An Investigation into the Partitioning of Polychlorinated Dibenzodioxins and Polychlorinated Biphenyls in Estuaries

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### Introduction

Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Biphenyls (PCBs) have received widespread attention in recent years due to their toxicity, persistence and liability to bioaccumulate<sup>1</sup>. Despite considerable research into their biological effects, sources and general environmental fate, very little information is available to describe the behaviour and transport of these compounds in the environment. In particular, quantitative data are required to allow detailed modelling of sorption processes and subsequent transport in marine systems.

The sorption of PCDDs and PCBs onto natural particles in marine systems is dependent on the basic physicochemistry of these hydrophobic and lipophilic compounds, and by the geochemistry of the sorbent<sup>2</sup>. Partitioning between the dissolved and solid phase in an estuary determines the subsequent transport and residence time in the system. The Humber estuary, UK for example has an estimated flushing time of 40 days compared with a residence time for sediments of 18 years<sup>3</sup>.

This investigation examines the solid phase partitioning of 2,3,7,8-TCDD and 22'55'TCB onto natural estuary suspended sediment populations from selected of UK estuaries. Detailed suspended sediment characterisation has allowed the study of the dependence of partitioning on solid phase geochemistry. A range of estuary types have been sampled for the experiments to represent varied estuarine conditions.

### Methodology

Partitioning behaviour has been examined using laboratory simulations of the estuarine gradient with the addition of [<sup>14</sup>C]-labelled compounds. Natural samples were taken from the Humber, Dart, Beaulieu and Clyde estuaries and used as soon as possible following collection to minimise sample degradation. At each estuary, freshwater end member and saline end member samples were collected. Two compounds were chosen for study; 2,3,7,8-TCDD, the most toxic of the dioxin congeners, and 22'55'TCB (IUPAC 52), one of the more abundant PCB congeners.

Each partitioning experiment was conducted in a 50ml centrifuge tube. A  $0.02\mu$ m spike of the [<sup>14</sup>C]labelled compound in hexane was added to each tube and evaporated. End member samples from the estuary were then admixed to represent the estuarine gradient and added in 20ml quantities to each tube and equilibrated for 12h on a shaker. Following equilibration, each tube was centrifuged at 3000rpm for 30m to separate the dissolved and solid phases. A 4ml sub-sample of the dissolved phase

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was pipetted into a vial containing 10ml of Ultima Gold Liquid Scintillation Cocktail (LSC) and counted on a scintillation counter. The remaining sediment was resuspended by gentle shaking and removed from the tube. 4ml of hexane was added to the tube and shaken for 12h to extract any adsorbed [<sup>14</sup>C]-labelled compound from the glass walls. A 2ml sub-sample was then removed and added to LSC for counting. The partition coefficient,  $K_D$  was derived by mass balance calculation from the original concentration of [<sup>14</sup>C]-labelled compound added.

Some difficulty was experienced, particularly with the [<sup>14</sup>C]-2,3,7,8-TCDD, in achieving the desired level of experimental repeatability due to the very low solubilities of these compounds. As a result, all experiments were carried out in triplicate or quadruplicate.

In addition to the mixing experiments, suspended particulate matter (SPM) samples were collected by bulk filtration of each end member or approximated by bed sediments collected at the end member sites and sieved to  $< 63\mu$ m. These samples were characterised by surface area determination using BET N<sub>2</sub> adsorption<sup>4</sup>, Fe and Mn determined by acetic acid extraction followed by AAS, and Total Organic Carbon (TOC) determined operationally by mass loss on ignition. Less than  $63\mu$ m bed sediments were also analysed for apolar lipid content<sup>2</sup>.

#### **Results and Discussion**

Partitioning experiments have been carried out for all four UK estuaries. These estuaries have contrasting physicochemical characteristics ranging from the organic enriched Beaulieu estuary on the south coast of the UK to the tidally dynamic Humber estuary on the east coast, UK, characterised by sediments with a low apolar organic carbon content.

Results from the partitioning experiments have been plotted against salinity (conservative variable) for each estuary. Presenting data in this manner can be misleading as the effects of increasing ionic strength and the admixing of suspended sediment populations.



Figure 1. 22'55'-TCB - Log. K<sub>D</sub> against Salinity using Filtered and Unfiltered MEM Dart Estuary Water

To investigate the relative importance of these two effects, an experiment was conducted using estuary water where the MEM was prefiltered prior to mixing (ie. the characteristics of the suspended sediment population were kept constant). Figure 1 shows the result of this experiment.

In the natural (unfiltered) mixing case, the partition coefficient,  $K_D$  for 22'55'TCB decreases rapidly in the low salinity region resulting in a  $K_D$  at the MEM of one tenth the REM value. For the filtered MEM water experiment, the  $K_D$  rises gradually with salinity to a value representing twice the REM  $K_D$ . From this experiment we have concluded that the major influence on axial variations in  $K_D$  is the geochemistry of the suspended solid phase. From our previous work<sup>2</sup> and that of others<sup>5</sup> we might therefore expect to see some considerable variation in the magnitude and axial behaviour of  $K_D$ 's between different organochlorines and between different estuary systems.

This expectation is borne out in Figure 2 which shows the variation between  $K_D$  and salinity/suspended particle population for the four estuaries under study. The first observation is the significant variation in magnitude of  $K_D$  at the freshwater end of the estuary. In both the Dart and Beaulieu estuaries, rich in organic matter, the partition coefficient varies between 300,000 and 500,000 indicating high solid phase adsorption. In the relatively organic enriched Clyde estuary (apolar lipid content in sediment approximately 6.5 +/- 5.0 mg/g), the initial  $K_D$  is approximately 175,000 compared with a value of 50,000 in the Humber estuary (apolar lipid content in sediment approximately 1.6 +/- 0.7 mg/g)<sup>2</sup>.



Figure 2. 22'55'-TCB - Log. K<sub>D</sub> vs Salinity in Natural Estuary Waters

The relatively organic rich estuaries of the Beaulieu, Dart and Clyde exhibit a sharp decrease in  $K_D$  towards the MEM resulting in  $K_D$  values within the range 25,000 - 130,000. This behaviour is in sharp contrast with the Humber estuary where the  $K_D$  rises gradually with salinity to a MEM value comparable to the other estuaries.

Within estuaries an interplay exists between the destabling effects of an increase in ionic strength tending to aggregate colloidal material thus increasing the apparent  $K_D$ , and the estuarine gradient in sediment geochemistry from organic rich lithogenic material at the REM (high relative  $K_D$ ) to mineral dominated marine material at the MEM (low relative  $K_D$ ). In organic rich estuaries, the geochemistry appears to dominate the sorption behaviour and this is confirmed by the mixing experiment conducted using filtered MEM water (Figure 1) which demonstrated the increase in  $K_D$  with salinity once solid phase geochemical variability had been eliminated. In contrast the Humber estuary, with relatively low organic content in suspended sediments results in a low REM  $K_D$  followed by an increase of  $K_D$  with salinity possibly as a result of destabilisation and aggregation processes.

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Experiments were repeated for 2,3,7,8-TCDD on samples from the Humber and Clyde estuaries. The high  $K_D$  values for 2,3,7,8-TCDD resulted in experimental difficulties in accurate dissolved concentration determination. Figure 3 summarises the experiments on Humber and Clyde particle populations for both 22'55'TCB and 2,3,7,8-TCDD.



Figure 3. Log. K<sub>p</sub> vs Salinity for 22'55'TCB & 2,3,7,8-TCDD in Humber/Clyde Natural Waters

 $K_{\rm D}$  values for 2,3,7,8-TCDD in both Humber and Clyde waters are much higher than those for 22'55'TCB. This difference between the two compounds is consistent with their physicochemical properties (eg. solubility for 22'55'TCB ~0.046mg/l<sup>6</sup>, for 2,3,7,8-TCDD ~0.019 $\mu$ g/l<sup>7</sup>). The difference in  $K_{\rm D}$  between the two compounds does not, however affect the variation of  $K_{\rm D}$  with salinity. The interplay between the sorbent and the ionic gradient is also likely to explain the observed 2,3,7,8-TCDD data trends.

Results from these experiments clearly indicate the dominance of solid phase geochemistry in determining sorption preferences of chlorinated compounds such as PCBs and dioxins. Long sediment residence times in estuaries (~years) and other aquatic systems (eg. rivers, lakes) place an importance on this understanding of partitioning behaviour helping to quantify fluxes from coast to sea and to highlight regions where preferred sediments may accumulate to the detriment of resident biota populations.

### References

<sup>1</sup>Tanabe, S. (1988): PCB problems in the future: foresight from current knowledge. Environ. Poll. 50, 5-28.

<sup>2</sup>Tyler, A.O., Millward, G.E., Jones, P-H., Turner, A. (1994): Polychlorinated Dibenzo-para-dioxins and Polychlorinated Dibenzofurans in Sediments from UK Estuaries. Estuarine and Coastal Shelf Science, In Press.

<sup>3</sup>Turner, A. (1990): Chemical Dynamics in North Sea Estuaries and Plumes. PhD Thesis, University of Plymouth.

<sup>4</sup>Millward, G.E., Turner, A., Glasson, D.R., Glegg, G.A. (1990): Intra- and inter-estuarine variability of particle microstructure. The Science of the Total Environment 97/98, 289-300.

<sup>5</sup>Preston, M.R., Raymundo, C.C. (1993): The Associations of Linear Alkyl Benzenes with the Bulk Properties of Sediments from the River Mersey Estuary. Environmental Pollution 81, 7-13.

<sup>6</sup>Hutzinger, O., Safe, S., Zitko, V. (1974): The Chemistry of PCBs. CRC Press 1974.

<sup>7</sup>DoE Working Group (1989): Dioxins in the environment. Pollution Paper No. 27. HMSO.