

NRA National R&D Project 330

The Distribution of PCDDs and PCDFs
in Surface Freshwater Systems.

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1. Introduction

This report summarises the work that has been carried out since the first Interim Progress Report of June 1992. The first report described the work that had taken place since the beginning of the project, including meetings and discussions, a literature review, and the collection of information to prepare for the field programme. This included questionnaires sent out to 6 NRA regions, and the replies that had been received.

This report describes the progress that has been made since June 1992 and outlines the work plan for the next phase of the project.

2. Meetings

The Third Project Meeting was held on 2nd July 1992 at AEA Technology, Harwell. Those present were Dr G Brighty and Mr G Miller of NRA Anglian Region, and Dr P Ambidge, Dr W McKay and Dr C Fletcher of AEA Environment & Energy. At the meeting, most of the sampling sites were selected. It was agreed that in addition to water samples, sediment samples would be collected and stored, increasing the contract value by £13 K. To assist interpretation of the results of PCDD/F analysis, it was decided that suspended particulate loading, total organic carbon (TOC) and dissolved organic carbon (DOC) would also be determined in water samples. PCDD/Fs are hydrophobic and so have an affinity for organic matter, both particulate and dissolved. The above parameters provide information on the particulate and dissolved phases in the water column, and allow greater insight into the partitioning of PCDD/Fs in the water column. In sediment samples, it was decided that dry weight, loss on ignition (a surrogate measure of organic carbon content) and a basic particle sizing into the sand (>63 µm) and fine particulate (<63 µm) fractions, would provide sufficient supplementary information to assist in interpretation.

3. Site Selection

Following discussions at the Third Project Meeting, and further consultation with NRA representatives, the sites given in Table 1 were included in the sampling programme. All sites were sampled between 8/7/92 and 14/8/92, with the exception of Welsh Region sites. Information on Welsh Region sites was received at a later date, and sampling was carried out in October 1992.

In total, 40 water samples and 36 sediment samples were collected from 28 sites. There was no available muddy sediment to sample at 4 of the sites (above the point source at Mag Brook and R. Spenn in Yorkshire, and above and below the afforested area on the R. Irfon, Wales). At two sites, R. Calder and R. Don in Yorkshire, water samples could not be taken at exactly the same site as sediment samples, due to unavoidable bed disturbance when entering the water. In each case, a more suitable water sampling point was located as close as possible to the sediment sampling sites. The original site for sampling the River Granta (Anglian Region) was at Linton. On arrival at the site, no sediment could be found and so a site 3 km further downstream at Hildersham was chosen as a surrogate site.

The R. Spenn in Yorkshire was not originally one of the choices for sampling. However, when visiting the Yorkshire region, we were informed that there had been a fire at Allied Colloids a few weeks previously. The chemical content of the water used to put out the fire would have damaged the sewage treatment works, so the works were by-passed and the water went directly into the Spenn. All life in the river was destroyed by this incident. It was strongly suggested that we should sample this river as a potential source of dioxins. The site was therefore added to the original choice.

4. Details of Sample Collection

At each site, the following samples were taken:

- 5 l water for PCDD/F analysis
- 1 l water for suspended particulate load determination
- 100 ml water for total organic carbon determination
- 100 ml water for dissolved organic carbon determination
- approximately 1 kg wet sediment for PCDD/F analysis
- 150 ml pot of wet sediment for determination of dry weight, organic carbon and particle size (fraction >63 μm)

4.1 Water samples

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. On return to the river bank, a hexane-rinsed aluminium foil lid insert was put in place to prevent contamination by the lid of the bottle.

The 1 l sample for particulate loading determination was also collected in this way, but the foil lid insert was not necessary.

The 100 ml amber glass bottles used for the determination of TOC and DOC were organic-free (fired in a furnace at 550°C for 5 hours). On sampling, lids were opened and closed beneath the water surface, and bottles were rinsed before sampling as described above. On the same day that samples were taken, the samples collected for TOC determination were acidified to ~pH2 with orthophosphoric acid. DOC samples were filtered using organic-free glass Millipore filtering equipment, and organic free filter paper. After filtration was complete, these samples were also acidified. The acidified TOC and DOC samples were kept in a cool box until return to the laboratory.

4.2 Sediment samples

Where the river water was deep, or sampling had to be carried out from the river bank, sediments were collected using a Gilson corer. Where the river was easily accessed, it was possible to wade into the water, and removed sediment cores using a pole attachment. Where the river bank was sheer, the pole was 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. This is necessary to preserve surface fine particulates and fine flocs. Fine material contains a higher concentration of dioxins than coarse particles, due to increased surface area, and so it is important to sample this surface layer. Also, internal consistency is maintained within a site by always taking exactly the same depth of material.

Once a sediment core had been extracted, the top 3 cm (representing surface sediment) was sliced off and placed into a 1 l amber glass bottle. Additional cores (10-15) were collected, and this method was repeated until the bottle had been filled. This gave approximately 1 kg of sediment, which was sufficient for PCDD/F analysis. Cores that had been disturbed, for example by the corer hitting an obstruction (e.g. a rock) during use, or by large air bubbles disrupting the sediment-water interface, were discarded.

The depth of 3 cm was taken to represent surface sediment material because benthic invertebrates living and burrowing in the sediment will be affected by contaminants in sediments to this depth, and any changes in the bottom-dwelling biota will be reflected through the foodchain. In addition, 3 cm is a feasible amount of sediment to be bulked from individual cores in order to carry out the sampling relatively quickly, and thus to maximise sampling efficiency.

A subsample of sediment was also taken for the determination of dry wet, loss on ignition (a surrogate measure of organic carbon content) and particle size analysis.

5. Documentation, Labelling and Storage

A field note book was taken to all sites and a note made of the date, site name, national grid reference, brief site description, weather conditions, and any other relevant details. Photographs were taken at most sites as a visual record. At each field site, all containers were clearly marked with a water-resistant paint pen before sampling commenced. Labels gave the date, the site name and the analysis to be carried out on the sample (e.g. 'dioxin water', 'dioxin sediment', 'TOC' etc.). At the end of each sampling day, individual labels were printed and stuck onto each bottle to confirm sample identity.

On return to the laboratory, all samples, with the exception of sediments for PCDD/F analysis, were placed in a cold room, or refrigerators, at 4°C until analysed. The sediment samples were air dried on return to the laboratory, and are being stored in amber glass jars until required.

6. Analysis of Water Samples

6.1 Determination of Particulate Loading

For each sample, the exact volume of water collected was recorded prior to filtration. The sample was drawn through pre-weighed filters (Millipore HVLP 0.45µm, 47 mm diameter polyvinylidene difluoride filter membrane) by a partial vacuum in the collecting vessel. The vacuum was generated by an electric air pump. Any residual particulate remaining in the sampling bottle was rinsed out using filtrate from the collecting vessel. The filter papers were dried in an oven to a constant weight, and the weight recorded. Particulate load (mg l⁻¹) was calculated by taking the difference between the loaded filter and blank filter, and dividing by the volume of sample filtered.

Results of particulate load determination on collected samples are given in Table 2.

6.2 Determination of total organic carbon (TOC) and dissolved organic carbon (DOC)

This determination was carried out at the National Rivers Authority's Severn Trent Laboratories. Results are given in Table 3.

6.3 Analysis of PCDD/Fs

It was agreed that initially, samples from seven background sites and seven potentially contaminated sites should be analysed to investigate the PCDD/F content of these samples. The background sites selected are given in Table 4, and the potentially contaminated sites in Table 5. It is hoped that results from these analyses will be presented at the next Progress Meeting.

7. Analysis of Sediment Samples

7.1 Determination of dry weight, organic content and particle size

A small subsample was removed from the 150 ml pot of sediment collected at each site in order to determine the dry weight (or water content) and loss on ignition (organic carbon content) of the sediment samples. The subsamples were placed into pre-weighed porcelain crucibles and weighed on three occasions, once wet, once after drying to constant weight in an oven (to determine dry weight) and once after igniting in a furnace at 550°C for 5 hours (to burn off organic carbon). These parameters are given in Table 6.

The remaining sediment samples were sent to ADAS Laboratories to determine the amount of sand (>63 µm) in each sample. The results are given in Table 6.

7.2 Analysis of PCDD/Fs

Samples are being stored at present, and depending on the outcome of the water sample analyses, may be analysed at a later date.

8. Summary

- All water and sediment samples have been collected.
- All determinations have been carried out on supplementary water and sediment parameters.

- Of the water samples collected for PCDD/F analysis, 7 background and 7 potentially contaminated samples have been selected, and are being analysed.
- The sediment samples for PCDD/F analysis have been dried and are being stored.

Table 1. Location and Description of Sampling Sites

NRA Region/River	Grid Ref	Site Location	Description	Associated Industry
Thames				
R. Thames	SU 720 742	Caversham Weir	diffuse sources	general urban
R. Thames	TQ 177 708	Teddington	diffuse sources	general urban
R. Thames	SU 106 937	Cricklade	background	
Anglian				
R. Cam	TL 431 527	Hauxton	above point source	Schering Agrochemicals
	TL 434 524		below point source	
R. Granta	TL 546 486	Hildersham	diffuse source	agriculture/pesticides
New River	TL 607 697	Wicken	background	
North West				
R. Alt	SD 292 051	Altmouth	diffuse	general urban
R. Mersey	SJ 616 878	Howley Weir	diffuse	general urban
R. Weaver	SJ 600 761	Acton	diffuse	general urban
R. Dane	SJ 932 637	Hugbridge	background	
Yorkshire (Central)				
Mag Brook (or R. Hall Dike)	SE 099 108	Honley	above point source/ background	STW/textiles
	SE 126 138		below point source	
R. Calder	SE 173 214	Mirfield	above point source	STW/chemical industry
	SE 199 199		below point source	
R. Aire	SE 426 260	Beale	above point source	STW/chemical works, power station
	SE 535 256		below point source	
R. Aire	SE 326 313	Fleet Weir	above point source	STW
	SE 379 286		below point source	
R. Spenn	SE 176 278	Dewsbury	above point source	STW/chemical industry*
	SE 231 206		below point source	
Yorkshire (South)				
R. Don	SK 389 912	Rotherham	above point source	STW/steel works
	SK 423 923		below point source	
R. Loxley	SK 298 896	near Sheffield	background	
Severn Trent				
R. Amber	SK 379 536	Ambergate	above point source	STW/textiles/colliery
	SK 353 517		below point source	
R. Derwent	SK 385 343	Church Wilne	above point source	STW/textiles
	SK 441 316		below point source	
R. Derwent	SK 347 484	Belper	above point source	STW/lubricating oils
	SK 347 457		below point source	
R. Erewash	SK 447 496	Eastwood	above point source	STW/textiles
	SK 464 454		below point source	
R. Lathkill	SK 223 646	Alport	background	
R. Derwent	SK 298 896	Froggatt	background	
Pressbrook	SK 385 601	Ogston	diffuse source	burial of rubble from Coalite explosion
R. Tame	SK 207 935	Lea Marston	above point source	lake purification system
	SK 214 945		below point source	
Welsh				
R. Irfon	SN 854 525	Abergwesyn	background	
R. Irfon	SN 920 471	Llangamarch Wells	diffuse source	major forestry
R. Lugg	SO 570 375	Hereford	diffuse source	agriculture

Table 2. Particulate loading of water samples

NRA Region/River	Site Location	Particulate load (mg l ⁻¹)
Anglian		
R. Cam	Hauxton (above)	2.7
	(below)	3.1
R. Granta	Hildersham	7.9
New River	Wicken	6.7
North West		
R. Alt	Altmouth	2.9
R. Mersey	Howley Weir	7.0
R. Weaver	Acton	17.7
R. Dane	Hugbridge	2.0
Yorkshire (Central)		
Mag Brook (or R. Hall Dike)	Honley (above)	1.3
	(below)	1.7
R. Calder	Mirfield (above)	0.4
	(below)	9.0
R. Aire	Beale (above)	9.5
	(below)	8.6
R. Aire	Fleet Weir (above)	7.6
	(below)	4.6
R. Spenn	Dewsbury (above)	1.3
	(below)	4.1
Yorkshire (South)		
R. Don	Rotherham (above)	3.5
	(below)	6.1
R. Loxley	near Sheffield	12.4
Severn Trent		
R. Amber	Ambergate (above)	8.9
	(below)	3.6
R. Derwent	Church Wilne (above)	6.3
	(below)	6.9
R. Derwent	Belper (above)	11.1
	(below)	9.4
R. Erewash	Eastwood (above)	7.1
	(below)	2.3
R. Lathkill	Alport	1.4
R. Derwent	Froggatt	3.0
Pressbrook	Ogston	5.8
R. Tame	Lea Marston (above)	8.3
	(below)	6.6
Welsh		
R. Irfon	Abergwesyn	0.5
R. Irfon	Llangammarch Wells	31.3
R. Lugg	Hereford	4.5

Thames Region results are not yet available.

Table 3. Results of total organic carbon (TOC) and dissolved organic carbon (DOC)

NRA Region/River	Site Location	TOC (mg l ⁻¹)	DOC (mg l ⁻¹)
Thames			
R. Thames	Caversham Weir	6.3	5.4
R. Thames	Teddington	6.5	6.2
R. Thames	Cricklade	4.9	4.6
Anglian			
R. Cam	Hauxton	(above)	6.9
		(below)	6.9
R. Granta	Hildersham	5.2	5.0
New River	Wicken	1.8	1.7
North West			
R. Alt	Altmouth	16.8	14.8
R. Mersey	Howley Weir	12.4	11.5
R. Weaver	Acton	9.8	8.0
R. Dane	Hugbridge	6.0	5.9
Yorkshire (Central)			
Mag Brook (or R. Hall Dike)	Honley	(above)	2.3
		(below)	18.0
R. Calder	Mirfield	(above)	7.9
		(below)	25.2
R. Aire	Beale	(above)	14.2
		(below)	15.0
R. Aire	Fleet Weir	(above)	10.4
		(below)	13.6
R. Spenn	Dewsbury	(above)	21.1
		(below)	20.2
Yorkshire (South)			
R. Don	Rotherham	(above)	7.5
		(below)	9.6
R. Loxley	near Sheffield	5.0	3.5
Severn Trent			
R. Amber	Ambergate	(above)	6.9
		(below)	7.1
R. Derwent	Church Wilne	(above)	3.2
		(below)	6.4
R. Derwent	Belper	(above)	5.4
		(below)	2.8
R. Erewash	Eastwood	(above)	12.9
		(below)	12.4
R. Lathkill	Alport	1.6	1.5
R. Derwent	Froggatt	2.8	2.7
Pressbrook	Ogston	8.1	7.5
R. Tame	Lea Marston	(above)	12.1
		(below)	12.0
Welsh			
R. Irfon	Abergwesyn	1.5	1.5
R. Irfon	Llangammarch Wells	1.8	1.8
R. Lugg	Hereford	2.5	2.3

* Sample broken in transit

Table 4. Background sites selected for PCDD/F analysis of water samples

<u>Region</u>	<u>Site Name</u>	<u>Date Sampled</u>
Thames	R. Thames, Cricklade	10.7.92
Anglian	New River, Wicken	15.7.92
North West	R. Dane, Hugbridge	22.7.92
Yorkshire	R. Loxley, near Sheffield	12.8.92
Severn Trent	R. Derwent, Froggatt	12.8.92
Severn Trent	R. Lathkill, Alport	14.8.92
Welsh	R. Irfon, Abergwesyn	21.10.92

Table 5. Potentially contaminated sites selected for PCDD/F analysis of water samples

<u>Region</u>	<u>Site Name</u>	<u>Date Sampled</u>	<u>Source</u>
Anglian	R. Cam, Hauxton	14.7.92	Schering Agrochemicals
North West	R. Mersey, Howley	21.7.92	general urban/STW/trade effluent
Yorkshire	R. Spenn, Dewsbury	4.8.92	STW/phenoxy acetic acid/fire at Allied Colloids before we sampled - fire water straight into river
Yorkshire	R. Don, Rotherham	11.8.92	Steelworks
Yorkshire	Mag Brook, Honley	4.8.92	STW/textiles
Severn Trent	R. Amber, Ambergate	28.7.92	STW/textiles/colliery
Severn Trent	R. Derwent, Belper	31.7.92	STW/lubricating oil industry

With the exception of the Mersey which had no discrete point source, the samples were all taken below potential point sources.
STW - Sewage Treatment Works

Table 6 Results of dry weight, loss on ignition and particle size determinations

NRA Region/River	Site Location	Dry weight (%)	LOI (%)	Sediment >63µm (%)	
Thames					
R. Thames	Caversham Weir	14.0	17.5	48	
R. Thames	Teddington	44.7	5.8	83	
R. Thames	Cricklade	12.5	20.0	30	
Anglian					
R. Cam	Hauxton	(above)	21.2	17.0	54
		(below)	15.3	16.4	29
R. Granta	Hildersham	18.9	14.1	47	
New River	Wicken	30.8	23.1	71	
North West					
R. Alt	Altmouth	49.5	8.9	56	
R. Mersey	Howley Weir	39.1	17.1	42	
R. Weaver	Acton	37.5	10.7	44	
R. Dane	Hugbridge	18.3	34.2	44	
Yorkshire (Central)					
Mag Brook (or R. Hall Dike)	Honley	(below)	6.9	35.1	45
R. Calder	Mirfield	(above)	29.8	15.8	64
		(below)	68.0	3.2	96
R. Aire	Beale	(above)	42.1	10.8	88
		(below)	21.3	22.3	34
R. Aire	Fleet Weir	(above)	55.4	10.9	86
		(below)	47.2	10.4	74
R. Spenn	Dewsbury	(below)	5.9	42.0	31
Yorkshire (South)					
R. Don	Rotherham	(above)	17.0	25.5	33
		(below)	39.9	19.4	74
R. Loxley	near Sheffield	8.4	24.0	24	
Severn Trent					
R. Amber	Ambergate	(above)	42.6	8.8	51
		(below)	17.4	17.8	45
R. Derwent	Church Wilne	(above)	38.7	11.6	55
		(below)	27.6	12.1	49
R. Derwent	Belper	(above)	21.2	18.2	29
		(below)	27.4	13.6	53
R. Erewash	Eastwood	(above)	29.9	25.0	40
		(below)	39.5	22.6	30
R. Lathkill	Alport	32.7	11.4	50	
R. Derwent	Froggatt	37.8	11.9	70	
Pressbrook	Ogston	16.5	16.4	15	
R. Tame	Lea Marston	(above)	31.2	16.8	56
		(below)	49.4	9.0	81
Welsh					
R. Lugg	Hereford	33.8	7.5	30	