Pesticides in Dee Estuary Sediments, NW England; Implications for Pollution Study of Coastal Environments

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Received 11 Aug 2002; revised 15 Mar 2003

Abstract

Core samples from the sediments of the Dee Estuary were collected from the chosen sites to study the distribution of pesticides in the sediments. The organic compounds were extracted by a microwave sample preparation system from 56 sediment samples and gas chromatography. Mass spectrometry (GC-MS) was employed for the organic compound analysis. Distribution of *n*-alkanes in the analysed sediments and calculation of their carbon preference index indicate a continental source for the organic compounds in all samples. Different search strategies were applied to find pesticides in the sediments. Maneb was the only pesticide found in the samples. The distribution of Maneb showed a zigzag pattern with depth in all the four studied areas in the Dee estuary, corresponding to the pattern of distribution of total organics. The highest concentration level of Maneb was 16.33 ng/g of sediment at a depth of 14 cm. The distribution of Maneb with depth is attributed to the seasonal application and release to the environment.

Keywords: *Pesticides, Maneb, Environmental Pollution, Dee Estuary, and Sediments.*

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Introduction

Pesticides, harmful substances for health, unlike most other classes of chemicals, are designed to be released deliberately into the environment to control pests and diseases, and thus it is important to assess any risk that may arise from their use. Huge amounts of pesticides are being used annually to protect crops. Most of these pesticides have short half-life and degrade to other compounds but some are more resistant and remain in water or soil (sediments) for long time and inter the food chain of animals and human (Calamari and Bacci, 1987). Several mass destruction of wild life, because of misuse of pesticides, are reported(Cooper, 1991). Numerous pesticide-related diseases are identified in human and domestic animals (Perry et al., 1989; Hodgson, et.al.,1991).All these facts make it necessary to monitor the release to and accumulation of pesticides in environment. An attempt has been made in this paper to elucidate the fate of pesticides in the Dee estuary sediments.

The Dee Estuary is located in the north west of England to the west of Chester (Fig. 1). This estuary consists of large areas of inter-tidal sand flats and mud with extensive salt marshes at the head of the estuary and along the eastern coastline. The axial distance from Chester to the mouth of the estuary (Liverpool Bay, Irish Sea) is 35 km. The estuary consists of about 87 km^2 of inter-tidal sand and mud flats and about 15 km^2 of salt marshes. The Dee Estuary is amongst five most important estuaries in Britain and ten most important in

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Europe for wild life especially waders and wild fouls (Gillham, 1978). It is a valuable staging post for migrating birds in both spring and autumn and supports large number of waders throughout the winter. The Dee Estuary and the adjacent areas form a complex ecological system in which a variety of plant and animal communities occur. The Estuary has been used for centuries by man and some uses have affected the ecology of the estuary seriously. In particular, reclamation of salt marsh, accumulation of industrial activities and discharge of waste materials have had serious consequences. The Dee Estuary is probably one of the most polluted environments in the UK in terms of trace metals (Cr, Cu, Pb, Hg, Ni and Zn) (Hunt, 1985; Turner et al., 1994; Taylor, 1986).

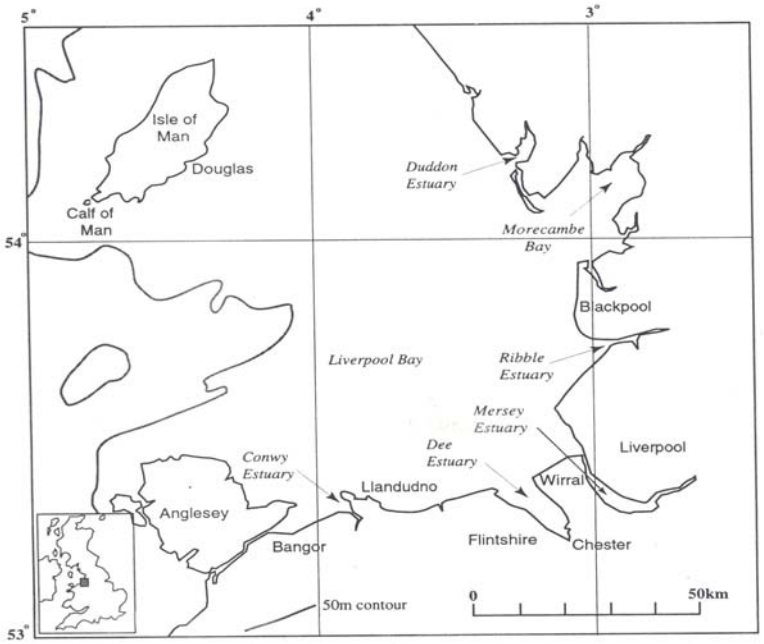


Fig. 1: Geographical Location of the Dee estuary in the England

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Sampling and Organic Material Extraction

Four sampling sites in the Dee Estuary were chosen. These sites are shown in Fig. 2 Sediment cores were collected from these sites.

Description of cores is provided in Fig. 3 The sampled cores are made mainly of clay-rich materials with intercalations of sandy layers, plant roots and dark swirl textures which probably are organic-rich materials. 56 samples were prepared from different depth of the four sampled cores. A mixture of dichloromethane as solvent and squalane as internal standard was used to dissolve the organic compounds in the sediments (Chau and Afghan, 1982). An MDS-2000 microwave digestion system with Teflon vessels in Manchester University was used to extract the organic materials. The total amounts of extracted organic components with depth are illustrated for each area in Fig. 4 The distribution of total organic materials (extracted from the sediment samples) shows a zigzag pattern for Greenfield area, Mostyn Quay area and Pincton Pool area. The distribution of total organic materials for Mostyn Dock area is uniform between depths of 6cm to depth of 18 cm.

Analysis and Results

A combination of gas chromatography-mass spectrometry(GC-MS) was used in this study to identify the samples (Lewis, 1997; Lithgow, 1997). A Hewlett Packard 5890 gas chromatograph coupled with a VG-Trio-1000 quadruple mass spectrometer fitted with 30m×0.32mm DB-5 Durabond FSOT column was used to identify the organic

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materials in the samples. 2,6,10,15,19,23-Hexamethyltetracosane (or squalane) was used as standard.

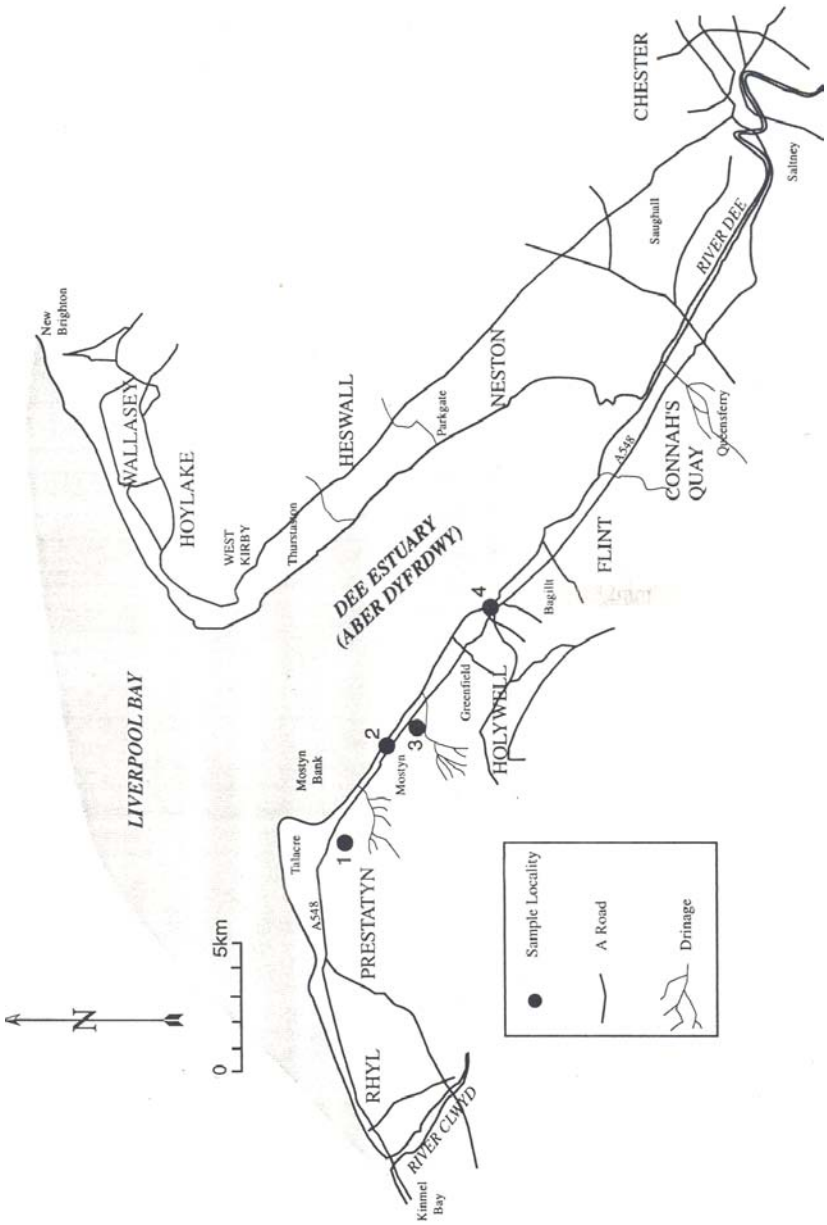


Fig. 2: SampleLocalities in the Dee area, 1= Pincton Pool area, 2= Mstyn Quay area, 3= Mostyn Docks area and 4= Greenfield area

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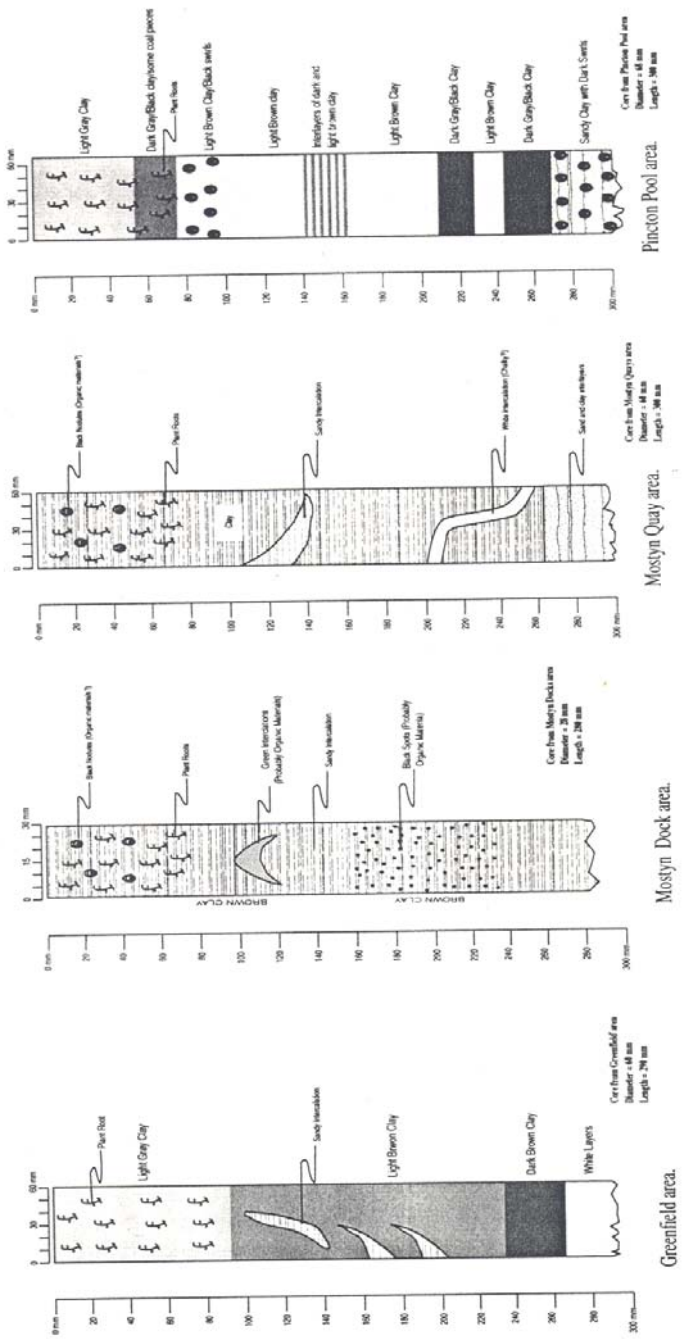


Fig. 3: Description of core samples collected from four sites in the Dee estuary

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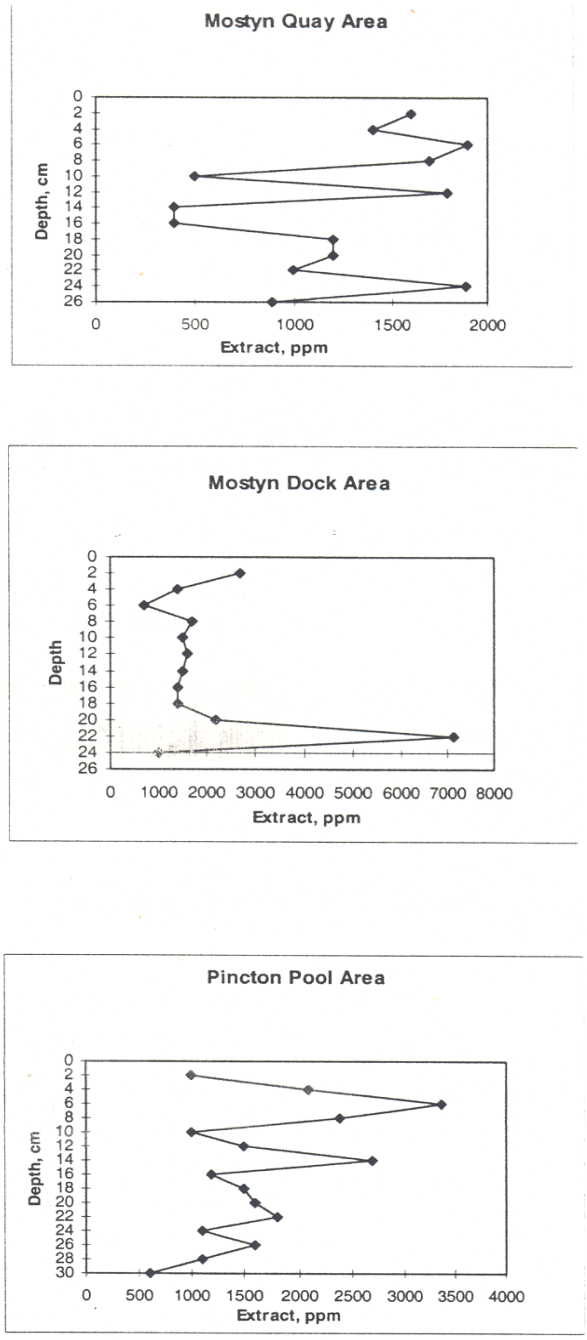


Fig. 4: Total Organic Compounds extract versus depth in three sites in the Dee estuary. The graphs show a zigzag pattern

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A study of carbon preference index (CPI) was carried out on *n*-alkanes in organic compounds in the sediments, in order to find out the source of the organic materials (Bray and Evans, 1961; Clark and Blumer, 1967; Scalan and Smith, 1970). The graphs in Fig.5 illustrate the relation between number of carbon in *n*-alkanes and depth of the samples in the Greenfield area as a representative for all four areas. Fig. 6 shows the relationship between CPI and depth for all areas. Calculated CPIs for all sites are higher than 1 indicating a continental source for the organic compounds in the sediments.

In order to investigate the presence of pesticides in the analysed samples threefold strategy was used as stated below:

a) Mass spectrums for all compounds were identified using Library of Mass Lab.

b) Ion search through all total ion chromatograms (TIC) was carried out for the key pesticide concentrations.

c) Visual comparison of all mass spectrums against authentic mass spectrum for all major pesticide groups was done.

Maneb was the only pesticide identified in the samples. Maneb is a protective fungicide effective against many diseases of foliage, particularly the blight of potato and tomato, as spray concentration of 150-200 g/100 litre (Worthing, 1979). The formula is $(C_4H_6MnN_2S_4)$ *x*, which is a polymeric salt of ethylenebisdithiocarbamic acid. The mass spectrum of Mane in the sediments is provided in Fig. 7 The highest concentration of Maneb is 2.07 ng/g sediment in the

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Greenfield area at a depth of 12 cm, 13.07 ng/g sediment in the Mostyn Docks area at a depth of 22 cm, 9.45 ng/g sediment in the Mostyn Quay area at a depth of 10 cm and 16.33 ng/g sediment in the Pincton Pool area at a depth of 14 cm (Rahbar Saadat, 1999). The concentration of Maneb in the sediments from four sites in the Dee estuary, with depth, are illustrated in Fig. 8.

Discussion and Conclusions

The main point to be discussed is lack of other types of pesticides species in the sediments of the studied area, the variation of Maneb concentration with depth and the lack of Maneb at the surface of the sediments almost in all studied areas. Two possibilities can be considered for the lack of other types of pesticides in the Dee estuary: a) no other types of pesticides are used in the area. This possibility could be reasonable since the whole Dee area is influenced by industrial activities rather than agricultural activities. b) Some other types of pesticides are used but since their half-life was very short, they are degraded and therefore are not present in the sediments anymore. This assumption could be correct because there are common pesticides (e.g. Malathion, a phosphororganic pesticide with a half-life of 3 to 7 days which rapidly degrades in aqueous environment; Garner et al., 1986; Howard, 1990). Either of the above mentioned considerations could be the reason for lack of the other types of pesticides in the Dee area.

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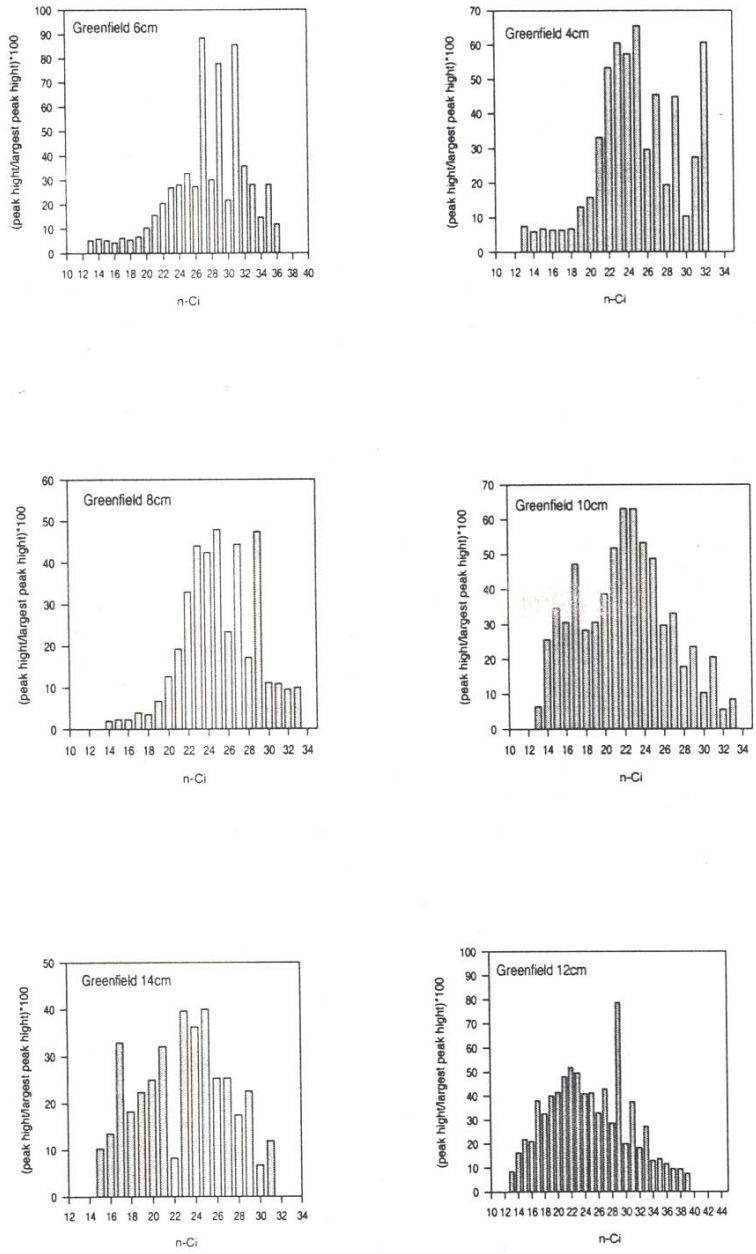


Fig. 5: Distribution of n-alkanes with different C number at different depth in the Greenfield site

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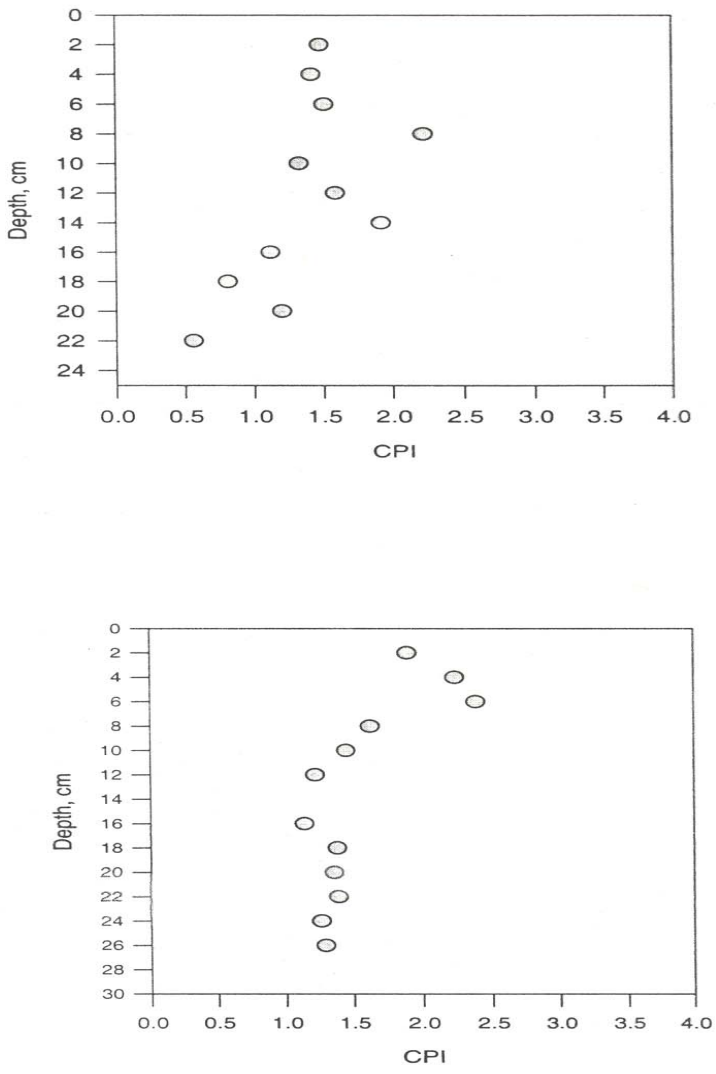


Fig. 6: Relationship between CPI (Carbon preference index) anceepth for samples from the Mostyn Dock site (top) and Mostyn Quay site (bottom)

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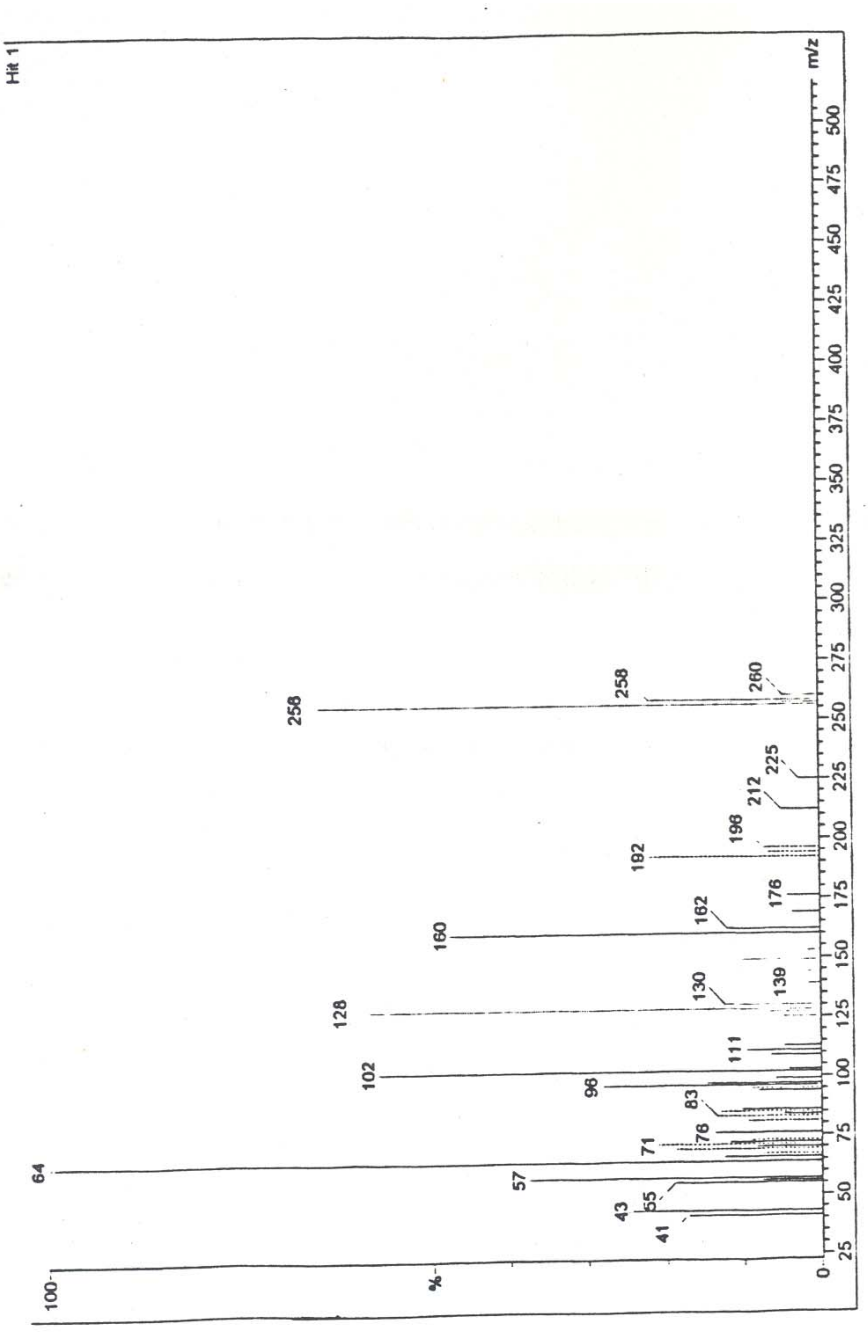


Fig. 7: Mass spectrogram of Maneb

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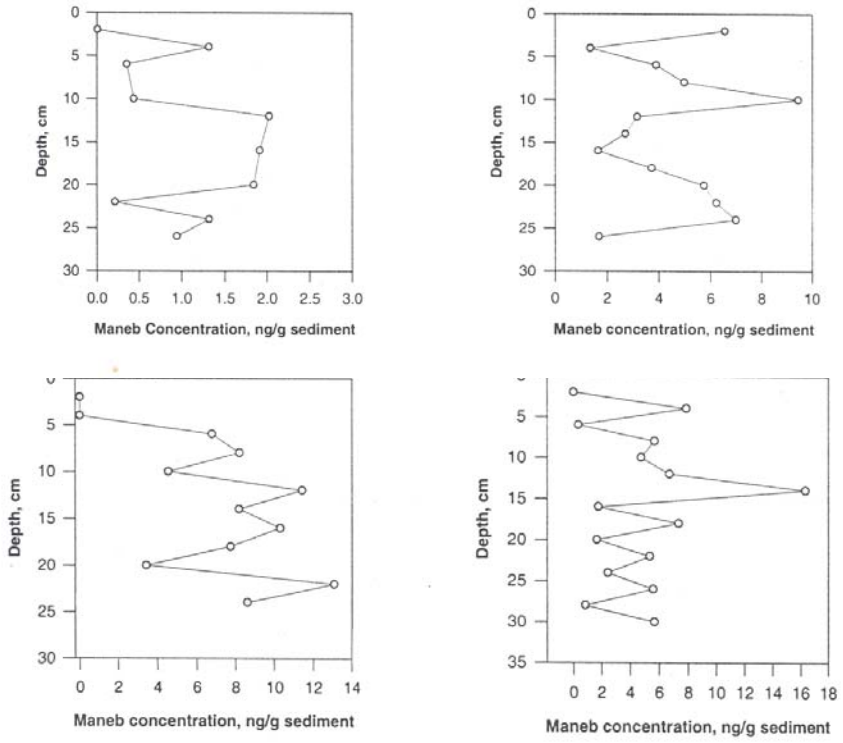


Fig. 8: Distribution of Maneb in the sediments by depth. From top left, clockwise greenfild site, Mostyn Quay site, Pincton Pool site and Mostyn Dock site

Three reasons can be considered for the zigzag distribution pattern of Maneb in the sediments with depth. a) The application of Maneb is in regular time intervals. Pesticides are used normally at spring and summer times and they are not applied at autumn and winter. Application of Maneb at spring and summer times will cause concentration of the pesticide in the sediments deposited at this time while the sediments deposited in autumn and winter will be free of pesticides. This produces a zigzag distribution pattern by depth in the sediments. b) The second probable reason for the zigzag behaviour

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could be the inhomogeneity in sediments. Organic materials can accumulate in the clay-rich parts of the sediments while their accumulation in the sand-rich parts is limited (Yaron et al., 1996). Study of cores from the areas shows interlayers of clay-rich materials with intercalation of sand-rich materials. Although this interlayering is not systematic, it still can cause the zigzag distribution pattern of Maneb. c) The third possibility is rhythmic concentration of organic materials in the sediments. Maneb is easily soluble in the organic materials (Worthing, 1979; Sensi and Chen, 1989); therefore it is reasonable to relate its concentration to the concentration of the total organic materials in the sediments.

Maneb has a very low concentration (almost absent) in the three sites in the studied areas at the surface of the sediments (up to a depth of 2cm). The possible reasons for this observation are a) because Maneb at the surface is in contact with more oxidised waters, it may degrade more quickly than Maneb at the depth. b) The absence of Maneb at the surface may be a result of lack of application of Maneb in the recent years. c) It may show a low-concentration point at the sequence of high-low distribution behaviour. Since Maneb at the surface of the sediments in the Mostyn Quay area reaches to 6.56 ng/g sediment, the third explanation seems to be more relevant for lack of Maneb at the surface of sediments in the other areas.

The distribution pattern of Maneb in the sediments by depth matches very closely with the distribution pattern of carbon preference

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index (CPI) and with total organic compounds extract.

In 1993, 703000 hectares of land was treated by Maneb in the Great Britain. 815 tons of this fungicide was applied in only England and Wales in 1991 (HMSO, 1996). In a monitoring by HMSO, 2085 ground water samples were analysed for Maneb. Limit of detection was 25 to 400 ng/litre, the highest concentration was 140,000ng/litre and the mean of concentration was 246.7 ng/litre (HMSO, 1996). Considering the highest concentration and assuming a weight of 1 g for one ml of water, the maximum concentration of Maneb is equivalent to 140 ng/g and the mean of concentration is 0.247 ng/g. Comparing these data with data obtained for Maneb concentration in the Dee estuary sediments, from this study, shows that the highest concentration in the Dee estuary sediments (16.33 ng/g sediment) is much higher than the mean of concentrations for groundwater samples and much lower than the recorded maximum concentration for the groundwater samples. Because the highest concentration of Maneb in the Dee estuary comes from sediments and from a depth of 14 cm, it is reasonable to consider that this amount does not represent the actual concentration at the time of application of Maneb and that a while after Maneb in sediments is subjected to degradation. Owing to the type of the sedimentary basin which is an estuary and because of the turbid nature of the sediments it is not possible to relate the thickness of the sediments to their age accurately but 14 cm of sediment may have been accumulated during few years which is a enough time

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period for degradation of much of the applied Maneb. If this assumption is true, then the amount of Maneb applied at the time corresponding to a depth of 14 cm had been substantial. Because Maneb in the sediments probably is not in direct contact with living organisms and because the concentration of Maneb in the sediments is not necessarily the same as its concentration in the aqueous environment and food chain of living organisms, it is not easy to assess the risk of Maneb in the sediments. Overall, the lack of other pesticides especially chlorinated pesticides with long half-life, which would had been accumulated in the sediments in case of application, and low concentration of Maneb in comparison with maximum concentration in the groundwater samples (especially at the surface of the sediments) make the Dee estuary a relatively clean environment in terms of pesticide pollution.

The following studies can be suggested in context of the present study to find out more about the fate of pesticides in the Dee estuary.

-Study of the concentration of Maneb and other possible pesticides in water of the estuary at different agricultural seasons to find the peak concentration of pesticides.

- Statistical investigation of amount and type of pesticides, which are used by farmers in the area and comparing the results with findings from this study.
- Study of the concentration of pesticides at depth higher than 35 cm to find any possible concentration of pesticides with long

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half-life especially chlorinated pesticides, which may have been used long time ago, and traces remain in the sediments.

Acknowledgements

We would like to thank Dr. Dave Cooke from Manchester University, Department of Earth Sciences for his constructive suggestions and his help in this study and Dr. Keith Hall from Manchester University, Department of Chemistry for providing the MassLab software. Constructive comments by two anonymous referees of the Journal of Engineering and environmental Geology of Teacher Training University improved the manuscript.

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