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

Executive Summary

Environmental and Water Resource Engineering Section
Imperial College of Science, Technology and Medicine

Anglian Region Operational Investigation

OI 420/9/A

NRA

National Rivers Authority

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NRA Report No OI/420/9/A

Supplement to the 1992 Imperial College report submitted to the National Rivers Authority, Anglian Region, in December 1992 NRA report No OI/420/8/A.

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Dissemination Status:
Internal: Released to Regions
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Research Contractor:
This document was produced under Anglian Region OI Contract 420 by:

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Background

The discovery that eels taken from the River Yare in 1985 contained elevated concentrations of mercury, almost twice the 0.3 mg kg^{-1} limit set by the 1984 EEC Directive (Council of European Communities, 1984), prompted a detailed investigation into mercury contamination within the River Yare system. The contamination was historical, originating from an industrial source that discharged (under licence) quantities of mercuric halides and copper to the public sewer during the late 1960s to mid 1970s. The original discharge consent for the chemical company permitted the emission of 2000 kg a^{-1} of mercury to the sewer. This limit was set by Norwich City Council, the regulatory authority at that time. The consent was reduced in the light of work published in the mid 1970s that highlighted the potential health effects associated with mercury and its organic derivatives (Smith and Smith, 1975). The consent limit currently stands at 48 kg a^{-1} and effective in house pollution control results in actual emissions that are well below this value. The industrial wastewaters are conveyed, via the public sewerage system, to Whitlingham sewage treatment works (STW) which removes, on average, 83% of the influent mercury, before discharge to the River Yare (Goldstone *et al.*, 1990). Although a significant reduction in the amount of mercury released from Whitlingham STW has occurred in the last 17 years the River Yare has undergone considerable cumulative loading of mercury within bottom sediments.

Sediment analysis undertaken in 1986 by Imperial College of Science, Technology and Medicine revealed the existence of a mercury contamination plume originating at Whitlingham STW (Bubb *et al.*, 1991). Mercury concentrations ranged from 0.05-32.9 mg kg^{-1} producing mean enrichment 2-30 times greater than catchment background levels. The discovery of methylmercury within the sediments was of particular concern because methylmercury has the potential to bioaccumulate and was the major causative agent responsible for 784 official cases of Minamata disease in the Minamata bay district, Japan, during the late 1950s and early 1960s that caused neurological and renal damage as well as fatalities (Smith and Smith, 1975). The occurrence of significant quantities of both inorganic and methylmercury within River Yare sediments and biota is consequently of concern, particularly since Eels are fished commercially on the Yare and are destined for human consumption. The Ministry for Agriculture, Fisheries and Food (MAFF), however, calculated that 0.5 kg of eel, taken from the contaminated stretch of the River Yare, could be consumed per week before any risk was posed to human health (Pers. comm. from MAFF, 1987).

It was in response to these concerns that Anglian Water Authority, and subsequently the National Rivers Authority (NRA), commissioned Imperial College to undertake research into mercury within the River Yare and the associated Broad systems. A routine monitoring program was established to assess temporal and spatial changes in the distribution of total and methylmercury within the sediments, while *in situ* and laboratory based experiments were employed to elucidate the factors controlling the behaviour and fate of mercury within the system. The ultimate aim of this program is to formulate management strategies for the River Yare that will safeguard the Water Quality Standards for mercury and minimise uptake by biota. This report forms an executive summary to '*Mercury and methylmercury in the River Yare, Norfolk*'; a detailed report submitted to the NRA (report No OI/420/8/A) in December 1992 by Imperial College, which contains a full description of experimental methods, result and data interpretation and operational management recommendations.

Findings

Annual monitoring of surficial sediments has identified a 17 km mercury enrichment zone stretching from Trowse in the West, at the upper tidal limit[1], to Hassingham in the East[2], located downstream of Rockland Broad and includes the interconnecting Broad (Surlingham, Wheatfen and Rockland) and Fleet areas. Inorganic mercury within the River Yare sediments forms a classic point source pollution plume which is centred 1-2 km downstream of Whitlingham STW and identifies Whitlingham as the contamination source. The occurrence of elevated loadings ≈4 km above the point source reflected the effect of tidal reversals that sweep contaminants upstream.

A quantitative assessment of the magnitude of mercury enrichment was gained by comparisons to average catchment background levels of 0.4 mg kg^{-1}. This value is consistent with the average shale value which is often used as a global baseline average for particulate associated metals (Salomons *et al.*, 1987). Surface sediments exhibited significant degrees of enrichment culminating in an 82 fold enrichment when the maximum observed concentration of 32.9 mg kg^{-1} was considered for the 1986 surficial sediment survey data. Since 1986, however, surficial sediments total mercury concentrations have declined significantly (Figure 1). This culminated in a 7 fold decrease in maximum surficial sediment mercury loadings by 1990, reducing concentrations to 0.01-4.68 mg kg^{-1}.

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

(i) The downstream movement and dispersion of particulate bound mercury by natural sediment transport processes, with subsequent dilution by 'fresh' unpolluted particulate matter.

(ii) The burial of mercury contaminated sediment beneath a 'cleaner' overlay of fresh uncontaminated sediment.

(iii) Remobilization of mercury from surficial sediments due to the action of complexing agents (chlorides, organics, etc.), changes in pH or redox potential, or mercury volatilisation.

(iv) Uptake by biota.

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1 Grid reference TG 244068

2 Grid reference TG 360045

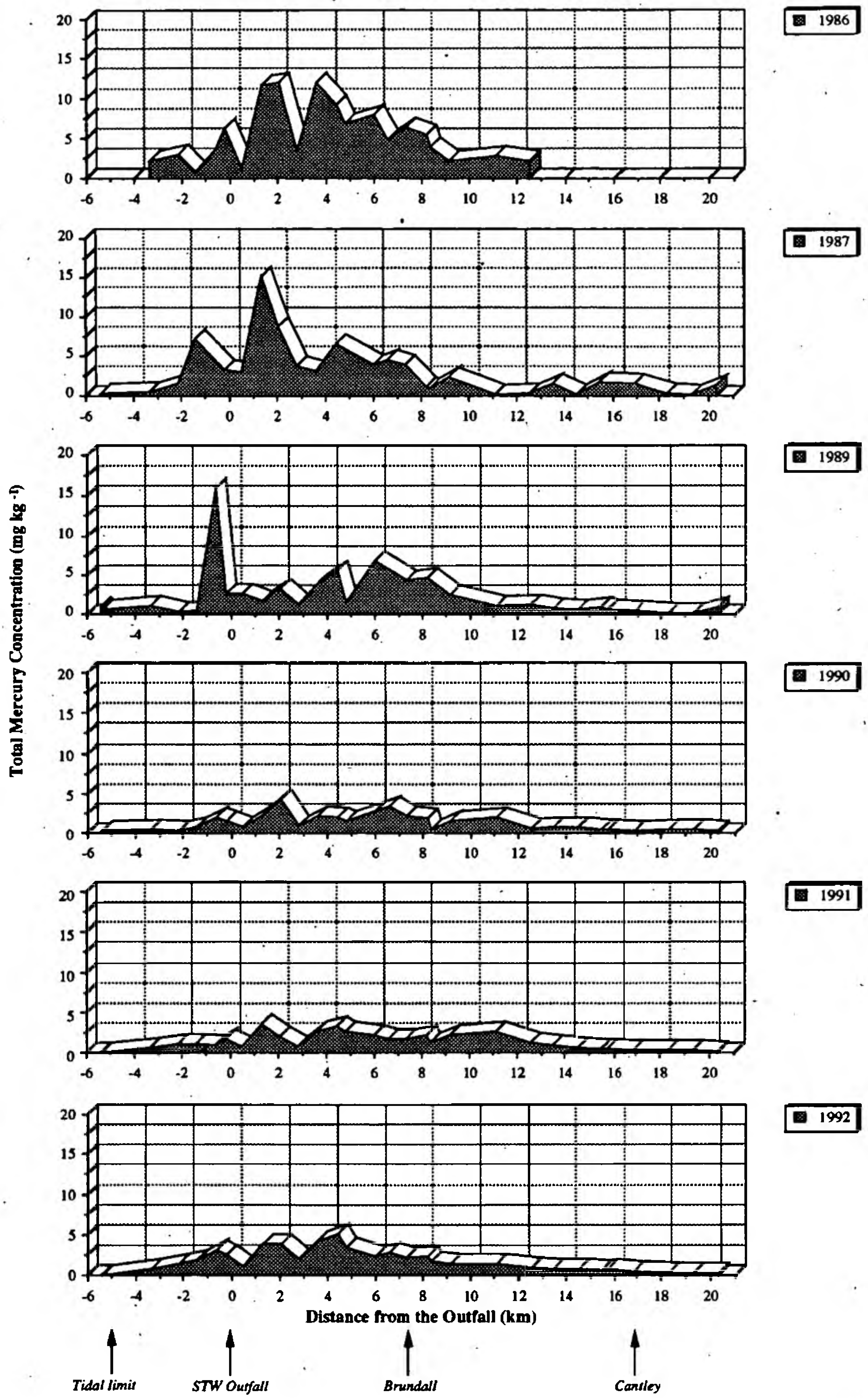

Figure 1. Longitudinal Distribution of Mean Transect Total Mercury loadings in River Yare Surficial Sediments.

Fluvial transportation of mercury contaminated particulates out of the study area is unlikely to be a dominant process operating within the River Yare system. The longitudinal distribution of sediment total mercury concentrations for the 1986-1992 surveys (Figure 1) gives no indication of a downstream shift in the pollution plume or an increase in loadings in the lower study reach. These results confirm the findings of the hydrological model exercise undertaken on the River Yare by Imperial College in 1986, which predicted that the dominant fluvial process was one of net particulate deposition, which would essentially fix contaminants within the sediment compartment (Imperial College, 1987). It is also unlikely that biota uptake or mercury desorption due to the formation of mercury complexes could account for the magnitude of the decline in surficial sediment mercury loadings. However in recent years saline intrusions have been pushing further inland and it is feasible that some degree of mercury remobilization from the sediment compartment will have taken place through the formation of soluble mercury-chloro complexes during these periods.

Evidence supplied from the succession of spatial surveys and a number of coring exercises indicates that the burial of contaminated sediment beneath a cleaner overlay, in the wake of tighter emission controls, is the main factor responsible for the observed decrease in surficial sediment mercury loadings. Total mercury concentrations of up to 36.9 mg kg^{-1} were detected at depth within sediment cores, the precise depth being dependent upon boat traffic disturbance and sedimentation rates, as dictated by hydrology, sediment supply and channel morphology. Maximum total mercury loadings generally occurred at depths between 20-24 cm but there were large variations. In areas of high sedimentation, such as at point bar localities (on the inside of meander bends) and in areas of quiescent flow, mercury was buried to depths in excess of 1 m. In areas of low sedimentation, maximum loadings occurred in surface sediments. Core profiles displayed a gradual decline in mercury towards surface deposits implying that the reduction in mercury inputs to the system has been effective in promoting a corresponding decline in recent sediments. Localised sediment disturbance by storms, boat traffic and dredging activities can, however, increase surface sediment mercury concentrations. Dredging operations during bridge construction for the A11 Norwich southern bypass road (located just upstream of the Whitlingham STW outfall), may have been the responsible for the slight increase in total mercury concentrations observed in the 1992 sediment survey which effected a 9 km reach downstream of the bridge site. It is also assumed that large scale sediment disturbance would increase methylmercury production and the potential for biological uptake as reduced metal species are exposed to oxygenated surface waters releasing more available metal ions to surface and interstitial waters. A full assessment on the impact of dredging activities and other forms of large scale sediment disturbance is needed to ensure that future capital works do not exacerbate the mercury problem on the Yare.

The distribution of total mercury within the river system was influenced by distance from the point source, sediment type and channel morphology. Highest mercury concentrations occurred in proximity to Whitlingham STW and in fine grained organic rich silt deposits that tended to occur in areas of quiescent water conditions such as at channel margins and in the shallower Broads. Coarser grained calcareous sand and gravel deposits contained lower concentrations of total mercury.

Although emission controls have been effective in promoting a decline in surficial sediment total mercury concentrations, methylmercury has not undergone a similar response. Methylmercury concentrations were highly variable, ranging from <0.1-29.47 $\mu g\ kg^{-1}$ on the River Yare (Figure 2) up to 33.4 $\mu g\ kg^{-1}$ in the shallower Broad systems, but have not declined since 1986. Methylmercury concentrations, therefore, failed to reflect the distribution of inorganic mercury. This suggests that methylmercury formation and subsequent retention within the sediment compartment were independent of total mercury concentrations and explains why some sediments with low total mercury concentrations contain marked enrichments of methylmercury. This point is illustrated further in Figure 3 which depicts the percentage methyl to total mercury concentrations against distance downstream. Although methylmercury generally contributed only a small fraction to the overall mercury burden, accounting for <1% of the total mercury present, this is still significant since methylmercury is the form most readily assimilated by aquatic organisms. Two areas consistently displayed high percentage methylmercury accounting for 1-7% of the total mercury present. The first area occurred at Trowse, 5 km upstream of Whitlingham STW and the second at Cantley, near to the British Sugar reprocessing factory, which lies ≈16 km below Whitlingham STW and downstream of the main contaminated zone. Enhanced methylation at these locations could be a temperature induced phenomenon promoted by the shallow water conditions at Trowse, which would facilitate heat penetration into the sediment, and the discharge of cooling water from the British Sugar plant at a temperature of 25°C at Cantley (NRA, Pers. Comm. 1988). Laboratory based tank experiments demonstrated that an increase in sediment temperature from 12°C to 22°C enhances methylmercury concentrations by ≈30% over a 10 day period. A similar conclusion was drawn from field data obtained from Rockland Broad where sediment methylmercury loadings decreased between 30-50% as seasonal temperatures shifted from ≈25°C to ≈6°C. Temperature is consequently an important control upon net methylation activity within aquatic sediments. Alternative explanations for the methylmercury anomalies at Trowse and Cantley could lie in the photochemical synthesis of methylmercury in the shallow water conditions at Trowse and enhanced bacterial activity at Cantley stimulated by the release of nutrient rich wastewaters from Cantley STW. There is no evidence to implicate British Sugar as a source of methyl- or total mercury to the River Yare system.

An *in situ* seasonal monitoring program in Rockland Broad (May 1991-March 1992) has partially elucidated the factors controlling the distribution and accumulation of methylmercury within the River Yare's sediment compartment by highlighting the importance of microbial activity and diagenetic (sediment ageing) processes in dictating methylation/demethylation

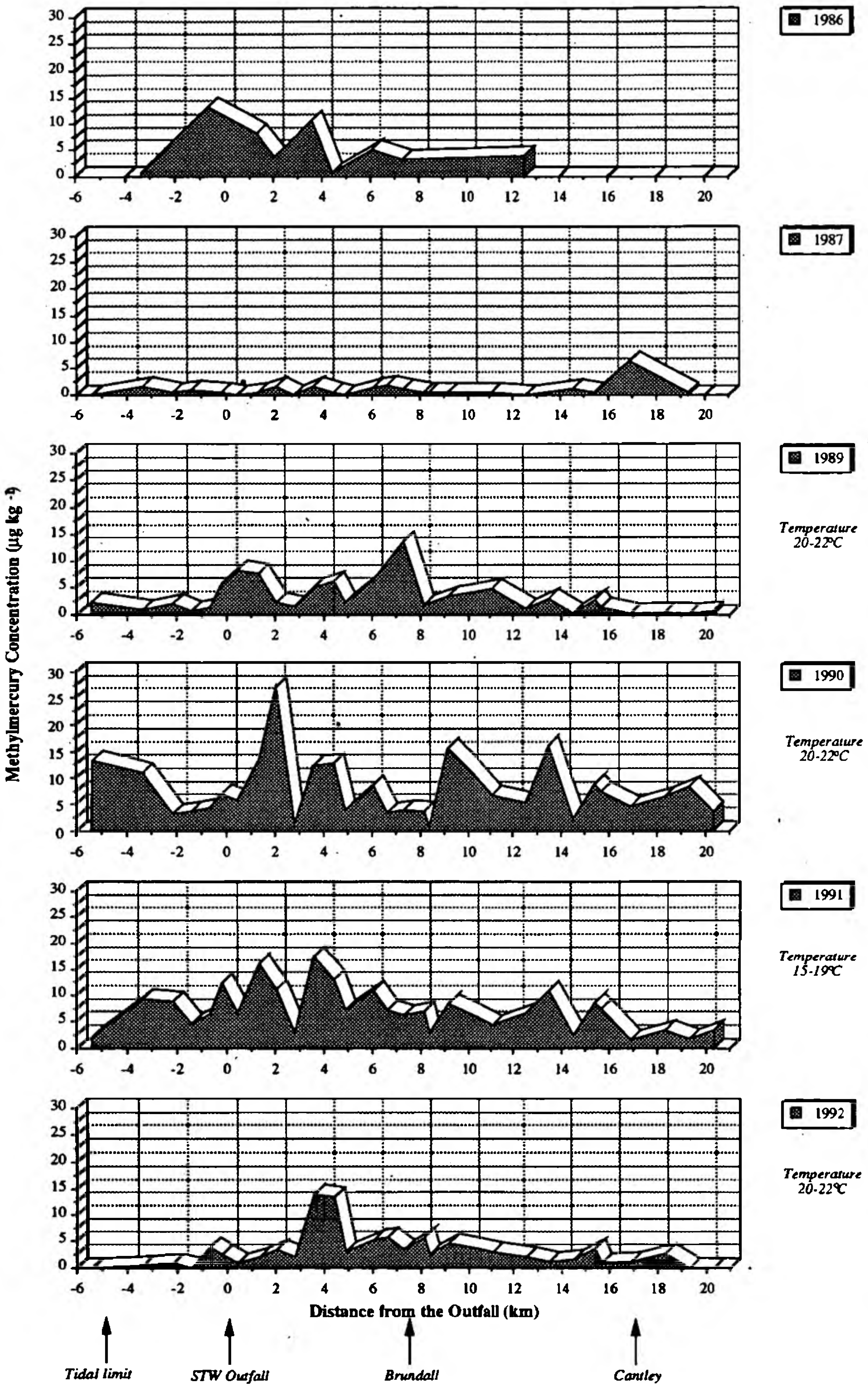

Figure 2. Longitudinal Distribution of Mean Transect Loadings of Methylmercury in River Yare Surficial Sediments.

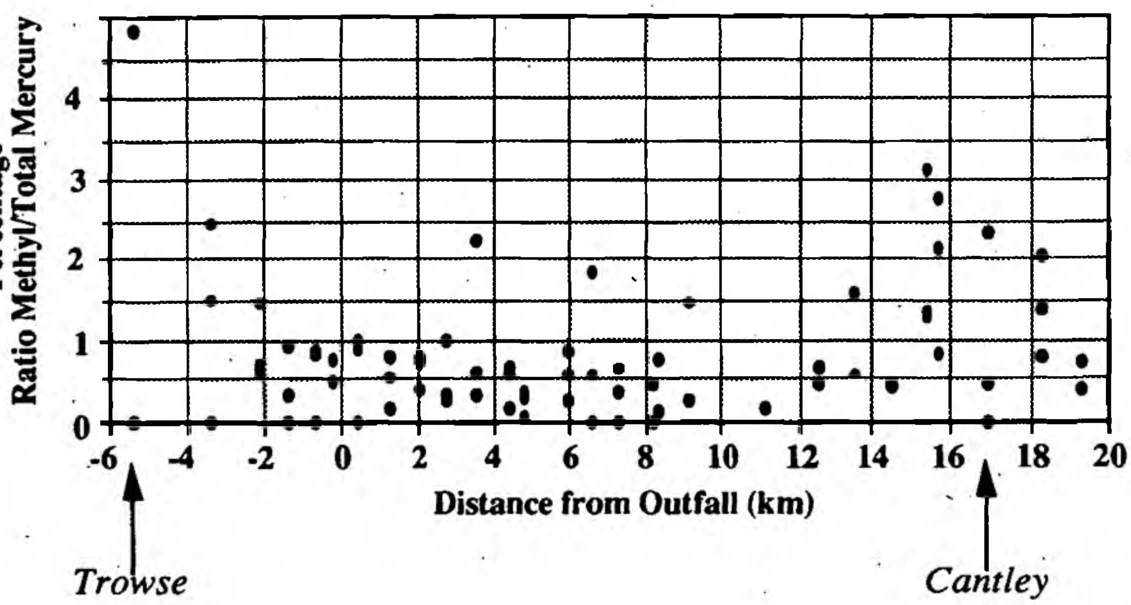

Figure 3. Percentage ratio of methylmercury to total mercury plotted against distance from Whitlingham STW.

reactions. It is the interaction between the methylation/demethylation processes that governs the net accumulation of methylmercury within the sedimentary compartment. Methylating bacteria thrive under moderately anaerobic conditions in subsurface layers, while demethylating bacteria predominate in surface aerobic zones. This encourages methylmercury to accumulate in subsurface layers (4-8 cm) where conditions are optimised for formation and subsequent retention. Under strongly reducing conditions, however, the formation of mercuric sulphide limits the availability of the mercuric ions (the component required for methylation) and alters the ecological succession to non-methylating bacteria, reducing methylmercury concentrations at depth. Detectable concentrations of methylmercury were rarely observed below 36 cm. The decline in levels of methylmercury at the sediment/water interface could also infer the diffusion of methylmercury into the water column, which represents a potential pathway for accumulation in aquatic biota.

Methylation/demethylation reactions are therefore controlled by dissolved oxygen, sulphur and the nature of the bacterial communities present but temperature also plays an important role leading to seasonal changes in methylmercury loadings. Maximum methylmercury production occurred in the summer when conditions were optimised for its formation and retention within the sediment system (high temperatures, low oxygen availability) and were lowest in the autumn when lower temperature conditions (≈6°C) reduced microbial activity, slowing down or halting bacterial mediated methylation reactions. Methylmercury was routinely detected at concentrations reaching 25-33 $\mu g\ kg^{-1}$ during the summer months and declined by ≈30-50% in the autumn. The behaviour of methylmercury is, however, highly variable. Some sediments contained undetectable methylmercury concentrations in the autumn, while others displayed levels comparable to summer concentrations. Further research is needed to further elucidate the factors controlling mercury methylation within the River Yare system.

Recommendations

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

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

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

1. The main recommendation is to refrain from all dredging operations unless they are essential.

2. If dredging activity is unavoidable then the following precautions should be taken:

2.1. Dredging should be undertaken in the late autumn or winter periods following a prolonged period of cold weather. This will minimise the activity of methylating and sulphate reducing bacteria and may help to minimise methylmercury formation.

Do not undertake dredging activities in:

- The spring and summer, or at other times of the year if temperatures are high.
- During period of saline intrusions.
- During periods of algal blooms.

2.2. Remove **all** contaminated sediments. This may require site investigations to determine the absolute depth of contamination at specific sites.

2.3. Attempts should be made to minimise sediment remobilization during the dredging operations by the adoption of appropriate dredging technologies.

2.4. All dredge spoil derived from the 'contaminated reach' should be properly disposed of in a licensed, fully clay lined, disposal site. This includes sediments from the Broads and small inlets and moorings. It **should not** be placed on the river banks, even for flood defence purposes. Uncontaminated sediment from the lower river reaches can be used for this purpose if necessary.

2.5. Prior notification of dredging operations should be made to the Broads Authority and a detailed log should be kept of all dredging operations undertaken on the contaminated reach. This should include:

i) reasons for dredging.

ii) written notification to the dredging contractor authorising the dredging operation, detailing any operational restrictions.

iii) definitive location of dredging.

iv) quantity and depth of sediment removed.

v) details of precautions taken to minimise remobilization and sediment re-entry into the system.

vi) precise location of dredge spoil disposal at the licensed disposal site.

3. An additional precaution that could be taken if the 'do nothing strategy' is subsequently adopted, is to minimise reworking of upper sediment layers by reducing disturbance by boating traffic in shallow water areas, such as the Broads. The options could range from a total ban on boat traffic through the Broads to a review of speed limit restrictions. This may help to reduce surface concentrations of total mercury by encouraging the deposition of clean sediment overlay.

4. Instrumental surveying of bottom sediments types should be undertaken to provide a detailed picture of bottom sediment characteristics. This would be invaluable for estimating the depth of contamination in specific river reaches and the mercury burden in the sediment compartment.

5. To undertake an additional coring exercise in the light of Point 4 to define the depth of contamination in areas of high particulate sedimentation.

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

6. To continue the annual monitoring of surficial sediments using the pre-designated transects and sampling strategy employed on former Yare surveys. Monitoring should be undertaken in July to minimise seasonal influences.

7. Routine monitoring to track the extent and frequency of saline intrusions on the River Yare is required in order to predict the impact of saline intrusions upon mercury remobilization from the sediment to the overlying water.

8. Further research to assess the impact of large scale sediment disturbance upon mercury mobility and availability needs to be undertaken, together with an assessment on the long term consequences of dredge spoil disposal.

9. To more fully elucidate the role of bacteria as methylating agents and to more clearly evaluate the links with the seasonal cycling of sulphur and iron.

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