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HALOGENATED HYDROCARBONS AND MERCURY IN SEDIMENTS FROM THE WESTON CANAL, MERSEYSIDE

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INTRODUCTION

The Weston Canal is part of an extensive canalisation of Merseyside river systems and associated with both the Weaver Navigation and the Manchester Ship Canal (MSC). The Weaver/Weston Canal system is regarded as estuarine in nature, with the limit of estuarine properties at Sutton Weaver, for the purposes of the River Quality Surveys.

This estuarine classification arises as a result of a hydrographically complex series of interactions between the Weston Canal, River Weaver/ Weaver Navigation and the MSC. The Weston Canal runs parallel to the Weaver/MSC for much of its course, giving onto the Runcorn and Weston Canal in the north through a lock system.

The Weaver Navigation debouches openly into the Manchester Ship Canal whose level is partially controlled by a water exchange with the Mersey at the Weaver sluices. Shipping movements are largely through the Eastham locks into the Manchester Ship Canal and it is this route through which most water is considered to exit the system (see Langston 1986) Most of the higher locks into the Ship Canal are now disused. The Weaver sluices are operated to admit water on certain high tides to maintain the level in the MSC. A weir on the Weaver navigation and the Frodsham Lock control levels in the Weston Canal which communicates with the MSC at the Weston Marsh Lock. Part of the system is shown in FIGURE 1.

The Weston Canal is considered to be of bad quality as shown on map NWWA 02 and defined in the associated documents (DoE 1986). In common with other waterways in the vicinity, the canal is heavily industrialised and receives a considerable quantity of industrial effluent. At least 516,975 cubic metres of effluent per day are consented for discharge into the canal according to Water Authority records which if fully utilised would correspond to a net flow through the canal of 5.98 cubic metres per second. There is no apparent abstraction of water from the canal and so it follows that the bad quality of the canal water is due directly to the effluents discharged into it rather than a further deterioration of the water from the Weaver which is classified as poor.

Among the substances consented for discharge by the North West Water Authority in the canal are mercury and chlorinated hydrocarbons, both in milligram per litre quantities as may be ascertained from copies of the consents held on the public register establised under the Control of Pollution Act (1974).

The plants adjacent to the Weston Canal are known to manufacture a range of halogenated compounds ranging from

chlorofluorocarbons (CFCs) to solvents such as perchloroethylene. Free chlorine is produced in a chlor-alkali plant, and as a result mercury is discharged to the canal despite the use of a reclamation plant. Deposits are regularly dredged from the canal and pumped to the lagoon and dumpsite marked "A" in FIGURE 1.

Given the nature of the processes in use and the effluents discharged, sediments were sampled and some determined for a range of chlorinated compounds and mercury. The remainder were used to establish microbial enrichment cultures with a view to isolating bacteria able to degrade halogenated hydrocarbons.

METHOD AND MATERIALS

Samples of sediment were obtained from the Weston Canal at the points indicated in FIGURE 1. Samples were obtained using a 10 centimetre Ekman grab transferred to a 350ml acid washed polythene bottle and transported to the analysing laboratory in the case of sample Nos: 6, 7, 8 & 10. All other samples were used for microbiological studies to be reported later. Samples were analysed for mercury using a cold vapour atomic absorption method. Volatile halogenated hydrocarbons were determined using a headspace method and quantified against an external standard of dichloromethane. Semi-volatile compounds were were extracted in toluene and estimated against a deuterated napthalene internal standard. All samples were run using capillary gas chromatography/ mass spectrometry.

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RESULTS

Results are given in TABLES I & II. TABLE I reports the results in mg/kg for each sediment on an "as received" basis by the analysing laboratory. TABLE II reports the results of these analyses adjusted for water losses at 105C, i.e. on a dry weight basis in mg/kg

Chemical	Sample No: (mg/kg wet weight) 6	7	8	10
Dichloroethane	3	Trace	-	-
Chloroform	-	60	1	-
Carbon tetrachloride	-	300	1	-
Trichloroethene	-	Trace	1	-
Tetrachloroethene	-	30	2	-
Hexachloroethane	-	Trace	-	-
Hexachlorobutadiene	6	4	-	-
Hexachlorobenzene	1	250	2	8
Dichlorobenzene	-	-	-	1
Mercury	94.5	39.2	13.4	31.4
Loss at 105C	52.7%	75.2%	77.9%	47.9%

TABLE I: Content of chlorinated hydrocarbons and mercury in sediments from the Weston Canal. All quantitiies are in mg/kg (ppm) wet weight.

Chemical	Sample No: (mg/kg dry weight) 6	7	8	10
Dichloroethane	6.3	N/A	-	-
Chloroform	-	241.9	4.5	-
Carbon tetrachloride	-	1209.6	4.5	-
Trichloroethene	-	N/A	4.5	-
Tetrachloroethene	-	120.9	9.0	-
Hexachloroethane	-	N/A	-	-
Hexachlorobutadiene	12.6	16.1	-	-
Hexachlorobenzene	2.1	1008.0	9.0	15.3
Dichlorobenzene	-	-	-	1.9
Mercury	199.7	158.0	60.6	60.2
Loss at 105C	52.7%	75.2%	77.9%	47.9%

TABLE I: Content of chlorinated hydrocarbons and mercury in sediments from the Weston Canal. All quantities are in mg/kg (ppm) dry weight. N/A (not applicable) applies to values given as "Trace" in TABLE I. Conversion formula used:

$$\frac{100}{100-x} \cdot y = z$$

where x = percentage weight loss at 105C
y = wet weight value in mg/kg
z = adjusted value Loss at 105C refers to weight loss of wet sample at this temperature as a percentage.

COMMENTS

From the results, it is clear that sediments of the Weston

Canal are very highly contaminated with chlorinated hydrocarbons and mercury. The sediments sampled ranged in type from fine black anoxic mud with relatively low water content to fluid blue and yellow deposits smelling strongly of hydrogen sulphide. These probably arise from the suspended solids content of the discharges. These deposits are regularly dredged and pumped to a settling lagoon marked "A" in FIGURE 1 (see:ENDS 1988).

The differences in the analysed components at each sampling site are probably a reflection of losses to the atmosphere of the more volatile components. The semi-volatile hexachlorobenzene was detectable some distance away from the discharge at site 10. The dichlorobenzene detected in sample 10 may be the result of chemical changes taking place after discharge of the effluent. It is more likely, however, to be due to an additional input since hexachlorobenzene is chemically extremely stable. Mercury levels also appear to diminish with increased distance from the discharge area, and this suggests that it is relatively conservative to the material removed by dredging.

In wet weight terms, the most highly contaminated sediment with respect to mercury was found at site No: 6 at a level of 94.5 ppm. (In dry weight terms this converts to 199.7 ppm). This concentration is not regarded as a special waste (DoE 1985). The same is true for the content, combined or separate, of chlorinated materials although it should be noted that several have proven carcinogenic properties in animal models. Moreover it is admitted that the 1% concentration used in defining special wastes is "suggested somewhat arbitrarily" (DoE 1985).

Carbon tetrachloride is used extensively in the production of chlorofluorocarbons (CFCs), in metal degreasing and and other solvent applications. The discharge of carbon tetrachloride is limited by EC directive 86/280/EEC to be complied with as of 1.1.88. This sets monthly emission standards of 1.5mg/l of effluent discharged whilst daily values are set at 3.0 mg/l. For the aquatic environment, quality objectives of 12 ug/l of CCl_4 are set. Given the levels found in the sediment it seems possible that these standards are not being met. Although carbon tetrachloride is not thought to biaccumulate significantly it is nonetheless capable of causing serious changes in cell metabolism which is refelected in mitotic repopulation of affected liver tissue (Droy et al. 1988).

The presence of such high levels of hexachlorobenzene in the sediments must be viewed with extreme concern due to its bioaccumulative and persistent character. Hexachlorobenzene is a well known by-product of chlorine, vinyl chloride and chlorinated solvent manufacture (see: eg Mumma & Lawless 1975). Inimical effects upon biological systems have been widely demonstrated.

Bacterial populations can be modified (Hamdy 1988) while in higher organisms such as birds, localisation of HCB and its metabolites has been found to occur in a wide range of organ systems including the bone marrow, adrenals, body fat and liver (Ingebrigtsen 1981). Brevik (1983) presents details of HCB in Norwegian environmental matrices from a variety of compartments including fish, human milk and fat, seabirds and aquatic invertebrates. HCB clearly has the potential to behave in a similar way to other organochlorine compounds in the wider environment. There is evidence of partial degradation of HCB burdens in mammals administered the chemical. Degradation products include chlorophenols and chlorobenzenes and a variety of sulphur containing chlorinated substances. The toxicological properties of most of these remain unknown (see Renner 1988).

Every effort should be made to minimise the discharge of this substance. The fate of HCB pumped into the lagoon as part of the dredge spoil should be determined since it is likely that a substantial proportion will be lost to the atmosphere. It would be desirable to obtain biopsy samples of human fat from members of the local community to assess exposure commitment to the various materials released from this plant. Further, urgent investigation of human breastmilk levels should be carried out since this constitutes a known and potentially important transfer mechanism. Finally, hexachlorobenzene is one of a number of possible by-products of halogenated hydrocarbon manufacturing processes. Others include the notorious polychlorinated dibenzo-p-dioxins, the polychlorinated dibenzofurans and octachlorostyrene. The sediments of the Weston Canal should be analysed for these materials as a matter of urgency as should other environmental matrices.

While carbon tetrachloride and hexachlorobenzene constitute the bulk of the halogenated contaminants in the Weston Canal, others such as chloroform and tetrachloroethene are present at levels which even in the absence of any other materials would constitute grounds for concern. Allan (1988) considers that 190 ug/l TCE found in the St Clair River, part of the highly polluted Great Lakes system is "extreme". Chloroform concentrations in Lake Ontario nearshore waters reach 0.1 ug/l. The sediment burden associated with these levels is not reported.

The full environmental implications of the series of discharges resulting in the contamination of the Weston Canal sediments are, of course, unknown. Of the chlorinated materials detected in the sediment analyses, all are contained in the EEC List I or "blacklist" (Gardiner and Mance 1984). Mercury discharges from the chlor-alkali industry are the subject of EC directive (OJ No: L81, 27.3.82). It is likely that this directive is being breached. This possibility is supported by the COPA

public register data which record over 90 breaches of statutory consent conditions in 1986. It seems that, on a fundamental level, the Weston Canal which is notionally part of the UK public waterways system is being used as part of an effluent treatment system. This in turn appears to involve at best simple volatilization of contaminants to the atmosphere. Moreover the process completely ignores any imperative to conform to a precautionary approach. Ultimately this may be putting both the wider environment and local communities at risk.

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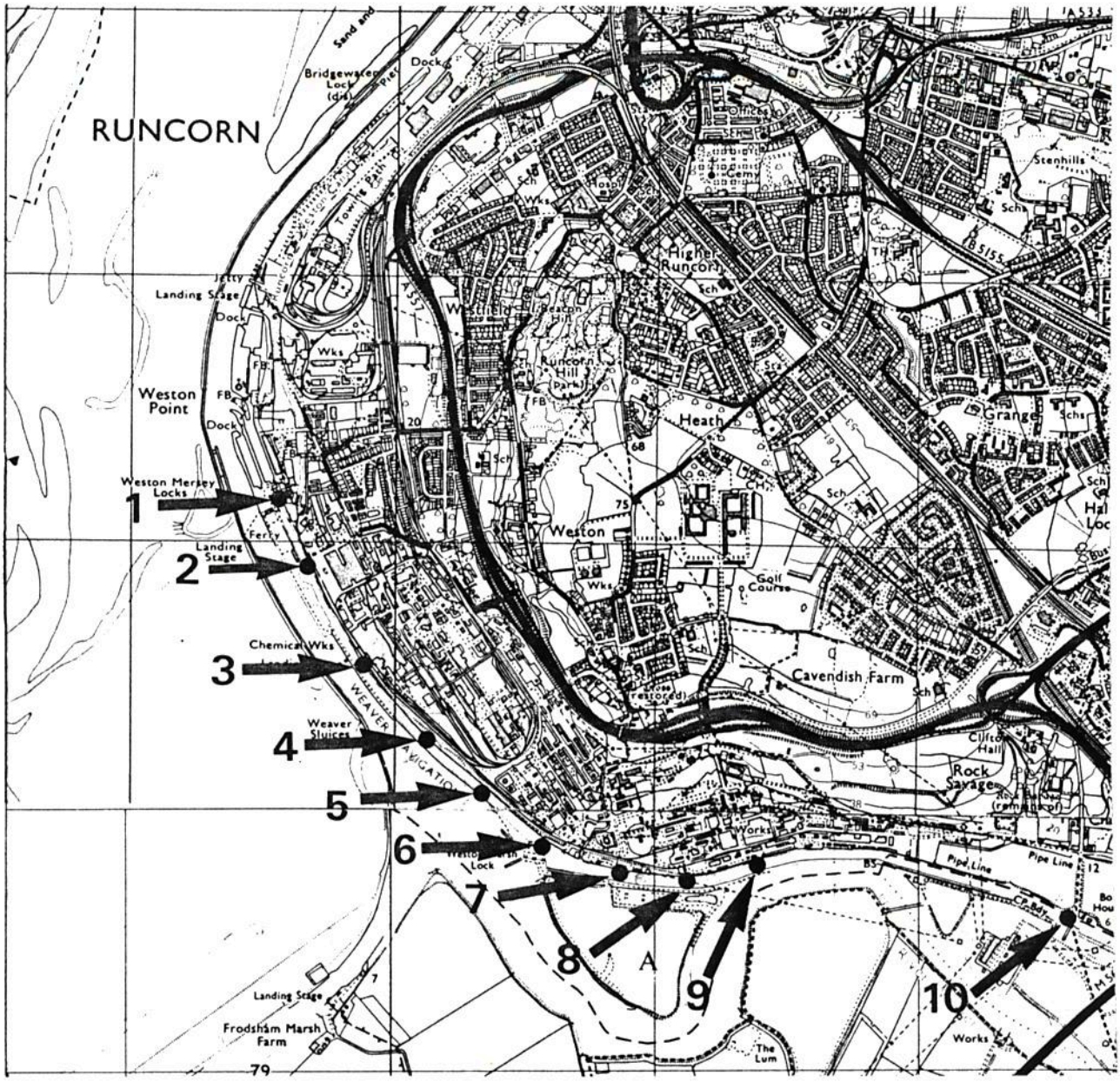

FIGURE 1: Sampling locations on the Weston Canal, Merseyside. Sample Nos: 1-5 and 9 were used to set up microbial enrichment cultures for microbes able to degrade halogenated hydrocarbons. Sample Nos: 6,7,8 & 10 were analysed for mercury and a suite of volatile and semi-volatile halogenated hydrocarbons. The results are reported in the text together with the sampling and analytical methods used. Samples were taken on 26 September 1988 between 1330 and 1500 hours.

Base Map is a composite at approximately the same scale of Ordnance Survey Pathfinder Series maps, Sheets: SJ 47/57 (Ellesmere Port [East]) and SJ 48/58 (Widnes), Scale 1:25,000