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Dieldrin in Fish and Shellfish from the Mersey Estuary and Liverpool Bay

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The Mersey Estuary is the outlet for one of the most extensive river catchment systems in Britain, covering an area of some 5000 sq km, and encompassing a large part of Cheshire and South Lancashire as well as the conurbations of Liverpool and Manchester. The modern history of the estuary is inextricably linked with the foundation of British industry, being amongst the first centres of manufacturing during the Industrial Revolution. The Mersey Basin also supports a human population of some 5 million and widespread dairy farming. Farm effluents also affect the upper river system of the Mersey catchment from which residual pesticides are dispersed to the estuary and the Irish Sea (NRA 1995).

In Britain, the use of chlorinated pesticides such as dieldrin has been banned for over 20 years because of their persistent character (WHO 1989). However, dieldrin, a product of peracid epoxidation of aldrin, has a long environmental residence time, and toxicological implications for biota (Boer and Brinkman 1994) because of its propensity to transfer along food chains. Organochlorines have been implicated in recent disturbing events including reproductive failure in seal populations (Reijnders 1986 ; Harding and Addison 1986; Morris et al. 1989) and impaired reproductive success in marine fish (von Westernhagen et al. 1981; Barnthouse et al. 1990). Such episodes are relevant to the circumstances of inner Liverpool Bay given its resident seal populations and organochlorine signature (Johnston et al. 1991; McNeish et a1.1997).

This paper reports upon one aspect of the organochlorine status of the Mersey Estuary and Liverpool Bay, namely the dieldrin concentrations of migratory roundfish and the more sedentary flatfish populations that dominate the commercial catch, fish landed by anglers and the food chains leading to marine mammals, including seals.

MATERIALS AND METHODS

Sampling was undertaken between 1992 and 1995 during all seasons of the year and using inshore fishing boats. Two sites were targeted in the inner Mersey Estuary, Eastham and Garston, and two as representing the outer Mersey Estuary/Liverpool Bay, namely Rock Channel and Great Burbo Bank (Figure 1). Populations of flatfish sampled were plaice (>25cm) (*Pleuronectes platessa*), dab (>20cm) (*Limanda limanda*), flounder (>25cm) (*Platichthys flesus*) and Dover sole (*Solea solea*). Roundfish taken for analysis were whiting (>27cm) (*Merlangius merlangus*) and cod (>35cm) (*Gadus morhua*). Site-species combinations where

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fishing was conducted successfully are shown in Table 1, except for plaice (Figure 2). Comparative samples were to be collected from the Solway Firth where, in practice, only flounder were caught in sufficient numbers. Small scale sampling of the invertebrate community of the Mersey Estuary was also undertaken. Species sampled included; shrimps (*Crangon vulgaris*), mussels (*Mytilus edulis*), starfish (*Asteria rubens*), whelks (*Buccinium undatum*) and hermit crabs (*Pagurus bernhardus*).

Muscle tissue was analysed from samples of flatfish and roundfish as this constitutes an integrated measure of exposure over long periods of time. Specimens were frozen upon landing, later defrosted, weighed, measured and dissected. Muscle samples were then refrozen to await analysis. Invertebrates were analysed on a composite soft tissue basis.

Analytical methods for dieldrin mainly followed techniques developed by the Ministry of Agriculture, Fisheries and Food (Allchin et al. 1989). Five grams of

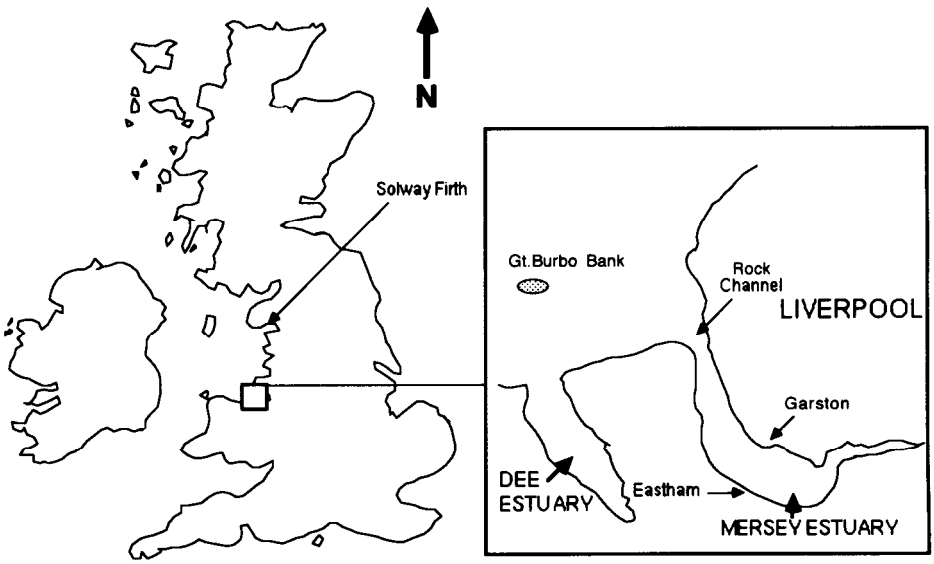

Figure 1. Sampling sites in the Mersey Estuary and Liverpool Bay

muscle tissue were ground with 30g of anhydrous Na_2SO_4 and then stored for 48h to complete dehydration. Samples were solvent-extracted for 4h with 120ml of n-hexane in a soxhlet assembly. Thimbles were spiked with decachlorobiphenyl as a recovery standard. After cooling, the extract was quantitatively transfered to a 100ml flask and made up to the mark. 50ml of extract were then removed for the gravimetric determination of hexane-extractable lipids (HEL).

Clean-up of the extracts was achieved using 5% deactivated Al_2O_3 topped with Na_2SO_4. To avoid exceeding the maximum lipid capacity of an Al_2O_3 column, typically 50mg, the appropriate volume of extract was calculated, reduced in volume to 1ml using a stream of nitrogen, and transferred quantitatively to the Al_2O_3 column. The column was then eluted with 20ml n-hexane, the first 16ml

collected and again reduced to 1ml volume. Fractionation was undertaken using 2g of 5% deactivated SiO_2 topped with Na_2SO_4. Cleaned-up extracts were fractionated by elution with 20ml of 2% tetrahydrofuran in n-hexane.

Analysis was undertaken on a Varian 3500 gas chromatograph (GC) fitted with an electron capture detector, a Varian 8035 autosampler and an automated DS651 data capture station. The GC was configured with a cool, on-column injector and a 3m long, 320µm i.d. deactivated fused silica retention gap connected to a 60m x 0.25 mm (i.d.) DB5 column of film thickness, 0.25µm. The GC was operated using H_2 as the carrier gas (40cm sec^{-1} average linear velocity), an injection volume of 1µl and an injector temperature of 60°C held for 1 min. with a temperature programme of 180°C min^{-1} to 280°C maintained to the end of the run. The initial column temperature was 80°C for 1 min., operated with a two-part temperature programme: 7.5°C min^{-1} to 200°C and 2.5°C min^{-1} to 280°C held for 5 min. The detector temperature was isothermal at 300°C and the make-up gas was N_2 used at 30ml min^{-1}. The internal standard was octachloronaphthalene

Quality assurance involved the use of rotating procedural blanks, and concentrating pesticide grade solvents to detect interfering peaks. Accuracy and precision were checked periodically by the analysis of standard reference material., SRM No. 1588 (Organics in Cod Liver Oil) (NIST, Maryland, USA). In this paper, unless otherwise stated, data are expressed on a wet tissue weight basis. Summary data in terms of hexane-extractable lipid (HEL) are also given in Table 1 and Figures 2-3.

RESULTS AND DISCUSSION

Data for dieldrin in muscle tissue of fish, except plaice, from the Mersey Estuary, Liverpool Bay and Solway Firth are summarised in Table 1.

Table 1. Dieldrin in fish from the Mersey Estuary and Solway Firth[a]

Species	Site	Wet wt. basis	HEL basis
Cod	Rock Channel	0.4 ± 0.2 (20)	131 ± 77 (20)
Whiting	Eastham	1.1 ± 0.4 (15)	407 ± 85 (15)
Whiting	Garston	1.0 ± 0.2 (22)	367 ± 67 (22)
Whiting	Rock Channel	0.4 ± 0.2 (22)	190 ± 76 (22)
Whiting	Gt.Burbo Bank	0.3 ± 0.1 (11)	120 ± 46 (11)
Dab	Rock Channel	4.5 ± 2.9 (11)	295 ± 142 (11)
Dab	Gt.Burbo Bank	1.2 ± 0.4 (44)	116 ± 27 (44)
Dover Sole	Garston	1.7 ± 1.0 (22)	480 ± 415 (22)
Dover Sole	Eastham	1.6 ± 1.5 (9)	774 ± 987 (9)
Dover Sole	Gt.Burbo Bank	0.9 ± 0.3 (22)	240 ± 100 (22)
Flounder	Garston	5.3 ± 2.1 (8)	1146 ± 486 (8)
Flounder	Rock Channel	1.6 ± 0.8 (11)	500 ± 225 (11)
Flounder	Gt.Burbo Bank	1.6 ± 1.4 (32)	320 ± 203 (32)
Flounder	Solway Firth	0.7 ± 0.3 (7)	145 ± 38 (7)

[a]All values in µg kg^{-1}, mean ± std. deviation. Replication in parentheses.

Concentrations in fish muscle were generally lowest in whiting (0.3-1.1 µg kg^{-1}) and cod (0.4 µg kg^{-1}), typical values for the latter being comparable to the north-

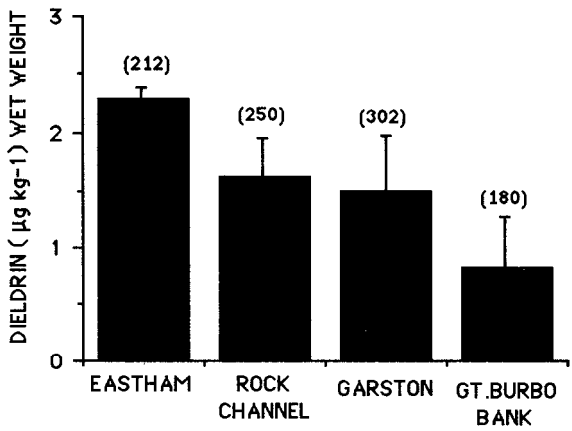

Figure 2 Dieldrin in plaice from Mersey Estuary sites. Values in parentheses are means on an HEL basis.

west Atlantic (0.2-0.3 µg kg^{-1}: Hellou et al. 1993). Highest levels of dieldrin were in flatfish, especially flounder from Garston (5.3 ± 2.1 µg kg^{-1}) and dab from Rock Channel (4.5 ± 2.9 µg kg^{-1}). These relatively high means may reflect the longer estuarine residence time of these two species of flatfish for feeding and breeding, but also their dietary preferences and the lipid content of their tissues. Particularly lipid-rich species from the Mersey Estuary, notably eels, have been reported as having high levels of dieldrin, 90 ± 60 µg kg^{-1} wet wt (Johnston et al . 1991).

Flatfish showed lower mean values for dieldrin at the outer estuary site of Gt. Burbo Bank than at the inner estuary sites, and most were in the range 0.9-1.6 µg kg^{-1}. The peak mean value, for plaice from Eastham, exceeded 2.0 µg kg^{-1} and dieldrin residues in this species showed a distinct seaward concentration gradient from the inner estuary to Great Burbo Bank. This latter site gave a lower mean value for dieldrin in plaice than for all other sites (Figure 2). Nearly all the mean values for dieldrin were below the 4 µg kg^{-1} given elsewhere as a nominal historical maximum level for dieldrin in muscle of fish in outer Liverpool Bay and the Irish Sea, and there is little distinction between these areas and other coastal sites around Britain, all of which show dieldrin values for flatfish and roundfish in the range 2-7 µg kg^{-1} (Franklin 1987).

Contemporary levels of dieldrin in the Mersey Estuary and the broader Irish Sea are extremely low compared with the British coastline two decades ago when, for example, values for fish from the Medway Estuary, off the south-east coast of England, were 7.4 - 210 µg kg^{-1} (Wharfe and Van der Broek 1978). However, contemporary levels of dieldrin in Mersey Estuary flounder, notably Garston (5.3 µg kg^{-1}), are still significantly higher than for the reference site at Solway Firth (0.7 µg kg^{-1}) (Table 1).

Invertebrates from Gt. Burbo Bank showed much higher dieldrin levels than in all fish species from this site (Figure 3). Mean values for whelk (4.7 ± 2.4 µg kg^{-1}) and hermit crab (12.9 ± 6.9 µg kg^{-1}) were, respectively, similar to and 2-3x greater than the highest mean for flatfish, namely flounder from Garston.

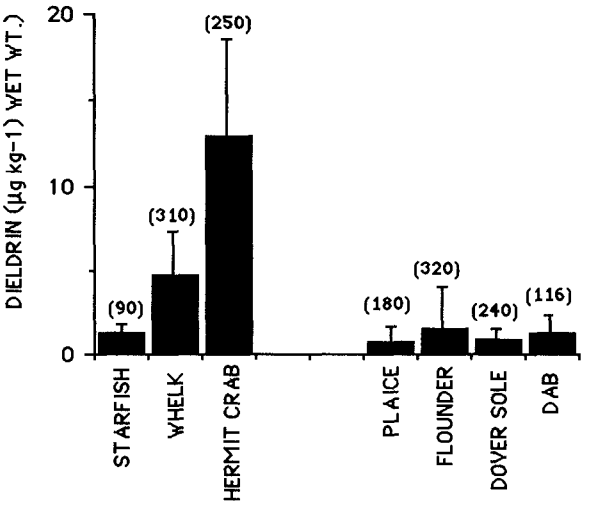

Figure 3 Dieldrin (mean ± SD) in invertebrates and fish from Gt. Burbo Bank. Values in parentheses are means on an HEL basis.

Since the whelk and hermit crab were sampled from Gt. Burbo Bank, which is generally less exposed to land-based sources of dieldrin than inner estuary sites, there are clearly factors of diet or age, or an unidentified offshore source of dieldrin, that give a clear distinction between different taxonomic groups or genera of marine invertebrates.

Shrimps and blue mussels from New Ferry gave lower mean values for dieldrin, of 0.8 µg kg^{-1} and 3.0 µg kg^{-1}, respectively. Dieldrin levels in mussels from the Mersey Estuary are not significantly elevated against a benchmark for most of the rest of the British coastline of 1-3 µg kg^{-1} (Franklin and Jones 1993). This range itself is much reduced compared with more than a decade ago (<1 - 413 µg kg^{-1}; Cowan 1981; 2-300 µg kg^{-1}; Murray 1982). Concentrations of dieldrin in the muscle of six fish species. sampled within the Mersey Estuary were between 0.3 and 2.3 µg kg^{-1}, a range that is again placed in perspective when it is considered that 2-4 µg kg^{-1} was typical of outer Liverpool Bay ten years ago (Franklin 1987).

Moreover, in this respect Liverpool Bay is considered not to differ from other coastal sites around Britain. Approvals for products containing dieldrin in the UK ceased in March, 1989 due to concerns over food chain bioaccumulation, and the impact upon non-target species, including predatory birds and mammals (Carson 1991). Residual dieldrin levels in fish thus appear to be reflecting the termination of approved use of this cyclodiene pesticide, since the residual concentrations are low for what still constitutes one of Britain's most vulnerable estuaries in terms of industrial and agricultural effluents. It is apparent that, at least in respect of specific chlorinated pesticides, the Mersey Estuary ecosystem continues to benefit from investment in sewage treatment and the increased regulatory controls over effluent discharges (Head and Jones 1991; NRA 1995).

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