

Dioxins in UK Estuaries

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Introduction

Estuaries receive waste from a number of diffuse and direct sources including outfalls, dump sites¹, landfill sites², and by atmospheric deposition³. The hydrodynamics of estuaries and coastal waters ensure that hydrophobic pollutants are widely distributed. Waters around the United Kingdom are significantly polluted with hydrophobic organic pollutants and it is suggested that such contamination may be adversely affecting marine life.

The problems associated with the analysis of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs and PCDFs) at the trace concentrations found in environmental samples have resulted in little comprehensive research on the behaviour of PCDDs and PCDFs in estuaries and coastal waters. Quantitative information on partitioning behaviour and sorption reaction kinetics is not yet available; much of which is required as a precursor to modelling PCDD/PCDF transport and fate in complex marine systems.

Approach and Methodology

The first objective of the current three year study has been to establish a primary database of estuarine data for general reference and calibration of future model developments. Such datasets are currently not available for UK estuarine and coastal waters. Over a period of 1 year, sediments samples have been taken using grab and core samplers from a number of key coastal locations around the UK including the Mersey, Tees, Tyne, Tweed, core samples from the Irish Sea and axial surveys of the Dee, Clyde and Humber.

Sample analysis has been carried out using methods adapted from analysis of soil samples. Samples were solvent extracted and the extractant concentrated. Liquid chromatography was then used to elute the extractant and the PCDD/PCDF collected, concentrated to a suitable volume. The PCDD/PCDF analysis was carried out by passing the sample through a gas chromatogram directly interfaced to a high resolution mass spectrometer (VG 70S) operating in the selected ion monitoring mode (SIM). Homolog groups and specific

congeners were identified and quantified by reference to ¹³C PCDD/PCDF IQSs.⁴

To supplement the PCDD/PCDF data, all samples were analysed for particulate CHN using a combustometric technique, lipid content using the Dole & Meinhurtz solvent extraction method and specific surface areas (SSA) established using BET N₂ adsorption⁵.

Results and Discussion

Homolog	Sediment Samples PCDD/DF (ppt dry weight)							
	Clyde Estuary Stations (Distance from Glasgow, km)					Morcambe Bay (Core Sample)		
	1 (3km)	2 (4km)	3 (5km)	4 (10km)	5 (22km)	0 cm	14cm	28cm
2,3,7,8 TCDD	16	7	19	9	1.5	6	0.3	0.3
TCDD	86	40	110	75	17	6	3	2.5
PeCDD	180	87	120	104	47	<0.6	<5.0	<3.0
HxCDD	100	85	100	73	34	10	<5.0	<5.0
HpCDD	800	405	550	528	79	40	18	10
OCDD	3500	1855	2180	1990	108	150	50	35
2,3,7,8 TCDF	28	17	20	17	3.5	2	3.0	0.5
TCDF	210	106	230	96	15.9	21	15	8
PeCDF	170	135	240	100	14.5	16	6	<3.0
HxCDF	320	310	420	210	28	35	<5.0	<5.0
HpCDF	350	260	460	350	35	22	10	9.0
OCDF	270	135	190	140	5.9	22	15	13
Total PCDD	4666	2472	3060	2770	285	206.6	81	55.5
Total PCDF	1320	946	1540	896	99.3	116	51	38
Nato/CCMS Equivalent	57	36	60	37.6	7.6	3.7	1.7	1.2

Table 1. PCDD/PCDF Concentrations in Morcambe Bay and Clyde Estuary Sediments.

Table 1 summarises results from analyses carried out on core samples from Morcambe Bay and the axial survey of the Clyde. The samples from Morcambe Bay are representative of a UK coastal shelf sea environment receiving waste from a number of industrialised estuaries (Clyde, Mersey, Dee, Severn). The Clyde is an industrialised estuary with direct pollutant inputs from the City of Glasgow via industrial/domestic sewage outfalls.

Due to their ubiquity in the marine environment, it is difficult to determine 'background' concentrations of PCDD/DF in the marine environment. Turkstra and Pols (1989) regarded total PCDD/PCDF sediment concentrations of between 10 and 100 ppt as background levels in their study of the Noordzeekanaal in the Netherlands. Norwood et al (1989) in a study of Narragansett Bay obtained a value of < 0.93 ppt 2,3,7,8 TCDD at their "relatively clean reference site". Set against these assessments, the levels of PCDDs and PCDFs found in Clyde sediments may be regarded as elevated and those in Morcambe Bay as background. PCDDs and PCDFs were, however, concentrated in the surface sediments in Morcambe Bay whereas PCB concentrations increased with depth.

The source of PCDD/PCDFs to the Clyde estuary is not clear. Sample homolog

profiles from local incineration sources and direct sewage inputs may help in the future to elucidate the source. From the axial distribution of PCDDs and PCDFs (discussed below) however, it would seem likely that a direct source(s) to the estuary is present.

Due to their hydrophobicity, the transport and axial distribution of PCDDs and PCDFs in estuaries is dominated by the physicochemical characteristics and transport mechanisms of estuarine sediments. Generally, organic micropollutants are expected to favour fine sediments with high surface areas, high organic carbon content and high lipid content. Clyde sediments in the lower estuary tend to be of marine origin with high grain size and low organic content compared with the upper estuary's finer, organic rich sediments. An expected general decrease in total PCDD and PCDF concentration was therefore observed down the estuary.

An initial examination concludes that the dispersive hydrodynamics of the estuary and the effectiveness of an estuary as a filter for fine grained sediments received from its tributary rivers, is probably responsible for the observed dilution. In this case however, the homolog profiles have been examined more closely to see the way in which individual chloro-homolog groups, with their varying toxic significance, are affected by estuarine transport.

Homolog	Clyde Estuary Stations				
	1 (3km)	2 (4km)	3 (5 km)	4 (10 km)	5 (22km)
TCDD	1.8	1.6	3.6	2.7	6.0
PeCDD	3.9	3.5	3.9	3.7	16.5
HxCDD	2.1	3.5	3.3	2.6	12.0
HpCDD	17.2	16.4	18.0	19.2	27.7
OCDD	75.0	75.0	71.2	71.8	37.8
TCDF	15.9	11.2	14.9	10.7	16.0
PeCDF	12.9	14.3	15.6	11.2	14.6
HxCDF	24.2	32.6	27.3	23.4	28.2
HpCDF	26.5	27.5	29.9	39.1	35.2
OCDF	20.4	14.3	12.3	15.6	5.9

Table 2. Homolog concentrations as a percentage of total PCDD/PCDF

Table 2 shows individual homolog concentrations as a percentage of the total PCDD/PCDF concentration. In the upper estuary (sites 1,2), octachlorinated congeners dominate the dibenzodioxin pattern. Downstream at sites 3 and 4, a reduction in relative OCDD concentration is noted, compensated by an relative increase in HpCDD concentrations. At the outer estuary site 5, a significant decrease in OCDD is compensated by relative increases in all the lower chlorinated homologs. The pattern for PCDF homologs is less clear but a downstream decrease in OCDD concentration relative to the other homologs is also obvious. In the Humber, a similar pattern is observed from sediments taken axially down the estuary with OCDD relative concentrations decreasing from 69.9 % to 50.8 % and TCDD increasing from 0.2 % to 18 %.

Two possible explanations of these observations can be made. Several studies of PCB behaviour indicate that metabolic biodegradation of a PCB can occur⁸, a first stage of which

is often dechlorination⁹. This would result in a coupled relative increase in lower chlorinated congeners and decrease in higher chlorinated congeners as a function of the pollutant's residence time in the estuary. Bearing in mind the widely reported persistence of PCDDs and PCDFs¹⁰, the extent of the apparent 'dechlorination' may be unlikely.

An alternative explanation is based on the observed dependence of geochemical behaviour on the basic physicochemical properties of the compound and in particular the octanol-water partition coefficient¹¹ (often used to express the hydrophobicity of the compound). Variations in the partitioning behaviour of individual congeners on the basis of their chlorinity would infer differential transport within the estuary system resulting in changes in the relative homolog concentrations as observed in Clyde and Humber sediments.

Initial studies of PCDD and PCDF contamination in UK estuaries have therefore concluded that PCDD and PCDF transport and distribution is significantly affected by the hydrodynamics of the estuary and the physicochemical characteristics of sediment within the estuary. Axial variations in the relative concentrations of individual chlorohomologs suggests that dechlorination or differential geochemical transport may be important mechanisms in the behaviour of PCDDs and PCDFs in estuarine environments.

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