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Mercury, Methylmercury and Copper in the River Yare, Norfolk

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

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## Summary Report to the Environment Agency Project No. OI/420/10/A

Since 1986 Imperial College has produced 3 reports to the National Rivers Authority for Project OI/420/10/A, this is a summary of the third and final report submitted by Imperial College of Science, Technology and Medicine, London, to the Environment Agency on the mercury, methylmercury and copper contamination in the River Yare, Norfolk. The report 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 Environment Agency in the management of the contaminated reach of the R. Yare and the surrounding environments it effects.



Figure 1. River Yare Sampling Transect Locations.

River bottom sediment samples were collected annually by Imperial College along transects for a 30 km stretch of the river, with each transect containing at least 3 grab samples with the exception of 1987 when only one sample per location was collected (Figure 1).

Sediments were seived to <1 mm, digested with a modified aqua regia in a microwave digester and analysed for Hg and Cu using the appropriate atomic absorption method. Sediments were subsequently extracted for methyl mercury which was determined using atomic fluorscence, the methods are described within the report. Fish, eel and roach, were supplied by the NRA and were analysed for mercury and methyl mercury. Quality control was maintained through the use of certified reference materials, duplicate digestions and replicate analyses.

Mercury and copper contamination were first identified in the River Yare in 1984 when the then Anglian Water Authority had samples of roach analysed for Hg and were found to have an average Hg concentration of 0.44 mg kg<sup>-1</sup>. A subsequent investigation of river 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 (Figure 1).

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 mg kg<sup>-1</sup> 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. The concentration of Hg in the final effluent has been reduced to less than 0.2 µg l<sup>-1</sup> since 1994 from 20 µg l<sup>-1</sup> in 1986. The copper concentration has been reduced by 33% to an average of 5 µg l<sup>-1</sup> in the final effluent discharged to the R. |Yare. Highly contaminated bottom sediments have gradually become buried by a cleaner overlay of sediments. Sediment cores collected in 1995 show that the most contaminated sediment near the STW is now buried 25-35 cm below the sediment surface (Figure 2).

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Figure 2. Distribution of Hg and Cu with depth in cores collected at Whitlingham, Rockland Broad and Cantley in 1995.

Remobilisation of contaminated sediments by 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. As shown in Figure 2 Hg is buried in the sediments of Rockland Broad. 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.

As a result of this study it has been recommended that:

- 1. Emissions of Hg and Cu to the river from Whitlingham STW must continue to be strictly monitored by the Environment Agency.
- 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. 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

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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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