Sampling methods used to investigate PCDD/F concentrations in UK freshwater systems.

Fletcher, C. L., McKay, W. A. & Ambidge, P. F.
AEA Technology, 364 Harwell, Didcot, Oxfordshire OX11 0RA, UK

1. Objectives

Little information is available on either the concentrations or fate of PCDD/Fs in UK lakes and rivers[1]. This paper discusses the sampling methods used in two investigations that are being carried out to increase our knowledge of these organic pollutants in UK freshwaters. The investigations differ in their aims, and this paper describes the differing sampling strategies required. Some preliminary results are presented from one of the studies.

2. Approach and Methods Used

2.1 Study description

The first study, funded by the UK Department of the Environment (Air Quality Division) (DoE), aimed to (i) investigate the fate of airborne PCDD/Fs deposited into freshwater systems, including their facility for transfer through the aquatic foodchain, (ii) investigate the feasibility of using enclosed lake systems from around the UK to help quantify changes in input of atmospherically-derived PCDD/Fs in the environment, both spatially and temporally. The second study, a national R&D project funded by the UK National Rivers Authority (NRA), was designed to identify potential sources (point and diffuse) of PCDD/Fs to UK rivers, and to investigate these by analysing water and surface sediment samples from appropriate locations.

2.2 Methods of sample collection for PCDD/F analysis

(a) DoE study. To meet the first aim of the DoE project, surface sediment and fish samples were taken from four sites in the UK (Fig. 1). Surface sediment samples were taken using a Kajak-Brinkhurst corer[2], a gravity corer which is relatively light and ideal for taking short cores from lakes. Like the other types of corer descibed in the following sections, the Kajak-Brinkhurst corer maintains an intact sediment-water interface, which is important to ensure that no fine material

(and associated contaminants) is lost from the sediment surface when sampling. Once a sediment core had been extracted, the top 3 cm (taken to represent surface sediment) was sliced off. Benthic invertebrates living and burrowing in the sediment will be affected by contaminants in sediments to this depth. Any changes in the bottom-dwelling biota will affect dependent organisms higher up the foodchain. Also, 3 cm is a feasible amount of sediment to be bulked from individual cores in order to carry out the sampling relatively quickly.

Fish samples were taken to provide an indication of the fate of atmospherically-derived PCDD/Fs in the foodchain. Fish (pike, perch, roach) from the English sites were caught by anglers. Lough Neagh roach were caught by trawling, and eels by eel lines. Brown trout from Dry Loch were caught by setting nets overnight, and retrieved the following day.

To fulfil the second objective of the DoE project, long sediment cores were taken from Eleven Acre Lake and Lough Neagh. Long cores provide an historical perspective of PCDD/F accumulation, and indicate the relative importance of recent inputs to long term deposition to these freshwater systems. The sediment cores from Eleven Acre Lake were taken by piston coring[3]. The core tubes used for this corer are of a larger diameter than those normally used, and so allow a greater amount of sediment to be sampled for every core taken. Cores from Lough Neagh were taken using a mini-Mackereth corer[4]. This type of corer uses gas pressure to force the core tube into the sediment, and therefore requires a large enough boat to accommodate a gas cylinder. Both corers allowed about 1 m depth of sediment to be collected

(b) NRA study The aim of the NRA study was to identify industrial or agricultural practices which result in a potential discharge of PCDD/Fs into river systems. Water and surface sediment samples were taken from a number of sites where potential point or diffuse sources had been identified. Background sites were also sampled to provide a comparison. Twenty eight different sites were visited nationally. Water samples for PCDD/F analysis were collected in hexane-washed amber glass bottles. When sampling, the lids of the bottles were removed and recapped beneath the water to avoid contamination by the surface microlayer. The bottles were rinsed twice with river water before the final sample was collected. Hexane-rinsed aluminium foil lid inserts were put in place to prevent contamination by the lid of the bottles. Sediments for this study were collected using a Gilson corer with pole attachment. This is an ideal corer to use where it is possible to wade into the water. Where the river bank is sheer, the pole can also be lowered into the water from the bank. In some cases, the river was shallow and the core tubes could be manually inserted into the sediment. Both these methods allow the recovery of samples with an intact sediment-water interface. As with the DoE study, the top 3 cm (taken to represent surface sediment) was sampled.

3. Results

Some preliminary sediment results are available from the DoE study. Fig.1 illustrates the location of the sample sites, the total PCDD/F concentrations and I-TEQs (ng kg^{-1} dry weight) in surface sediments. This diagram shows the concentrations of PCDD/F found in these different catchment and lake types in the UK. It shows that surface sediments provide a reservoir for PCDD/Fs from which accumulation the foodchain may occur. Congener profiles from Eleven Acre Lake and Lough Neagh surface sediments (Fig. 2) are similar, with the predominance of the higher chlorinated dioxin isomers giving fairly typical 'combustion' profiles (a result of long range transport of combustion products). Marsworth Reservoir sediments contain higher concentrations of tetra-CDD and tetra-CDF. These lower chlorinated species contribute to the relatively high TEQ value seen in Fig. 1. Dry Loch also exhibits a different congener profile. The large input of octa-CDF may be the result of atmospheric deposition from regional sources, e.g. Glasgow or Belfast.

Results from sediment core analyses enabled a sediment inventory (PCDD/F accumulation over the last 90 years) to be calculated. Comparing this with the recent inventory calculated from surface sediments, results showed that 5%-10% of the total PCDD/F accumulation since 1900 had occurred in the last 5 years. This indicates that 90% or more of the PCDD/F reservoir is held at depths greater than about 3 cm in the sediment.

4. Conclusions

A number of techniques are available to sample aquatic media for PCDD/F analyses. Consideration to the aims and objectives of a study enable an appropriate sampling strategy to be developed and applied.

Acknowledgements We are very grateful to the UK Department of the Environment (Air Quality Division) and to the National Rivers Authority (Anglian Region) for supporting these studies.

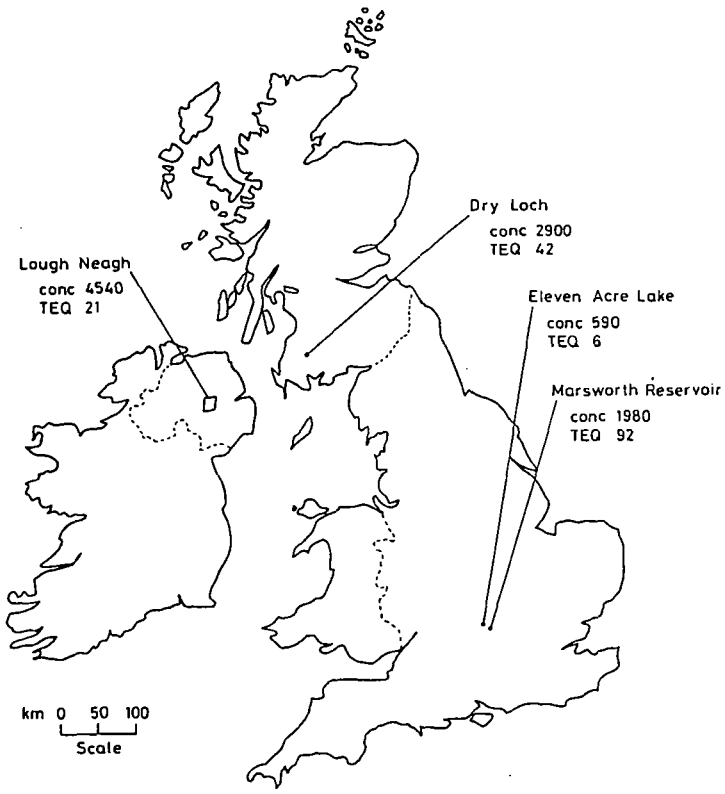
References

[1]Fletcher CL & McKay WA. Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in the aquatic environment - a literature review. *Chemosphere* 1993;26:1041-1069

[2]Brinkhurst RO, Chua KE & Batoosingh E. Modifications in sampling procedures as applied to studies on the bacteria and tubificid oligochaetes inhabiting aquatic sediments. *J. Fish. Res. Bd. Can* 1969;26:2581-2593.

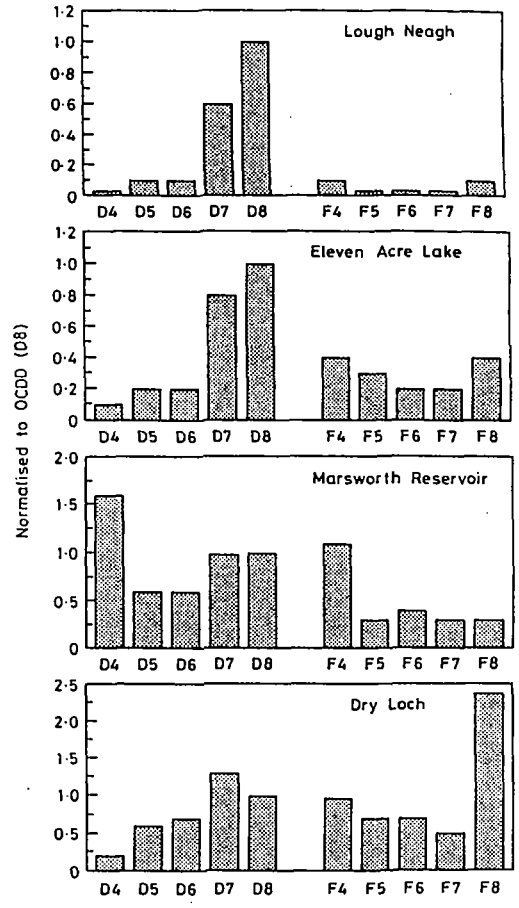
[3]Wright HE Cores of soft lake sediments. *Boreas* 1980;9:107-114.

[4]Mackereth FJH. A short core sampler for sub-aqueous lake sediments. *Limnol. Oceanogr.*1969;14:145-150.



conc = Total concentration of PCDD/Fs (ng kg^{-1} dry weight, or ppt)
TEQ = Toxic Equivalent (ng kg^{-1} dry weight, or ppt)

Figure 1. Location of sampling sites, showing concentration and TEQ of PCDD/Fs in surface sediments.



D = PCDD
F = PCDF
4,5 etc. = Number of substituted chlorine atoms

Figure 2. Congener profiles of PCDD/Fs in surface sediments at the four sample sites