7.5					<b>45</b> i	31.1				7.5	6.7
245		7.4	7.3	7.3	7.2	7.7		<b>45</b> iii						
<b>25</b> i	11.1	7.6	7.7	7.4	7.3	7.3		45v						6.7
<b>25</b> iii				7.1	7.6			46	32.5				7.2	7.1
25v		7.1	7.4	7.3	7.5			47	33.5				7.2	7.1
	12.53	7.4	7.5	7.2	7.4			48	34.5				7.5	7:1
26i	14.33													

†Site numbers in brackets are for the 1989 survey, all others apply to every survey year
 \*Distance from Whitlingham STW, negative values indicate upstream, positive values downstream
 Blank spaces indicate no data was collected

## 6. Cores taken at 3 locations in the R Yare pollution plume

## Whitlingham core

depth	Hg	Cu	Mg	Ca	Al	Ti	Mn	Fe	Р	S	Eh	PH
_(cm)	(mg kg <sup>-1</sup>	)(mg kg <sup>-1</sup> )	$(\mathbf{g} \mathbf{k} \mathbf{g}^{-1})$	( <u>e kg<sup>-1</sup>)</u>	$(g kg^{-1})$	$(g kg^{-1})$	<u>(e ke<sup>-1</sup>)</u>	(g kg <sup>-1</sup> )	(g kg <sup>-1</sup> )	(g kg <sup>-1</sup> )	(mV)	-
0 - 5	4.10	36.1	1.84	99.9	7.9	0.112	0.480	22.9	3.72	7.40	-135	7.13
510	5.59	33.6	1.54	87.0	7.8	0.141	0.367	15.8	2.41	5.87	-131	7.03
10 - 15	10.06	53.5	2.17	107.1	7.9	0.094	0.422	20.3	3.48	5.92	-134	6.98
15 - 20	14.42	75.4	2.62	92.4	11.8	0.178	0.478	23.1	3.95	6.47	-126	6.95
20 - 25	20.23	77.3	2.68	87.4	13.0	0.208	0.485	23.6	4.16	6.33	-123	6.92
25 - 30	17.80	69.7	2.41	80.0	10.4	0.151	0.437	20.9	3.80	6.61	-128	6.95
30 - 35	20.37	79.5	2.56	87.1	10.1	0.130	0.490	23.1	4.40	7.08	-117	6.95
35-40	8.54	49.2	1.90	62.6	10.3	0.197	0.360	16.7	3.21	4.41	-126	6.93
40 - 45	6.39	39.0	4.03	86.2	10.8	0.139	0.590	24.4	2.48	5.22	-147	6.9
<b>45 - 5</b> 0	5.46	35.1	6.00	94.6	14.8	0.177	0.696	28.2	2.30	5.83	-133	6.86
50 - 55	0.71	20.5	7.85	62.1	25.6	0.310	1.059	35.7	1.79	3.52	-103	6.89
55 - <del>6</del> 0	0.84	22.3	7.81	65.7	13.3	0.105	0.929	32.3	1.67	3.43	-154	6.89
60 - 65	0.86	23.2	5.07	66.2	12.4	0.135	0.728	26.5	1.70	3.60	-91	7.04
65 - 70	0.56	46.1	2.03	91.5	10.1	0.187	0.332	19.9	2.08	6.26	-116	6.87
70 - 75	0.87	73.8	2.59	117.0	14.0	0.282	0.411	26.3	2.45	8.55	-160	6.89

### **Rockland core**

depth	Hg	Cυ	Mg	Ca	Al	Ti	Mn	Fe	P	S	Eh	pН
(cm)	(mg kg*l	)(mg kg <sup>-1</sup> )	) (g kg <sup>-1</sup> )	( <u>e ke<sup>-1</sup>)</u>	(g kg <sup>-1</sup> )	(g kg <sup>-1</sup> )	(g kg <sup>-1</sup> )	(g kg-1)	(g kg <sup>-1</sup> )	(g kg <sup>-1</sup> )	(mV)	_
0 - 5	0.51	29.8	5.18	81.1	9.49	0.182	0.852	24.6	3.49	4.76	-110	7.2
5 10	0.56	33.3	5.61	83.9	10.53	0.189	0.900	26.5	3.62	5.71		7.2
10 - 15	0.54	32.3	5.18	79.0	10.12	0.173	0.808	24.5	3.32	5.29	-90	7.0
15 - 20	0.77	35.9	5.70	81.3	15.89	0.253	0.818	26.7	3.29	6.17		7.0
20 - 25	0.80	41.3	5.46	83.1	13.37	0.176	0.932	26.7	3.68	6.11	-100	6.9
25 - 30	1.04	48.0	4.95	91.5	12.21	0.168	0.909	27.1	3.98	6.95		6.9
30 - 35	1.34	49.9	5.62	100.2	16.47	0.259	0.933	28.6	4.03	7.14	-116	6.8
35-40	1.60	50.4	5.14	106.2	16.04	0.262	0.776	26.7	3.74	7.07		6.8
40 - 45	1.59	51.5	5.10	105.3	17.17	0.272	0.705	26.0	3.42	7.32	-88	6.8
45 - 50	1.55	47.6	5.19	120.6	18.75	0.313	0.756	26.6	3.50	7.74		6.8
50 - 55	1.33	37.3	3.97	102.4	12.35	0.210	0.611	20.8	2.79	<b>6</b> .69	-70	6.8
55 - 60	1.30	35.8	4.19	143.2	17.38	0.309	0.689	22.5	2.85	8.30		6.8
60 - 65	0.98	39.0	4.28	129.9	15.93	0.286	0.661	23.4	2.78	<b>9.6</b> 0	-50	6.9
65 - 70	1.05	39.0	4.25	125.8	14.39	0.222	0.622	23.6	2.61	10.38		6.9
70 - 75	0.40	32.4	3.81	132.5	15.20	0.279	0.578	21.5	2.24	10.49	-106	6.9
75-80	0.42	36.0	4.31	146.9	18.77	0.328	0.599	23.1	2.29	11.78		6.9
80-85	0.42	35.1	4.01	153.5	13.66	0.216	0.574	22.2	1.87	11.83	·223	7.1
85-90	0.11	13.7	1.94	187.1	5.63	0.092	0.318	9.5	0.47	8.13	-257	7.1
90-95	0.01	3.3	1.05	332.2	1.18	0.019	0.298	2.3	0.21	3.35		

## **Cantley** core

depth	Hg	Cu	Mg	Ca	A)	Ti	Mn	Fe	P	S	Eh	pН
(cm)	(mg kg <sup>-1</sup>	)(mg kg <sup>-1</sup> )	(g kg <sup>-1</sup> )	( <u>e</u> kg <sup>-1</sup> )	(g kg <sup>-1</sup> )	(g kg <sup>-1</sup> )	(g kg*1)	(mV)				
0-5	0.577	11.60	6.57	56.5	11.9	0.142	1.098	28.5	1.67	3.46	152	7.76
5 10	0.240	9.84	9.55	62.6	17.2	0.153	0.958	39.0	1.26	5.43		7.72
10 - 15	0.059	6.93	9.94	51.6	21.2	0.211	0.735	36.6	0.72	7.52	130	7.55
15 - 20	0.048	6.68	10.29	52.1	24.0	0.206	0.786	37.5	0.67	6.97	155	7.34
20 - 25	0.047	6.96	10.21	52.4	20.6	0.193	0.760	34.9	0.78	5.55	-230	7.18
25 - 30	0.048	14.22	1.93	167.1	7.5	0.136	0.292	9.6	0.47	8.09	-226	7.13
30 - 35	0.044	6.26	9.41	47.4	14.8	0.136	0.795	33.1	0.77	4.64	-200	7.09
35-40	0.040	6.21	9.62	49.0	14.1	0.150	0.831	33.2	0.84	4.35	-157	7.04
40-45	0.045	5.27	9.89	50.4	16.0	0.132	0.864	35.3	0.75	4.79	-80	6.95
45-50	0.020	5.43	9.46	50.4	14.7	0.133	0.811	34.0	0.68	5.79	-103	6.99

		COREI			CORE 2			CORE 3			CORE 4			CORE 5	
Depth	Hg	Cu	MeHg	Hg	Cu	McHg	Hg	Çu	Mellg	Hg	Cu	MeHg	Hg	Cu	Meflg
(cm)	(mg kg <sup>-1</sup> )	(mg kg <sup>+1</sup> )	(µg kg <sup>-1</sup> )	(mg kg <sup>-1</sup> )	(mg kg <sup>- 1</sup> )	(µg kg <sup>-1</sup> )	(mg kg <sup>-1</sup> )	(mg kgʻ <sup>1</sup> )	(µg kg <sup>=1</sup> )	(mg kg <sup>-1</sup> )	(mg kg <sup>+1</sup> )	(µg kg <sup>-1</sup> )	(mg kg <sup>-1</sup> )	(mg kg <sup>-1</sup> )	(µg kg <sup>-1</sup> )
0.2.5	1.84	114	3.3	0.90	98	1.6	0.78	82	6.8	2.30	126	2.1	3.18	141	3.9
2.5-5			2.3			0.5			4.8			1.9			2.7
5-7.5	1.72	104	0.7	0.97	89	<0.1	0.87	87	1.4	3.15	168	0.7	4.24	161	<0.1
7.5-10			na			na			<0.1			<0.1			<0.1
10-12.5	1.08	97	na	0.97	97	na	0.90	91	<0.1	3.27	150	<0.1	3.69	167	<0.1
12.5-15			na			na			<0.1			<0.1			<0.1
15-17.5	1.06	97	na	0.94	97	na	0.82	98	<0.1	2.40	118	<0.1	3.22	162	<0.1
17.5-20			na			na			<0.1			<0.1			<0.1
20-25	1.01	99		1.46	118		2.15	121		4.25	225		2.78	150	
25-30	1.49	125		1.61	124		1.96	120		4.58	174		2.78	162	
30-35	1.69	192		1.20	101		1.61	155		3.76	143		2.48	148	
35-40	1.82	224		2.35	118		3.45	184		5.15	155		2.87	140	
40-45	0.86	218		1.37	125		3.58	209		5.33	102		3.11	195	
45-50	1.23	238		1.69	76		3.34	200		6.88	253		3.22	219	
50-55	1.05	239		1.18	63		3.21	178		7.10	236		4.43	229	
55-60	1.32	209		2.38	65		4.16	166		9.89	251		5.02	235	
60-65	0.66	172		2.22	74		ns	ns		7.29	249		6.14	209	
65-70	1.56	195		7.92	108		ns	ns		7.36	246		4.95	179	
70-75	1.51	198		5.78	111		ns	ns		5.94	248		6.05	224	
75-80	3.03	230		2.75	72		ns	ns		ns	ns		6.83	222	
80-85	3.21	191		1.43	41		ns	ns		ns	ns		ns	ns	

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APPENDIX 2 Concentrations of mercury, copper and organomercury found in cores taken from Thorpe St Andrews (Chapter 5)

na=not analysed, ns=no sample as end of core was reached

# Field monitoring of dredging at Thorpe St Andrews and elutriate test results

<b>—</b>		Co	proentration of dis	solved oxygen (mg ]	1,	
Time (h)	Site 1	Site 2	Site 3	Maximum	Minimum	Mean
-17 -3 -2 -1	9.84	9.27	9.47	9.84 9.45	9.27	9.53
-3	8.78	8.08	9.45	9.45	8.08	8.77
-2	8.93	9.14	9.24	9.24	8.93	9.10
-1	9.19	9.1	9.23	9.23	9.1	9.17
0	8.37	9.14	8.92	9.14	8.37	8.81
1 2 3	8.25	8.61	9.23	9.23	8.25	8.70
2	8.33	9.29	9.04	9.29	8.33	8.89
	8.56	9.62	9.62	9.62	8.56	9.27
4	8.79	9.07	9.32	9.32	8.79	9.06
5	8.71	9.31	9.87	9.87	8.71	9.30
6	8.86	9.22	9.41	9.41	8.86	9.16
5 6 7 8 9 10	8.99	9.41	9.42	9.42	8.99	9.27
8	9.02	10.13	9.53	10.13	9.02	9.56
9	9.2	9.74	10	10	9.2	9.65
10	9.46	9.84	10.35	10.35	9.46	9.88
11	9.41	9.52	9.55	9.55	9.41	9.49
12	9.06	9.42	9.4	9.42	9.06	9.29
13	9.15	9.62	9.24		9.15	9.29
14	9	9.63	9.41	9.62	9.15	
15	9.21	9.12	9.48	9.63	9	9.35
16	9.39	10.64	9.48 9.84	9.48	9.12	9.27
17	9.39			10.64	9.39	9.96
18	9.45	10.43	9.92	10.43	9.39	9.91
19	9.45	10.28	9.82	10.28	9.45	9.85
19		10.51	10.28	10,51	9.41	10.07
20	9.45	10.4	10.95	10.95	9.45	10.27
20 21 22	9.39	10.37	10.18	10.37	9.39	9.98
22	9.39	10.19	10.26	10.26	9.39	9.95
23	9.25	10.62	10.32	10.62	9.25	10.06
24	9.43	10.00	9.56	10.00 10.55	9.43	9.66
26	9.42	10.55	9.8	10.55	9.42	9.92
28	9.62	10.63	9.84	10.63	9.62	10.03
30	9.77	10.27	10.68	10.68	9.77	10.24
32	9.71	10.85	10.66	10.85	9.71	10.41
34	<b>9</b> .6	10.95	10.89	10.95	<b>9</b> .6	10.48
38	9.6	10.14	10.79	10.79	9.6	10.18
42	9.8	9.97	10.12	10.12	9.8	9.96
46	9.41	9.9	10.4	10.4	9.41	9.90
50	10.77	10.73	10.00	10.77	10.00	10.50

Dissolved oxygen content before, during and after dredging

### Water conductivity

				ctivity (µS cm)		
Time (h)	Site 1	Site 2	Site 3	Maximum	Minimum	Mean
-17 -3 -2 -1 0	0.80-4	0.806	0.806	0.806	0.804	0.805
-3	0.784	0.784	0.788	0.788	0.784	0.785
-2	0.770	0.778	0.780	0.780	0.770	0.776
-1	0.774	0.780	0.774	0.780	0.774	0.776
0	0.768	0.774	0.778	0.778	0.768	0.773
1	0.760	0.768	0.756	0.768	0.756	0.761
2	0.760	0.766	0.764	0.766	0.760	0.763
3	0.780	0.794	0.784	0.794	0.780	0.786
4	0.800	0.804	0.800	0.804	0.800	0.801
5	0.794	0.796	0.800	0.800	0.794	0.797
6	0.798	0.794	0.800	0.800	0.794	0.797
2 3 4 5 6 7 8 9 10 11 11	0.808	0.802	0.812	0.812	0.802	0.807
8	0.814	0.814	0.820	0.820	0.814	0.816
9	0.820	0.812	0.808	0.820	0.808	0.813
10	0.822	0.822	0.818	0.822	0.818	0.821
11	0.824	0.822	0.818	0.824	0.818	0.821
12	0.824 0.822	0.822 0.822	0.804	0.822	0.804	0.816
13	0.816	0.824	0.818	0.824	0.816	0.819
14	0.818	0.820	0.824	0.824	0.818	0.821
15	0.820	0.822	0.824	0.824	0.820	0.822
16	0.846	0.832	0.832	0.846	0.832	0.837
16 17	0.812	0.818	0.834	0.834	0.812	0.821
18	0.834	0.828	0.830	0.834	0.828	0.831
19 20 21 22	0.830	0.826	0.830	0.830	0.826	0.829
20	0.830	0.826	0.832	0.832	0.826	0.829
21	0.840	0.826	0.828	0.840	0.826	0.831
22	0.900	0.828	0.828	0.900	0.828	0.852
23	0.860	0.828	0.834	0.860	0.828 0.828	0.831
24	0.882	0.824	0.828	0.882	0.824	0.845
26	0.902	0.824	0.828	0.902	0.824	0.851
26 28	0.902	0.824	0.822	0.902	0.822	0.849
30	0.862	0.818	0.822	0.862	0.818	0.849
32	0.790	0.820	0.822	0.822	0.790	0.834
34	0.834	0.820	0.824	0.822	0.820	
38	0.876	0.820	0.824	0.876	0.820	0.826
42	0.836	0.832	0.824	0.836	0.824	0.840 0.831
46	0.820	0.826	0.820	0.826	0.820	0.831
50	0.772	0.760	0.768	0.826	0.760	0.822

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ater pH			Wat	ler pH		
Time	Site 1	Site 2	Site 3	Maximum	Minimum	Mean
-17 -3 -2 -1	7.90	7.91	7.95 8.02	7.95 8.02	7.91	7.92
- 3	8.00	8.01	8.02	8.02	8.00	8.01
-2	8.03	8.03	8.03	8.03	8.03	8.03
-)	8.05	8.04	8.04	8.05	8.04	8.04
0	7.92	8.05	8.04	8.05	7.92	8.00
1	7.92	8.05	8.02	8.05	7.92	8.00
2	7.93	8.06	8.04	8.06	7.93	8.01
3	7.94	8.10	8.08	8.08	7.94	8.04
4	7.95	8.07	8.06	8.07	7.95	8.03
5	7.95	8.09	8.11	8.11	7.95	8.05
5 6 7	7.96	8.09 8.08	8.07	8.07	7.96	8.04
7	7.98	8.07	8.10	8.10	7.98	8.05
8 9	7.98	8.14	8.12	8.14	7.98	8.08
9	8.01	8.12	8.11	8.12	8.01	8.08
10	8.13	8.12	8.10	8.13	8.10	8.12
11	8.12	8.12	8.11	8.12	8.11	8.12
12	8.00	8.12	8.12	8.12	8.00	8.08
12 13	8.01	8.15	8.12	8.15	8.01	8.09
14	8.10	8.15	8.13	8.15	8.10	8.13
15	8.02	8.14	8.15	8.15	8.02	8.10
16	8.02	8.15	8.13	8.05	8.02	8.10
17	8.03	8.17	8.17	8.17	8.03	8.12
18	8.04	8.17	8.17	8.17	8.04	8.13
19	8.04	8.19	8.17	8.19	8.04	8.13
20	8.05	8.23	8.20	8.23	8.05	8.16
21	8.05	8.20	8.20	8.20	8.05	8.15
22	8.05	8.20	8.19	8.20	8.05	8.15
23	8.04	8.20	8.20	8.20	8.04	8.15
24	8.05	8.22	819	8.22	8.05	8.15
26	8.05	8.19	8.19 8.19	8.19	8.05	8.14
28	8.06	8.29	8.20	8.29	8.06	8.18
30	8.06	8.24	8.20	8.24	8.06	8.17
32	8.06	8.22	8.21	8.22	8.06	
34	8.06	8.23	8.23			8.16
34	8.05	0.43 0 11	8.23	8.23	8.06	8.17
42	8.05	8.22 8.17	0.42 9.19	8.22	8.05	8.16
			8.18	8.18	8.05	8.13
<b>46</b> 50	8.03	8.18	8.16	8.18	8.03	8.12
	8.24	8.20	8.15	8.24	8.15	8.20

### Water temperature

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<b>T</b> <sup>2</sup> <b>A</b> >			Temper	ature (DC) Maximum	<b>.</b>	
Time (h)	<u>site</u> ]	site2	site3		Minimum	Mean
-17 -3 -2 -1	9.3 9.1	9.2 9.1	9.3 9.2	9.3 9.2	9.2 9.1	9.3 9.1
• • •	9.1	9.1	9.2	9.2	9.1	9.1
-2	9.1	9.1	9.1	9.1	9.1	9.1
-1	9.1	9.1	9.1	9.1	9.1	9.1
0	9.1	9.1	9.1	9.1	9.1	9.1
1	9.1	9.1	9.0	9.1	9.0	9.1
2	<b>9</b> .1	9.0	9.1	9.1	9.0	9.1
3	<b>9</b> .1	9.1	9.1	9.1	9.1	<b>9</b> .1
4	9.1	9.1	9.1	9.1	9.1	9.1
5	9.1	9.0	9.1	9.1	9.0	9.1
6	9.1	9.1	9.1	9.1	9.1	9.1
7	9.1	9.0	9.0	9.1	9.0	9.0
8	9.0	8.9	8.9	9.0	8.9	8.9
9	8.9 8.9	8.8	8.9	8.9	8.8	8.9
10	8.9	8.8	8.8	8.9	8.8	8.8
ii	8.8	8.8	8.8	8.8	8.9 8.8 8.8 8.8 8.8 8.7	8.8
12	8.8	8.8	8.7	8.8	8.7	8.8
13	8.7	8.7	8.7	8.7	8.7	8.7
14	8.7	8.6	8.6	8.7	8.6 8.5 8.5 8.5 8.3	8.6
15	8.6	8.5	8.6	86	85	8.6
15 16	8.5	8.5	8.5	8.6 8.5	8.5	8.5
17	8.4	8.3	83	8.4	83	8.3
18	8.3	83	8.3 8.3	8:3	83	8.3
iõ	8.3	8.3 8.2	8.2	8.3	8.3 8.2	8.2
19 20 21 22	8.2	8.1	8.1	8.2	8.1	8.1
21	8.1	8.0	8.0	8.1	8.0	8.0
22	8.0	8.0	8.0	8.0	8.0	8.0
23	8.0	8.0	7.9	8.0	70	8.0
23	70	7.9	7.9	7.9	7.9 7.9	5.U 7 A
26	7.9 7.9 7.8 7.9 7.7	78	7.9	70	7.8	7.9
20	7.7	7.8 7.8 7.9 7.7	7.9 7.9 7.8	7.9 7.9 7.9 7.9 7.7	7.0	7.9
20	7.8	7.0	7.9	7.5	7.8 7.8	7.8
28 30 32	7.9	ע.ו ר ר	7.7	7.5 C C	1.8	7.9 7.7
34	7.1	1.1	7.7	1.1	7.7	1.1
34	7.5	7.5 7.3 7.3	7.4	7.5	7.4	7.5 7.3 7.3
38	7.3 7.3	1.5	7.3 7.3	7.3 7.3	7.3 7.3	7.3
42	1.5	1.5	1.5	1.3	1.5	7.3
46	7.3 7.5	7.3 7.5	7.3 7.5	7.3 7.5	7.3 _7.5	7.3
50	1.5	1.3	1.5			7.5

## Metal concentrations in the water column before, during and after dredging and for elutriate tests

### Manganese

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15.5         183         190         5         164         2           17         176         196         7         184         2           19         187         204         9         180         1           26         194         210         13         158         1	
17         176         196         7         184         22           19         187         204         9         180         1           26         194         210         13         158         1	
19 187 204 9 180 1 26 194 210 13 158 1	
26 194 210 13 158	
20 00 01 170 1	
50 182 222 38 188 22 56 172 775 50 777 77	

Iron\_

	<b>F</b> 1	Con	centration of iron ()	ug ( <sup>-1</sup> )		
-	Elutriat			Field monitoring		
<u>Time (h)</u>	<u>Dissolved</u>	Total	Time (h)	Dissolved	Total	
9	925	883	-17	545	706	
11	983	883 985	-i	522	755	
12.5	922	1022	i	509	787	
14	901	985	i	540	824	
15.5	922	1280	š	572	844	
17	868	1194	ž	627	873	
19	711	1338	ó	625	892	
26	684	1007	13	712	1007	
33	559	901	17	595	909	
36	525	955	21	700		
39	593	902	26		961	
42				670	904	
	515	978	32	<b>62</b> 1	932	
50	589	882	38	657	945	
56	507	685	50	656	865	

Mercury

	Conce Elutriate	ntration of mercury (	μg -1)
Time_(h)	Total	Time (h)	Field Total
9	0.39 0.35	-17	0.04
11		-1	0.04
12.5	0.45	1	0.08
14	0.5	3	0.)
15.5	0.57	5	0.14
17	0.53	7	0.22
19	0.42	9	0.28
26	0.35	13	0.34
33	0.28	17	0.31
36	0.22	21	0.2
39	0.2	26	0.12
42	0.17	32	0.13
50	0.12	38	0.07
56	0.08	50	0.02

### Copper

	Conce Elutriate	ntration of copper (	ug 1 <sup>-1</sup> )
Time (h)	<u>T</u> etal	Time (h)	Field Total
9	9.55	-17	2.05
11	8.57	-]	0.9
12.5	9.31	1	3.21
14	9.54	3	1.03
15.5	10.42	5	1.82
17	12.46	7	8.83
19	11	9	5.37
26	9.88	13	7.26
33	9.48	17	7.27
36	7.21	21	3.51
39	6.41	26	3.3
42	4.44	32	3.82
50	5.7	38	2.38
56	5.2	50	3.69

# APPENDIX 3 Concentrations of metals in dredge spoil extracts and plants

### Aqua regia digestates

Loc <sup>†</sup>	Irc	on (mg kg	ς <sup>-1</sup> )	Mang	anese (n	ng kg <sup>(1</sup> )	Potas	sium (m	g kg <sup>-1</sup> )	Сор	per (mg	kg <sup>-1</sup> )	Mer	cury (mg	: kg <sup>-1</sup> )
	Mean	std dev	%RSD	Mean	std dev	% RSD	Mean	std dev	%RSD	Mean	std dev	% RSD	Mean	std dev	% RSD
1	14675	199	1.4	147.9	4.2	2.8	559	37	6.7	49.69	0.23	0.5	7.32	0.77	10.5
2	25888	90	0.3	346.1	1.1	0.3	1205	51	4.3	46.80	0.65	1.4	1.45	0.03	1.7
3	31253	632	2.0	385.9	1.3	0.3	1637	123	7.5	101.10	1.48	1.5	4.57	0.27	5.8
4	33062	401	1.2	531.8	10.2	1.9	1523	135	8.9	68.26	0.05	0.1	4.64	0.07	1.6
5	33554	613	1.8	399.6	3.5	0.9	1385	86	6.2	113.86	0.42	0.4	3.81	0.38	9.9
6	23258	256	1.1	368.8	0.6	0.2	1066	25	2.3	97.48	1.65	1.7	1.01	0.09	8.9
7	24031	420	1.7	359.1	11.1	3.1	992	52	5.3	81.80	0.28	0.3	0.84	0.05	5.8

### **DTPA** extracts

Loc <sup>†</sup>	İn	on (mg kj	g <sup>-1</sup> )	Mang	anese (п	ng kg <sup>-1</sup> )	Pota	ssium (m	g kg <sup>-1</sup> )	Coj	oper (mg	kg <sup>-1</sup> )	Me	rcury (mg	(kg <sup>-1</sup> )
	Mean	std dev	%RSD	Mean	std dev	%RSD	Mean	std dev	%RSD	Mean	std dev	% RSD	Mean	std dev	%RSD
1	198.1	8.9	4.5	9.51	0.34	3.6	63.0	3.5	5.5	15.19	0.36	2.4	nd		
2	329.7	15.5	4.7	24.05	0.55	2.2	172.7	6.6	3.8	9.76	0.19	1.9	nd		
3	210.4	7.5	3.6	16.66	0.35	2.1	287.6	.1.2	0.4	30.54	0.94	3.1	nd		
4	386.2	12.3	3.2	35.85	0.34	0.9	78.6	4.3	5.4	17.84	0.38	2.1	nd		
5	646.2	24.4	3.8	28.32	1.04	3.7	15.6	0.8	5.0	33.16	1.00	3.0	nd		
6	392.1	7.8	2.0	14.85	0.56	3.8	197.2	2.0	1.0	20.49	0.72	3.5	nd		
7	400.9	17.3	4.3	18.22	0.47	2.6	142.3	3.2	2.3	21.18	0.56	2.7	nd		

### Dilute nitric acid extracts

Loc <sup>†</sup>	lro	on (mg kg	<sup>-1</sup> )	Mang	anese (n	ng kg <sup>-1</sup> )	Pola	sium (m	g kg <sup>-1</sup> )	Cop	oper (mg	kg <sup>-1</sup> )	Mer	cury (mg	(kg <sup>-1</sup> )
	Mean	std dev	%RSD	Mean_	std dev	%RSD	Mean	std dev	%RSD	Mean	std dev	%RSD	Mean	std dev	%RSD
1	5375	254	4.7	124.4	4.6	3.7	150	7.1	4.8	30.43	1.35	4.4	2.43	0.10	4.0
2	14020	512	3.7	330.2	9.5	2.9	361	3.6	1.0	29.77	1.19	4.0	0.54	0.02	3.3
3	13182	278	2.1	254.0	7.5	2.9	459	10.7	2.3	59.35	0.86	1.4	1.59	0.04	2.4
4	15443	275	1.8	454.7	11.7	2.6	314	5.6	1.8	39.17	1.82	4.6	2.46	0.11	4.6
5	15730	717	4.6	334.5	14.1	4.2	180	6.8	3.8	67.55	1.55	2.3	2.61	0.11	4.1
6	12227	263	2.2	305.3	11.7	3.8	505	1.9	0.4	60.16	2.25	3.7	0.55	0.02	3.1
7	10931	510	4.7	304.1	12.8	4.2	330	14.6	4.4	52.60	<u>1.70</u>	3.2	0.42	0.03	7.6

Location on transect

std dev = standard deviation, %RSD= % relative standard deviation

nd = not detected i.e. below detection limit

All concentrations are averages of 3 digestions or extractions

Location	iron (	mg kg <sup>-1</sup> )	Mangane	se (mg kg <sup>-1</sup> )	Potassiu	m (mg kg <sup>-1</sup> )	Copper	(mg kg <sup>-1</sup> )	Mercury	(mg kg <sup>-1</sup> )
	Plant	Root	Plant	Root	Plant	Root	Plant	Root	Plant	Root
ī	95.0	74.0	25.0	13.1	8836	3856	13.2	12.2	0.066	0.164
2	101.3	202.0	25.9	22.1	12736	4171	9.8	14.2	0.025	0.133
3	38.1	62.2	26.3	15.5	15988	10391	7.3	9.4	0.034	0.159
4	73.4	151.2	24.2	21.0	13313	8356	15.3	14.2	0.105	0.165
5	7.5	143.5	22.7	25.3	9695	7147	8.7	8.6	0.04	0.287
6	56.0	526.3	23.8	27.6	14046	8039	15.3	12.8	0.028	0.138
7	90.8	611.6	25.6	29.9	12461	6998	15.2	14.4	0.224	0.087

All concentrations are averages of 3 different plants from each location

# APPENDIX 4 Fish surveys of the R Yare and Ormesby Broad

R	Yare	eels	1993

No	Length (cm)	Weight (g)	Age (y)	Hg (mg kg <sup>-1</sup> )	MeHg (mg kg <sup>-1</sup> )	Ratio MeHg:Hg
1	51		19+	0.101	0.12	11
2	55	276.8	19+	0.094	0.09	96
3	47	150	19+	0.086	0.09	105
4	59	280.4	15+	0.113	0.04	35
5	47	205.9	18+	0.104	0.05	48
6	42	115	20+	0.3	0.12	40
7	35	<b>9</b> 5.8	21+	0.602	0.09	15
8 9	69	480	21+	0.123	0.14	114
9	44.5	119.1	19+	0.128	0.15	117
10	55	210	17+	0.089	0.09	101
11	54	156	18+	0.087	0.1	115
12	46.5	115	17+	0.162	0.08	49
13	48	150	18+	0.179	0.1	56
14 15	50	178	17+	0.12	0.1	83
15	47	98	20+	0.055	0.06	109
16 17	34	65.3	14+	0.116	0.12	103
17	42	122	18+	0.059	0.04	68
18	40.5	121	•	0.06	0.05	83
19	39	114.6	19+	0.339	0.06	18
20	35	81.1	19+	0.225	0.04	18 18
21	50	161	19+	0.259	0.06	23
22	34	80	15+	0.229	0.07	54
22 23	41	92.7	19+	-		
24	34	73.5	20+	0.082	0.07	85
25	33	63.4	14+	0.123	0.14	114

### R Yare eels 1994

No	Length	Weight	Sex*	Age	Hg	MeHg (mg kg <sup>-1</sup> )	Ratio
	(cm)	(g)		(ÿ)	(mg kg <sup>-1</sup> )	(mg kg * )	MeHg:Hg
Ĭ	36.0 36.2	102.2 101.9	រញារា	11	0.362 0.357 0.262	0.308 0.340	0.85 0.95
2	36.2	101.9	M	11	0.357	0.340	0.95
3	39.7 39.2	137.5	່ມານກ F	14	0.262	0.269	1.03
4	39.2	123.6	. <b>F</b>	ij	0.155	0.134	0.86
5 6 7 8	34.5	85.9	ມກາ	9	0.155	0.112	0.73
6	50.1	249.0	F	13	0.132	0.087	0.66
7	36.9 50.7	76.4	F	9 17	0.238	0.184	0.77
8	50.7	218.2	F	17	0.128	0.114	0.89
9 10	44.5	151.7	F	21	0.296	0.238	0.80
10	45.3	159.4	F F F F F F F F M	13	0.296	0.299	1.01
11	40.4	114.7	F	8	0.113	0.099	0.88
12	39.0	109.5	F	12	0.227	0.205	0.90
13	34.9	69.8	M	14	0.286	0.219	0.77
14	46.0	153.7	F	12	0.274	0.272	1.00
15	34.2 31.7	77.1	រភាភា	16	0.187	0.131	0.70
16	31.7	61.5 85.3	М	13	0.284	0.245 0.178	0.86
17	33.6	85.3	imm	10	0.195	0.178	0.91
18	37.5	93.5	imm	17	0.270	0.239	0.89
19	33.4	62.6 51.2	imm	17 13	0.203	0.183	0.90
20 21	30.1	51.2	i៣រា F F F F F F	6	ns 0.351	ns 0.355	<b>n</b> 5
21	37.1	64.5 73.7 539.3	F	12	0.351	0.355	1.01
22	34.6	73.7	F	11	0.257	0.205	0.80
22 23	65.5	539.3	F	14	0.153	0.205	0.84
24	47.4	183.4	F	14	0.312	0.300	0.96
25	56.5	283.6	F	12	0.295	0.232	0.79
26 27 28 29	41.6	109.7	F	14	0.115	0.116	1.01
27	33.6	79.5	imm F F F	10	0.231	0.157	0.68
28	41.0	114.9	F	13	0.220	0.191	0.87
29	48.9	175.8	F	14 11	0.267	0.233 0.301 0.297	0.87
30	45.0 33.2	130.5	F	11	0.301 0.371	0.301	1.00
31	33.2	64.9	រំហារប	17	0.371	0.297	0.80
32	32.4	45.6	imm	12	0.350	0.299	0.85
31 32 33 34	38.3	100.7	M	15	0.351	0.295	0.84
34	54.7	285.3	F	11	0.237	0.207 0.383	0.87
35	52.0	254.4	F	16	0.401	0.383	0.95
36	38.0	115.7	រំពារា	12	0.410	0.364	0.89
37	36.0	87.9	imm	12 15	0.309	0.258	0.83
38	36.9	83.4	F	13	0.376	0.315	0.84
39	39.6	100.7	F	8	0.125	0.116	0.93
40	30.0	46.0	រំពាររា	14	0.501	0.426	0.93 0.85
41	32.7	59.6	imm	14	0.194	0.161	0.83
42	53.0	271.9	F	15	0.303	0.280	0.92
43	42.7	145.3	F F F	14	0.280	0.234	0.84
44	42.0	112.7	F	14	0.316	0.330	1.04
45	34.2	85.7	imm	15	0.350	0.355	1.02
46	24.7	30.7	imm	6	0.218	0.178	0.81
46 47	44.3	129.0	F	14	0.222	0.195	0.88
48	41.9	130.5	F	14	0.222 0.305	0.229	0.75
49	34.3	74.5	М	i2	0.059	0.057	0.96
50	49.8	196.7	F	14	0.057	0.059	1.04
51	31.0	52.0	imm	12	0.076	0.067	0.88

# Ormesby Broad eels 1995

No	Length	Weight	Age	Sex	M Hg	uscle tiss MeHg	ue % Ratio	Liver tissue Hg MeHg & Ratio		
	(cm)	(g)	(y)	JCA	(mg kg <sup>-1</sup> )	(me ke <sup>-1</sup> )	MeHg:Hg		(mg kg <sup>-1</sup> )	% Ratio MeHg:Hg
1	47.9	175.3	12		130.7	101	77.3	332.1	61.9	18.6
	48.1	194.4		М	105.9	87.3	82.4	116.3	29.5	25.4
2 3 4	38.2	79.3	12	?	112.7	90.1	79.9	90.9	16.9	18.6
4	60.5	420.8	13	F	132.0	104.7	79.3	52.0	7.6	14.6
5	47.0	192.6	13	F	62.4	57.5	92.2	26.8	5.3	19.8
6	56.5	335.2	16	Ň	98.4	77.2	78.5	32.2	4.5	14.0
7	59.9	454.2	12	F	161.1	134.3	83.4	68.5	11.4	16.6
5 6 7 8	58.8	387.6	13	M	118.4	88.2	74.5	55.9	10.3	18.4
9	48.2	228.7	12	M	<b>95.0</b>	82	86.3	60.6	10.3	17.0
10	52.5	302.9	13	F	101.3	83.1	82.0	162.6	21.6	13.3
11	50.0	253.9	10	F	101.3	90.8	88.7	40.6	9.2	22.7
12	49.0	236.5	12	M	87.9	71.4	81.2	32.6	5.1	15.7
13	55.0	343.9	15	M	128.1	103.9	81.1	116.4	18.2	15.6
14	35.0	91.3	8	M	108.9	<b>95</b> .4	87.6	43.9	8.7	19.8
15	44.0	160.3	12	F	185.8	164.4	88.5	43.9	9.5	21.5
16	52.5	228.6	-	F	165.8 167.2	132.5	79.2	252.0	52.1	<b>2</b> 1.5 <b>2</b> 0.7
17	50.7	279.1	16	F	148.5	132.5	79.2 79.9			
17	51.0	279.1	15	г М	148.5			52.0	8.2	15.8
10 19		462.8	15			95.9	77.5	38.2	9.5	24.8
	61.0			F	88.6	73	82.4	57.6	16.5	28.7
20	72.0	899.8	15	F	104.2	80.6	77.4	64.2	13.1	20.4
21	55.0	303.4	12	F	32.4	28.6	88.3	3.6	0.7	19.5
22	57.0	250.8	12	M	37.5	30.5	81.4	24.1	3.8	15.7
23	39.0	74.6	12	F	270.5	201.9	74.6	97.0	14.5	15.0
24	49.7	215.4	13	F	37.7	30.2	80.1	16.9	2.9	17.2
25	58.6	451.0	17	F	42.5	33.7	79.3	14.4	2.2	15.2
26	77.0	890.8	18	F	88.4	72	81.4	29.9	8.5	28.4
27	58.4	422.1	15	nd	120.3	99.3	82.6	33.0	7.9	<b>23.9</b>
28	52.3	369.1	14	nd	76.4	57.7	75.5	27.6	4.5	16.3
29	54.5	247.1	14	nd	62.9	48.7	77.5	33.6	6.8	20.3
30	53.1	292.4	14	nd	116.5	106.3	91.2	8.9	1.8	20.2
31	47.0	210.1	15	nd	142.6	121.7	85.3	46.6	4.8	10.3
32	55.0	357.9	13	nd	82.3	67.8	82.4	24.0	4.6	19.2
33	50.0	262.5	-	nd	14.7	11.3	76.9	125.2	20.5	16.4
34	47.0	188.5	12	nđ	131,9	108.6	82.4	32.9	5.6	17.0
35	40.0	121.0	14	nd	145.3	103.8	71.4	90.9	17.2	18.9
36	50.0	214.0	11	nđ	143.2	114.6	<b>8</b> 0. <b>0</b>	144.4	19.8	13.7
37	40.8	108.0	11	nd	119.1	92.1	77.3	29.5	7	23.7
40	57.0	309.9	14	nd	41.2	36.5	88.6	6.0	0.8	13.3
41	55.1	361.3	-	nd	90.1	69.8	77.5	59.4	12.8	21.6
42	48.2	208.4	14	nd	46.9	39.2	83.6	9.2	1.5	16.3
44	49.8	192.1	11	nd	285.0	232.4	81.6	153.1	34.2	22:3
45	54.0	317.5	13	nd	49.9	39.9	80.0	37.2	5.4	14.5
46	52.6	342.3	15	nd	78.1	63.2	81.0	44.4	9.3	21.0
49	56.3	325.2	14	nd	74.1	61	82.3	33.9	3.3	9.7
50	<b>5</b> 3.0	325.9	14	nd	64.7	<b>5</b> 4.6	84.4	28.3	3.5	12.4
51	<b>5</b> 0.0	257.4	15	nd	123.3	92.1	74.7	70.6	17.3	24.5
53	53.8	385.0	15	nd	48.8	39	79.9	120.5	24.1	24.5 20.0
55 54	53.8 52.0	280.1	13	nd	40.0 99.9	84.2	84.3	241.6	51.9	
	52.0 73.0	1000.8	18		131.1		87.7	142.1		21.5
<b>5</b> 5				nd		114.9	87.7 80.9		23.7	16.7
57	<b>52.0</b>	<b>299</b> .4	14	nd	34.5	27.9		20.9	5.1	24.4
59	50.0	279.4	16	nd	<u>99.0</u>	83.7	84.6	4.7	1	21.2

nd - not determined or immature, M = male, F = female

R Yare roach 1993

No	Length (cm)	Weight (g)	Age (Y)	[Hg]	[MeHg]	Ratio MeHg:Hg
1	15.6	66.2	4	0.197	0.14	71
4	17.7	93.2	2	0.159	0.11	7Ō
3	17.2	93.4	5	0.105	0.07	67
4	14.6	54.1	4	0.142	0.07	49
5	15	59.5	4	0.17	0.12	71
6	17	92.1		0.23	0.08	35
7	15.7	69.7	4	0.146	0.16	109
8	19.9	148.7	5	0.182	0.09	49
9	18.5	110.8	5	0.209	0.16	77
10	24.4	269.1	8	0.221	0.16	72
11	17.5	104.2	4	0.139	0.06	43
12	14	44.3	4	0.141	0.1	71
13	18	105.4	5	0.168	0.14	83
14	21.4	170.8	6	0.164	0.17	104
15	17	97.9	5	0.192	0.09	47
16	17.8	105.3	Ś	0.106	0.09	85
17	16.3	75.6	4	0.169	0.11	65

## R Yare roach 1994

No	Length (cm)	Weight (g)	Sex*	Age (y)	[Hg] (ms ks <sup>-1</sup> )	[MeHg]	Ratio MeHg:Hg
1	20.2 20.8	136.2 176.2	nd	4+	0.1168	0.1081	0.93
1 2 3 4 5 6 7 8 9	20.8	176.2	nd	5+	0.0615	0.0598	0.97
3	18.9	135.9	М	5+	0.0599	0.0417	<b>0</b> .70
4	22.1	223.9	F	5+	0.0593 ·	0.0466	0.79
5	21.1	178.5	F	5+	0.0943	0.0798	0.85
6	19.1	137.5	F	5+	0.0386	0.0404	1.05
7	18.7	135.0	M	5+	0.0369	0.0305	0.83
8	18.6	123.5	F	5+	0.0420	0.0311	0.74
9	16.6	82.0	M	5+	0.0370	0.0365	0.99
10	17.3	101.5	F	5+	0.0307	0.0262	0.85
11	18.3	112.3	M	5+	0.0273	0.0259	0.95
12	19.1	129.2	М	6+	0.0785	0.0676	0.86
13	20.6	173.3	F	5+	0.0473	0.0404	0.85
14	18.2	104.2	F	5+	<b>0</b> .0331	0.0308	0.93
15	20.3	162.6	F	5+	0.0279	0.0250	0.89
16	18.0	110.8	М	5+	0.0505	0.0352	0.70
17	16.0	73.0	М	4+	0.0490	0.0464	0.95
18	21.5	220.2	F	5+	0.0714	0.0568	0.80
19	17.3	100.8	F	5+	0.0546	0.0523	0.96
20	18.0	111.1	F	4+	0.0392	0.0375	0.96
21	17.9	96.8	Ň	4+	0.0326	0.0260	0.80
22	20.5	180.4	F	-	0.0472	0.0385	0.82
23	19.5	147.2	F	5+	0.0702	0.0586	0.84
24	21.5	222.7	F F M	6+	0.0476	0.0447	0.94
25	18.0	105.9	м	6+	0.0318	0.0268	0.84
26	23.0	245.2	F	5+	0.0646	0.0557	0.86
27	21.5	223.5	Ē	Š+	0.0445	0.0403	0.91
28	20.5	155.3	Ň	5+	0.0481	0.0426	0.89
29	17.8	104.1	F	5+	0.0532	0.0406	0.76
30	21.5	207.5	Ē	5+	0.0478	0.0394	0.82
31	18.5	109.9	Ē		0.0940	0.0941	1.00
31 32	19.2	135.0	Ē	4+	0.0775	0.0567	0.73
33	16.6	85.8	Ē	5+	0.0617	0.0564	0.91
34	20.8	85.8 108.2	Ē	5+	0.0552	0.0479	0.87
35	20.2	159.8	Ê	5+	0.1210	0.1144	0.95
36	19.4	143.6	<b>W</b> - <b>-</b> - <b>- - -</b>	5+	0.0447	0.0287	0.64
37	19.1	127.9	м́	5+	0.0675	0.0537	0.80
38	16.9	90.8	F	5+	0.0447	0.0358	0.80
39	17.3	102.9	м́	5+	0.0406	0.0325	0.80
40	17.8	106.0	M F	5+	0.0547	0.0469	0.80

\*nd = not determined, M = male, F = female, imm=immature

ns = no sample

# Ormesby Broad roach 1995

No	Length	Weight	Sex*	Age	Hg	MeHg	% Ratio
	(cm)	(g)		(y)	(mg kg <sup>+1</sup> )	(mg kg <sup>-1</sup> )	MeHg:Hg
1	16.5	68.9	4	F	ns	ns	
2	14.2	42.8	3.	F	87.2	69.5	79.8
3	19.5	107. <b>2</b>	4	F	66.2	55.7	84.1
4	14.0	34.1	3	F	51.7	38.1	73.7
5	16.5	66.2	4	М	93.8	81.9	87.3
6	14.0	36.8	3	М	77.7	62.4	80.3
7	12.5	25.4	3	М	71.5	56.7	79.2
8	12.0	22.9	3	М	60.8	52.4	86.1
9	12.5	24.9	3	F	<b>5</b> 0.5	39.3	77.7
10	17.0	74.2	4	М	<b>6</b> 6.8	54.3	81.3
11	16.3	62.1	4	М	84.2	64.3	76.3
12	12.6	25.3	3	F	<b>99</b> .3	78.1	<b>78</b> .6
13	12.0	22.4	3	F	46.8	39.0	83.4
14	12.0	24.8	3	F	48.9	45.2	92.5
15	12.5	25.3	3	F	41.0	35.2	85.9
16	17.8	89.9	4	М	58.9	44.8	76.1
17	16.5	57.0	4	F	69.4	55.7	80.3
18	18.5	89.4	4	F	55.6	40.5	72.7
19	13.3	32.6	4	F	54.1	45.2	83.6
20	12.3	25.4	3	F	47.0	36.2	77.0
21	18.0	83.6	4	F	70.6	62.4	88.4
22	15.0	55.8	4	F	52.1	38.1	73.1
23	12.5	25.2	3	F	55.4	45.7	82.5
24	17.5	87.4	4	F	44.1	33.8	76.7
25	14.6	46.8	3	F	26.6	22.4	84.2
26	19.5	111.2	4	F	58.2	41.4	71.2
27	16.6	61.4	4	F	57.9	49.0	84.7
28	17.0	68.8	4	Μ	87.8	69.5	79.2
29	12.2	25.1	3	М	57.5	43.8	76.2
30	12.1	23.1		F	<b>2</b> 7.7	24.6	88.8
31	13.5	31.8	3 3	F	42.0	33.6	80.1
32	12.4	25.3	3	F	48.9	36.2	74.0
33	19.5	110.0	4	F	38.2	31.4	82.3
34	12.4	28.9	3	F	19.4	17.6	90.8
35	16.8	65.8	4	F	87.8	67.1	76.5
36	13.3	36.6	3	F	33.7	25.7	76.2
37	12. <del>9</del>	26.1	3	F	39.3	32.4	82.4
38	12.6	<b>29</b> .7	3	М	<b>2</b> 9.6	22.4	75.7
39	18.5	105.2	4	F	47.2	42.9	90.7
40	17.3	71.7	4	F	49.3	36.2	73.4
41	16.5	69.1	4	М	49.6	40.0	<b>8</b> 0.6
42	16.5	61.4	4	М	46.9	41.0	87.3
43	14.3	39.1	3	Μ	34.4	25.7	74.7
44	13.2	30.8	3	F	46.7	37.6	80.5
45	12.0	24.0	3	M	51.7	39.5	76.4
46	13.7	37.9	3	F	37.6	32.4	86.2
47	13.3	34.3	3	F	54.3	44.3	81.6
48	19.8	128.0	5	F	51.6	38.1	73.8
49	12.5	25.6	3	Μ	47.0	39.0	83.0
50	12.4	27.1	3	М	34.7	27.7	79.8

M = male, F = female ns = no sample

### APPENDIX 5 Site licence for operation of Griffin Lane dumpsite

Norfolk County Council Highways Department Waste Disposal Section

Licence no. NFK/LS/007/O under the Control of Pollution Act 1974, 21 July 1986

#### Schedule of Conditions Landfill Site - Griffin Lane, Thorpe (TG 285 081) Licence Holder - May Gurney and Co mpany Limited

- 1. The licence holder shall obtain approval from the Waste Disposal Authority for any proposed change in the actual conduct of operations from the proposals shown in the licence application, as altered by any previous changes approved by the Waste Disposal Authority, before the proposed change is implemented.
- 2. The site shall be used only for the deposit of river dredgings.
- 3. An identification board of durable material and finish shall be displayed at the site entrance, giving the name, address, and telephone number of the operator.
- 4. The site shall be manned and supervised during operating hours.
- 5. Measures, to the satisfaction of the Waste Disposal Authority, shall be taken to prevent unauthorised access to the site.
- 6. Dredgings deposited on the site shall be levelled as soon as reasonably possible after deposit. A vehicle suitable or this purpose shall be provided at the site.
- 7. Dredging and landfill operations shall be scheduled in such a way as to ensure that mercury-contaminated sediments are covered with non-contaminated sediments or soil to a depth of not less than 0.2 metres.
- 8. Measures, to the satisfaction of the Waste Disposal Authority, shall be taken to ensure that any surface water run off from the site is directed back into the river.
- 9. Until final restoration, completed areas of landfilling shall be graded and maintained in a tidy condition to the satisfaction of the Waste Disposal Authority.
- 10. Measures, to the satisfaction of the Waste Disposal Authority, shall be taken to ensure that mud, debris or any other material is not deposited on any surrounding roadway by vehicles leaving the site.
- 11. Measures, to the satisfaction of the Waste Disposal Authority, shall be taken to ensure that the site is suitable for any proposed agriculture or other after use, before such use is implemented.
- 12. A record shall be kept of the quantities of material deposited at the site, and copies shall be sent to the Waste Disposal Authority at agreed intervals.
- 13. The terms of this licence shall be made known to any person who is given responsibility for the management or control of the site.