

Source and Fate of Polychlorinated Dibenzo-p-dioxins, Polychlorinated Dibenzofurans and Polychlorinated Biphenyls in Estuary Systems; A Major UK Estuary Study

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Introduction

The impact of tighter regulation of European water quality is resulting in an increased awareness of the influence of trace organic contaminants in marine ecosystems. In many cases however, limited scientific knowledge of the mechanisms and kinetics dominating contaminant behaviour in estuary systems is hampering model development and the effective implementation of new legislation.

Ongoing research has demonstrated the complexity of chlorinated organic pollutant geochemistry in aquatic environments. The importance of congener specific physicochemical properties is well established¹, but only recently has the geochemistry of the solid phase sorbent been shown to be significant². Strong variations in such controlling variables are commonplace in dynamic estuarine systems.

Approach and Methodology

This paper presents the second report of a current three year research programme studying the transport and fate of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) in aquatic systems. In 1991 a pilot survey of the Clyde estuary in Scotland was carried out³. This was followed in the summer of 1992, by a major survey where over 40 samples of bed sediment, inter-tidal sediment and suspended particulate matter (SPM) were collected and analysed.

Sediment samples were collected using grab and corer techniques. Bulk water samples were filtered in all-glass apparatus for SPM collection. All samples were analysed for

PCDDs, PCDFs (2,3,7,8-substituted congeners) and PCBs (total and ICES 7 congeners). The analytical methodology, carried out to an established protocol⁴, is given in a previous paper³. In addition to the organic micropollutant analyses, determinations of carbon content (combustion technique), specific surface area (SSA) (BET N₂ adsorption) and lipid content (solvent extraction) were also made.

Results and Discussion

The Clyde estuary is situated on the west coast of Scotland and is an industrialised estuary with direct pollutant inputs from the city of Glasgow via industrial/domestic sewage outfalls and atmospheric deposition from incinerator and other diffuse combustion sources.

In total, 42 km of the estuary was sampled from the weir to the inner firth. Concentrations of total PCDD, PCDF and PCB varied considerably within the estuary. Maximum values for total PCDD and PCDF were 9200 and 2500 ppt respectively compared with 4700 and 1500 ppt in the 1991 survey. Total PCB concentrations varied from 1 to 3000 ppb. Significant changes in other variables were also observed; lipid content ranged from below detection (0.3 mg/g approx) to 13.8 mg/g, SSA varied from < 1 to 12.5 m²/g.

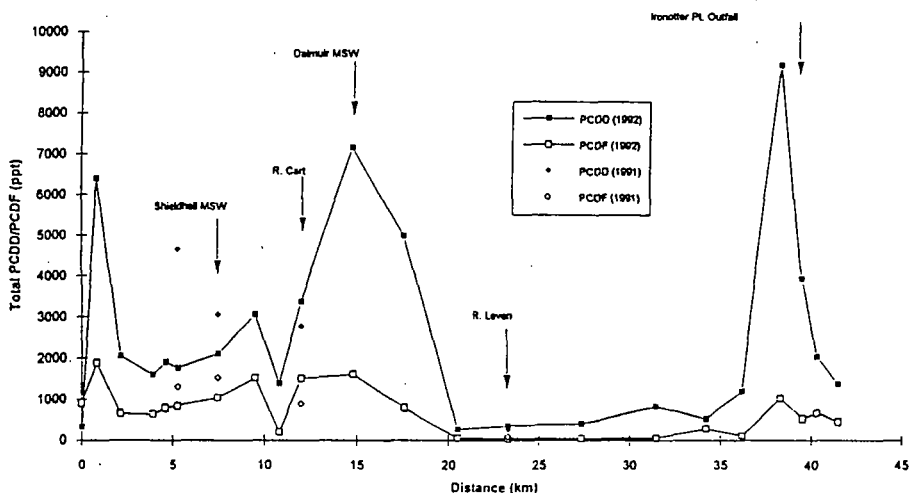


Figure 1. Axial Variation of Total PCDD and PCDF with Distance Down-estuary.

Figure 1 shows the axial variation of total PCDD and PCDF with distance down-estuary (1991 and 1992 surveys). Major anthropogenic inputs to the estuary are also marked. The estuary is characterised by three peaks in concentration. Close to the weir, a peak in PCDD/PCDF concentration coincides with the highest PCB concentration measured in the estuary (3000 ppb), and may be due to co-contamination⁵. The second peak occurs at the confluence of the River Cart with the Clyde estuary (12km), and is examined in more detail. Concentrations in the middle of the estuary (21 - 35 km) are low, coinciding with sediments of low lipid content (< 1.5 mg/g) and SSA (< 2 m²/g). The third PCDD/PCDF peak occurs in the inner firth in the vicinity of a long outfall at Ironotter Point.

Although the 1992 survey generally confirms observations of a systematic variation in PCDD:PCDF ratio in the 1991 survey (approx 2), there is significant change in PCDD:PCDF ratio in the vicinity of the River Cart confluence coinciding with a peak in total PCDD/PCDF concentration. In the upper estuary (0 - 12 km) PCDD:PCDF ratios range from 0.4 to 2.4 (avg. 2.2). In the mid-estuary region (12 - 35 km) PCDD:PCDF ratios vary from 4.4 to 9.7 (avg. 6.3). Samples taken in the River Cart at the interface between the upper and mid estuary regions have PCDD:PCDF ratios of 27.7 and 39.9. Two major factors appear to influence the distribution of PCDD/PCDF within the estuary; solid phase sorbent characteristics and pollutant input sources.

Generally, the estuary may be classified into regions of fine sediment with high surface areas and lipid content favourable for the adsorption of lipophilic contaminants² and areas of coarse sediment of marine origin with low lipid content. The upper estuary and inner firth have high SSA and lipid content compared with the middle estuary. Broadly, this pattern is reflected in the PCDD/PCDF distribution.

If the PCDD and PCDF concentrations are normalised for lipid and SSA, the peak concentrations occur in the middle estuary. Assuming that the PCDD and PCDF is bound in the lipid fraction of the sediment, these mid-estuary sediments hold a far greater contaminant load than those of the more lipid rich upper estuary sediments. Dilution effects may in part explain these observations; PCDD/PCDF inputs in the upper estuary bound to lipid-rich sediments are transported down-estuary and diluted by coarser lipid depleted sediments in the mid-estuary region.

The Clyde estuary is subject to a multiplicity of potential sources of PCDD/PCDF/PCB. The estuary is known to receive direct waste input from the iron/steel industry, PCB dump leachate and PCP as well as other diffuse combustion sources. The profile of homolog groups in environmental samples is well established as a signature of PCDD/PCDF source⁶.

In this study concentrations of each homolog group, tetra- through octa-, have been normalised against total PCDD and total PCDF to produce homolog profiles. From the distribution of relative homolog concentrations, the upper estuary was identified as a region of significant homolog profile variation. This has been investigated in detail by mapping sample homolog profiles. Results for an up-estuary area (5 - 18 km) are shown in Figure 2.

Homolog profiles at stations 7 and 8, although biased to the octa- homolog show significant concentrations in all other homolog groups similar to that expected in combustion source profiles. The River Cart joins the Clyde estuary 12 km from the weir. Sample I11 in the White Cart Water and I12 in the Black Cart Water have completely different homolog profiles dominated by the octa- homolog group. The White Cart Water receives waste from an outfall known to discharge PCP waste. PCP homolog profiles also exhibit the dominance of the octa- homolog group.

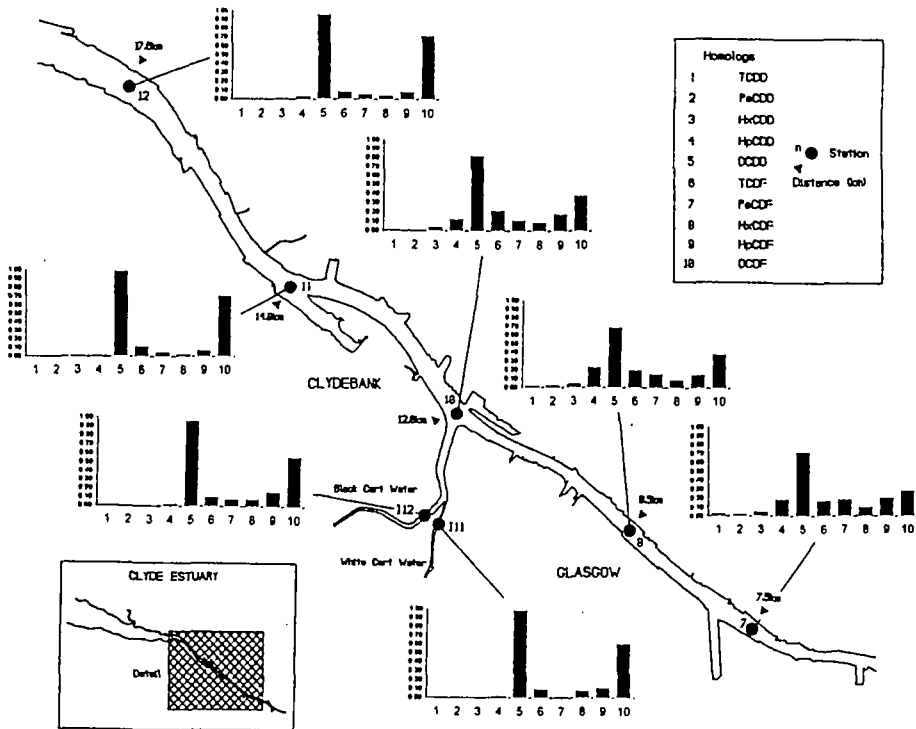


Figure 2. Homolog Profiles for Samples in the Clyde Estuary (5 - 18 km)

Downstream of the River Cart confluence, the homolog pattern in the estuary also changes significantly, showing the same octa-homolog dominance as the River Cart samples. The change in homolog profiles also coincides with a variation in PCDD:PCDF ratio and a peak in PCDD and PCDF concentration. The conclusion from these observations is that the River Cart tributary is making a significant estuary input of PCP derived PCDD/PCDF which dominates the downstream PCDD/PCDF distribution.

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