

Draft Final Report

R&D Project 330

Distribution of PCDDs and PCDFs in Surface  
Freshwater Systems

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July 1993

ENVIRONMENT AGENCY



124277

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## FOREWORD

Project 300: PCDDs and PCDFs in surface freshwater systems was funded by the National Rivers Authority as a National R&D Research Project, under contract NRD023.

We are grateful to the National Rivers Authority, for funding this project, and to all NRA personnel involved, particularly Dr G C Brighty (R & D Coordinator) and Mr G Miller (Project Leader). Special thanks go to: Mr C Wheeler, Mr N Dunlop (Thames Region), Mr K Rutterford, Mr I Hill, Mr M Sharp (Anglian Region), Mr G Edwards, Ms J Hill, Mr R Macklewade (North West Region), Mr P Reeves, Mr P Hufton, Mr K Selby, Ms J Stone (Severn Trent Region), Mr R Armitage, Mr P Baker, Mr J Meynell (Yorkshire Region), Mr T Whittaker (Welsh Region) who cooperated and helped greatly in the planning and execution of the field programme. We would like to acknowledge a number of other AEA staff who have contributed to various aspects of this study: A McMahon, C. Brock, C Halliwell, Y Jackson and K Mori. The maps in Appendix B were based on Ordnance Survey mapping with the permission of the Controller of Her Majesty's Stationary Office, © Crown copyright.

## **EXECUTIVE SUMMARY**

Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) are present naturally in the environment, but these natural sources are of relatively little importance compared with the emission of PCDD/Fs into the environment as unwanted by-products of anthropogenic processes. This study was initiated by the National Rivers Authority with the overall objective of determining the distribution of PCDD/Fs in surface freshwater systems of England and Wales.

The study involved the sampling and analysis of 40 sites for surface waters and 36 sites for deposited surface sediment from both potentially polluted and background areas. The concentrations in the water samples were extremely low (total concentration  $<6 \text{ ng kg}^{-1}$ , TEQ  $<0.07 \text{ ng kg}^{-1}$ ). PCDD/Fs were detected in all the sediment samples, and total concentrations and TEQ values varied considerably between sites (300 - 16 000  $\text{ng kg}^{-1}$  total concentration, 2-120  $\text{ng kg}^{-1}$  TEQ). These values are comparable to the PCDD/F range found in UK soils, and to surface river sediments in Europe.

PCDD/F concentrations and TEQ values at background sites and at sites associated with specific types of industrial and non industrial sources have been determined. A sampling protocol for water and sediment sampling suitable for future NRA applications has also been described. Finally, the study recommends future studies for PCDD/F monitoring to the NRA after consideration of the project findings.

## **KEYWORDS**

Dioxins, furans, PCDD, PCDF, sediments, water, rivers



## 1. INTRODUCTION

Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) are chlorinated tricyclic aromatic compounds and are present naturally in the environment as a result of combustion events such as forest fires. However, these natural sources are of relatively little importance compared with the emission of PCDD/Fs into the environment as unwanted by-products of anthropogenic processes. PCDD/Fs are globally distributed and found in all environmental media. They are chemically stable, have low solubilities in water, and have been shown to accumulate in the foodchain. Interest in PCDD/Fs has increased over the last 20 years, as awareness of the anthropogenic contribution has increased, and as analytical capabilities have improved to an extent which allows the detection of these compounds to parts per quadrillion levels (ppq), i.e. parts in  $10^{15}$ . Although there are 210 PCDD/Fs, most are thought to pose no human health risk (DoE 1989). Attention has been focused on seventeen PCDD/Fs with chlorines substituted in the 2,3,7,8 positions (termed the 2,3,7,8 congener group). This relates to concerns regarding their toxicity, carcinogenic potential and potential effects on animal reproductive and immunological systems (DoE 1989; Broman *et al* 1991; Clement 1991). The presence of these PCDD/Fs in the environment has evoked great public and media concern, not only in the UK but in other parts of Europe and America.

There is, however, no published information on the background levels of PCDD/Fs in natural freshwaters in the UK, or on the concentrations in potentially contaminated UK freshwater sites. The National Rivers Authority (NRA), the corporate body responsible for control of pollution of inland waters in England and Wales, therefore commissioned this project to help assess the extent of PCDD/F contamination in surface freshwater systems of England and Wales, and to define whether these contaminants present a major problem in terms of water quality and foodchain accumulation.

The overall project objective was to determine the distribution of PCDDs and PCDFs in surface freshwater systems, and initially had the following specific objectives:-

1. To select relevant industrial/non-industrial sources of PCDD/Fs which should be monitored.
2. To identify industrial/non-industrial catchments where such monitoring could be undertaken.
3. To develop a field sampling strategy for selected sites.

4. To develop a sampling protocol suitable for future NRA application.
5. To determine background levels of PCDD/Fs in surface freshwater systems (excluding sediments).
6. To determine levels of PCDD/Fs associated with specific types of industrial/non-industrial sources in freshwater systems (excluding sediments).
7. To assess critically the sampling strategy and progress after year 1 and suggest modifications for year 2, as appropriate.
8. To recommend future studies for PCDD and PCDF monitoring to NRA in the light of project findings.

During year 1 it was decided, after consultation with the NRA's project manager, to carry out all the sampling that year and to include sediments in the sampling programme. The objectives outlined above were thus modified somewhat, with (5) and (6) now including sediments and (7) no longer being appropriate.

The following report details the results of this study and how the above objectives were successfully addressed.

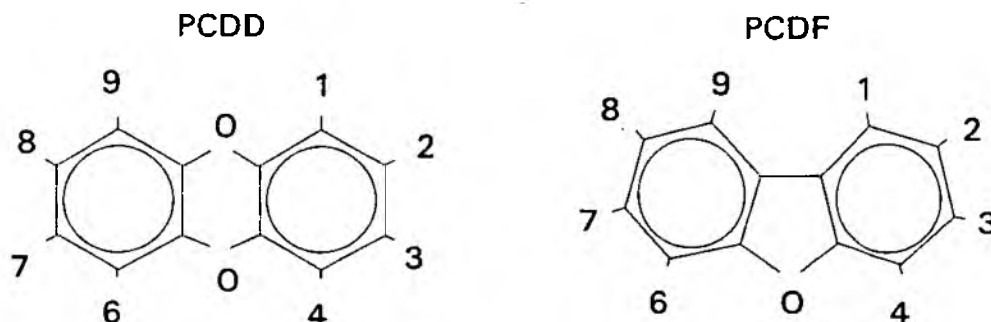
The project began with a literature review that identified industrial and non-industrial sources of PCDD/Fs to inland waters. Based on this, a questionnaire was sent out to those NRA Regions containing a representative cross-section of the identified sources. In total, 7 of the 10 NRA Regions were selected and asked to identify sites where sampling should be undertaken. After selecting suitable sites, a field sampling strategy was developed to collect both water and sediment samples for PCDD/F analysis. Some additional parameters were measured to improve the assessment and help extrapolation of the data. This report describes the project, and also provides recommendations for future studies and strategy concerning PCDD/Fs in the UK aquatic environment.

## 2. STRUCTURE AND PROPERTIES OF PCDD/Fs

### 2.1 General background

In order to understand the environmental concerns regarding PCDD/Fs in the aquatic environment, and the rationale behind the NRA's decision to commission this study, it is necessary to have some understanding of the structure and properties of PCDD/Fs. The following description is taken from a recent UK Department of the Environment funded review carried out by Fletcher & McKay (1993).

The chemical structures of PCDD/Fs given below show the positions (between 1 and 8) at which chlorine atoms can be substituted in place of hydrogen ions. There are a large number of combinations of chlorine substitutions possible, with 75 PCDDs and 135 PCDFs having been identified. Each individual compound differs only in the number and position of its chlorine atoms. The number of these atoms is indicated in the nomenclature of PCDD/F isomers, by a prefix; mono (M), di (Di), tri (Tr), tetra (T), penta (Pe), hexa (Hx), hepta (Hp) and octa (O) (after DoE 1989). The position of the chlorine atoms is given by preceding numbers, for example, 2378-TCDD represents tetrachlorodibenzo-p-dioxin, with chlorines in the 2,3,7 and 8 positions.



Seventeen of the possible 210 PCDD/Fs have chlorines substituted in the 2,3,7,8 positions and are thought to pose a risk to human health due to their toxicity, carcinogenic potential and potential effects on animal reproductive and immunological systems (DoE 1989; Broman *et al* 1991; Clement 1991). Of these seventeen PCDD/Fs, the most toxic isomer is 2378-TCDD, and as a consequence most toxicological studies have concentrated on this. Animal studies on the toxic affect of 2378-TCDD have shown that this isomer is fatal to certain species (e.g. the guinea pig) at very low levels. Studies have also shown a large variation in the susceptibility of different animal species to 2378-TCDD. It is the results of the long-term exposure of PCDD/Fs to animals that has suggested the most important implications for human health. Species such as rats, mice, monkeys and rabbits developed conditions such

as chloroacne (skin condition), liver damage and tumours, and suffered depression of the immune system and adverse effects on fertility (DoE 1989). Certain incidences (e.g. the industrial accident at Seveso, accidental contamination of rice by PCB oil in Yusho) have resulted in illness and death to human populations, but because PCDD/Fs were emitted in association with other organic contaminants, the effects of exposure cannot be attributed to PCDD/Fs alone. Studies are still continuing to determine the effects of PCDD/Fs on human health.

In order to account for the differing toxicities of different PCDD/F isomers, a weighting system has been developed which relates the seventeen 2378-substituted isomers to the most toxic, 2378-TCDD. Each of the 17 isomers are given a toxic equivalent factor (TEF) which, when multiplied by the concentration, gives a toxic equivalent (TEQ). 2378-TCDD has a TEF of 1.0. One drawback of this terminology is that different methods of calculating TEQs have been developed. However, the two most widely used methods, the NATO/CCMS international TEQ (I-TEQ) (NATO-CCMS 1988) and the Nordic TEQ (NTEQ), are very similar. In this study we have used the NATO/CCMS TEQ (I-TEQ), however, the only difference from the Nordic TEQ is the TEF assigned to 12378-PeCDF (0.05 using the I-TEQ method, 0.01 using the NTEQ method). Table 2.1 gives the toxicity factors used in this study.

In this study, results are reported giving both the total concentration of PCDD/Fs and the TEQ. All PCDD/Fs are pollutants, and as such, a measure of all 210 PCDD/Fs allows the extent of contamination at a site to be examined. The total concentrations of each homologue group are reported, i.e. groups of dioxins and furans with the same number of chlorines substituted. The TEQ measures the toxicity of a sample, and accounts for the 17 toxic PCDD/F isomers only.

## **2.2 Behaviour in the aquatic environment**

PCDD/Fs are highly hydrophobic which is reflected in their strong binding with organic matter (dissolved and particulate), particularly the lipid fraction, and their high laboratory-derived octanol-water partition coefficient ( $K_{ow}$ ). Concentrations of dissolved organic carbon (DOC) in rivers depend on environmental conditions but have an estimated global average of 5.8 mg l<sup>-1</sup> with a lipid content typically <1% (Meybeck 1982; Krogh & Lange 1932). Particulate organic carbon (POC) concentrations range from 1-3 mg l<sup>-1</sup> (about 1-6% of the suspended load) with a POC:DOC ratio of ~0.8, and a lipid fraction in the order of 10%. These conditions in the water column result in PCDD/Fs being rapidly absorbed by suspended particulate matter and subsequently deposited in fine sediment in river systems. The fate of

these particulates is important not only for determining the levels present in the water column, but for determining the extent of their deposition and incorporation in bottom sediments. Suspended and deposited particles therefore play an important role in determining the environmental fate of PCDD/Fs.

An equilibrium exists in the water column between the concentration of PCDD/Fs in true solution ('free'), those associated with dissolved or colloidal organic matter, and with particulate matter (Servos *et al* 1989). This equilibrium is important in determining the relative importance of the major exposure routes of PCDDs to fish (e.g. gill uptake versus foodchain uptake) and also to the transfer efficiency within these routes. For example, the uptake of PCDD/Fs through fish gills may be reduced in the presence of dissolved organic carbon (DOC), as the concentration in the truly dissolved phase is decreased. In early studies of PCDD/F accumulation in fish (e.g. Branson *et al* 1985; Muir *et al* 1986) gill uptake was thought to be the most significant pathway. However, the uptake of PCDD/Fs directly from the aqueous phase through gill membranes could not explain the occurrence of some isomer residues in the fish, and uptake through the foodchain and inadvertant ingestion of sediment during feeding are now thought to be more important routes (Muir *et al* 1986; Muir & Yarechewski 1988).

**Table 2.1 International Toxic Equivalent Factors (I-TEF) for the 2378-substituted isomers.**

Isomer	I-TEF
2378-TCDD	1.0
12378-PeCDD	0.5
123478-HxCDD	0.1
123678-HxCDD	0.1
123789-HxCDD	0.1
1234678-HpCDD	0.01
OCDD	0.001
2378-TCDF	0.1
23478-PeCDF	0.5
12378-PeCDF	0.05
123478-HxCDF	0.1
123789-HxCDF	0.1
123678-HxCDF	0.1
234678-HxCDF	0.1
1234678-HpCDF	0.01
1234789-HpCDF	0.01
OCDF	0.001

### 3. IDENTIFICATION OF POTENTIAL SOURCES OF PCDD/FS TO THE AQUATIC ENVIRONMENT

A literature review by McMahon (1992) carried out as part of this study identified potential PCDD/F sources relevant to this project. The main sources of PCDD/Fs fall into three classes; industrial discharge, industrial deposition and non-industrial sources. Table 3.1 identifies types of manufacture and related industries in each class. From these sources, PCDD/Fs may be discharged directly into watercourses, or may be emitted into the atmosphere and deposited by both wet and dry deposition. As described in Section 2.2, the hydrophobic and lipophilic properties of PCDD/Fs means that these compounds formed during industrial processes and dispersed onto land or into water will adsorb strongly to organic material, both in the particulate and dissolved phases, whether in soil or water.

**Table 3.1 Potential sources of PCDD/Fs to the aquatic environment**

Source	Type of practice	Examples
Industrial discharge	Chemical manufacture	Chlorinated phenolics PCBs Chlorinated phenoxy acetic acids Chlorinated pesticides Chlorinated herbicides Agrochemicals Disinfectants Bleaches
	Paper manufacture	Production of paper products from chlorine bleached wood pulp
	Metallurgical	Metal smelters e.g. iron and steel works, non-ferrous scrap
	Sewage Treatment Work	
Industrial deposition	Combustion plant	Municipal incinerators Clinical waste incinerators Chemical waste incinerators Industrial waste incinerators Sewage sludge incinerators Power stations Metal smelters
Non-industrial sources		Motor vehicles Domestic fires Forest fires Stubble burning Cigarettes

#### 4. IDENTIFICATION OF SUITABLE UK SAMPLING SITES

In order to identify suitable sampling sites on a national scale, a questionnaire was devised and sent to seven NRA Regions (Thames, Anglian, Northumbrian, North West, Severn-Trent, Yorkshire and Welsh). The aims of the questionnaire were to identify suitable sites for taking samples for PCDD/F analysis based on (a) a previous history of dioxin contamination in the area, (b) a previous history of the presence of a 'dioxin indicator' chemical (e.g. chlorophenols, PCBs, PAHs etc.) or (c) the proximity of a potential source of dioxins, based on the information given in Table 3.1. The response from Northumbrian Region showed that there were no suitable freshwater sites in the region, and so no further contact was made with this region. An example of the questionnaire and the responses from the six regions sampled are given in Appendix A.

On return of the questionnaires, detailed discussions took place with local NRA staff who were able to provide more detailed descriptions of the sampling sites suggested. Initially it was hoped that samples for PCDD/F analysis could be taken at the same time that the NRA took a routine sample, and from NRA routine sampling sites. However, this was impractical for several reasons. Firstly, many of the sites were monitored at monthly intervals or longer, and thus difficult to schedule into sampling trips. Secondly, the routine monitoring sites were often from locations such as bridges, with no access to the river bank itself, which was required for the sampling of water and sediments (see Section 5). Thirdly, where access to the river was possible at routine monitoring points, there was often no sediment available in the immediate locality. As it was preferable to sample waters and sediment as close together as possible, it was decided to sample both independently of the NRA routine sampling, although as near to the established routine sampling points as possible.

The questionnaire replies suggested a wide choice of river sites, and after consultation with the NRA project managers, a total of 40 sample points were selected, giving a broad range of potential point sources, diffuse sources and background sites from 28 different rivers in 6 different NRA regions. Table 4.1 documents the 40 sample sites, and a fuller description of each site, with a site map, is given in Appendix B.

Forty water samples and 36 sediment samples were successfully collected from the 28 sites. The shortfall in sediments reflects the non-availability of muddy sediment 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. Further details of the above sites are given in Appendix B.

**Table 4.1      Location and Description of Sampling Sites**

NRA Region/River	Grid Ref	Date	Site Location	Source	Associated Industry
<b>Thames</b>					
R. Thames	SU 720 742	8.7.92	Caversham Weir	diffuse sources	general urban
R. Thames	TQ 177 708	9.7.92	Teddington	diffuse sources	general urban
R. Thames	SU 106 937	10.7.92	Cricklade	background	
<b>Anglian</b>					
R. Cam	TL 434 524	14.7.92	Hauxton	above point source	Schering Agrochemicals
	TL 431 527	14.7.93		below point source	
R. Granta	TL 546 486	15.7.92	Hildersham	diffuse source	agriculture/pesticides
New River	TL 607 697	15.7.92	Wicken	background	
<b>North West</b>					
R. Alt	SD 292 051	21.7.92	Altmouth	diffuse	general urban
R. Mersey	SJ 616 878	21.7.92	Howley Weir	diffuse	general urban
R. Weaver	SJ 600 761	22.7.92	Acton	diffuse	general urban
R. Dane	SJ 932 637	22.7.92	Hugbridge	background	
<b>Yorkshire (Central)</b>					
Mag Brook (or R. Hall Dike)	SE 099 108	4.8.92	Honley	above point source/ background	STW/textiles
	SE 138 126	4.8.92		below point source	
R. Calder	SE 173 214	5.8.92	Mirfield	above point source	STW/chemical industry
	SE 201 198	5.8.92		below point source	
R. Aire	SE 426 260	6.8.92	Castleford	above point source	STW/chemical works, power station
	SE 535 256	6.8.92		below point source	
R. Aire	SE 326 313	7.8.92	Fleet Weir	above point source	STW
	SE 379 286	7.8.92		below point source	
R. Spenn	SE 176 278	4.8.92	Dewsbury	above point source	STW/chemical industry
	SE 231 206	4.8.92		below point source	
<b>Yorkshire (South)</b>					
R. Don	SK 398 912	11.8.92	Rotherham	above point source	STW/steel works
	SK 423 923	11.8.92		below point source	
R. Loxley	SK 298 896	12.8.92	near Sheffield	background	
<b>Severn Trent</b>					
R. Amber	SK 379 536	28.7.92	Ambergate	above point source	STW/textiles/colliery
	SK 353 517	28.7.92		below point source	
R. Derwent	SK 385 343	30.7.92	Church Wilne	above point source	STW/textiles
	SK 441 316	30.7.92		below point source	
R. Derwent	SK 347 484	31.7.92	Belper	above point source	STW/lubricating oils
	SK 347 457	31.7.92		below point source	
R. Erewash	SK 447 496	13.8.92	Eastwood	above point source	STW/textiles
	SK 464 454	13.8.92		below point source	
R. Lathkill	SK 223 646	14.8.92	Alport	background	
R. Derwent	SK 244 755	12.8.92	Froggatt	background	
Pressbrook	SK 385 601	14.8.92	Ogston	diffuse source	burial of rubble from Coalite explosion
R. Tame	SK 207 935	20.10.92	Lea Marston	above point source	lake purification system
	SK 214 945	20.10.92		below point source	
<b>Welsh</b>					
R. Irfon	SN 854 525	21.10.92	Abergwesyn	background	
R. Irfon	SN 920 471	21.10.92	Llangammarch Wells	diffuse source	major forestry
R. Lugg	SO 570 375	22.10.92	Hereford	diffuse source	agriculture

## 5. SAMPLE COLLECTION AND STORAGE

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 (TOC) determination
- 100 ml water for dissolved organic carbon (DOC) 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  $<63 \mu\text{m}$ )

### 5.1 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 submerged beneath the water, and 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. A 1 l sample for particulate loading determination was also collected in this way, but the foil lid insert was not necessary. Once the lids were in place they were secured with tape.

Water samples were also collected for TOC and DOC determination, the difference between the two being a measure of the POC content. The concentrations of POC and DOC are likely to have an impact on the proportion of PCDD/Fs present in 'solution' and so indirectly on their bioavailability and toxicity (see Section 2.2). Particulate-associated PCDD/Fs also have the potential to be incorporated into deposited sediments which provide a long term reservoir. In association with this, the amount of suspended particulates in the water column were also determined.

The 100 ml amber glass bottles used for the determination of TOC and DOC were free of organics, having been fired in a furnace at  $550^{\circ}\text{C}$  for 5 hours. On sampling, lids were again opened and closed beneath the water surface, and the bottles rinsed before sampling as described above. On the same day that samples were taken, the samples collected for TOC determination were acidified to  $\sim\text{pH}2$  with orthophosphoric acid. DOC samples were filtered using glass Millipore filtering equipment with glass-fibre filter papers. The glassware and filter papers were cleaned of organics prior to use by heating to  $550^{\circ}\text{C}$  in a furnace. 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.

## 5.2 Sediment samples

Section 2.2 described how PCDD/Fs in association with contaminated sediments can enter fish through the foodchain, through inadvertent consumption of sediment itself, and through the desorption of the PCDD/Fs into the river water and uptake across gill membranes. The surface sediments are therefore of most immediate concern in terms of PCDD/F contamination.

A precise definition of 'surface sediment' (in terms of depth of sediment that is likely to be in intimate contact with the overlying water or feeding biota) is not possible because of differing sediment accumulation rates in different rivers. In this study, a depth of 3 cm was assumed to represent surface sediment material. Any benthic invertebrates living and burrowing in the sediment to this depth are likely to be accessible to species higher up the foodchain. Also, the top 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. Ten to fifteen cores were required to provide the quantity of surface sediment (about 1 kg wet weight) required for PCDD/F analysis. Internal consistency is maintained within a site by always taking exactly the same depth of material.

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 remove sediment cores using the Gilson corer with 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 without the need for a corer. Both these methods allow the recovery of samples with an intact sediment-water interface. This is necessary to retain the fine particulates at the sediment surface which would otherwise be resuspended and lost from the sample when the water was syphoned off from the top of the core. Fine material contains a relatively higher concentration of dioxins than coarse particles, due to increased surface area, and so it is important to sample this surface layer.

Once a sediment core had been extracted, the surface 3 cm of sediment was sliced off and placed into a 1 l amber glass bottle. Additional cores were collected, and this method was repeated until the bottle had been filled. 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.

In addition to collecting wet sediment for PCDD/F analysis, additional samples were taken to determine the water content of the sediment, the organic carbon content and particle size (<63 µm diameter). Section 2.2 described how particulate-associated PCDD/Fs become incorporated into bottom sediments, and so the determination of sediment parameters such as those described can assist in the interpretation of PCDD/F results.

After sediment sampling was complete at each site, the equipment was thoroughly washed with demineralised water to ensure that cross-contamination between sites did not occur.

### **5.3 Documentation, Labelling and Storage**

A field note book was taken to all sites and the date, site name, national grid reference, brief site description, weather conditions, and any other relevant details were recorded. Photographs were also taken at most sites as a visual record. All containers were clearly marked with a water-resistant paint pen before sampling commenced, giving the date, the site name and the analysis to be carried out on the sample. 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, were placed in a cold room, or refrigerators, at less than 5°C. The sediment samples for PCDD/F analysis were air dried and stored in amber glass jars prior to analysis.

### **5.4 Suitability of sampling strategy for future NRA applications**

The sampling strategy described above is suitable for use as an NRA sampling protocol and could be applied to routine monitoring using individuals with the appropriate expertise. The main necessity for collecting both water and sediment samples as described above is to be able to access the river itself. Before sediment sampling can take place, areas of sediment accumulation have to be located. Depending on the site, sediment may be located easily, but often a considerable amount of searching is required to locate areas of accumulating sediment, particularly if a river has a stoney or rocky bed. Also, experience is required to differentiate between accumulating sediment and bank or bed material. The coring method itself requires some expertise, since it is not always straightforward to retrieve cores with the sediment-water interface intact. This sampling strategy is applicable to a wide variety of river types. A basic sampling protocol is given in Appendix C.

## **6. ANALYSIS OF SAMPLES AND RESULTS**

### **6.1 Water samples**

#### **6.1.1 Determination of particulate loading**

For each sample, the volume of water collected was recorded prior to filtration. The sample was then drawn through pre-weighed filters (Millipore HVLP 0.45µm, 47 mm diameter polyvinylidene difluoride filter membrane) by a partial vacuum to a 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 (to an accuracy of 0.1 mg l<sup>-1</sup>) 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 Appendix D (Table D.1).

#### **6.1.2 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. A brief method description is given here, and further analytical details can be obtained from Mr P. Smith of NRA Severn Trent if required.

Filtered, acidified water samples (see Section 5.1) for DOC analysis were sparged with carbon dioxide-free nitrogen or argon to remove inorganic CO<sub>2</sub>. The samples were then oxidised under the action of ultra violet radiation in the presence of potassium persulphate to oxidise organic matter to CO<sub>2</sub>, which was measured on an infra-red detector. In the unfiltered TOC samples, inorganic CO<sub>2</sub> was removed in the same way, and the samples were injected into a furnace at between 700° and 900°C to produce CO<sub>2</sub>. This was measured in the same way as for DOC.

DOC results were subtracted from TOC at each site to provide a measure of POC. Results are given in Appendix D (Table D.2).

#### **6.1.3 Analysis of PCDD/Fs**

Of the 5x1 l water samples collected for PCDD/F analysis, 1-2 l was taken for each extraction. A 50 µl aliquot of a standard solution containing <sup>13</sup>C<sub>12</sub>-labelled 2378-PCDD/Fs was added to each litre prior to extraction. The composition of the standard is given in Appendix E (Table

E.1). The standard was added as an internal quantitation standard and also to act as an internal retention time reference in the gas chromatograph analysis. Each of the 1 l samples was extracted using 2 x 50 ml of n-hexane. The two hexane extracts from the two samples were mixed together and reduced to a volume of about 10 ml by freeze-drying. The sample extract was then put onto an acid clean-up column (pre-washed using 50 ml n-hexane) containing, in order, anhydrous sodium sulphate, 50/50 (w/w) concentrated sulphuric acid/Celite 545, 9/1 (w/w) anhydrous sodium sulphate/sodium hydrogen carbonate, 60-120 mesh silica gel and anhydrous sodium sulphate. The column was washed with 90 ml n-hexane to ensure complete elution of PCDD/Fs. This clean-up method was based on that of di Domenico *et al* (1979).

The 100 ml elution volume obtained from the column clean-up stage was reduced to about 2 ml in volume by freeze-drying, and was transferred to a prewashed chromatography grade basic alumina (Woelm) column. The column was washed with 10 ml n-hexane containing 2% dichloromethane and the washings discarded. A subsequent wash, using 10 ml of a 25/75 (v/v) n-hexane/dichloromethane mixture, was used to elute the PCDD/Fs. The eluent was reduced in volume to about 1 ml, and 100 µl of a solution of <sup>37</sup>Cl<sub>4</sub>-labelled 2378-TCDD in n-dodecane was added. The sample was then reduced to a final volume of 100 µl. The <sup>37</sup>Cl<sub>4</sub>-labelled TCDD was used as a recovery standard in the analysis to calculate the recovery efficiency of the extraction and clean-up procedure and as an internal quality control standard. The use of stable isotope labelled standards for internal quantitation and quality control has been described by Ambidge *et al* (1990).

The analysis of the 100 µl concentrated extract from the sample for PCDD/Fs was carried out using capillary gas chromatography-high resolution mass spectrometry (GC/HRMS) operating the VG Autospec mass spectrometer in the multiple ion detection mode via voltage scanning and using group switching. The column used was SGE BP5 50m capillary column (0.25 mm i.d., 0.2 µm film) initially at a temperature of 180°C. The sample was injected via a split/splitless injector in the splitless mode and after 1 minute the column was temperature programmed to 220°C at 10°C/min. A second temperature programme at 4°C/min to 280°C, at which the temperature of the column was held for 30 min, was used to elute the PCDD/Fs.

The results of PCDD/F analysis on the water samples showed that they were below the analytical limit of detection, which is give in Appendix E (Table E.2).

## 6.2. Sediment Samples

### 6.2.1 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 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 Appendix D (Table D.3).

The remaining sediment samples were sent to ADAS Laboratories to determine the amount of sand (<63 µm) in each sample. The results are also given in Appendix D.

### 6.2.2 Analysis of PCDD/Fs

Sufficient ground, dried sediment (about 100 g) was taken from each sample and weighed into a Soxhlet thimble. To this, 50 µl of a standard solution containing <sup>13</sup>C<sub>12</sub>-labelled 2,3,7,8-substituted PCDD/Fs was added (composition given in Appendix E, Table E.1). This acted as an internal quantitation standard and as an internal retention time reference in the gas chromatographic analysis.

The sample was extracted using 250 ml of an 80/20 (v/v) n-hexane/acetone mixture for 4 hours. The extract was washed using 50 ml M NaOH followed by a distilled water wash. The hexane layer was retained and reduced to a volume of about 10 ml by freeze-drying. This was put onto a prewashed column containing, in order, anhydrous sodium sulphate, 50/50 (w/w) concentrated sulphuric acid/Celite 545, 9/1 (w/w) anhydrous sodium sulphate/sodium hydrogen carbonate, 60-120 mesh silica gel and anhydrous sodium sulphate. The column was washed with 90 ml n-hexane to ensure complete elution of PCDD/Fs. This clean-up method was based on that of di Domenico *et al* (1979).

The 100 ml elution volume obtained from the column clean-up stage was reduced to about 2 ml in volume by freeze-drying, and was transferred to a prewashed chromatography grade basic alumina (Woelm) column. The column was washed with 10 ml n-hexane containing 2% dichloromethane and the washings discarded. A subsequent wash, using 10 ml of a 25/75 (v/v) n-hexane/dichloromethane mixture, was used to elute the PCDD/Fs. The eluant was reduced in volume to about 1 ml, and 100 µl of a solution of <sup>37</sup>Cl<sub>4</sub>-labelled 2378-TCDD in n-dodecane was added. The sample was then reduced to a final volume of 100 µl. The <sup>37</sup>Cl<sub>4</sub>-labelled



TCDD was used as a recovery standard in the analysis to calculate the recovery efficiency of the extraction and clean-up procedure and as an internal quality control standard. The use of stable isotope labelled standards for internal quantitation and quality control has been described by Ambidge *et al* (1990).

The analysis of the 100 µl concentrated extract from the sample for PCDD/Fs was carried out using capillary gas chromatography-high resolution mass spectrometry (GC/HRMS) operating the VG Autospec mass spectrometer in the multiple ion detection mode via voltage scanning and using group switching. The column used was SGE BP5 50m capillary column (0.25 mm i.d., 0.2 µm film) initially at a temperature of 180°C. The sample was injected via a split/splitless injector in the splitless mode and after 1 minute the column was temperature programmed to 220°C at 10°C/min. A second temperature programme at 4°C/min to 280°C, at which the temperature of the column was held for 30 min, was used to elute the PCDD/Fs.

The results of PCDD/F analysis on the sediment samples taken are given in Appendix E, Tables E.3-E.22, and are shown in Figures 6.1 - 6.20. Where the concentration of one of the toxic isomers fell below the limit of detection, the TEQ was calculated using the analytical detection limit. This gave the highest likely TEQ value for the sample. The Figures give the total PCDD/Fs in each homologue group, and the percentage contribution of the 17 toxic isomers to the total TEQ. Only those isomers which contribute 4% or greater to the total are given.

### Explanatory Sheet for Figures 6.1-6.20

The x-axis labelling of Figures reporting total concentrations of PCDD/F homologue groups is as follows.

D4 = TCDD  
D5 = PeCDD  
D6 = HxCDD  
D7 = HpCDD  
D8 = OCDD

F4 = TCDF  
F5 = PeCDF  
F6 = HxCDF  
F7 = HpCDF  
F8 = OCDF

The x-axis labelling of Figures reporting percentage contribution of individual isomers to TEQ is as follows.

The numbers indicate the position of the substituted chlorine atoms

The letters D and F represent dioxins and furans respectively

e.g. 2378D = 2378-TCDD

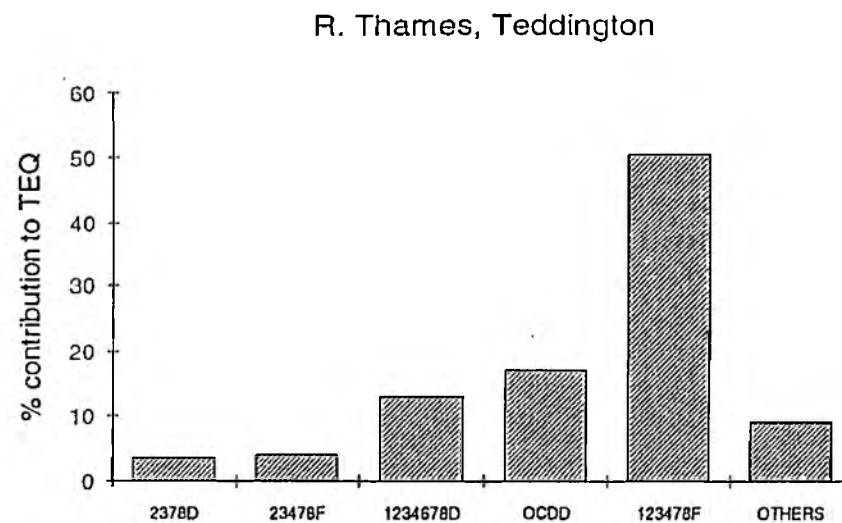
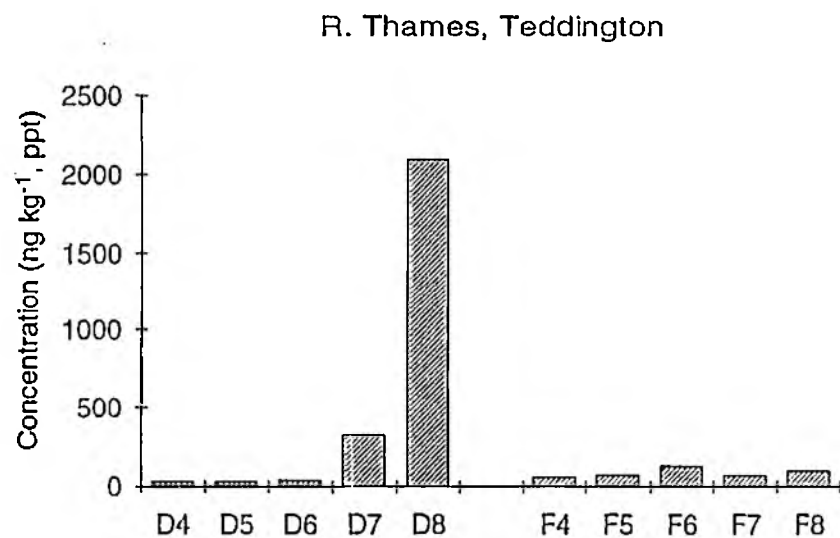
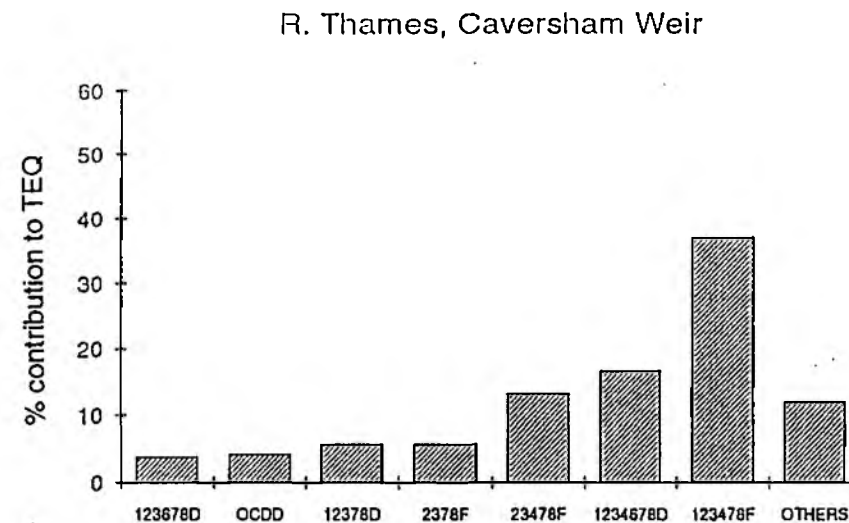
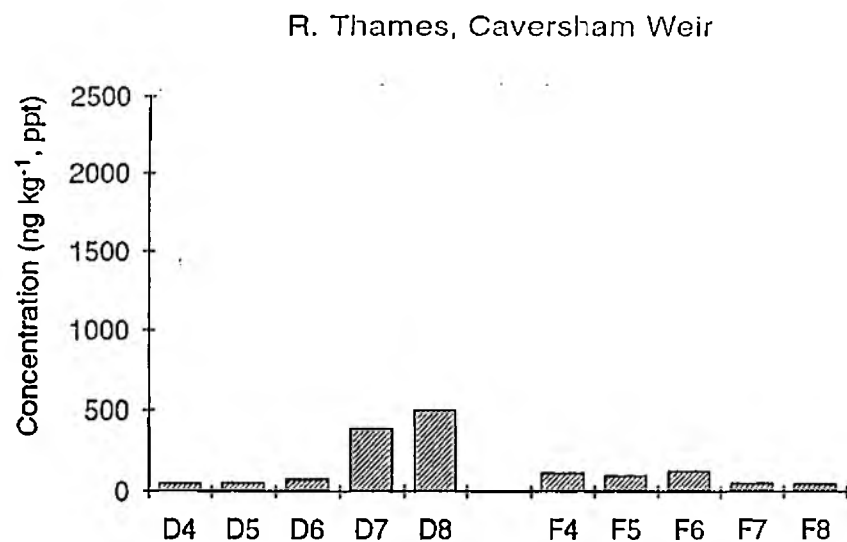
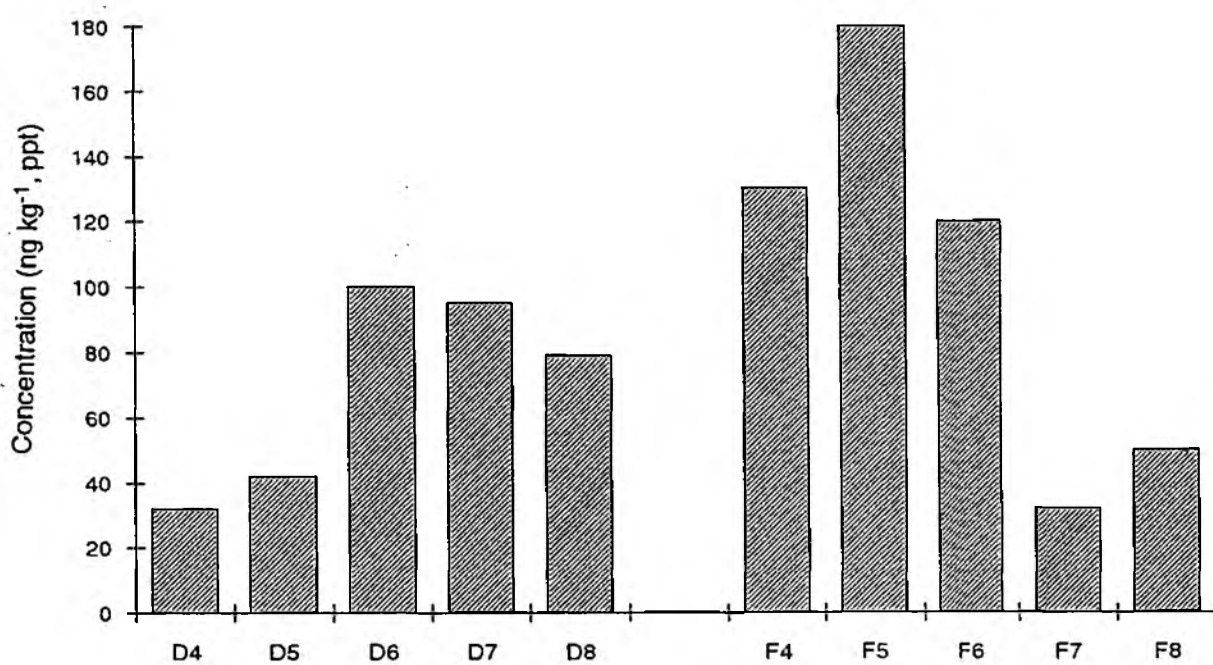


Figure 6.1 Homologue group concentrations and isomer contributions to TEQ for the River Thames at Caversham Weir and Teddington

# R. Thames, Cricklade



# R. Thames, Cricklade

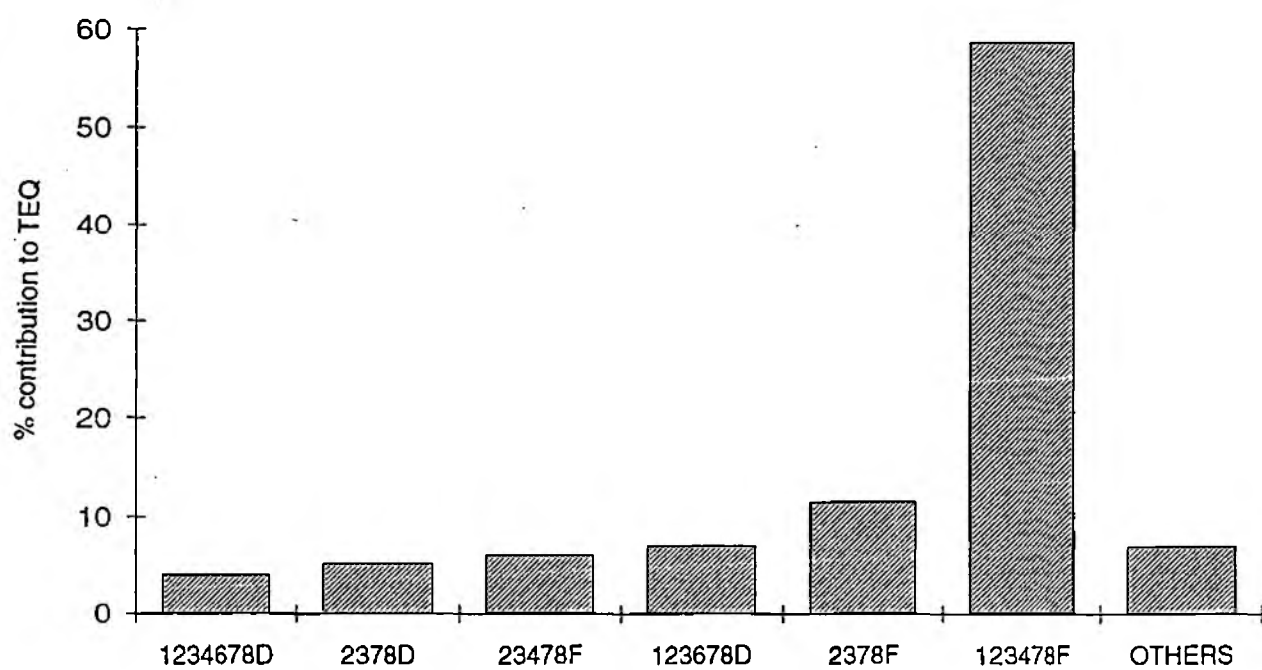


Figure 6.2 Homologue group concentrations and isomer contributions to TEQ for the River Thames at Cricklade

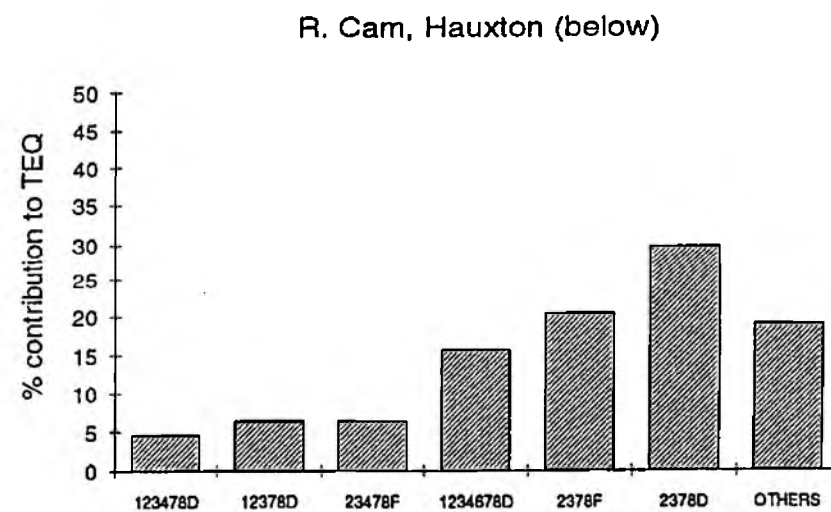
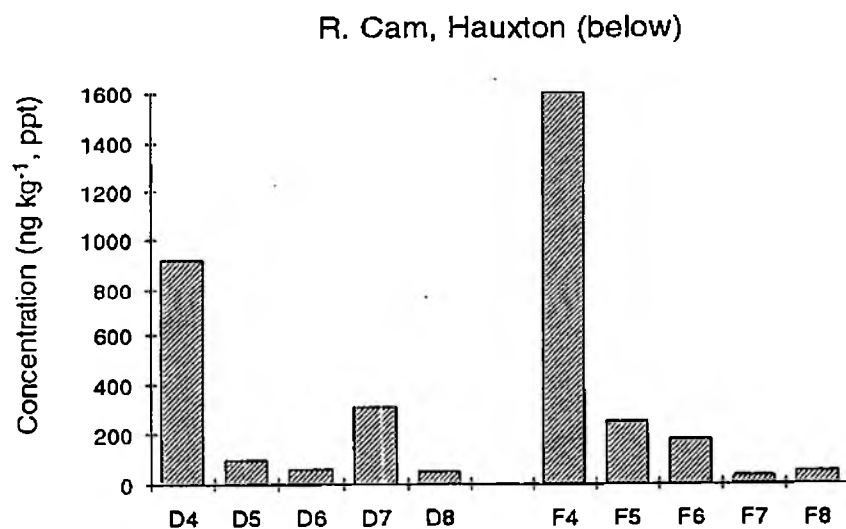
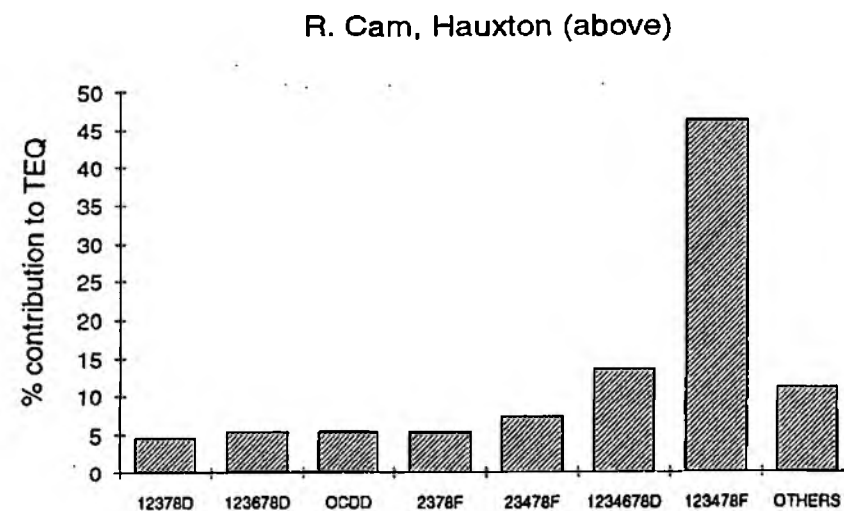
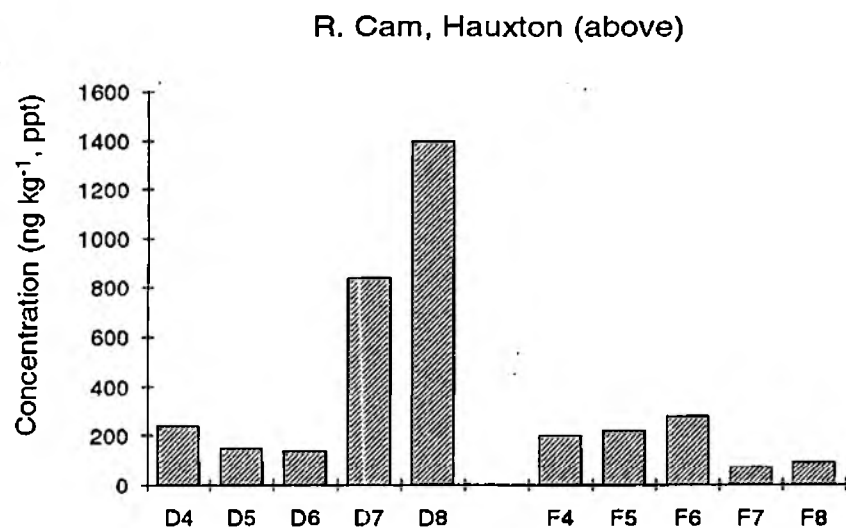


Figure 6.3 Homologue group concentrations and isomer contributions to TEQ for the River Cam above and below the potential point source at Hauxton

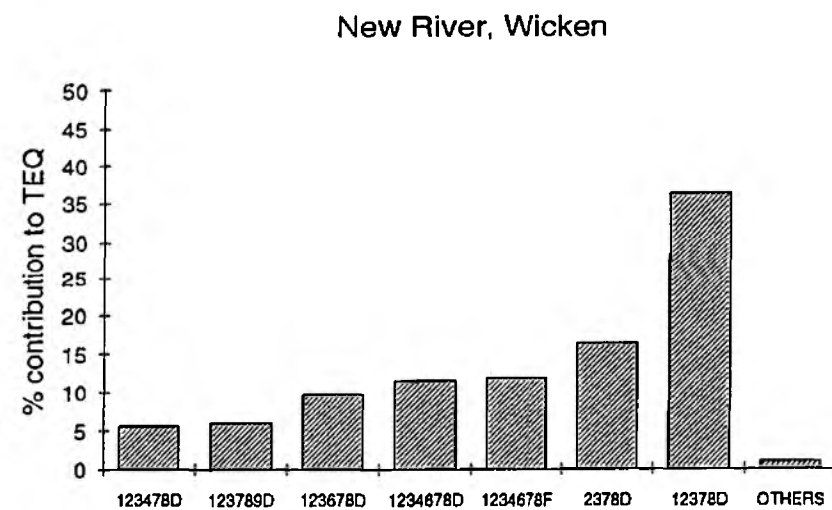
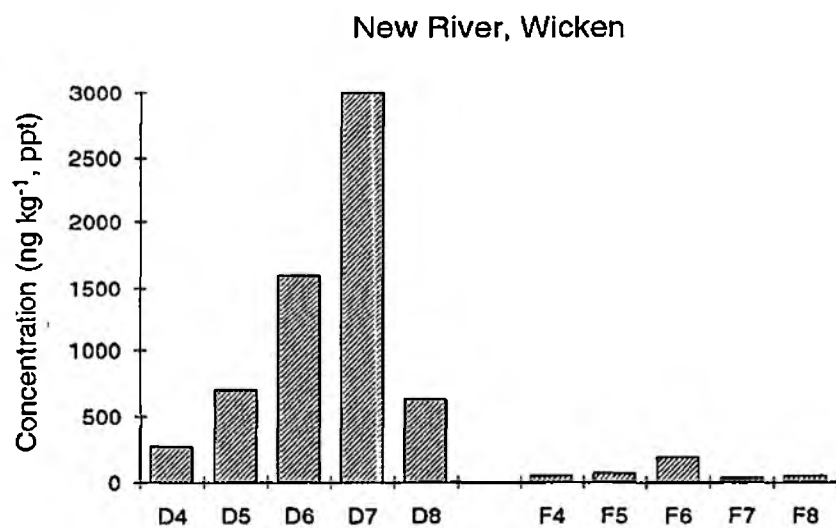
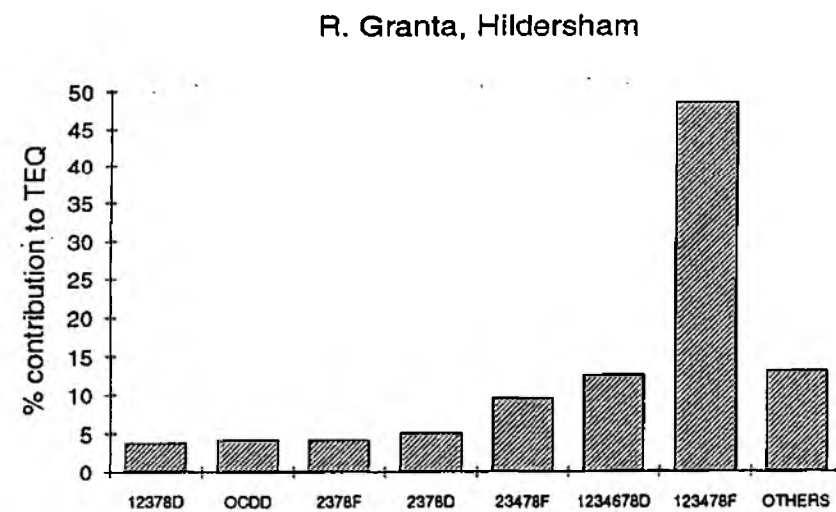
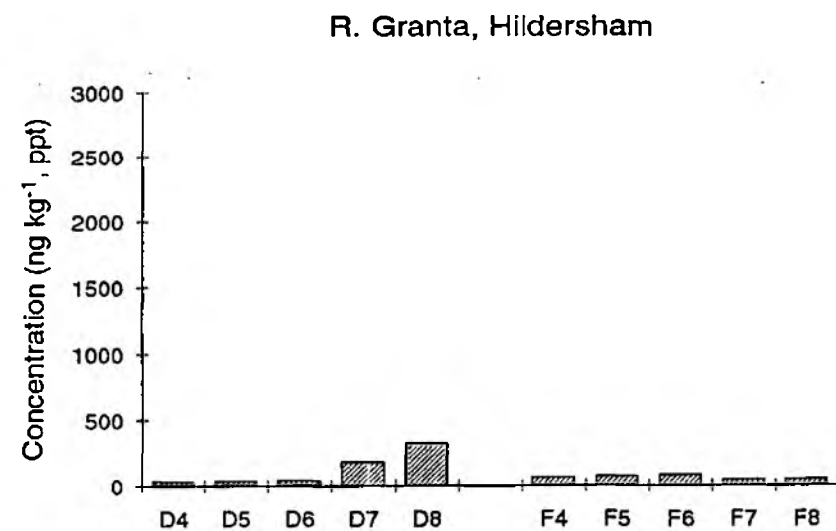


Figure 6.4 Homologue group concentrations and isomer contributions to TEQ for the River Granta at Hildersham and the New River at Wicken

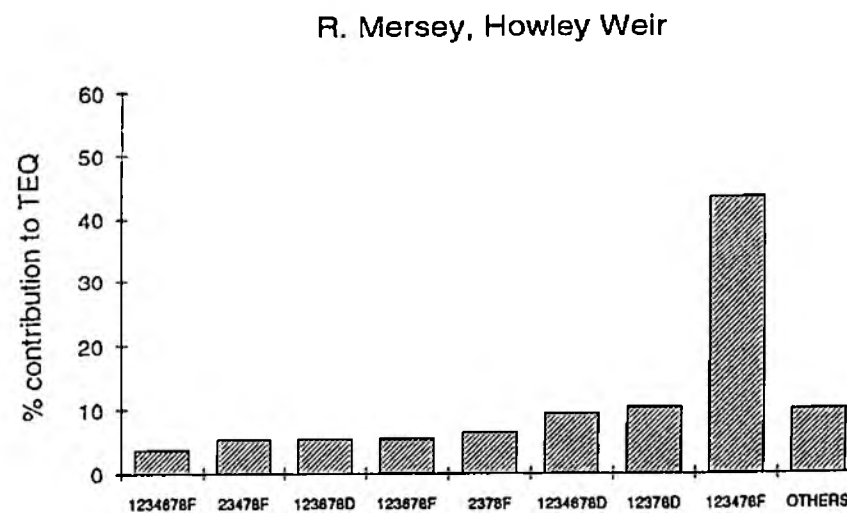
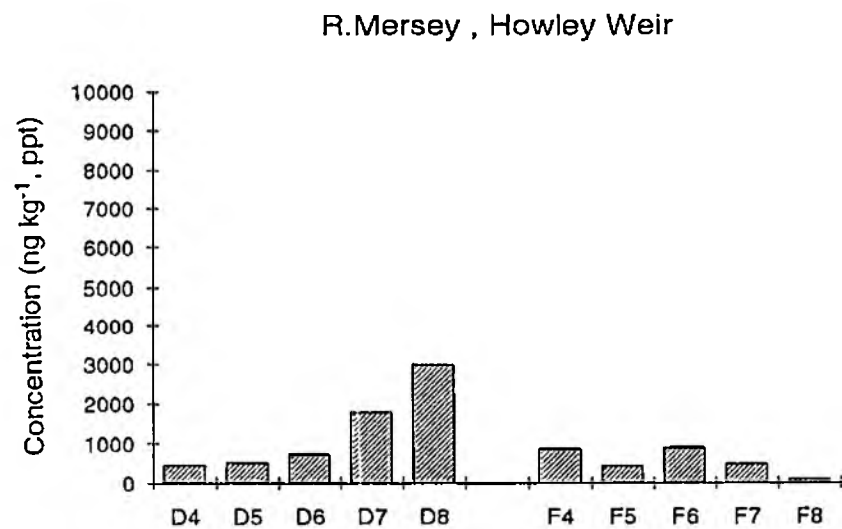
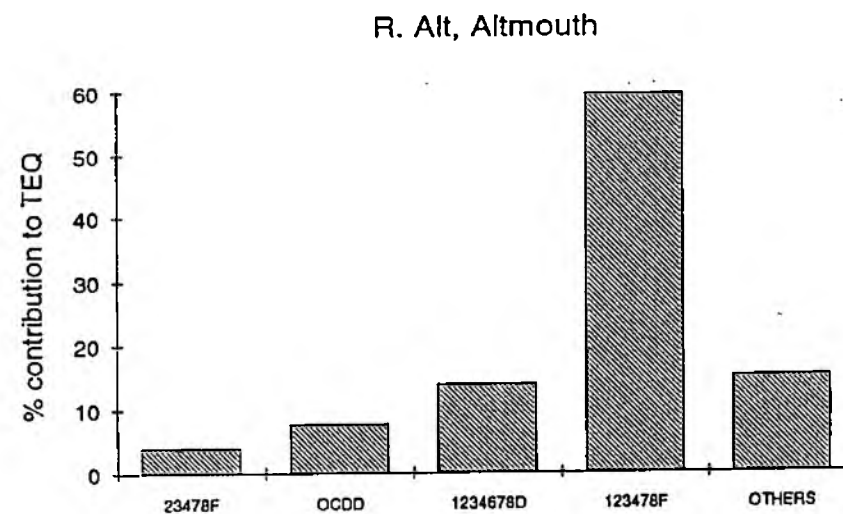
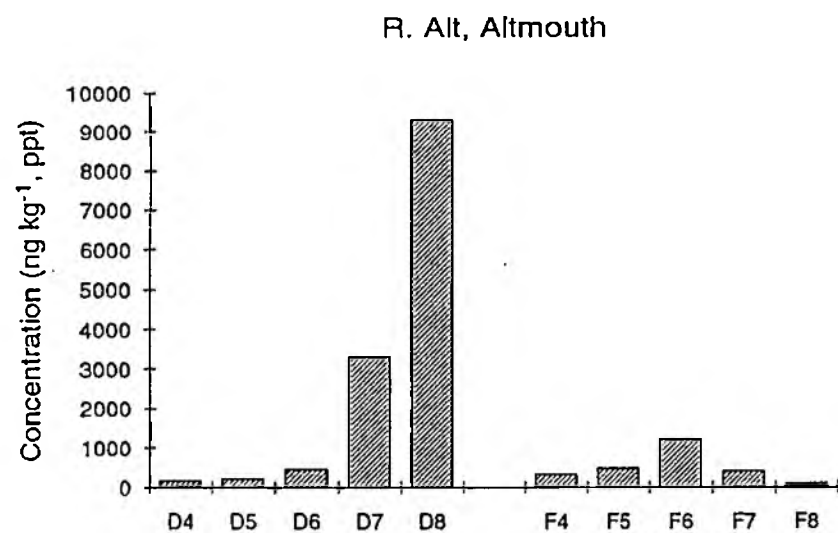


Figure 6.5 Homologue group concentrations and isomer contributions to TEQ for the River Alt at Altmouth and the River Mersey at Howley Weir

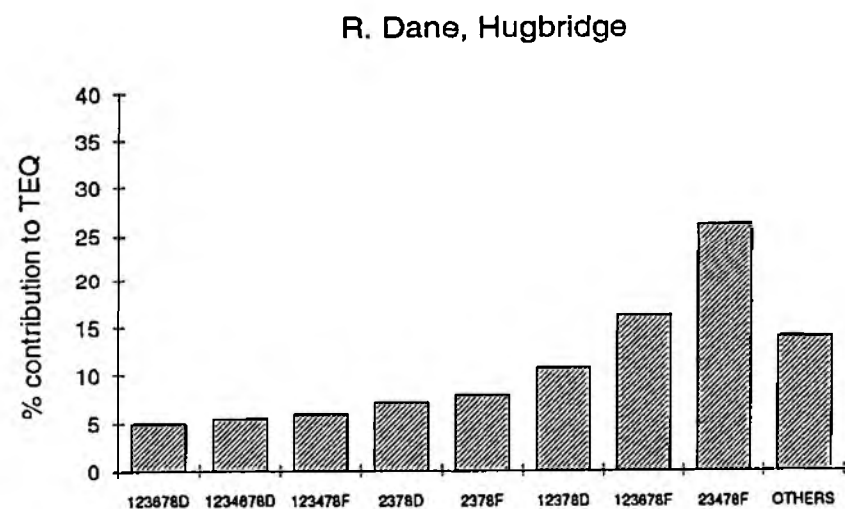
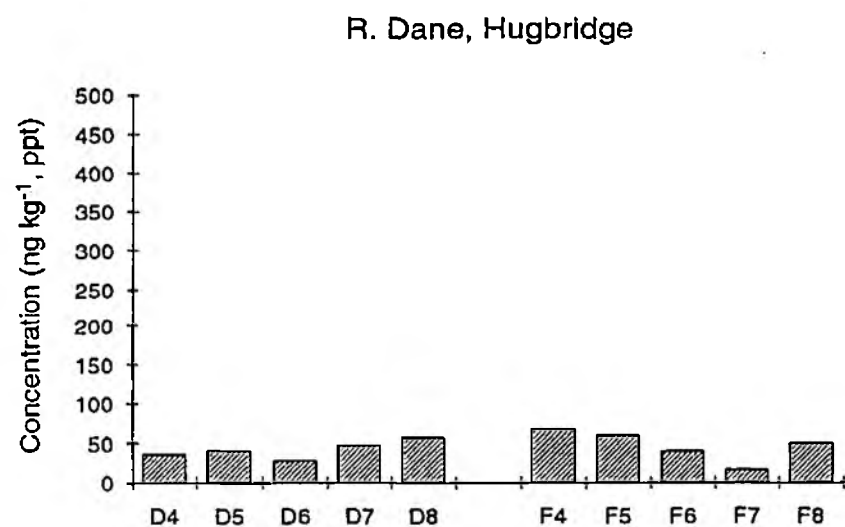
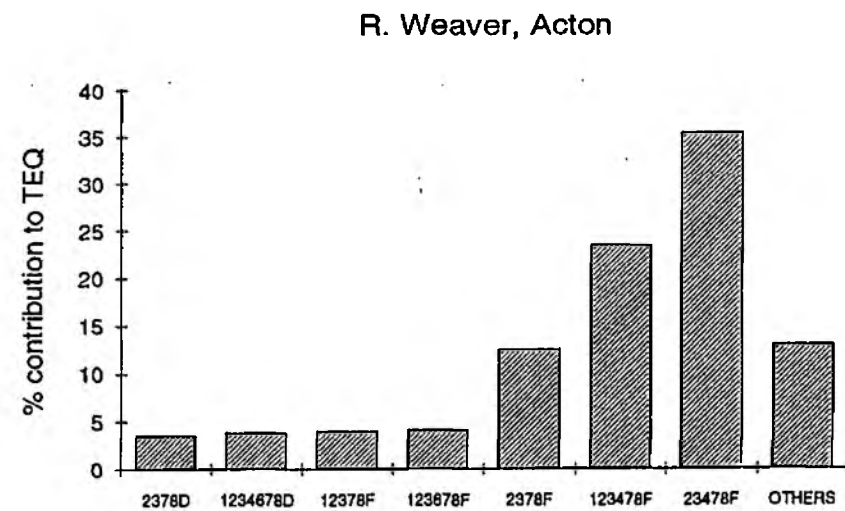
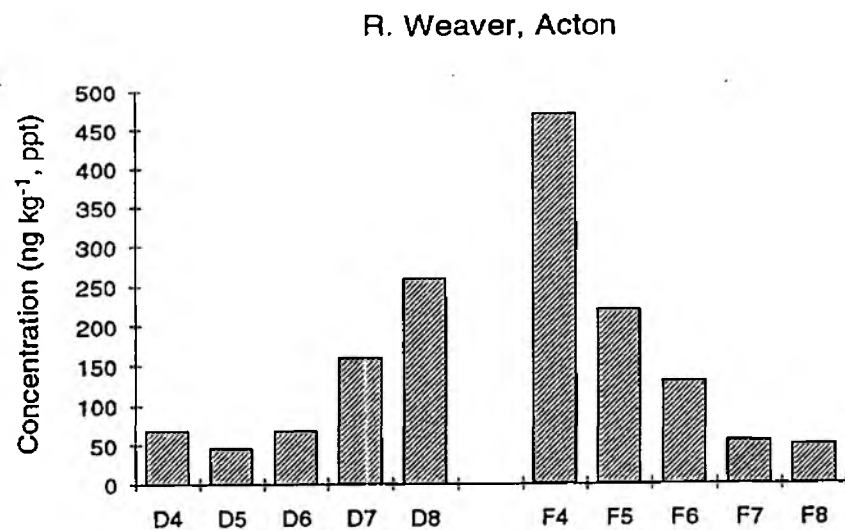


Figure 6.6 Homologue group concentrations and isomer contributions to TEQ for the River Weaver at Acton and the River Dane at Hugbridge



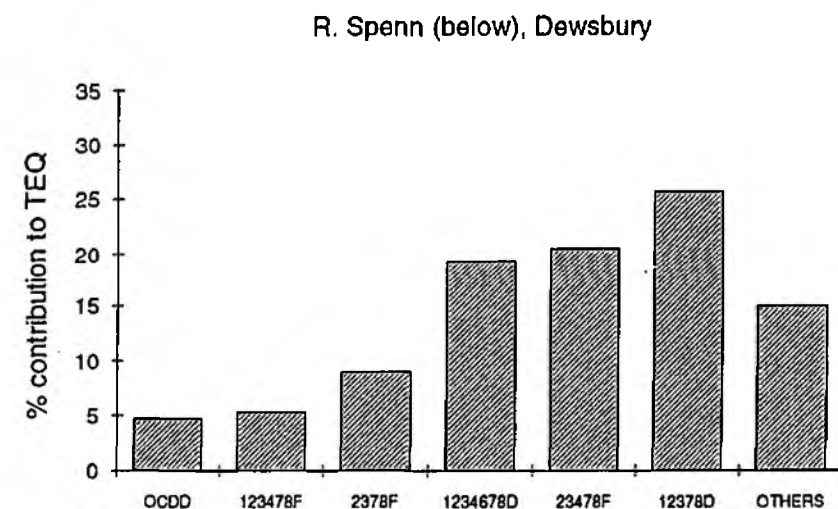
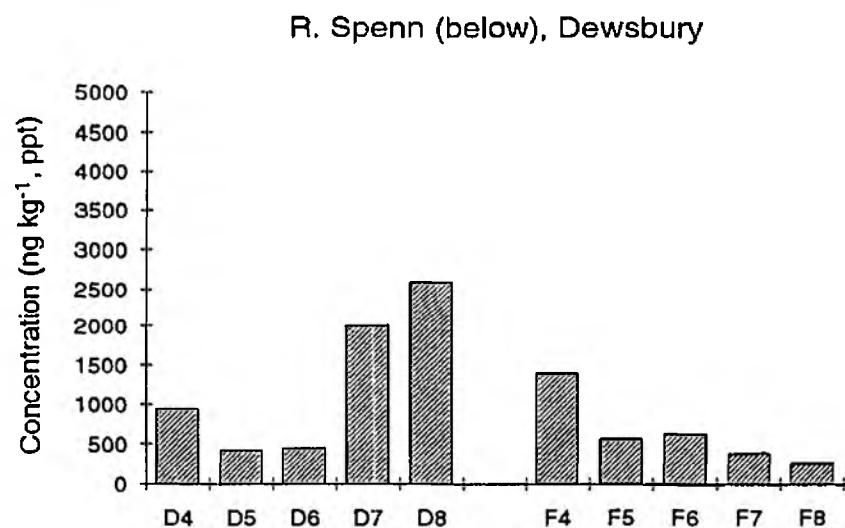
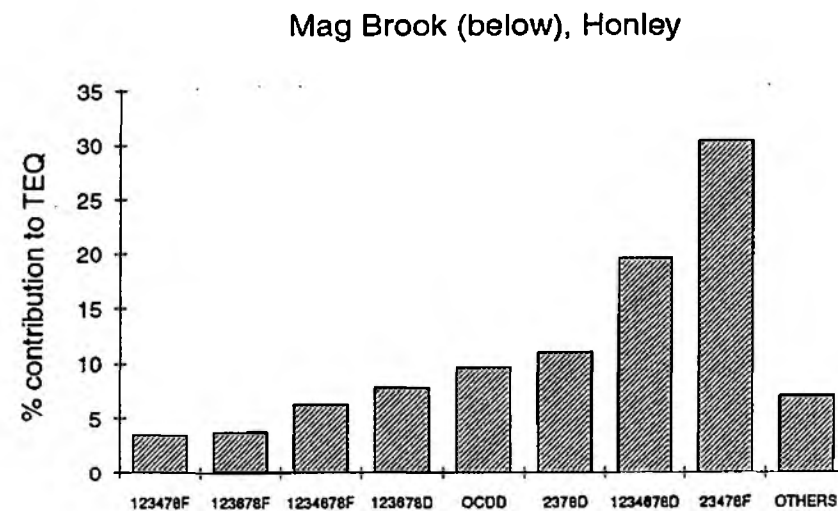
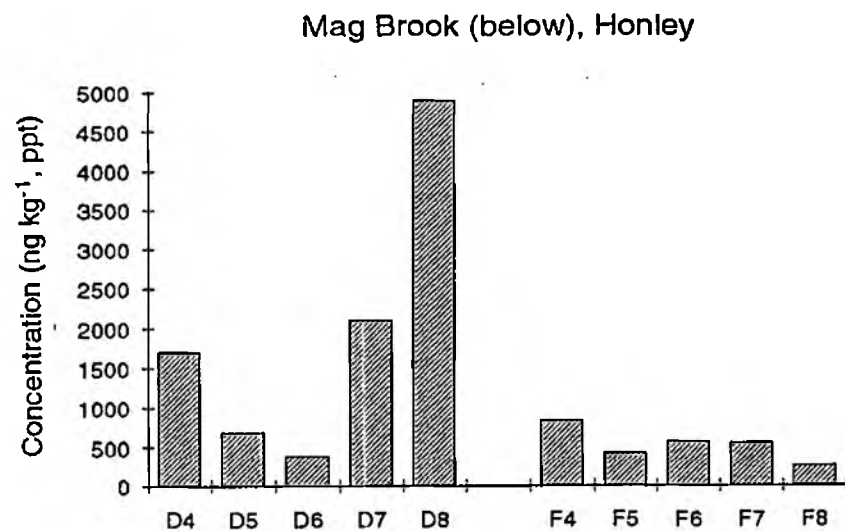


Figure 6.7 Homologue group concentrations and isomer contributions to TEQ below the the potential point sources at Mag Brook, Honley and the River Spenn, Dewsbury

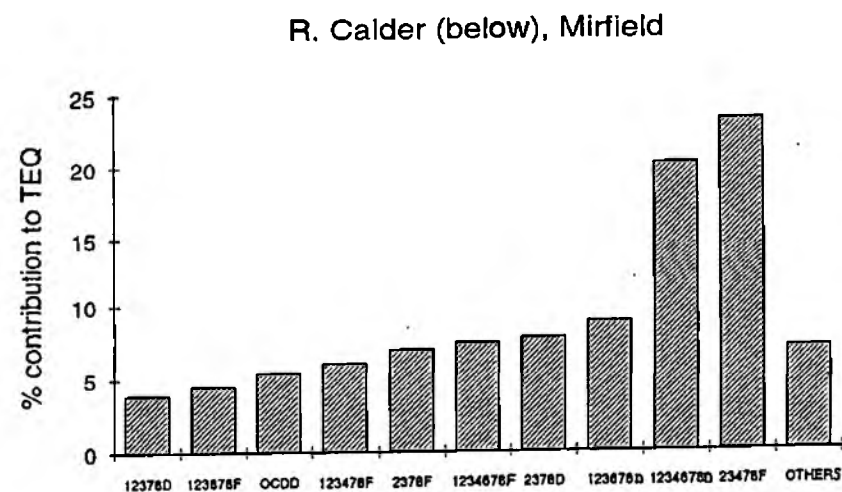
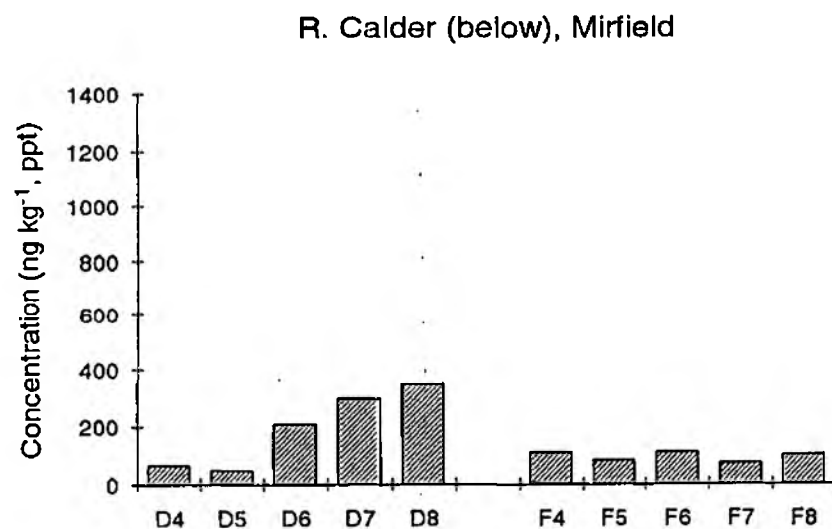
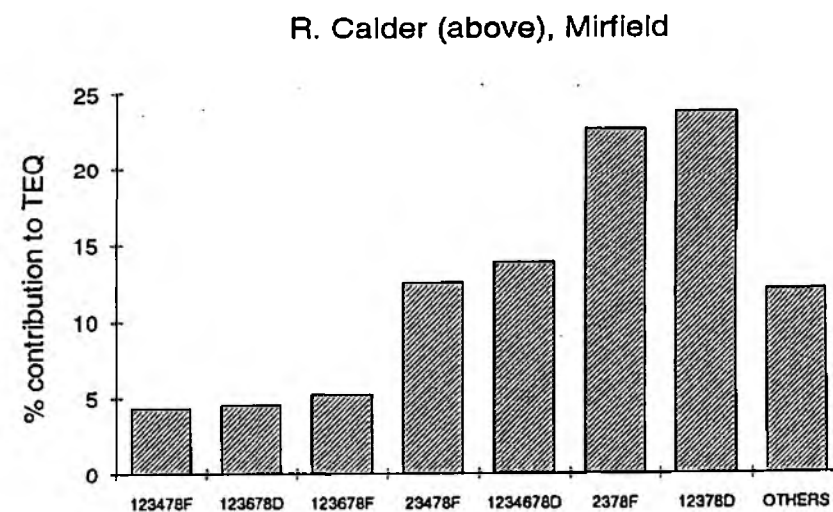
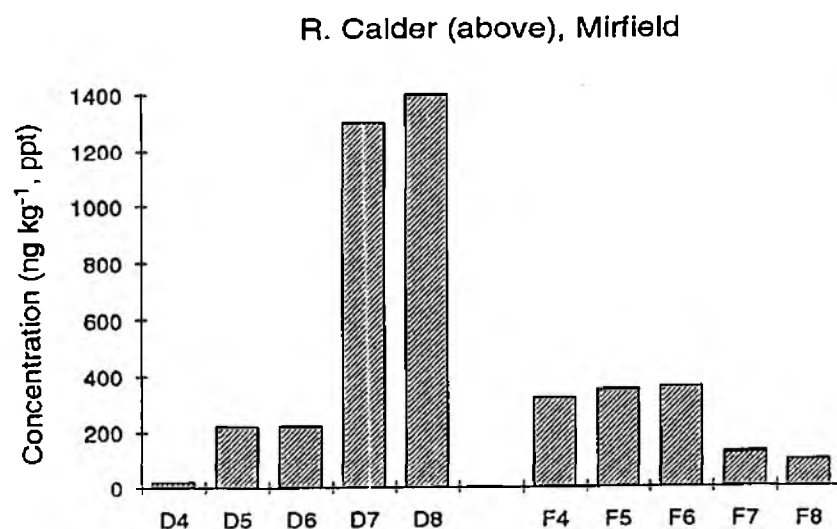


Figure 6.8 Homologue group concentrations and isomer contributions to TEQ for the River Calder above and below the potential point source at Mirfield

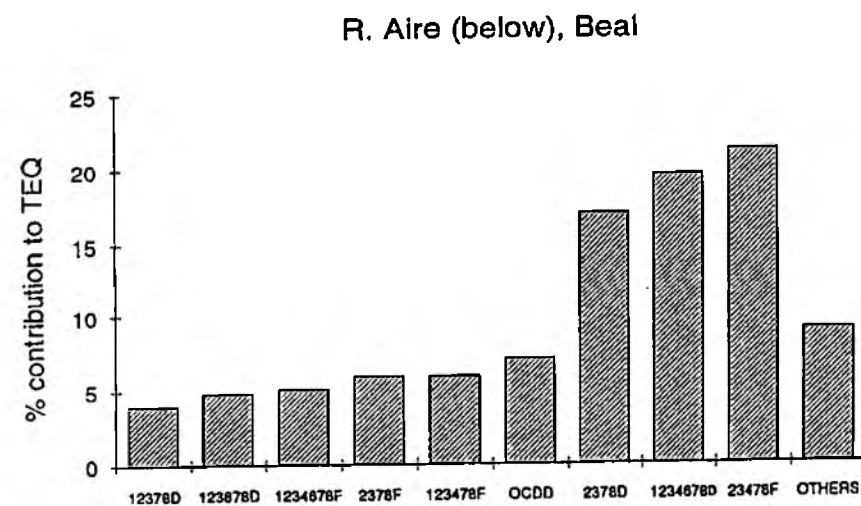
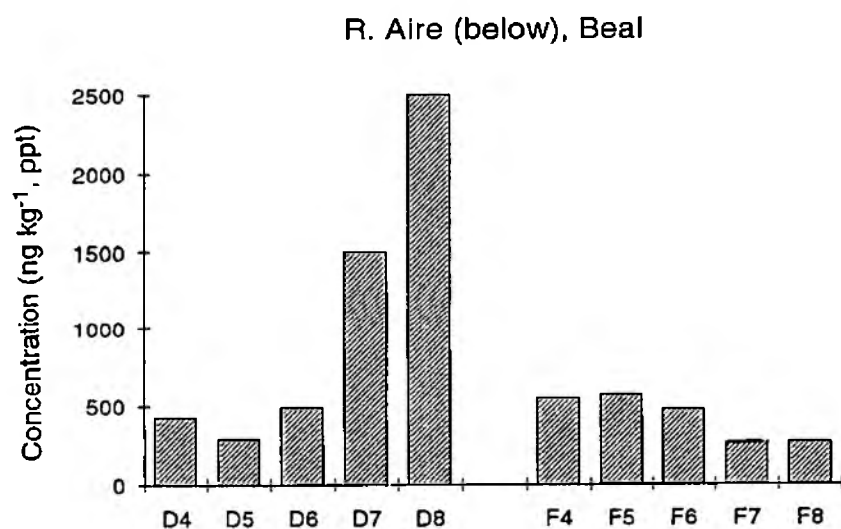
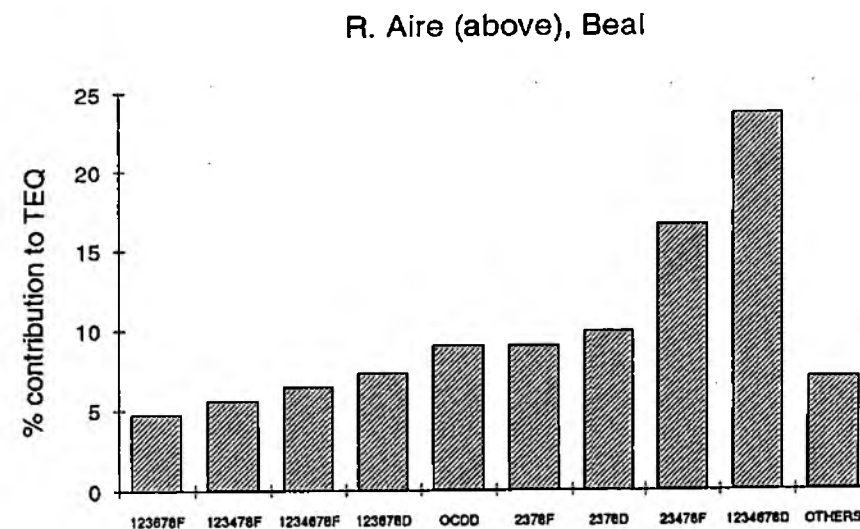
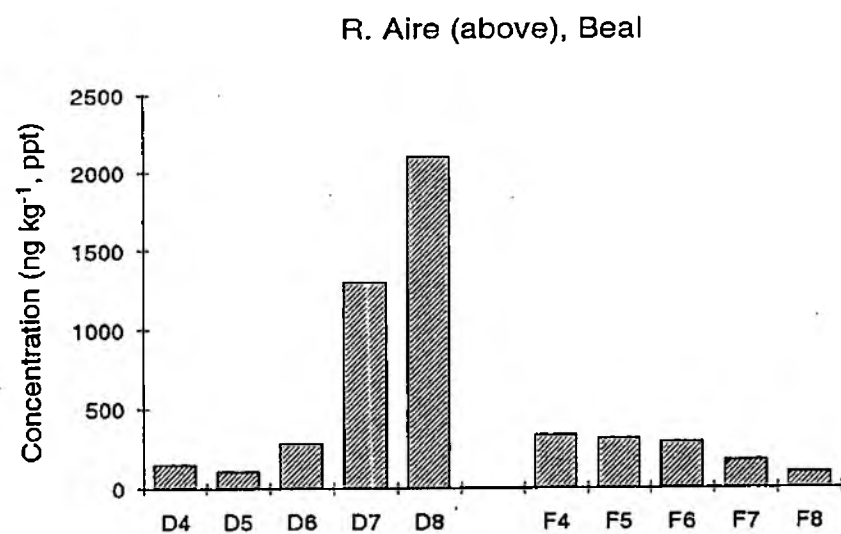


Figure 6.9 Homologue group concentrations and isomer contributions to TEQ for the River Aire above and below the potential point source at Beal

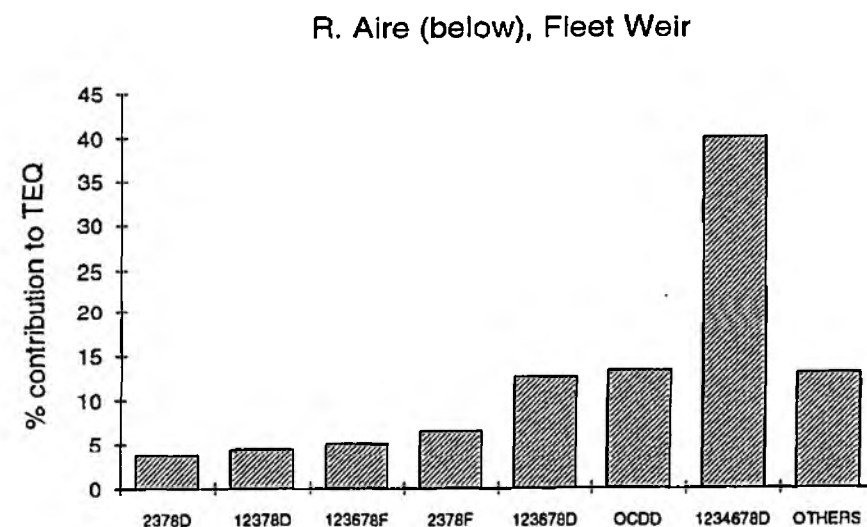
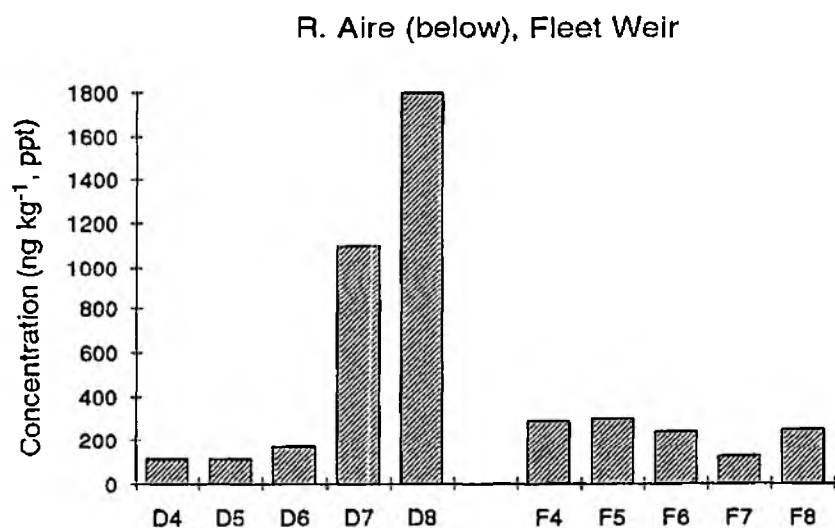
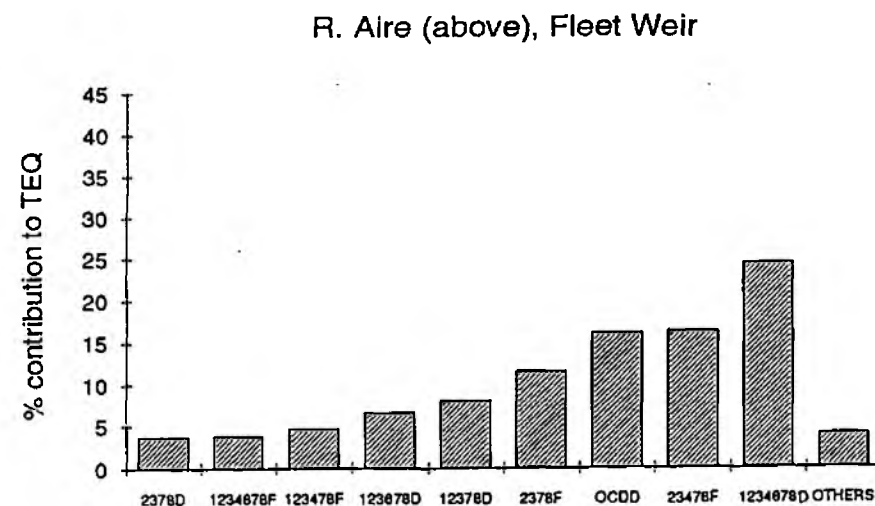
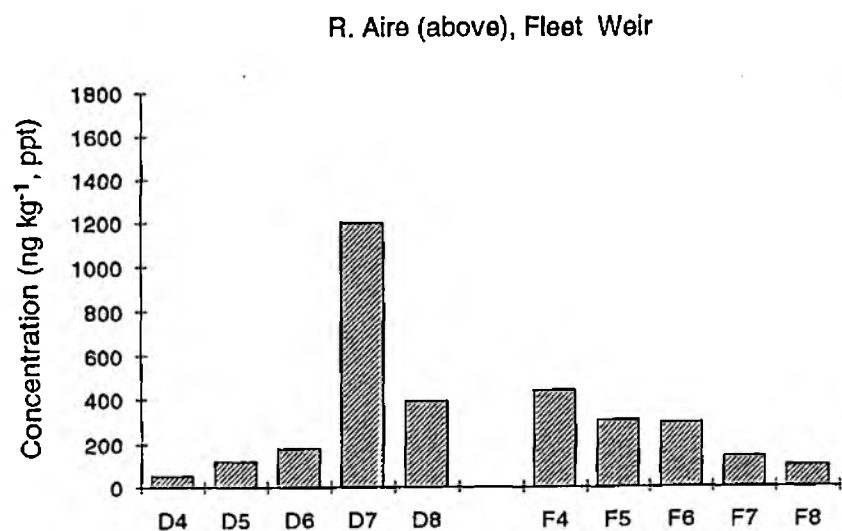


Figure 6.10 Homologue group concentrations and isomer contributions to TEQ for the River Aire above and below the potential point source at Fleet Weir

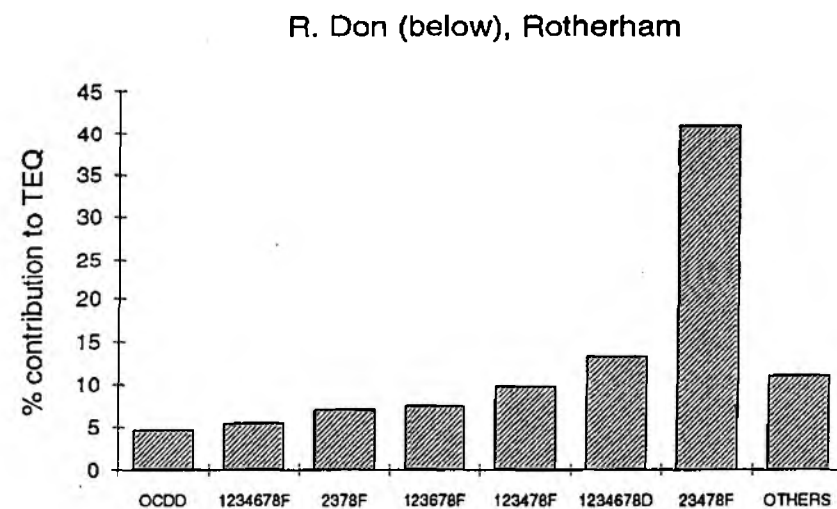
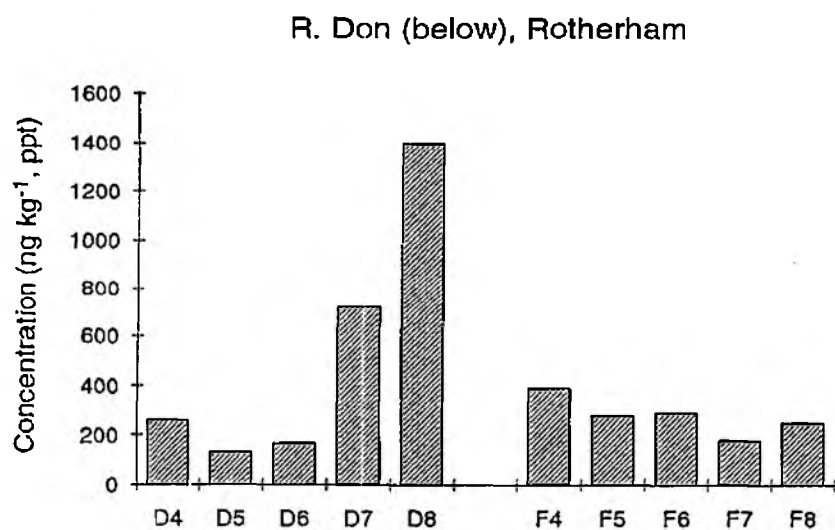
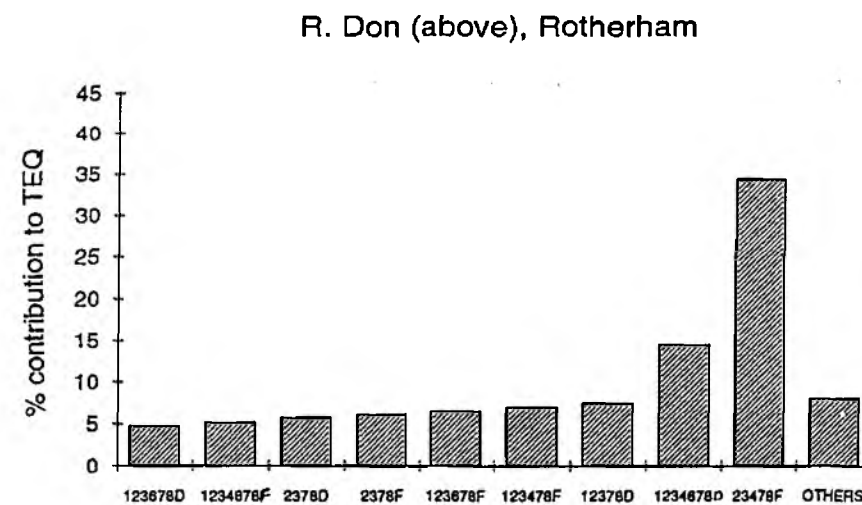
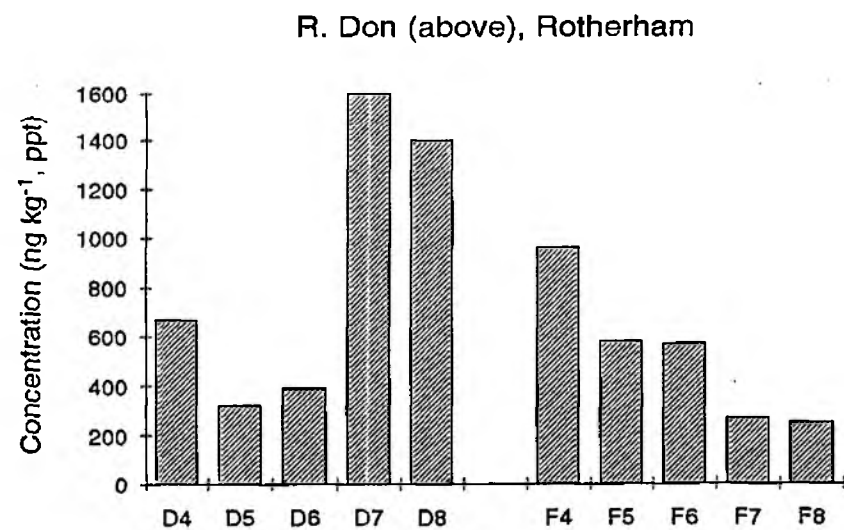


Figure 6.11 Homologue group concentrations and isomer contributions to TEQ for the River Don above and below the potential point source at Rotherham

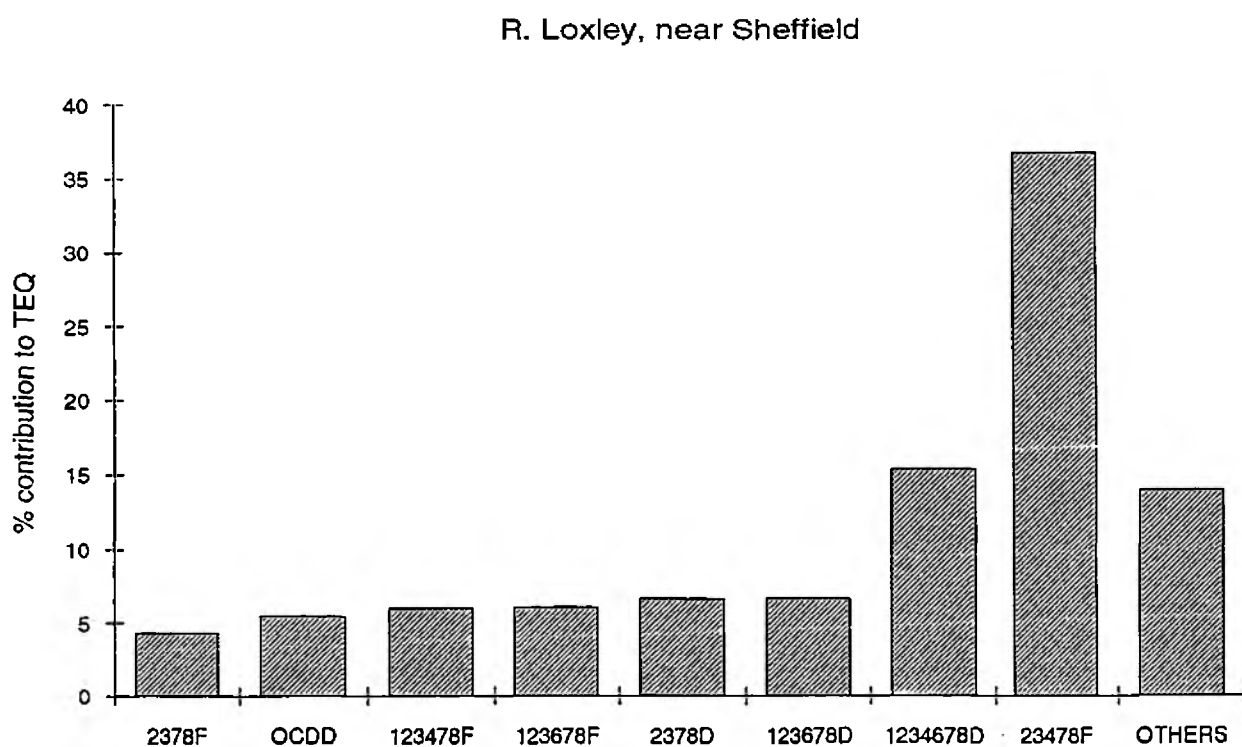
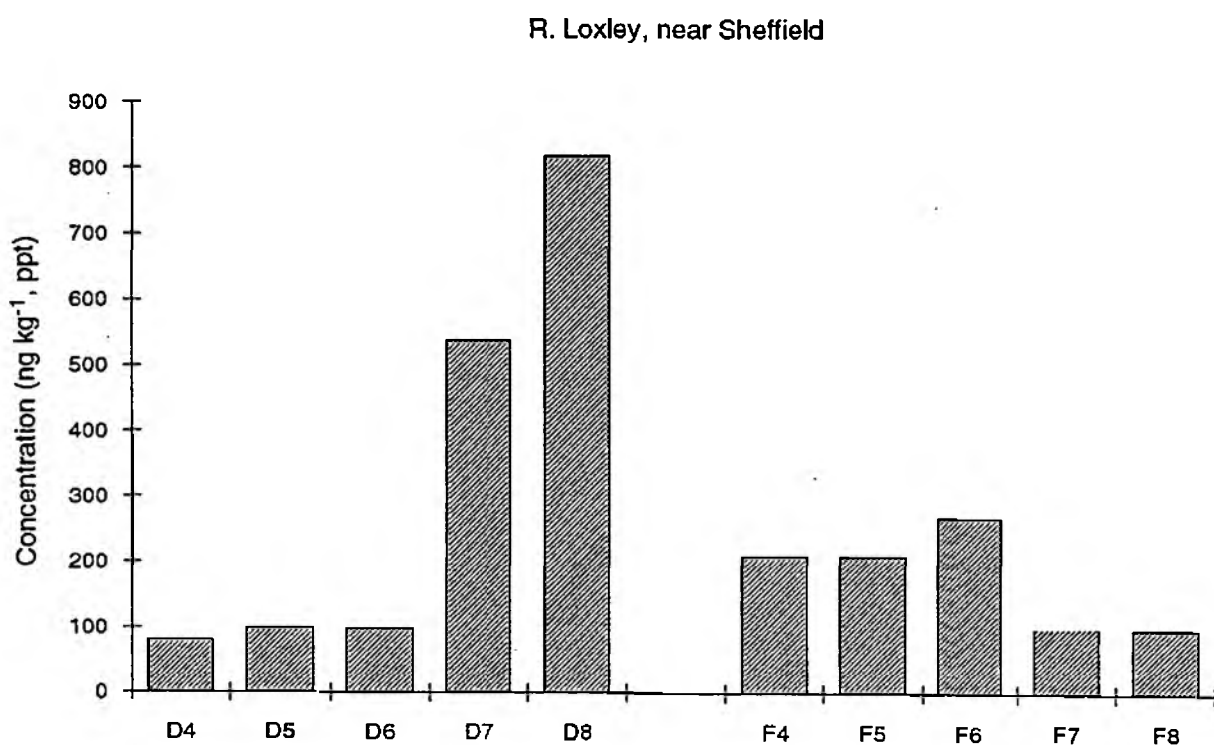


Figure 6.12 Homologue group concentrations and isomer contributions to TEQ for the River Loxley near Sheffield

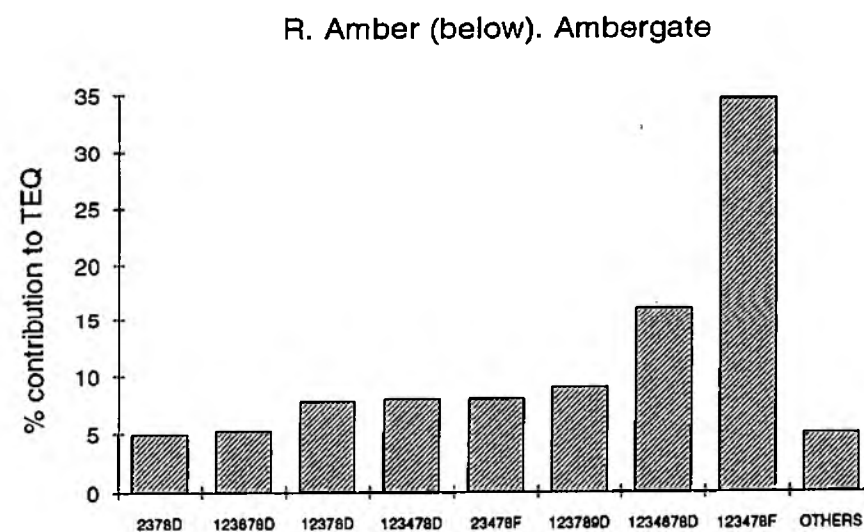
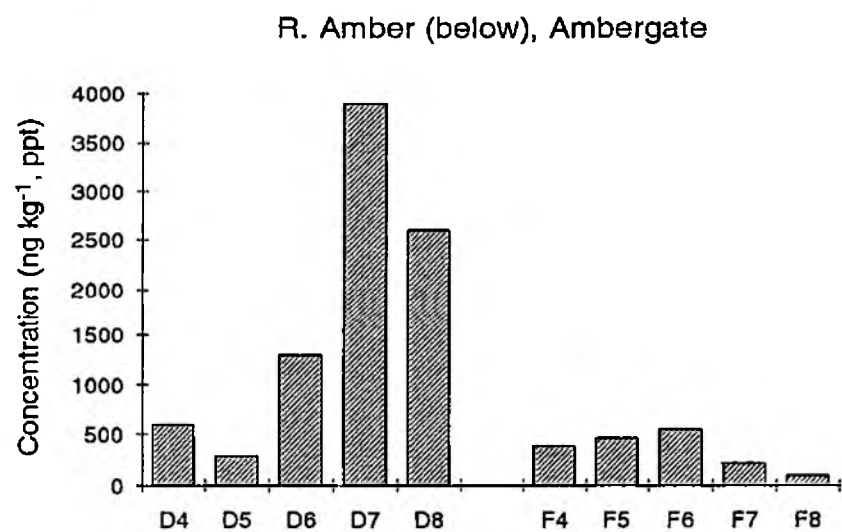
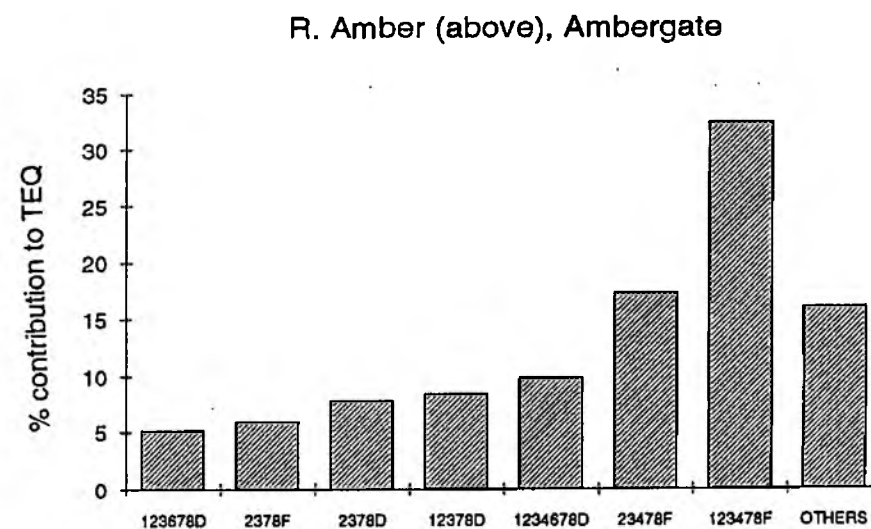
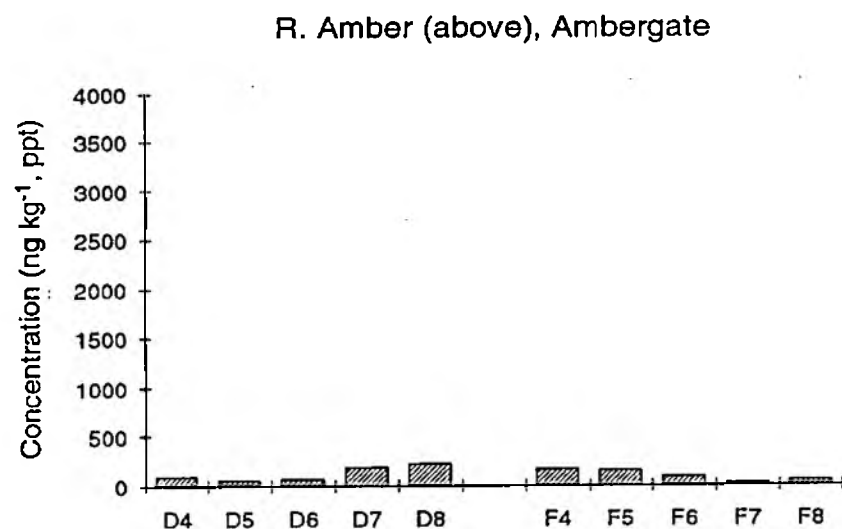


Figure 6.13 Homologue group concentrations and isomer contributions to TEQ for the River Amber above and below the potential point source at Ambergate



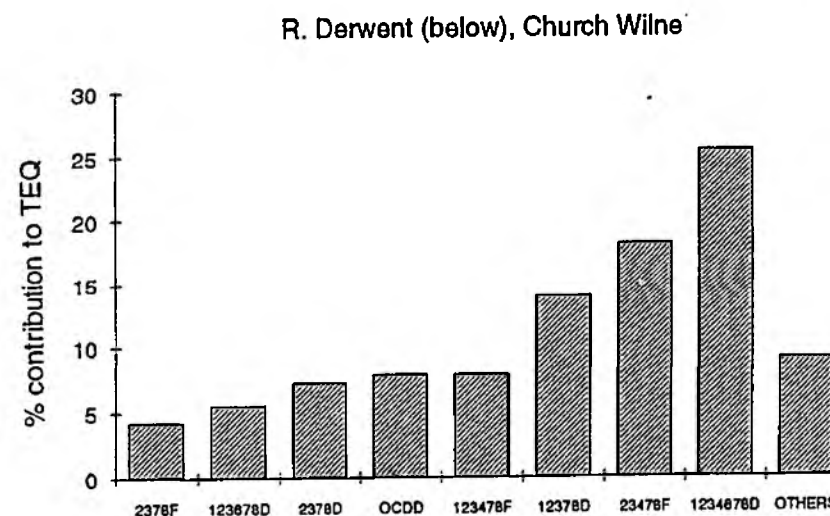
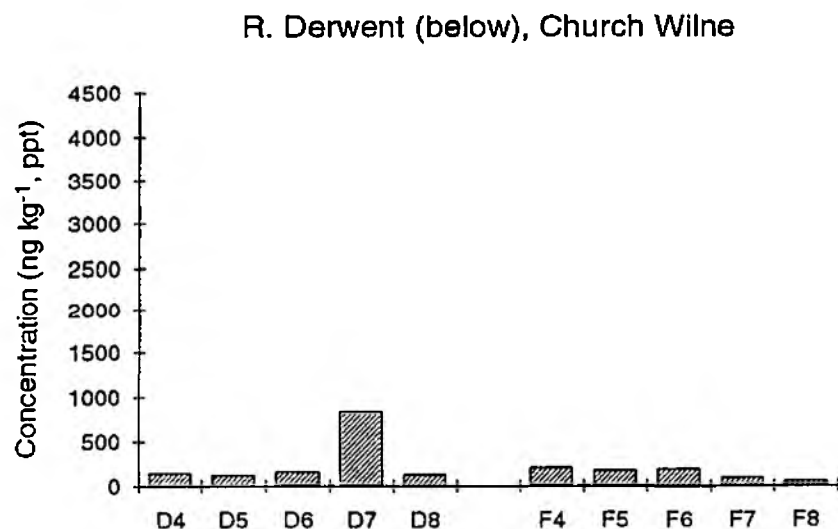
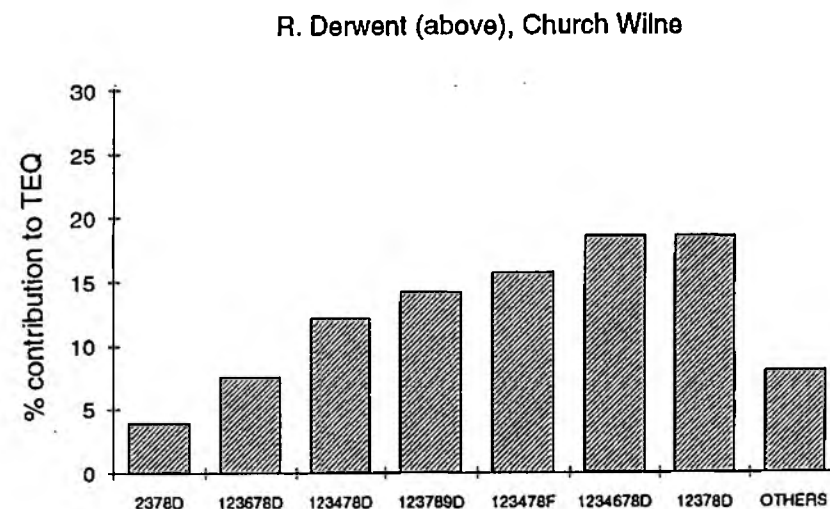
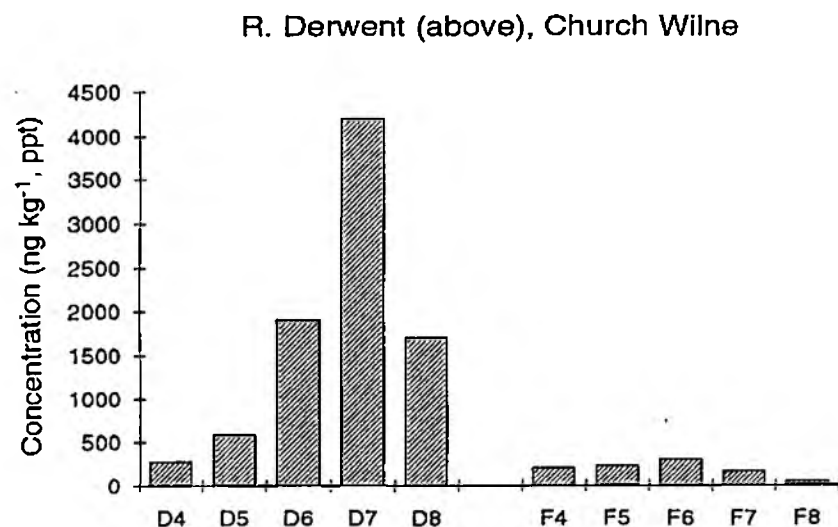


Figure 6.14 Homologue group concentrations and isomer contributions to TEQ for the River Derwent above and below the potential point source at Church Wilne



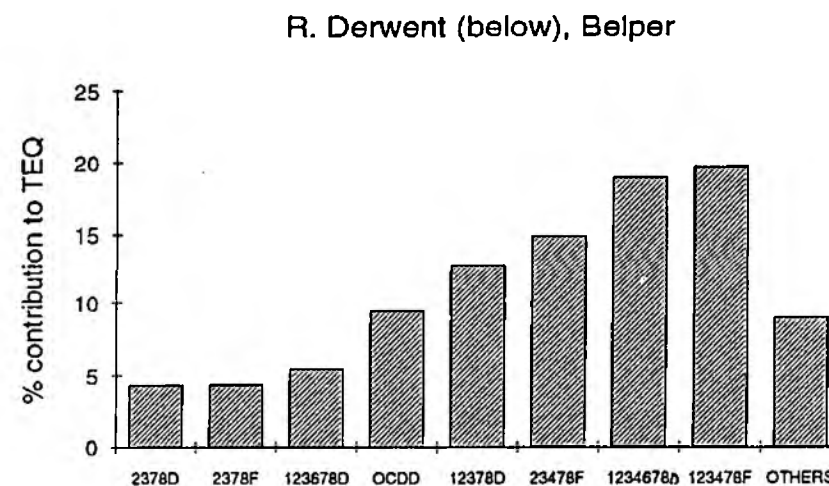
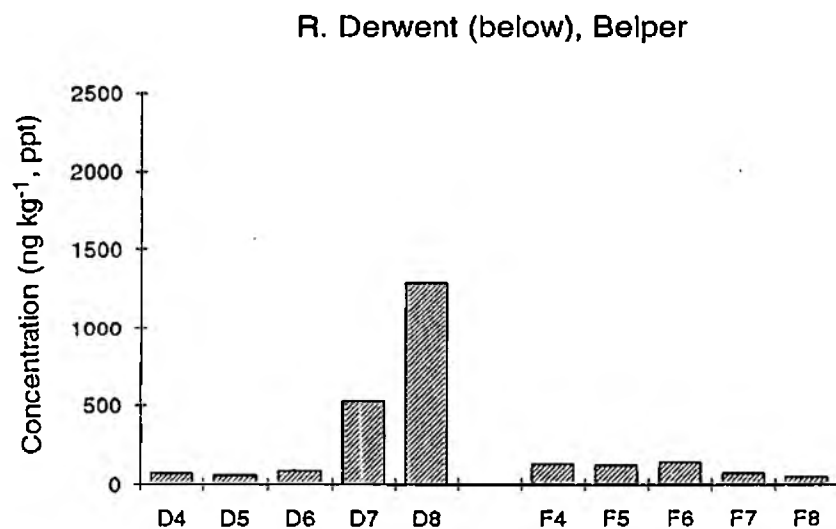
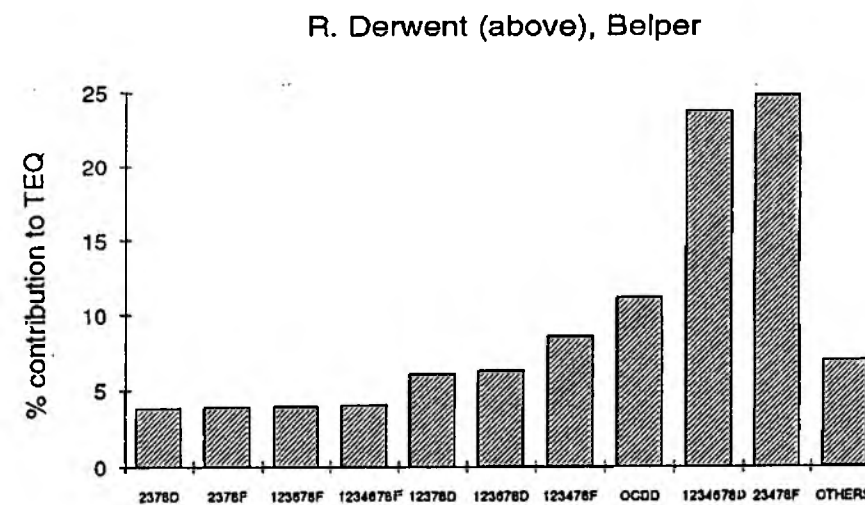
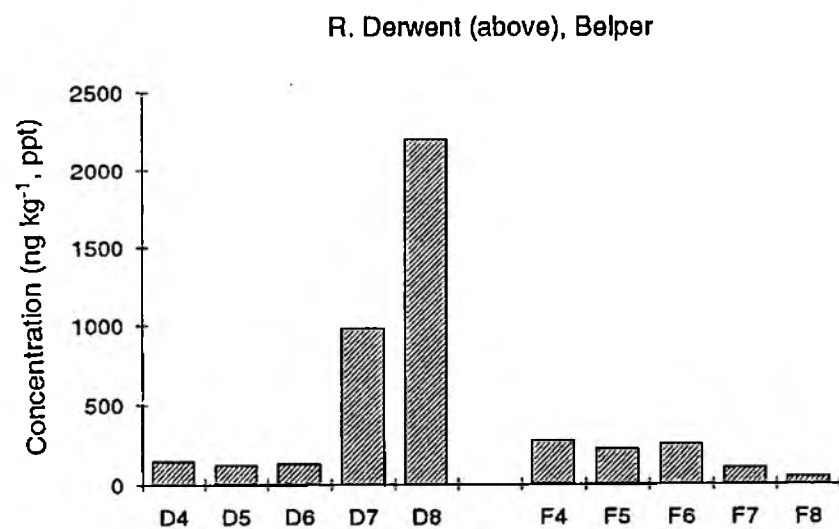


Figure 6.15 Homologue group concentrations and isomer contributions to TEQ for the River Derwent above and below the potential point source at Belper

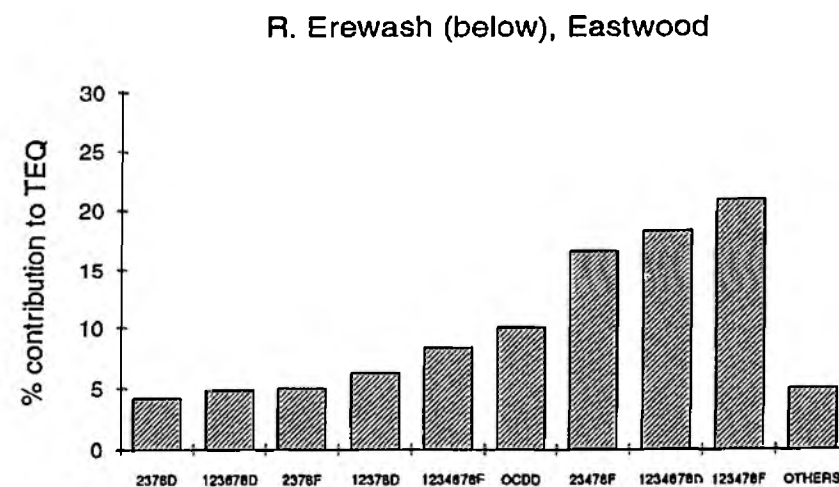
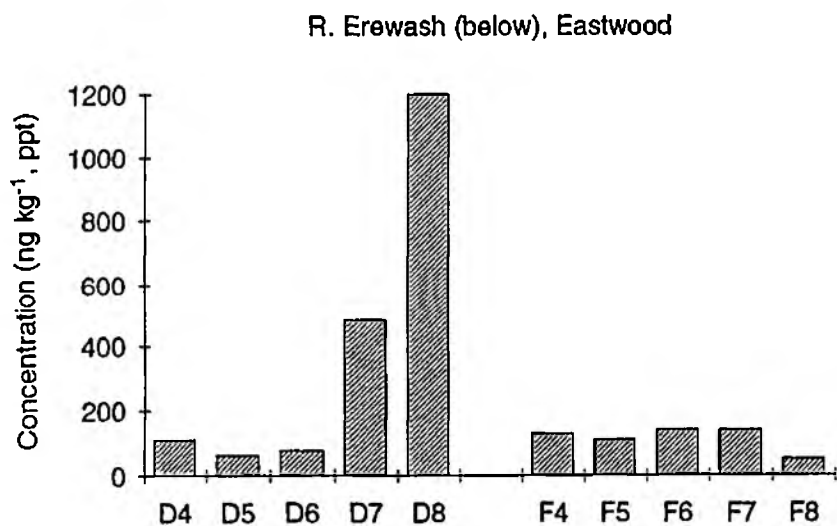
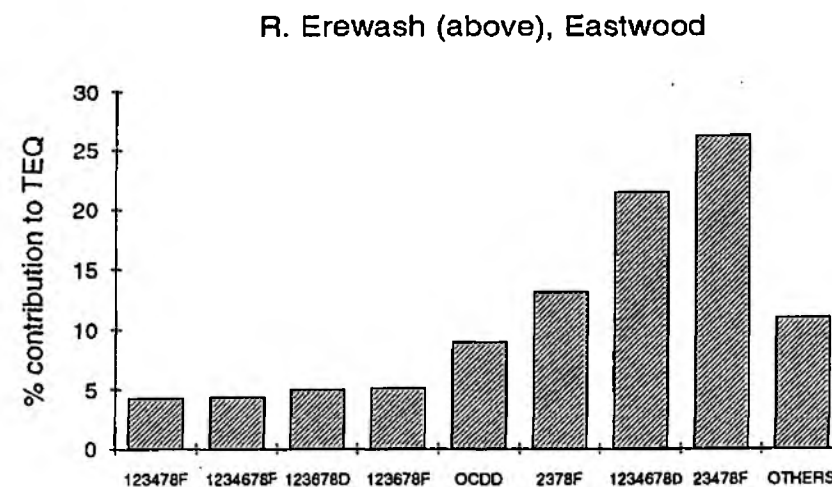
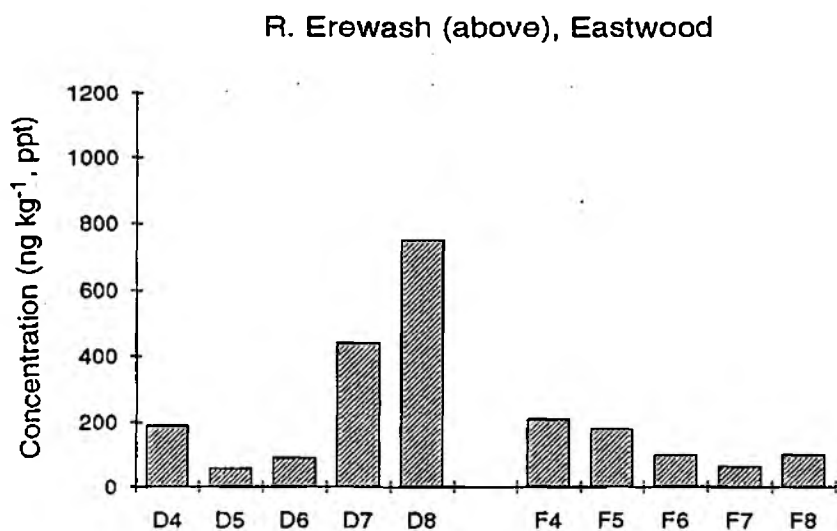


Figure 6.16 Homologue group concentrations and isomer contributions to TEQ for the River Erewash above and below the potential point source at Eastwood

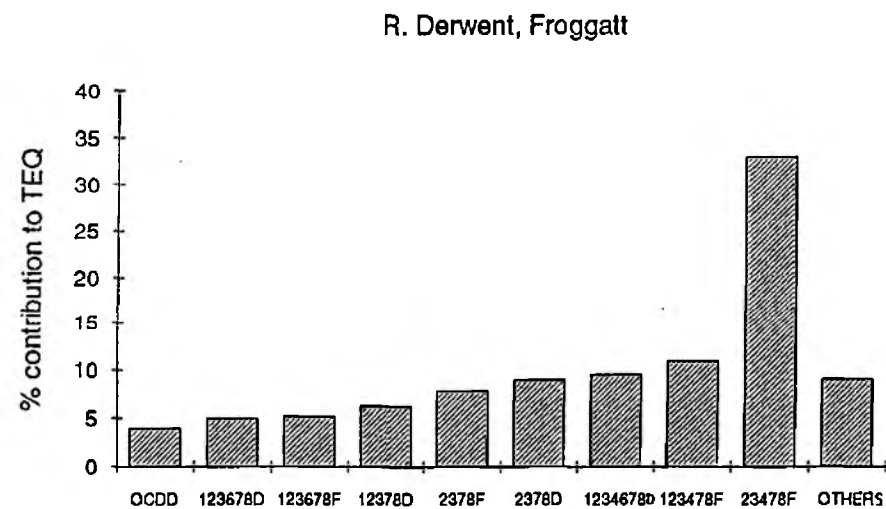
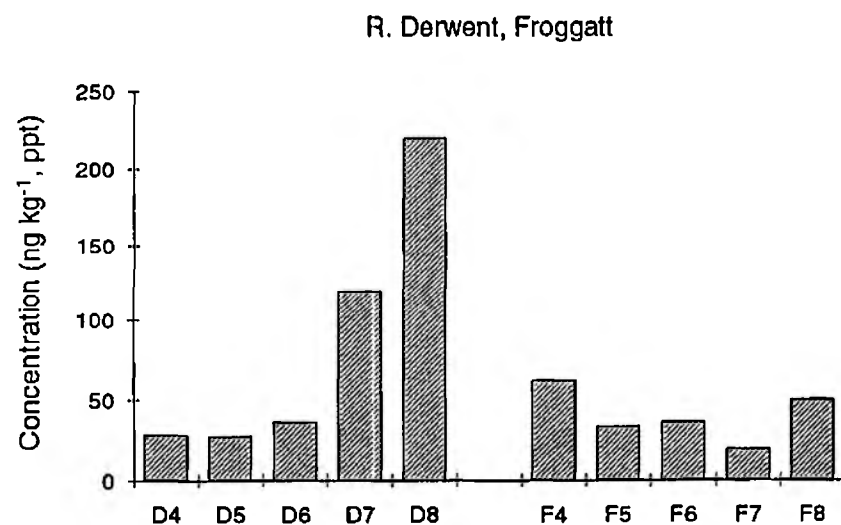
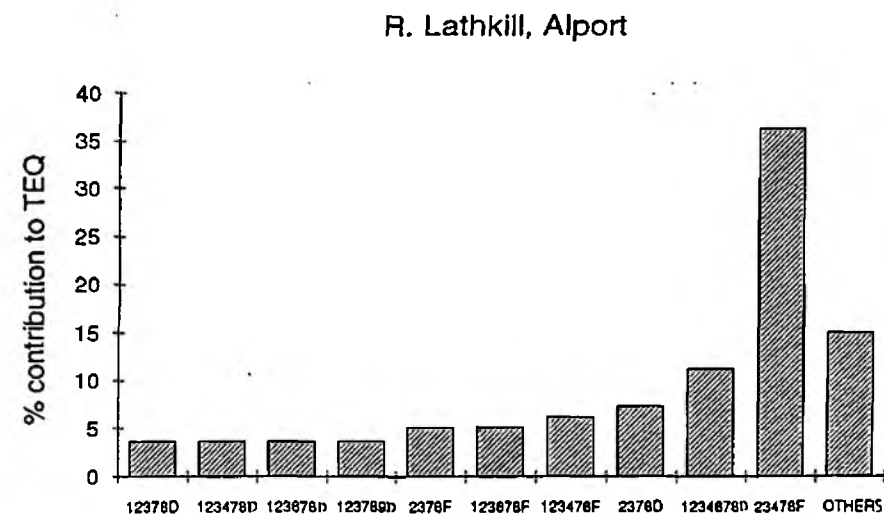
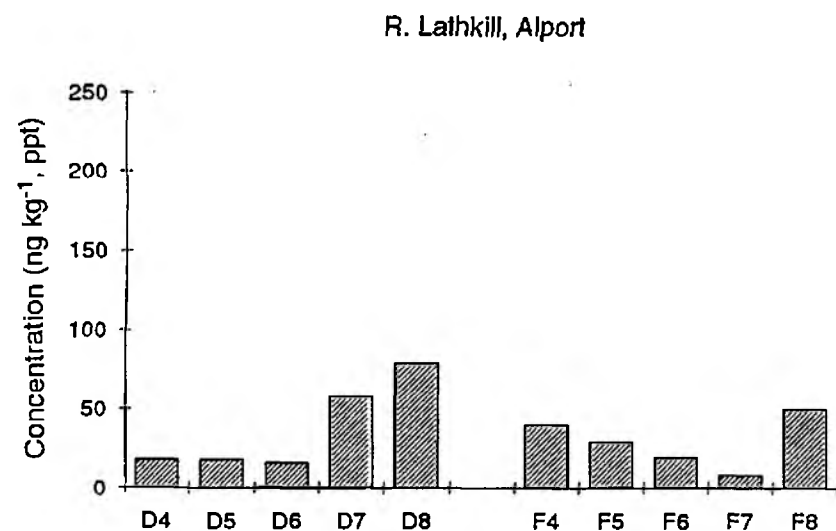


Figure 6.17 Homologue group concentrations and isomer contributions to TEQ for the River Lathkill at Alport and the River Derwent at Froggatt

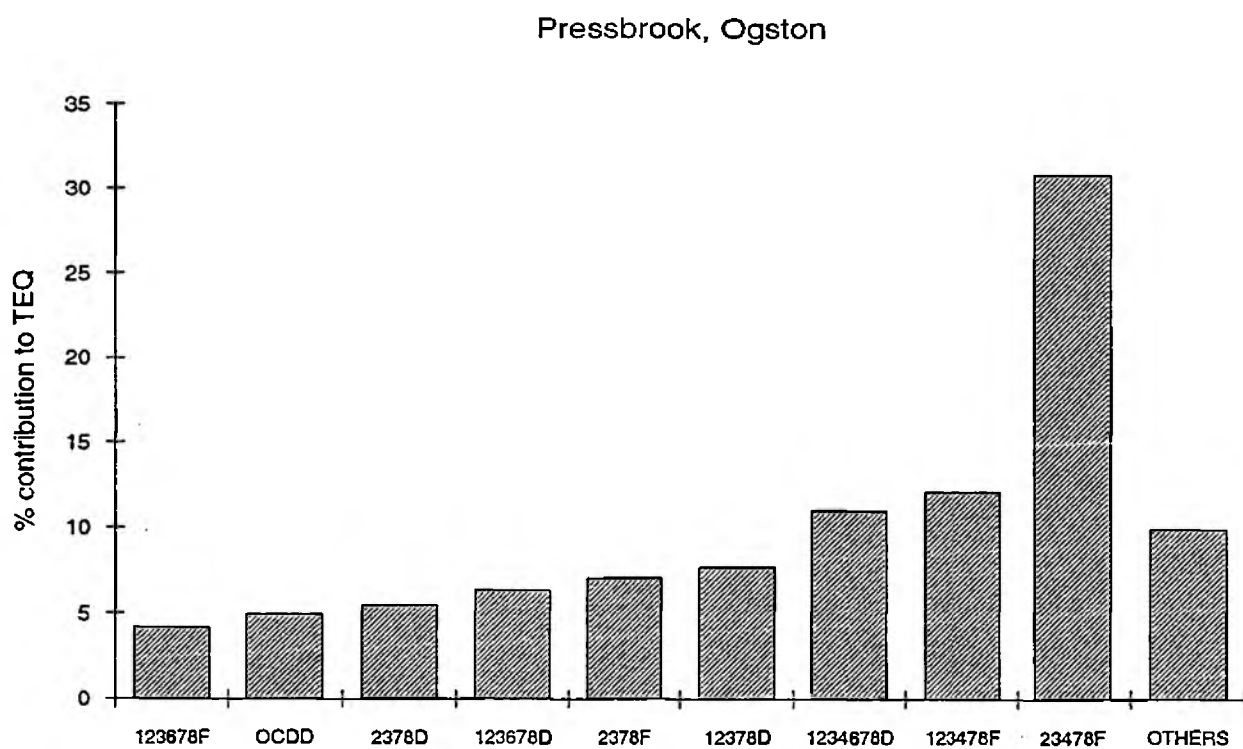
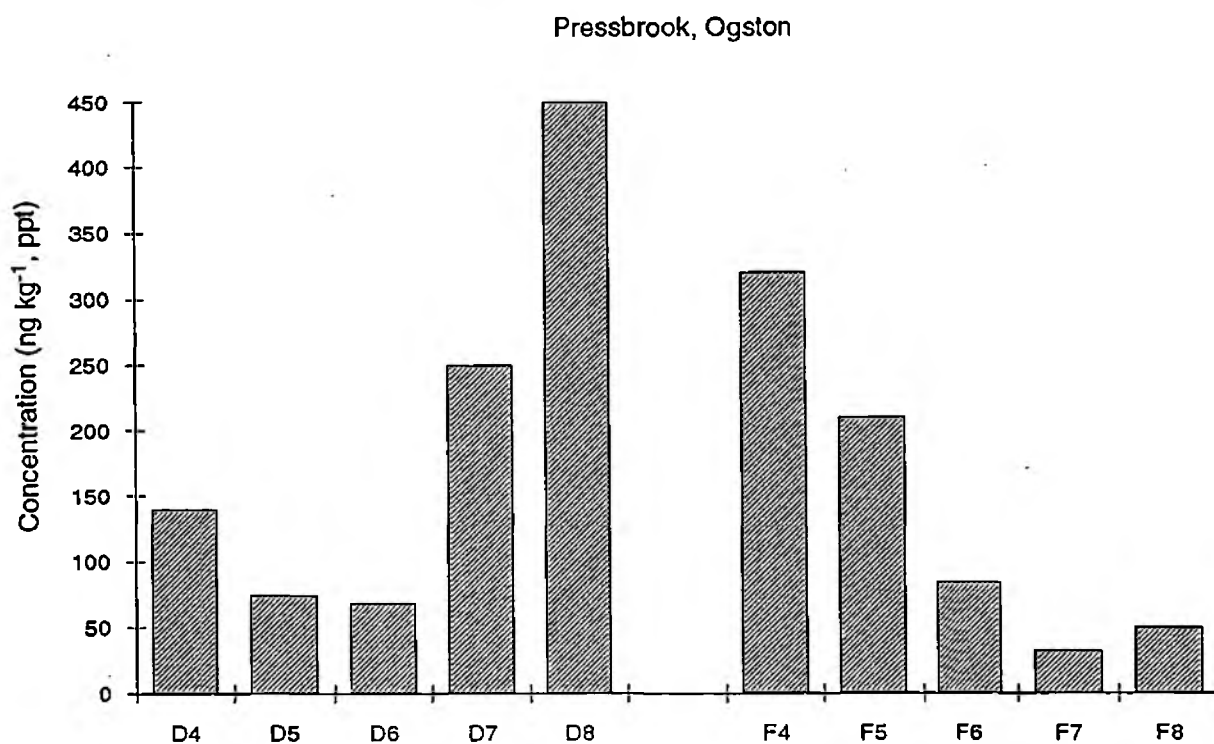


Figure 6.18 Homologue group concentrations and isomer contributions to TEQ for Pressbrook at Ogston

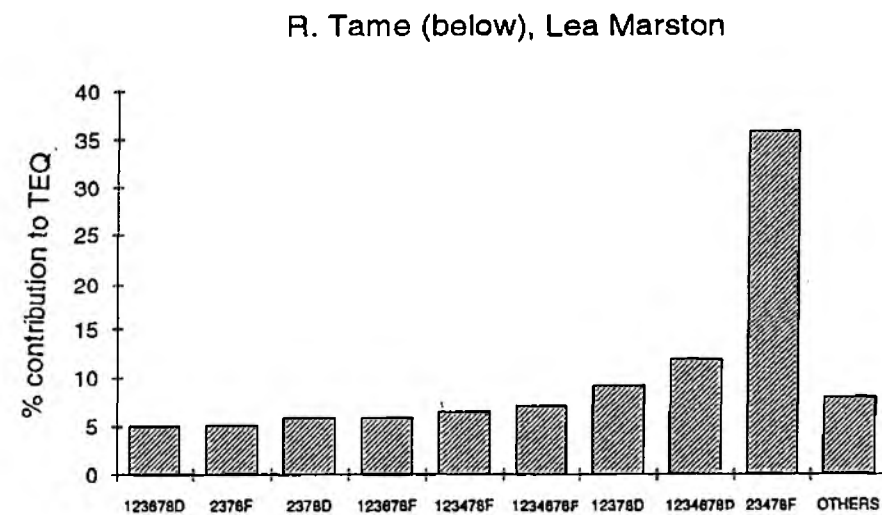
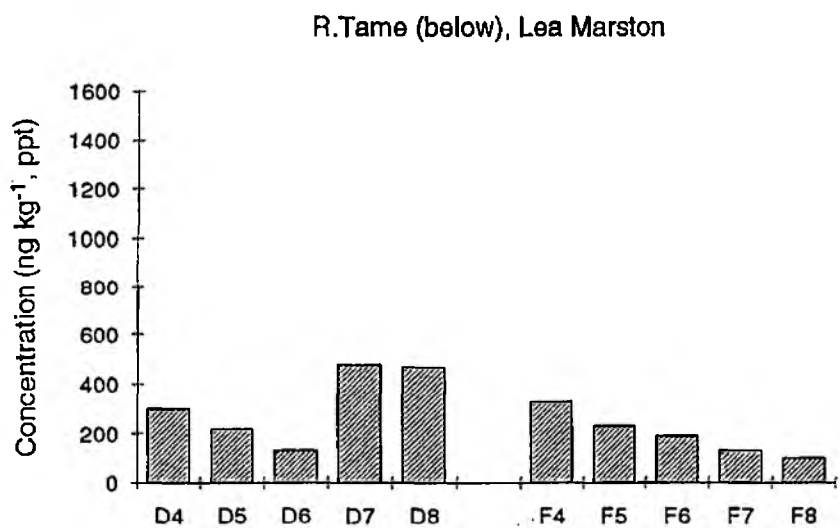
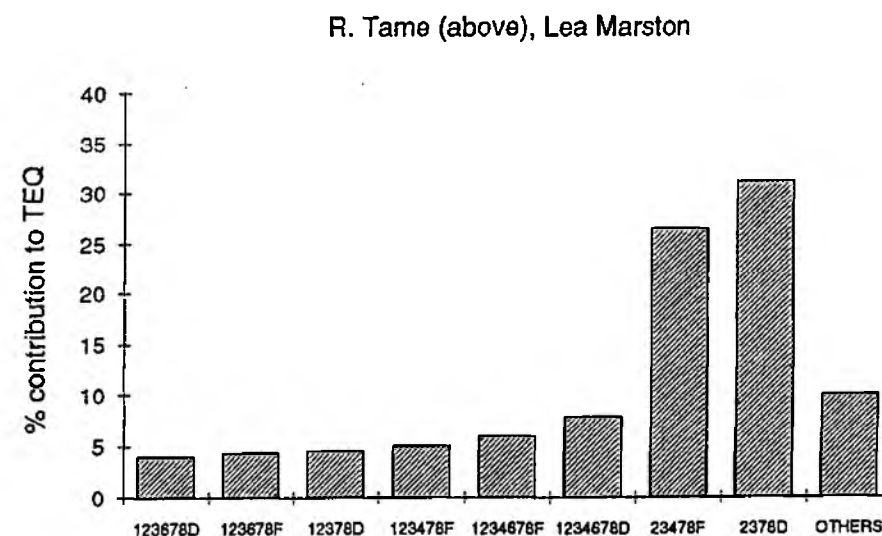
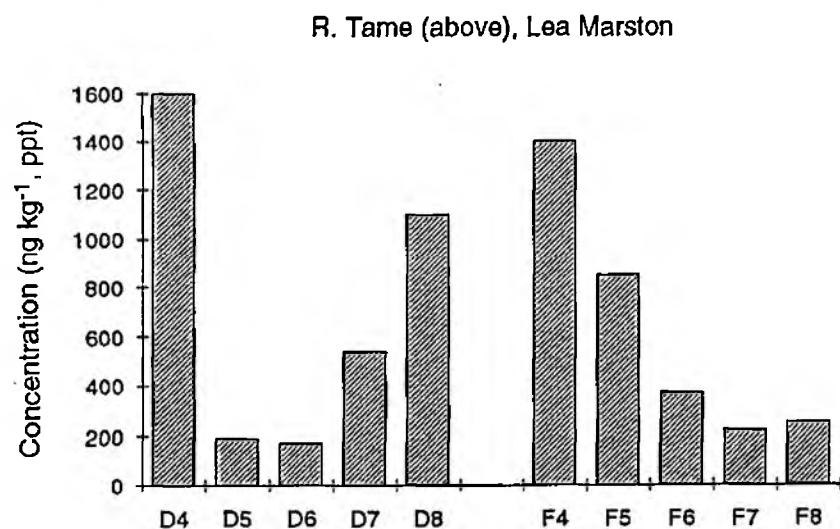


Figure 6.19 Homologue group concentrations and isomer contributions to TEQ for the River Tame above and below the potential point source at Lea Marston

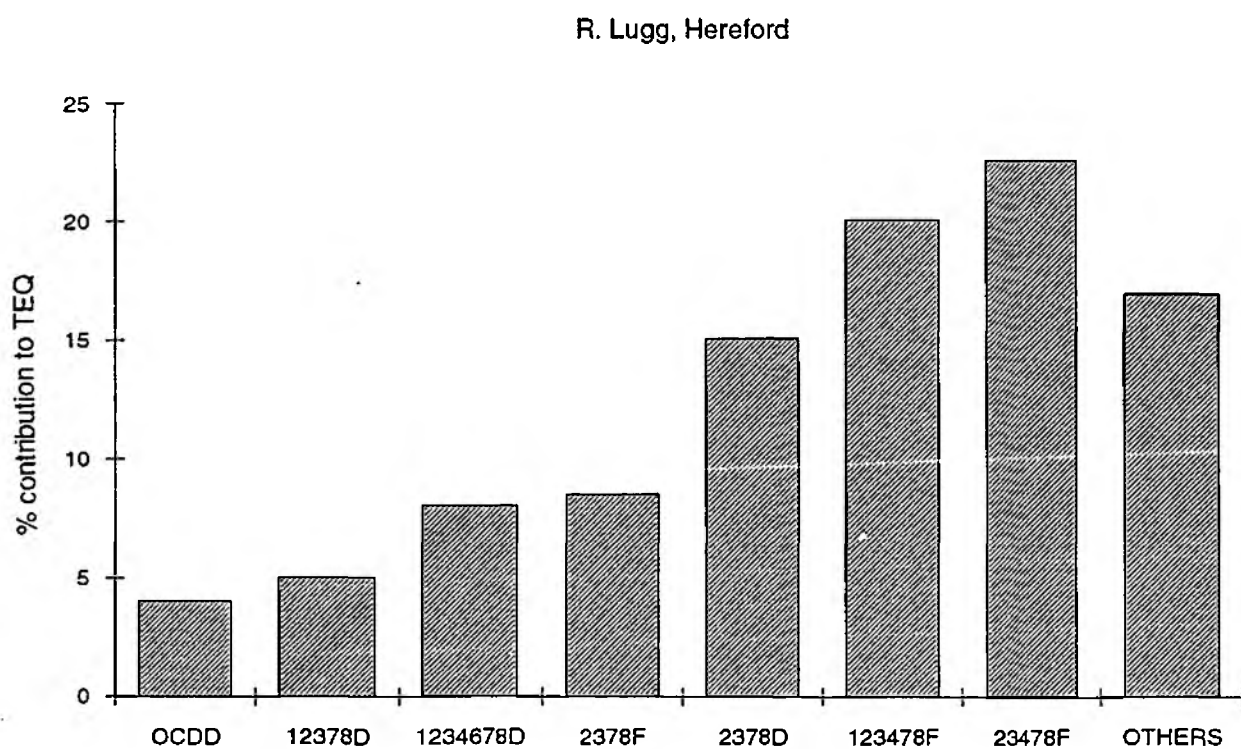
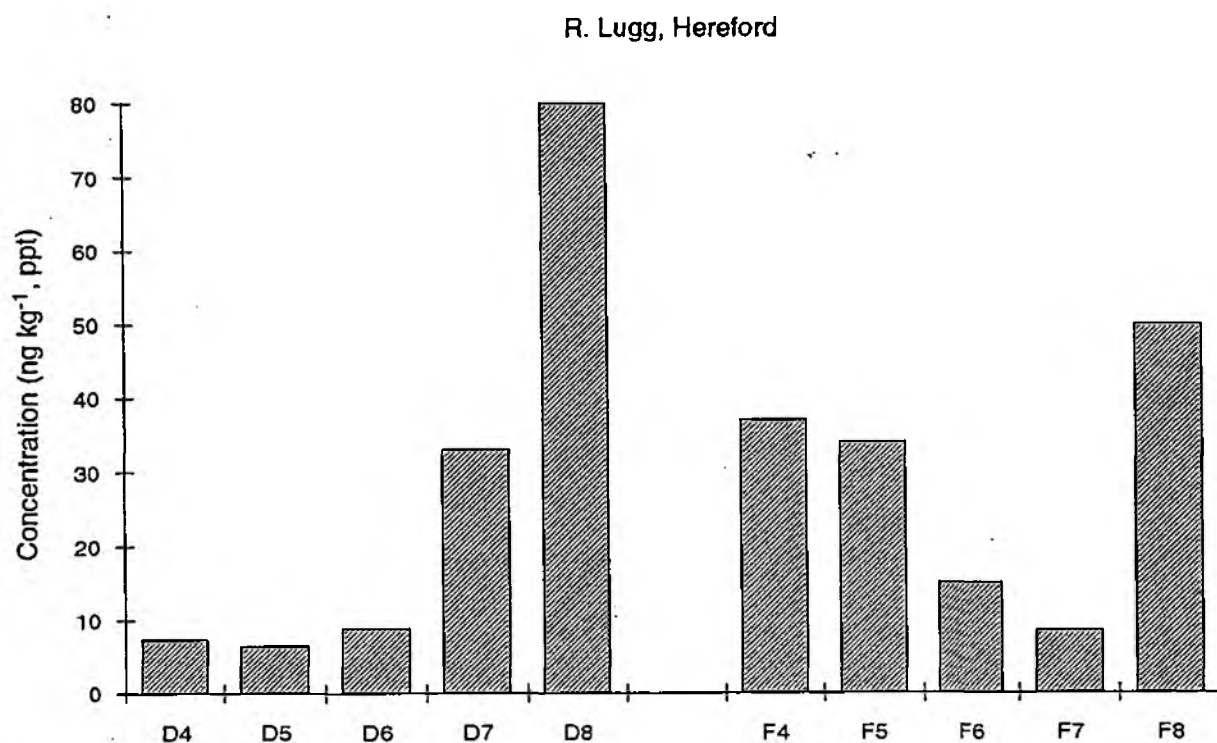


Figure 6.20 Homologue group concentrations and isomer contributions to TEQ for the River Lugg at Hereford

## **7. DISCUSSION**

### **7.1 Discussion of results - water samples**

The PCDD/F analysis of the 40 water samples provides a useful baseline, with all the results giving concentrations and TEQs of less than  $6 \text{ ng kg}^{-1}$  and  $0.07 \text{ ng kg}^{-1}$  respectively.

### **7.2 Discussion of results - sediment samples**

The PCDD/F results of the 36 sediment samples provide a valuable data set for UK freshwaters. Table 7.1 ranks the samples in terms of their total PCDD/F content and of their TEQ value. As explained in Section 2.1, the results of the analyses are given in two forms, the total PCDD/Fs in a sample and its TEQ. The total concentration (i.e. the sum of all the homologue groups) is a measure of the contamination level of a sample, whereas its TEQ is a measurement of the toxicity derived from the 17 toxic PCDD/Fs. Whilst there is generally a strong positive relationship between the increasing PCDD/F total concentration of a sample and its TEQ value, the relative proportions of toxic to non-toxic isomers do vary (see Fig 7.1) probably reflecting the variability of the initial homologue profiles in the original source material.

Table 7.1 presents the sites in order of total concentration and TEQ, from highest to lowest. The mean and standard deviations of these two data sets reflect the wide range of results, with the mean total concentration being  $4444 \pm 3794 \text{ ng kg}^{-1}$ , and mean TEQ being  $28.6 \pm 29.2 \text{ ng kg}^{-1}$ . Another useful way of describing the average of such a data set is to use the median, or middle value. The median for total concentration is  $3258 \text{ ng kg}^{-1}$  and for TEQ is  $16.7 \text{ ng kg}^{-1}$ . The histograms in Fig 7.2 show the number of sites in different total concentration and TEQ classes (the total concentrations are expressed as ppb). The histograms are skewed to the lower end of the scales, showing that there are a greater number of less contaminated and less toxic sites. The information given in Table 7.1 is combined with site locations on a map of England and Wales in Fig. 7.3.

The specific project objectives pertaining to background PCDD/F concentrations, and the concentrations associated with specific industrial/non-industrial sources are addressed in the following sections.

### 7.2.1 Background sites

Originally, seven river sites were chosen to provide information on background levels of PCDD/Fs in UK freshwaters. These were the Thames at Cricklade (Thames Region), New River at Wicken (Anglian Region), Dane, at Hugbridge (North West Region), Loxley near Sheffield (Yorkshire Region), Lathkill at Alport, Derwent at Froggatt (Severn Trent Region) and Irfon at Abergwesyn (Welsh Region). As it was not possible to collect sediment from the Irfon (see Section 4), six sites remain for comparison. When looking at the location of these sites in Table 7.1 it is apparent that the total concentration and TEQ in the Loxley and New River sediments are higher than at the other background sites. New River appears as the fourth most toxic river out of the 36 sites sampled despite its Grade 1 (i.e. very clean) NRA classification (I. Hill, pers. comm.). The site is surrounded by agricultural land so pesticide runoff is possible, and the sediments have a relatively high organic content (Table D.3) suggesting that PCDD/Fs would have an affinity with such sediments (see Section 2.2). River Loxley, although chosen as a background site, may possibly receive enhanced atmospheric deposition of PCDD/Fs from combustion sources. PCDD/Fs produced by combustion sources are emitted into the atmosphere and transported over long distances. It is possible that atmospheric emissions from Sheffield and surrounding industrial areas result in a higher PCDD/F concentration and TEQ here than at other background sites.

The four remaining background sites appear at the bottom of the ranking table, having among the lowest PCDD/F contamination and toxicity of the data set. The R. Lugg, a river in a low lying agricultural area of Herefordshire that was selected to explore effects of intensive agriculture in the catchment (non-point source). Its position as the least contaminated and least toxic site in Table 7.1 suggests that it is better included in the 'background' category.

Excluding the New River and R. Loxley, but including R. Lugg, a general statement of background PCDD/F concentrations and toxicity in UK freshwaters can be made. It would appear from the sites sampled that the total PCDD/F background concentrations are < 1000 ppt, with a TEQ < 6 ppt. Whilst the homologue group and TEQ profiles do vary, most show a predominance of OCDD and, to a lesser extent, HpCDD. Koester & Hites (1992) have shown that atmospheric deposition processes tend to favour the deposition of these higher chlorinated dioxins, giving rise to higher concentrations in the environment. It seems reasonable to suggest that the observed PCDD/Fs in the background river sediments result from atmospheric deposition, either onto the catchment or directly onto the water surface, resulting in a profile dominated by the higher chlorinated dioxins. Furans are also present in these homologue group profiles, particularly in the Thames at Cricklade and the Dane. Whilst dioxin and furan



isomers both contribute to the TEQ of these background sites, the highest percentage contribution is generally provided by 23478-PeCDF. The New River homologue and TEQ profiles differ from those described above, supporting the suggestion of an undefined source of PCDD/Fs to the river. The homologue group profile is dominated by dioxins, with HpCDD and HxCDD being present in the highest concentrations. PCDDs rather than PCDFs contribute most to the TEQ at this site, with over 35% contributed by 12378-PeCDD.

### 7.2.2 Non-point source sites

#### (i) General Urban

No potential point sources were identified for the discharge of PCDD/Fs in the Thames and North West Regions. In both regions, sites were chosen as representative of general urban inputs into major rivers. In the Thames Region these were the Thames at Caversham Weir, Reading and at Teddington, West London (Fig 6.1). In the North West, sites were chosen on the R. Alt, Merseyside the R. Mersey at Warrington and the R. Weaver south of Warrington (Figs. 6.5 and 6.6). Table 7.1 shows that the Thames sites are below the average total concentration and TEQ (both mean and median). Teddington is downstream of Caversham Weir and has a higher total concentration, but the TEQs of the two sites are very similar. The R. Weaver has a similar total concentration to the Thames at Caversham, but has a higher TEQ. Sediments from the Mersey and Alt are much more polluted and toxic. They contain the highest TEQs of all 36 samples, and the Alt has the highest total concentration. It is worth noting that the Alt site was a considerable distance downstream and so probably acts as a source of PCDD/F to its estuary. Looking at the homologue profiles, the Mersey is similar to the Thames at Caversham, and the Alt is similar to the Thames at Teddington. OCDD makes the largest contribution to total PCDD/Fs at the latter four sites, with a significant input also from HpCDD. The Weaver has a different total concentration profile, with TCDF being the dominant homologue group. In terms of TEQ, the greatest contribution (>35%) to these sites is made by 123478-HxCDF, with the exception of the Weaver whose most important isomer is 23478-PeCDF. The isomer 123478-HxCDF contributes almost 60% of the toxicity to the Alt.

#### (ii) Agricultural.

The R. Granta at Hildersham and R. Lugg at Hereford were chosen to assess the effect of pesticide use in agricultural areas. As has been shown, the R. Lugg has the lowest total concentration and TEQ of the data set and so is better placed in the background category. The Granta also shows little evidence of contamination, with a total concentration of <1000 ppt and TEQ <10 ppt. The total concentration profile show a dominance of OCDD and, to a lesser extent, HpCDD. In terms of TEQ, over 45% is contributed by 123478-HxCDF (Fig. 6.4). Both the Lugg and Granra indicate that agricultural areas contribute little to PCDD/F

contamination in rivers. However, as discussed earlier, the New River is also situated in an agricultural area and has much higher levels of PCDD/Fs, which suggests that an unidentified source of PCDD/Fs may be responsible for the observed measurements. It is not possible to determine whether the observed levels are pesticide-derived or due to another source.

### (iii) Others

The Pressbrook was chosen as a site possibly containing PCDD/F contamination from the nearby burial of rubble from an explosion at the Coalite plant near Bolsover. Its position in Table 7.1 (26th in both columns) does not suggest a high level of contamination in comparison with other sites, although the total concentration and TEQ are higher than the Derwent at Froggatt and the Lathkill which are background sites in the Severn Trent Region. The homologue group profile for the site (Fig. 6.18) shows a predominance of OCDD with less HpCDD, but also shows a relatively high concentration of TCDF and PeCDF. The isomer 23478-PeCDF contributes the greatest percentage to TEQ, at over 30%. Stack, incinerator and boiler samples from the Coalite works show a strong predominance of TCDD in total PCDD/F and TEQ results (Berryman *et al* 1991). This feature is not observed in the Pressbrook which suggests that Coalite rubble alone is not a predominant source of PCDD/Fs in the area.

## 7.2.3 Point source sites

### (i) Textile industries and sewage treatment works

Four sites were chosen as indicators of any contribution of textile works (and associated sewage treatment works) to PCDD/Fs concentrations in rivers. These were R. Amber, R. Derwent and R. Erewash in Severn Trent and Mag Brook in Yorkshire. Sediment samples were taken above and below the potential point source at the three Severn Trent sites, and below only at Mag Brook as sediments could not be located upstream.

The R. Amber receives a relatively large amount of effluent compared to the size of the catchment, as in addition to the textile industry and sewage treatment works there is a colliery in the area. Table 7.1 shows that there is a large difference in total concentrations and TEQs of PCDD/Fs between the above and below point source sample sites. The upstream site is within the top ten of cleaner sites in both columns, whereas the downstream site has the third largest total concentration and TEQ of all the sites. This is the largest difference between above and below sites measured. The contribution of homologue groups to the total concentration changes from the above to below sites, and it seems likely that the textile industry and/or the sewage treatment works and colliery are contributing to the elevated PCDD/F levels in the river. At the above site, all dioxin and furan groups are present at low

levels, with a small excess of OCDD and HpCDD. Below the point source, HpCDD dominates the homologue profile with significant contributions from OCDD and HxCDD. At both sites, the isomer 123478-HxCDF contributes the highest percentage to TEQ (Fig. 6.13).

The potential point sources identified on the River Derwent at Church Wilne were a textile industry which produces acetate and has dealt with speciality chemicals e.g. flame retardants, and a sewage treatment works. The location of accumulating sediments was difficult, which resulted in the above sample being taken some distance upstream near Derby (see Map B5.2). The results from this upstream site showed total concentrations and TEQs of PCDD/Fs to be higher than downstream (Fig. 6.14). Table 7.1 shows the upstream site to be in the top five most contaminated and toxic of those sampled. This site is clearly being contaminated with PCDD/Fs from another source, perhaps in Derby, and any contribution from the textiles factory is not contributing significantly to the PCDD/F loading of the river. The total PCDD/F profiles for both sites showed a dominance of HpCDD. In terms of TEQ, dioxin isomers dominated at the above site, with 12378-PeCDD and 1234678-HpCDD contributing most. Downstream, dioxins also made a large contribution to TEQ, with 1234678-HpCDD contributing >25%.

The R. Erewash site also receives effluent from a textiles industry. Table 7.1 shows that the results from above and below the potential point source are positioned close together, although both total concentration and TEQ are higher downstream. The total concentration of PCDD/Fs and the TEQ at both sites are lower than the average (mean and median) given for the data set. The homologue group profiles are similar for both sites, with a predominance of OCDD and to a lesser extent HpCDD. In both cases, both dioxins and furans contribute to TEQ, with the largest percentage being provided by 23478-PeCDF upstream and 123478-HxCDF downstream (Fig. 6.16). The results suggest that although the total concentration and TEQ of PCDD/Fs are marginally higher downstream, the potential point source does not make a significant difference to the PCDD/F loading of the river.

No accumulating sediment was located upstream of the potential point source on the Mag Brook, so a below point source sample only was taken. Table 7.1 shows the Mag Brook to be among the most contaminated of those sampled, having the second highest total concentration and sixth highest TEQ in the Table. The homologue group profile (Fig. 6.7) shows a dominance of OCDD with a significant contribution also by HpCDD and TCDD. Dioxins and furans both contribute to the TEQ, with 23478-PeCDF having the highest percentage (>30%).

(ii) Chemical industries and sewage treatment works.

The rivers identified as having a potential point source of PCDD/Fs from chemical industries were the rivers Calder, Aire and Spenn (Yorkshire Region), which had associated sewage treatment works, and R. Cam (Anglian Region). Sediment samples were collected above and below the potential point sources at all sites except the Spenn, where accumulating sediment could not be located above the potential source.

River Calder results show that the sample taken above the potential source has a higher PCDD/F total concentration and TEQ than below, and Table 7.1 shows the difference to be relatively large (a factor of 3 for total concentration and 6 for TEQ). The sediment characteristics of the samples suggest a possible explanation, with the samples downstream having a very high sand content (only 4% of material being  $<63\ \mu\text{m}$ ) and low organic content ( $<4\%$ ). The comparable figures upstream were 36% and 16% respectively. The affinity of PCDD/Fs to organic material and the likelihood of higher organic concentrations in finer grained sediment would suggest that total concentrations would be lower under the described sedimentary conditions downstream. As suggested for the Derwent at Church Wilne, it is possible that an unidentified source of PCDD/Fs is present upstream, contributing to the higher PCDD/F concentrations and toxicity measured. The lack of organic-rich accumulating sediment at the downstream location may also reflect rapid the transportation of PCDD/Fs in suspension away from the site. Table D.1 shows that there is a high suspended load at Calder below, which coupled with a low sedimenting environment, would support this point. It is also possible that the potential point source identified is not emitting PCDD/Fs to any large extent, and so the concentrations upstream have been diluted by the downstream sample point. This is supported by similar homologue group profiles at both sites, whichs show a predominance of OCDD and HpCDD (Fig. 6.8). Both 12378-PeCDD and 2378-TCDF provide 20% of the TEQ at the upstream site, with 23478-PeCDF and 1234678-HpCDD contributing the largest percentage downstream.

Table 7.1 shows that the total PCDD/F concentration and TEQ of both upstream and downstream samples from the R. Aire at Beal fall into the upper half of both columns, indicating that the samples are among the more polluted in the data set. In addition to the chemical industry identified as a potential point source of PCDD/Fs to the river, there is also a power station in the vicinity which may contribute to the PCDD/F levels in the river via atmospheric deposition. The downstream site has a higher total concentration and TEQ than the upstream site, and both homologue group profiles show a predominance of OCDD and HpCDD. The isomers 1234678-HpCDD and 23478-PeCDF contribute the most to TEQ upstream, and these plus 2378-TCDD provide the greatest contribution to TEQ downstream

(Fig. 6.9). It is clear that the sediments downstream are more highly contaminated than above the potential source, but it is not possible to determine whether this is due to the chemical works identified, or whether atmospheric deposition from the nearby powerstation also has an effect.

No accumulating sediments were located above the potential point source in the Spenn, so sediment results were taken from downstream only. The original potential point source selected was a chemical industry producing phenoxy-acetic acid. About two weeks before sampling, a fire had broken out at a second chemical works in the catchment. 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. Life in the river was severely damaged by this incident. Table 7.1 shows that the Spenn is the 4th most contaminated and 8th most toxic of those sampled. The homologue group profile again shows high concentrations of OCDD and HpCDD, and also a relatively high concentration of TCDF and TCDD. The isomer 12378-PeCDD contributes the highest percentage to TEQ (Fig. 6.7). This site is more highly contaminated by PCDD/Fs than many other sites, but the extent to which the fire at the second chemical works contributed to this contamination is unknown.

The chemical works at Hauxton on the R. Cam produces agrochemicals, and samples were taken above and below the effluent pipe from the works. The results from this site are unusual because although the total concentration of PCDD/Fs is similar upstream and downstream, the TEQ is much higher above the potential point source (Table 7.1). The homologue group profiles show that although the total concentration is similar at both sites, the structure of the groups that make up the total is different (Fig. 6.3). The most noticeable feature is that although most of the homologue groups have decreased in concentration downstream, TCDD and TCDF have dramatically increased, which gives a similar total concentration to the upstream site. However, of these large TCDD and TCDF groups, only a small proportion (1% or less) are the toxic 2378-substituted isomers, resulting in the low TEQ value downstream (see Table E.5). A possible explanation for these results is that there is an unidentified source of PCDD/Fs further upstream, contributing to a large total concentration and TEQ at the above point source site. The upstream sample was taken above a weir where accumulating muddy sediment was plentiful. Emergent and submergent macrophytes were present, providing a favourable sedimentary environment for the deposition of particulates and associated PCDD/Fs (the R. Tame at Lea Marston, described later, provides an example of the settling of particulate-associated PCDD/Fs under favourable conditions). Below the weir, the potential point source appears to have contributed a large concentration of total TCDD and TCDF to the PCDD/F loading of the river, although the toxicity of these groups is very low.

### (iii) Others

Other potential point sources investigated are steelworks and sewage treatment works (R. Don, Rotherham), lubricating oils manufacture and sewage treatment works (R. Derwent, Belper), and sewage treatment works alone (R. Aire, Fleet Weir). R. Tame at Lea Marston provided a slightly different situation, where river water containing sewage treatment works effluent passed through a system of purification lakes, and samples were taken above and below the largest lake.

The R. Don at Rotherham is another example of a site which has a higher PCDD/F total concentration and TEQ above the potential point source than below it. The ranking in Table 7.1 shows both the upstream and downstream samples are in the upper half of the table, indicating that both sites have a relatively high level of contamination and toxicity. Both sampling sites are in a highly industrialised area and it would not be unreasonable to assume that another unidentified source is contributing to the PCDD/F concentration and toxicity above the steelworks. The homologue group profiles differ between the two sites which suggests that sources of PCDD/Fs change downstream. Above the point source, highest concentrations are present in the HpCDD group, followed by OCDD, and this pattern is reversed downstream (Fig. 6.11). Furan groups are present in higher concentrations at the upstream site, particularly TCDF. It is possible that the effluent from the steelworks and sewage treatment works is contributing to the homologue profile described downstream, and that the PCDD/Fs contributed by the unidentified source upstream have settled out above this identified point source.

The R. Derwent at Belper also has a higher concentration of PCDD/Fs and a higher TEQ above the potential point source than below it. The sites appear either side of the median in Table 7.1. The homologue profiles at the two sites are very similar, with OCDD and HpCDD dominant in both (Fig. 6.15). A similar profile but lower concentration suggests that the potential point source is not contributing PCDD/Fs to the river to any significant level, and that the concentration is decreasing downstream due to dilution. A mixture of dioxins and furans contributes to the TEQ at both sites, with >20% being provided by 23478-PeCDF and by 1234678-HpCDD upstream, and 123478-HxCDF and 1234678-HpCDD contributing most to TEQ downstream.

Sediment samples from the R. Aire at Fleet Weir also have a higher total concentration and TEQ above the potential point source, in this case a sewage treatment works. Table 7.1 shows that in terms of total PCDD/F concentration, both samples fall in the lower half of the table, but are either side of the median in the TEQ column. The homologue group profiles show a

difference downstream and upstream suggesting a change in PCDD/F source over that distance (Fig. 6.10). Upstream, the profile is dominated by HpCDD, with other groups providing much lower concentrations. Downstream, the profile contains mostly OCDD and HpCDD. About 25% of the TEQ of both samples is provided by 1234678-HpCDD.

At R. Tame, Lea Marston, samples were taken before sewage treatment works effluent from Birmingham and the Black Country entered the lake purification system ('above' sample), and below the largest purification lake. As may be expected, total concentration and TEQ were higher above the lake than below it. The homologue group profile above the lake showed a dominance of TCDD/F, and both 2378-TCDD and 23478-PeCDF provided the greatest contribution to TEQ. Below the lake, the contribution of TCDD/F was still visible, but these groups had a lower concentration than HpCDD and OCDD. About 35% of the TEQ below the lake was provided by 23478-PeCDF (Fig. 6.19). This site at Lea Marston illustrates how PCDD/Fs attached to suspended particulates will settle out under favourable sedimentary conditions. Table 7.1 shows that as the river passed through the largest water purification lake, the total concentration of sediment-associated PCDD/Fs was reduced by 4000 ng kg<sup>-1</sup>, and the TEQ was reduced by almost 50%.

#### 7.2.4 General observations

The preceding sections described the range of PCDD/F concentrations and TEQs present at the 36 sampling sites, together with information on the homologue group profiles and the contributions of individual isomers to the TEQs. An overview of the data presented allows the following observations to be made.

- inspection of the homologue group profiles shows that the most common pattern in terms of contribution to the total concentration is, OCDD providing the highest concentrations, with the second highest contribution from HpCDD. Of all the sites, 24 (67%) conform to this pattern. These 24 sites include a geographical spread across different site types (including background, point- and non-point sources), and vastly differing concentrations, including both the Alt (most highly contaminated site) and the Lugg (least contaminated site). These homologue groups are also the two most important in a further four sites, but in the reverse order, so in the total homologue profiles of 28 sites (78%) are dominated by these two groups.
- the relative contributions of the seventeen 2378-substituted isomers to the TEQ shows that either 23478-PeCDF or 123478-HxCDF tend to dominate at over 70% of the sites. As

with homologue groups, these isomers dominate sites of varying type and varying TEQ values.

The similar homologue and TEQ profiles at many different sites makes it difficult to identify a 'fingerprint' pattern which can associate environmental levels with a particular PCDD/F source. The fingerprint method, using homologue group profiles, has been used by various authors to try and associate environmental levels of PCDD/F with particular sources. This approach, although successful in some cases, should be used with a certain amount of caution. Fingerprinting can be useful when the point source produces a distinct homologue pattern. For example, measurements from the waste incinerator stack at Coalite Chemicals works, Derbyshire, show a clear predominance of the TCDD group (Berryman *et al* 1991). This homologue group can also clearly be seen in soil samples in the area (MAFF 1992). The procedure of fingerprinting becomes more difficult when a number of different sources of PCDD/Fs may produce similar homologue profiles. For example, Hagenmaier *et al* (1986) observed a predominance of OCDD and HpCDD in R. Neckar and R. Danube sediment samples, and suggested that the major source of these higher chlorinated dioxins was pentachlorophenol, as this chemical displayed a similar homologue profile. However, similar profiles observed in sediments of the Great Lakes were interpreted as being a result of atmospheric deposition of combustion-derived PCDD/Fs, due to a strong similarity of sediment profiles with those of air particulates (Czuczwa & Hites 1986). Chromatograms produced during PCDD/F analysis contain additional information on other individual isomers present in samples. It is possible that such information could be used to match source patterns with those found in the environment more closely.

Since no published data is available on levels of PCDD/Fs in UK freshwaters, information on UK background and urban soils provides a useful comparison. Data are available on the total concentration of PCDD/Fs in urban and rural UK soils in England, Wales and lowland Scotland (Creaser *et al* 1989, 1990). Both urban and rural soils show a predominance of OCDD with the second largest contribution from HpCDD in the homologue profiles, as seen in the majority of UK river sites. PCDD/F concentrations in urban UK soils are about an order of magnitude greater than in semi-urban and rural areas. The range of urban PCDD/F soil concentrations in England and Wales varies considerably, and the results show a mean total PCDD/F concentration of 12 010 ng kg<sup>-1</sup> but a median of 1436 ng kg<sup>-1</sup>. In order for an easier comparison with the sediment data set, results from a typical London and Sheffield soil have been taken from Creaser *et al* (1990). The total concentration of PCDD/Fs in the London soil were 2794 ng kg<sup>-1</sup>, and 5270 ng kg<sup>-1</sup> in the Sheffield soil. The London soil is similar to the Teddington sediment total concentration given in Table 7.1, and the Sheffield soil is



comparable with sediment samples of higher than average contamination. The mean total concentration for UK background soils is  $453 \text{ ng kg}^{-1}$ , which agrees with the background river sites at the bottom of Table 7.1. TEQ values were not available from the soils studies. PCDD/Fs have been measured in London air and the % contribution of isomers to TEQ has been calculated (Clayton *et al* 1992). The most dominant isomer measured in London air was 23467-PeCDF, which contributed 27% to the TEQ. This is one of the isomers which provides a large contribution to TEQ at many of the river sites in this study (see above).

### 7.3 Other international studies.

Results from this study can also be placed in a broader context by comparing them with studies that have been carried out on freshwater systems in other parts of Europe, in North America and Japan (see Fletcher & McKay 1993, and Table 7.2).

Two rivers which can be compared with UK background total concentrations are the Hamburg background (Götz *et al* 1990) and the Elk River (Reed *et al* 1990), see Table 7.2. The background concentration in the vicinity of Hamburg was taken as a comparison with Hamburg Harbour sediments, and River Elk samples were taken to provide baseline levels prior to the operation of a refuse-derived fuel power electricity generating station in Minnesota. Total PCDD/F concentrations from both studies fall within the range of background rivers in the UK. TEQ values are not available for comparison.

The remaining studies reported in Table 7.2 give an indication of the range of PCDD/Fs found in polluted waters. The highest total PCDD/F concentration reported is in a Norwegian fjord, and, though not strictly comparable, shows the severe pollution levels that have been identified in natural waters, in this case due to a magnesium production plant (Knutzen & Oehme 1989). The median total PCDD/F concentration taken from the UK study (3260 ppt) is comparable to less polluted parts of the Rhine (Evers *et al* 1988) and to rivers such as the Neckar and Danube (Hagenmaier *et al* 1986). Evers *et al* (1988) investigated the level of PCDD/F contamination in River Rhine sediments by measuring concentrations in sediments at various locations along the river. The Rhine is polluted by effluents from chemical and mining industries, and receives runoff from agricultural areas. As might be expected, the authors found that sediments from the upper reaches of the river (e.g. Basel, Table 7.2) contained lower concentrations of PCDD/Fs than at lower lying, more industrialised parts of the river. The highest PCDD/F concentrations were found in sediments of the Ruhr, a heavily industrialised tributary of the Rhine (Table 7.2), although these high levels seemed to have relatively little impact on the receiving waters of the Rhine. The most highly contaminated sample in the UK study (R. Alt,

>15 000 ppt) is approaching the level of contamination seen in these areas of the Rhine, and also the R. Elbe (Götz *et al* 1990, 1992).

Attempts have been made in some studies to attribute sources to the PCDD/Fs identified. Evers *et al* (1988) compared congener profiles from Rhine sediments with those from commercial PCB mixtures, and pulp and paper mill sludges, which contain high levels of 2378-TCDF, and fly ash and PCB pyrolysates, in which certain HxCDF and HpCDF isomers predominate. However, the Rhine sediments did not contain these marker compounds and so sources could not be directly associated with municipal or chemical incineration processes. The authors indicated that the PCDD/Fs recorded might be incidental by-products of specific industrial processes such as chlorinated benzene production. Götz *et al* (1992) interpreted the pattern of HpCDFs in congener profiles as originating from both combustion and non-combustion sources. The study by Hagenmaier *et al* (1986), mentioned in Section 7.2.4, measured PCDD/F congener profiles in sewage sludge, pentachlorophenol (an industrially produced pesticide) and stack gases from a municipal waste incinerator plant. They first concluded that the major source of HxCDD, HpCDD/F and OCDD/F in sewage sludge was pentachlorophenol, and then compared these congener profiles with those from river and lake samples. The congener profiles from Rivers Neckar and Danube displayed a dominance of the above mentioned congeners, and Hagenmaier *et al* (1986) concluded that the major source of these higher-chlorinated PCDD/Fs in these rivers was pentachlorophenol. The congener profile from Lake Constance showed a more even distribution between PCDD/F congeners, more akin to municipal waste stack gases, which suggested that atmospheric inputs may have played a more important role in the deposition of PCDD/Fs to Lake Constance than to the rivers studied.

Many rivers in the UK study receive effluents from sewage treatment works. It is difficult, however, to distinguish their contribution from that of other sources investigated due to similarities in homologue patterns (the sample from R. Aire at Fleet Weir below a sewage treatment works has the same pattern of OCDD/HpCDD dominance seen at many other sites). However, concern over the levels of PCDD/Fs in sewage sludge has prompted much research into the importance of various inputs to sewage treatment works, particularly in Germany and Scandinavia, because sewage sludge is often used as a fertilizer on agricultural land. Sources vary depending on the uptake of the plant, and, in addition to industrial waste water effluents, sources can include combustion products from incinerators and vehicle exhausts via atmospheric transport and urban runoff (Näf *et al* 1990). Inputs to a wastewater treatment plant in Stockholm, Sweden, were investigated and compared with outlet waste water and digested sludge (Näf *et al* 1990). PCDD/F congener profiles from inlet and outlet water were

similar, dominated by OCDD. The urban runoff pattern, also sampled, differed from this indicating the importance of industrial and domestic waste water inputs as opposed to runoff. The outlet water contained an order of magnitude lower concentration of PCDD/Fs on a N-TEQ basis than the inlet water. The authors showed that the major proportion of PCDD/Fs received by the plant were removed in digested sludge.

The observation of a relatively small input from surface runoff inputs from was also made by Horstmann *et al* (1992), who investigated the relative contribution of surface runoff and household wastewater to PCDD/F levels in sewage sludge in Germany. The PCDD/F pattern was similar for household waste and sewage sludge, but different for surface runoff. A crude mass balance indicated that 3-5 times more OCDD found in sewage sludge originates from households than for runoff. The authors also found that a large proportion of PCDD/Fs in sewage sludge came from unidentified 'other sources'.

Attempts have been made to determine the relative importance of inputs contributing to PCDD/Fs present in household waste. Rappe *et al* (1990) investigated the PCDD/F content of household hypochlorite bleach and liquid soap in Sweden, and found that although PCDD/F levels in the bleach were low, liquid soap did contain 2378-substituted PCDD/Fs, including 2378-TCDD. This may have been because liquid soaps are a by-product of the pulp industry, and the process of bleaching pulp is known to produce PCDD/Fs (Rappe *et al* 1990). Rappe & Anderson (1992a) measured the PCDD/F concentrations in wastewater from washing machines and dishwashers, as the detergents used contain substances which may generate PCDD/Fs during washing cycles. However, the contribution of these detergents to sewage sludge was found to be extremely low. Another possible input of PCDD/Fs to sewage treatment works is human faeces. PCDD/Fs have been identified in human adipose tissue, milk and blood, and on investigation, Rappe & Andersson (1992b) showed that a series of 2378-substituted PCDD/Fs were found in faeces samples. The congener profiles correlated well with samples of human fat. However, the isomer profile found differed from that in sewage sludge, and the authors concluded that faeces cannot explain the levels of PCDD/Fs found in sewage sludge.

**Table 7.1 Sediment sampling sites ranked by total PCDD/F concentration and TEO**  
(ng kg-1 dry weight)

Rank	Site Location	Total PCDD/Fs	Rank	Site Location	TEQ
1	R. Alt, Altmouth	15 970	1	R. Alt, Altmouth	122.805
2	Mag Brook, Honley (below)	12 410	2	R. Mersey, Howley Weir	101.51
3	R. Amber, Ambergate (below)	10 390	3	R. Amber, Ambergate (below)	80.995
4	R. Spenn, Dewsbury (below)	9690	4	New River, Wicken	73.005
5	R. Derwent, Church Wilne (above)	9630	5	R. Derwent, Church Wilne (above)	70.11
6	R. Mersey, Howley Weir	9310	6	Mag Brook, Honley (below)	51.105
7	R. Aire, Beal (below)	7390	7	R. Don, Rotherham (above)	50.925
8	R. Don, Rotherham (above)	7050	8	R. Spenn, Dewsbury (below)	48.735
9	R. Aire, Fleet Weir (above)	6763	9	R. Calder, Mirfield (above)	44.205
10	R. Tame, Lea Marston (above)	6690	10	R. Aire, Beal (below)	35.355
11	New River, Wicken	6593	11	R. Tame, Lea Marston (above)	32.095
12	R. Aire, Beal (above)	5160	12	R. Cam, Hauxton (above)	26.0
13	R. Aire, Fleet Weir (below)	4500	13	R. Don, Rotherham (below)	25.645
14	R. Derwent, Belper (above)	4470	14	R. Aire, Fleet Weir (above)	24.2
15	R. Calder, Mirfield (above)	4450	15	R. Aire, Beal (above)	23.32
16	R. Don, Rotherham (below)	4070	16	R. Derwent, Belper (above)	19.765
17	R. Cam, Hauxton (above)	3646	17	R. Weaver, Acton	18.4
18	R. Cam, Hauxton (below)	3584	18	R. Tame, Lea Marston (below)	16.765
19	R. Thames, Teddington	2975	19	R. Derwent, Church Wilne (below)	16.530
20	R. Tame, Lea Marston (below)	2580	20	R. Loxley, near Sheffield	14.945
21	R. Derwent, Belper (below)	2556	21	R. Derwent, Belper (below)	13.735
22	R. Loxley, near Sheffield	2530	22	R. Aire, Fleet Weir (below)	13.495
23	R. Erewash, Eastwood (below)	2499	23	R. Thames, Caversham Weir	13.227
24	R. Erewash, Eastwood (above)	2180	24	R. Thames, Teddington	12.280
25	R. Derwent, Church Wilne (below)	2088	25	R. Erewash, Eastwood (below)	11.985
26	Pressbrook, Ogston	1678	26	Pressbrook, Ogston	9.060
27	R. Thames, Caversham Weir	1537	27	R. Amber, Ambergate (above)	8.955
28	R. Weaver, Acton	1527	28	R. Erewash, Eastwood (above)	8.385
29	R. Calder, Mirfield (below)	1449	29	R. Granta, Hildersham	7.820
30	R. Amber, Ambergate (above)	1147	30	R. Cam, Hauxton (below)	7.778
31	R. Granta, Hildersham	952	31	R. Calder, Mirfield (below)	6.445
32	R. Thames, Cricklade	860	32	R. Thames, Cricklade	5.786
33	R. Derwent, Froggatt	631	33	R. Derwent, Froggatt	5.605
34	R. Dane, Hugbridge	446	34	R. Dane, Hugbridge	4.208
35	R. Lathkill, Alport	335	35	R. Lathkill, Alport	2.753
36	R. Lugg, Hereford	281	36	R. Lugg, Hereford	1.985

**Table 7.2      Concentrations of PCDD/Fs in surface sediment samples**

Author	River/lake	Total PCDD	concentration in surface sediments (ppt)			
			Total PCDF	Total PCDD/F	I-TEQ	2378- TCDD
Evers <i>et al</i> (1988)	R. Rhine					
	near Basel	1170	862	2032	21	
	near Strasbourg	7711	1000	8711	27	
	near Dusseldorf	8595	9351	17 946	187	
	near Rotterdam	2057	4540	6597	78	
	R. Ruhr	8148	9212	17 360	310	
Hagenmaier <i>et al</i> (1986)	R. Neckar u/s Heidelberg	2730	950	3680		
	R. Danube at Ulm	2700	860	3560		
Götz <i>et al</i> (1990)	Hamburg Harbour			10 000 - 75 000		1 - 1500
	Hamburg background	160	51	211		<0.5
Götz <i>et al</i> (1992)	R. Elbe, Artlenburger	4740	10 850	15 590	167	1
	R. Elbe, Hamburg	11 480	13 300	24 780	127	n.d.
Knutzen & Oehme (1989)	Frierfjord, Norway			749 000	18 000 (Nordic TEQ)	110
Czuczwa <i>et al</i> (1985)	Lake Zurich	~2200	~790	~2990		
Reed <i>et al</i> (1990)	Elk River, Minnesota	29	665	694		n.d.
Czuczwa & Hites (1984)	Saginaw River	~57 000	~54 000	~111 000		~1000
	Lake Huron	~1990	~633	~2623		
Czuczwa & Hites (1986)	Lake Michigan	~1470	~275	~1745		
	Lake Erie	~1855	~70	~1925		~10
	Lake Ontario	~5120	~5030	~10 150		~20
Miyata <i>et al</i> (1988)	river samples, Osaka	5300- 14 000	2700- 16 000	8000- 30 000		

~ approximate values have been taken from illustrations

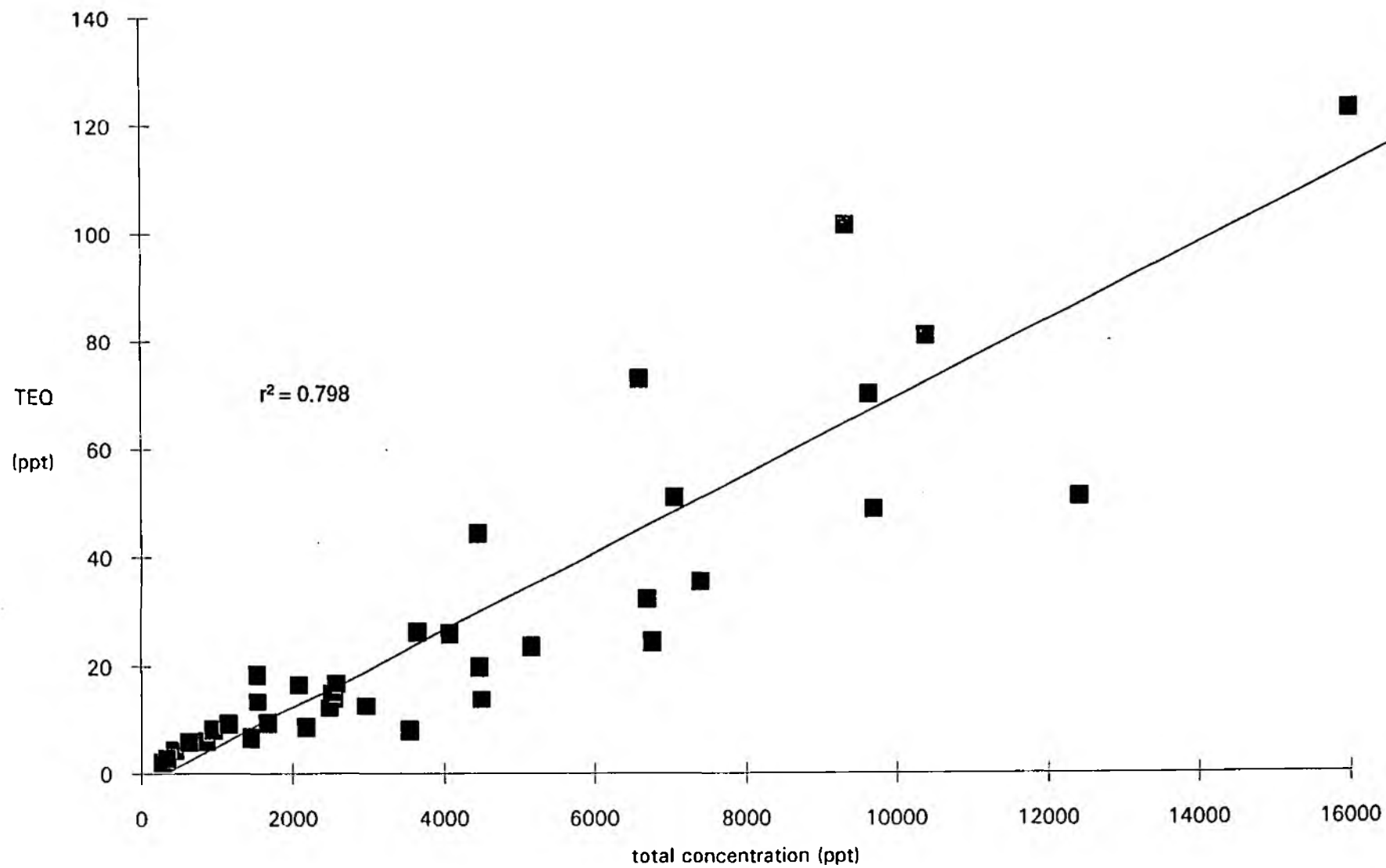


Figure 7.1 Relationship between total PCDD/F concentration and TEQ

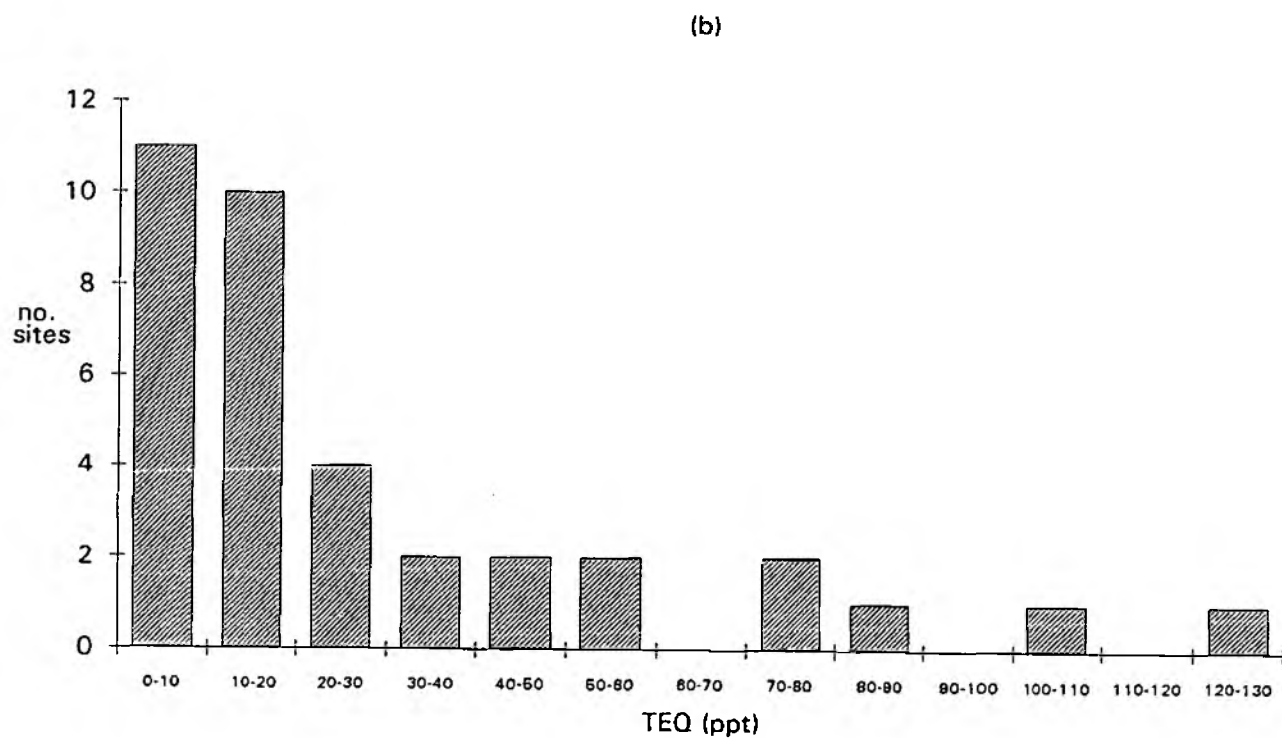
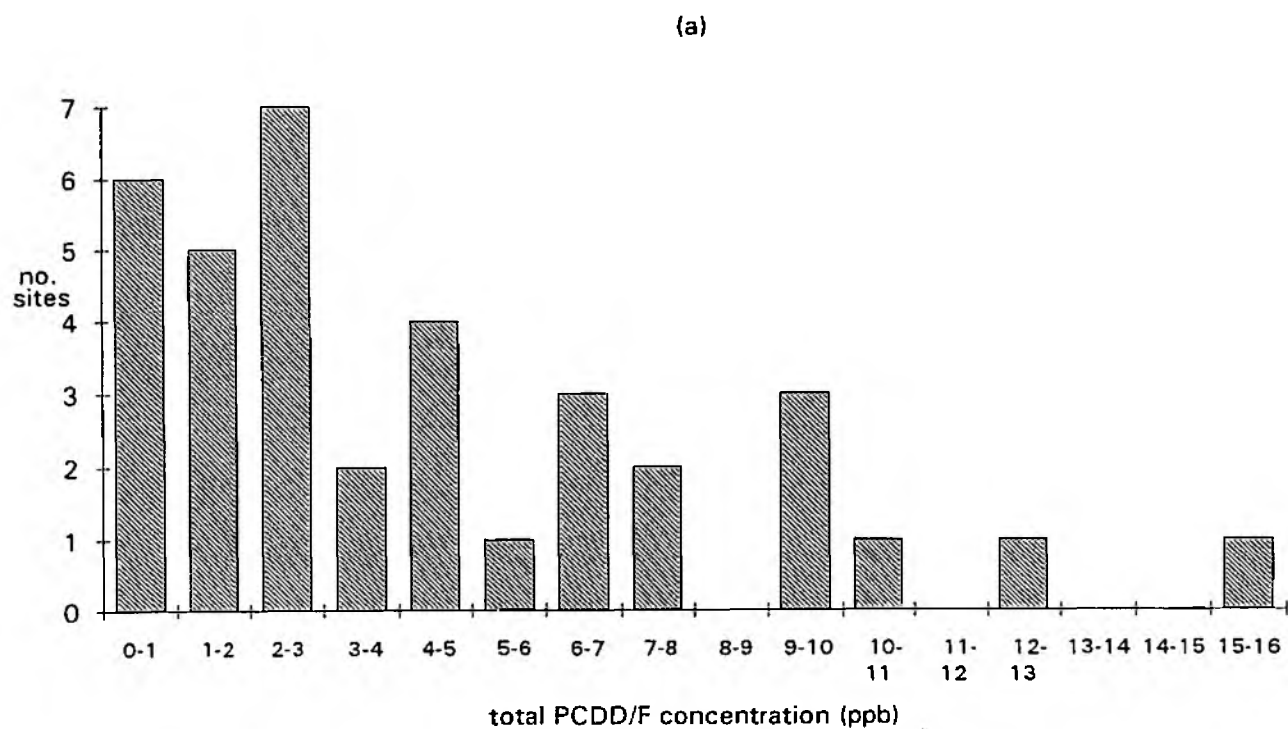


Figure 7.2 Histogram showing (a) the number of sites in each concentration class and (b) the number of sites in each TEQ class

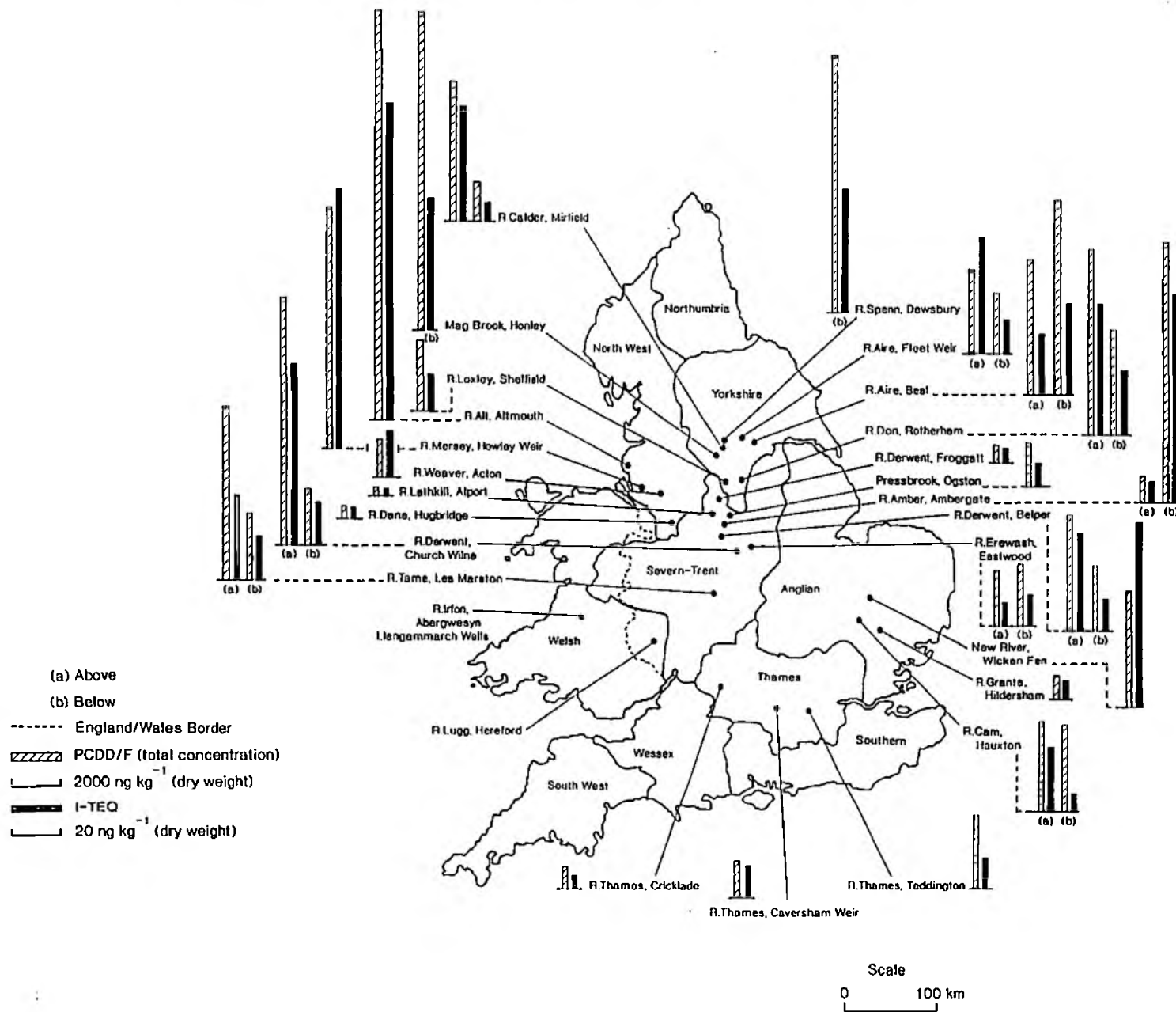


Figure 7.3 Sample site locations showing total PCDD/F concentrations and TEQ's at each site



## 8. CONCLUSIONS

A number of conclusions arise from the results of this study.

1. The analysis of 40 water samples from both potentially polluted and background areas showed PCDD/F concentrations to be below the limit of detection. This suggests that further routine monitoring of water samples is unnecessary unless specific pollution episodes warrant investigation. The sediment results have confirmed that bottom sediments provide a reservoir for PCDD/Fs, and would more usefully provide a means for monitoring PCDD/F levels in the aquatic environment.
2. The total concentrations and TEQs of PCDD/Fs presented here from a survey of 36 sediment sampling sites suggests that the levels present in fine riverine sediments across England and Wales can vary by at least a factor of 50, from 300-16 000 ng kg<sup>-1</sup> total concentration and 2-120 ng kg<sup>-1</sup> TEQ. These values are comparable to the range found in UK soils and of surface sediments in other parts of Europe.
3. It seems reasonable to assume that fine river sediment in England and Wales has a background total concentration in the order of 300-400 ng kg<sup>-1</sup> and a background TEQ of 2-4 ng-kg<sup>-1</sup>, originating primarily from direct deposition and indirect catchment runoff of atmospherically derived PCDD/Fs.
4. The sources of PCDD/Fs present in the rivers of England and Wales are not well defined, with the results of this study suggesting that unidentified point or diffuse sources may often completely mask the impact of identified potential point sources.
5. The information present in the literature on the homologue profiles of specific and diffuse sources is limited, and when coupled with the similarity in many of the homologue and TEQ profiles in the sediments sampled, this increases the difficulty of matching measured contamination with likely sources.

## 9. RECOMMENDATIONS FOR FUTURE WORK

1. The commonly adopted 'fingerprint' procedure for identifying sources is based on the matching of a limited number of homologue groups. Whilst used internationally, this technique clearly has its limitations. The gas chromatograms produced during analysis contain information on all 210 PCDD/F isomers. It is theoretically possible to extract this information to give much more detailed information on the samples analysed. A possible extension of the present study would involve extracting this information as the first step to developing a more sophisticated procedure for matching source to contamination.
2. Based on the results of this study, we would recommend that an attempt is made to identify the extent and source of the contamination observed upstream of sites on the rivers Derwent (Church Wilne and Belper), Calder, Hauxton, Don, and Aire (Fleet Weir).
3. This study was conducted on freshwaters only with the tidal limit of rivers providing a lower boundary for sampling. The contribution of riverine inputs to PCDD/F contamination of estuaries and coastal waters should be investigated. We would recommend that such a study should concentrate, at least initially, on the two rivers we have ranked highest in terms of TEQ, namely the Alt and Mersey.
4. In assessing the fate of particulate-associated PCDD/Fs in estuaries and coastal regions, an important consideration are the areas of tide-washed pastures around the coast which are regularly inundated with seawater. Fine particulates are deposited in these regions which are often grazed by sheep and cattle and occupied to differing extents by members of the public. It is possible that such land uses may provide a route for PCDD/Fs back to man. A limited investigation should be undertaken to determine whether this is a significant pathway.

## REFERENCES

- Ambidge, P. A. Cox, E. A., Creaser, C. S., Greenberg, M., Gem, M. G. de M., Gilbert, J., Jones, P. W., Kibblewhite, M. G., Levey, J., Lisseter, S. G., Meredith, T. J., Smith, L., Smith, P., Startin, J. R., Stenhouse, I. & Whitworth, M. (1990) Acceptance criteria for analytical data on polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. Chemosphere 21, 999-1006
- Berryman, R. J., Bennett, S. L., Ambidge, P. F., Lee, D. S. & McMorie, S. K. C. (1991) Investigation into emissions of dioxins and furans from the smokeless fuel plant and chemical wastes incinerator at the Coalite Works, Nr Bolsover, Derbyshire. AEA Environment and Energy Report AEA-EE-0223
- Branson, D. R., Takahashi, I. T., Parker, W. M. & Blau, G. E. (1985) Bioconcentration kinetics of 2,3,7,8-tetrachlorodibenzo-p-dioxin in rainbow trout. Environmental Toxicology & Chemistry 4, 779-788
- Broman, D., Näf, C., Rolff, C. & Zebühr, Y. (1991) Occurrence and dynamics of polychlorinated dibenzo-p-dioxins and dibenzofurans and polycyclic aromatic hydrocarbons in the mixed surface layer of remote coastal and offshore waters of the Baltic. Environmental Science and Technology 25, 1850-1864
- Clayton, P., Davies, B. J., Jones, K. & Jones, P. (1992) Toxic organic micropollutants in urban air. Warren Spring Laboratory Report LR 904 (PA).
- Clement, R. E. (1991) Ultratrace dioxin and dibenzofuran analysis: 30 years of advances. Analytical Chemistry 63, 1130-1139
- Creaser, C. S., Fernandes, A. R., Al-Haddad, A., Harrad, S. J., Homer, R. B., Skett, P. W. & Cox, E. A. (1989) Survey of background levels of PCDDs and PCDFs in UK soils. Chemosphere 18, 767-776.
- Creaser, C. S., Fernandes, A. R., Harrad, S. J. & Cox, E. A. (1990) Levels and sources of PCDDs and PCDFs in urban British soils. Chemosphere 21, 931-938.
- Cuzczwa, J. M. & Hites, R. A. (1984) Environmental fate of combustion-generated polychlorinated dioxins and furans. Environmental Science & Technology 18, 444-450
- Cuzczwa, J. M. & Hites, R. A. (1986) Airborne dioxins and dibenzofurans: sources and fates. Environmental Science & Technology 20, 195-200
- Cuzczwa, J. M., Niessen, F. & Hites, R. A. (1985) Historical record of polychlorinated dibenzo-p-dioxins and dibenzofurans in Swiss lake sediments. Chemosphere 14, 1175-1179
- di Domenico, A., Merli, F., Boniforti, L., Camoni, I., Di Muccio, A., Taggi, F., Vergori, L., Colli, G., Elli, G., Gorni, A., Grassi, P., Invernizzi, G., Jemma, A., Luciani, L., Cattabeni, F., De Angelis, L., Galli, G., Chiabrando, C. & Fanelli, R. (1979) Analytical techniques for

2,3,7,8-TCDD detection in environmental samples after the industrial accident at Seveso. Analytical Chemistry 51, 735-740

DoE (1989) Dioxins in the Environment. Department of the Environment Central Directorate of Environmental Protection. Pollution Paper No. 27. London: HMSO.

Evers, E. H. G., Ree, K. C. M. & Olie, K. (1988) Spatial variations and correlations in the distribution of PCDDs, PCDFs and related compounds in sediments from the River Rhine - Western Europe. Chemosphere 17, 2271-2288

Fletcher, C. L. & McKay, W. A. (1993) Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in the aquatic environment - a literature review. Chemosphere 26, 1041-1069

Götz, R., Friesel, P., Roch, K., Paepke, O., Ball, M. & Lis, A. (1992) Polychlorinated-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in bottom sediments of the River Elbe. Extended Abstracts of the 12th International Symposium on Dioxins and Related Compounds (Tampere, Finland August 1992). Volume 9, 83-86. Proceedings to be published in Chemosphere.

Götz, R., Schumacher, E., Kjeller, L.-O., Bergqvist, P.-A., & Rappe, C. (1990) Polychlorierte dibenzo-p-dioxine (PCDDs) und polychlorierte dibenzofurane (PCDFs) in sedimenten und fischen aus dem Hamburger hafen. Chemosphere 20, 51-73

Hagenmaier, H., Brunner, H., Haag, R. & Berchtold, A. (1986) PCDDs and PCDFs in sewage sludge, river and lake sediments from South West Germany. Chemosphere 15, 1421-1428

Horstmann, M., McLachlan, M. & Reissinger, M. (1992) Investigations of the origin of PCDD/F in municipal sewage sludge. Extended Abstracts of the 12th International Symposium on Dioxins and Related Compounds (Tampere, Finland August 1992). Volume 9, 97-100. Proceedings to be published in Chemosphere.

Knutzen, J. & Oehme, M. (1989) Polychlorinated dibenzofuran (PCDF) and dibenzo-p-dioxin (PCDD) levels in organisms and sediments from the Frierfjord, Southern Norway. Chemosphere 19, 1897-1909

Koester, C. J. & Hites, R. A. (1992) Wet and dry deposition of chlorinated dioxins and furans. Environmental Science and Technology 26, 1375-1382

Krogh, A. & Lange, E. (1932) Quantitative untersuchungen über plankton, kolloide und gelöste organische und anorganische substanzen in dem Füresee. Internationale Revue der gesamten Hydrobiologie 26, 20-53

MAFF (1992) Report of studies on dioxins in Derbyshire carried out by the Ministry of Agriculture, Fisheries and Food. MAFF Food Safety Directorate.

McMahon, A. W. (1992) Polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in freshwater systems. In 1st Interim Draft Report to National Rivers Authority (Ambidge, P. F., Fletcher, C. L. & McKay, W. A.) under National R&D Project 330. June 1992.

Meybeck, M. (1982) Carbon, nitrogen and phosphorus transport by world rivers. American Journal of Science 282, 401-450

Miyata, H. Takayama, K., Ogaki, J., Mimura, M. & Kashimoto, T. (1988) Study on polychlorinated dibenzo-p-dioxins and dibenzofurans in rivers and estuaries in Osaka Bay in Japan. Toxicology and Environmental Chemistry 17, 91-101

Muir, D. C. G. & Yarechewski, A. L. (1988) Dietary accumulation of four chlorinated dioxin congeners by rainbow trout and fathead minnows. Environmental Toxicology & Chemistry 7, 227-236

Muir, D. C. G., Yarechewski, A. L., Knoll, A. & Webster, G. R. B. (1986) Bioconcentration and deposition of 1,3,6,8-tetrachlorodibenzo-p-dioxin and octachlorodibenzo-p-dioxin by rainbow trout and fathead minnows. Environmental Toxicology & Chemistry 5, 261-272

Näf, C., Broman, D., Ishaq, R., Zebühr, Y. (1990) PCDDs and PCDFs in water, sludge and air samples from various levels in a waste water treatment plant with respect to composition changes and total flux. Chemosphere 20, 1503-1510

NATO/CCMS (1988) International Toxicity Equivalency Factor (I-TEF) method of risk assessment for complex mixtures of dioxins and related compounds. Pilot study on international information exchange on dioxins and related compounds. Report No. 176.

Rappe, C. & Andersson, R. (1992a) Analyses of PCDDs and PCDFs in wastewater from dish washers and washing machines. Extended Abstracts of the 12th International Symposium on Dioxins and Related Compounds (Tampere, Finland August 1992). Volume 9, 191-194. Proceedings to be published in Chemosphere.

Rappe, C. & Andersson, R. (1992b) Levels of PCDDs and PCDFs in human feces. Extended Abstracts of the 12th International Symposium on Dioxins and Related Compounds (Tampere, Finland August 1992). Volume 9, 195-198. Proceedings to be published in Chemosphere.

Rappe, C., Andersson, R., Lundström, K. & Wiberg, K. (1990) Levels of polychlorinated dioxins and dibenzofurans in commercial detergents and related products. Chemosphere 21, 43-50

Reed, L. W., Hunt, G. T., Maisel, B. E., Hoyt, M., Keefe, D. & Hackney, P. (1990) Baseline assessment of PCDDs/PCDFs in the vicinity of the Elk River, Minnesota generating station. Chemosphere 21, 159-171

Servos, M. R., Muir, D. C. G. & Webster, G. R. B. (1989) The effect of dissolved organic matter on the bioavailability of polychlorinated dibenzo-p-dioxins. Aquatic Toxicology 14, 169-184

## APPENDIX A

## QUESTIONNAIRE AND SAMPLE RESPONSE

### DISTRIBUTION OF PCDDs AND PCDFs IN SURFACE FRESHWATER SYSTEMS

1. This questionnaire is seeking to derive some basic information on the distribution of dioxins in surface **FRESH WATERS**. The following statements lead to Section 7 where the request for basic information is made.
2. Annex 1 overleaf contains a list of "typical" dioxin-forming industries. Some of these may be in your Region. These practices may not be directly associated with water (e.g. incineration stacks), but water may be downwind of them.
3. It should be possible to identify high/abnormally high levels of PAHs; PCBs; PCPs, Organochlorine pesticides from your Regional surface water quality monitoring programmes. Typically these would be levels at or in excess of EEC guidelines.
4. These chemicals are often associated with the dioxin-forming industries. Unless the site has already been tested for the presence of dioxins, there will be no firm information as to dioxin presence or levels. Indicator chemicals found in surface waters adjacent to or near recognised dioxin-forming industries represent the best clue as to their presence.
5. Due to the nature of dioxins, they readily become associated with particulate matter. It is proposed that sediment samples will be taken simultaneously and stored. If the water samples contain low dioxin levels, then sediments will be analysed. Sediments may also have been taken in your routine sampling programme and you may have information on the sediment type and usual sampling method.
6. It is the intention that sampling of surface waters ties in as close as possible to the routine sampling of these sites. This will give a longer dataset for the indicator chemicals and the dioxin levels will be provided for a recognised sampling point.
7. Annex 2 requests site information for those sites which you consider to be, potentially, contaminated with PCDDs or PCDFs. It covers the major headings which will enable us to select high priority sites across the UK, reflecting a variety of the industries listed in Annex 1 and from a variety of water body types (steams; rivers; ponds; lakes). Please limit your site selections to no more than 10.
8. If you can identify sites, it may be that the information available to you is superficial. If this is the case, AEA can contact the District Office for the more detailed information re the site access etc. Please give a further contact name and telephone number if this is the case.
9. If you have had any dioxin analysis undertaken for in your Region, please give some basic information as to when, where and how much PCDDs/PCDFs were found.



## ANNEX 1    POTENTIAL PCDD AND PCDF SOURCES FOR SURFACE FRESHWATER SYSTEMS

### INDUSTRIAL DISCHARGE

Chemical Manufacture	Chlorinated Phenolics PCBs Chlorinated phenoxy acetic acids Chlorinated pesticides Chlorinated herbicides Agrochemicals Disinfectants Bleaches                    etc.
Paper Manufacture	Production of paper Products from chlorine Bleached wood pulp
Metallurgical	Metal smelters e.g. Iron and steel works Non-ferrous scrap
Sewage Works	

### INDUSTRIAL DEPOSITION

Combustion Plant	Municipal Incinerators Clinical Waste Incinerators Chemical Waste Incinerators Industrial Waste Incinerators Sewage Sludge Incinerators Power Stations Metal Smelters
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### NON-INDUSTRIAL SOURCES

Motor Vehicles  
Domestic Fires  
Bonfires  
Cigarettes  
Stubble Burning  
Forest Fires (?)  
Accidental Fires

## DISTRIBUTION

A Ferguson	Anglian Region
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## Document Status and Use Note

This note provides details of how the attached document from the R&D programme is to be used and serves as a record of its status. Consequently, this note should not be removed from this document.

### 1. Document

Title **Draft Final Report - Distribution of PCDDs and PCDFs in surface freshwater systems**

#### Distribution Instructions

1 copy to :

G Miller	Project Leader (Anglian Region)		
G Brighty	R&D Scientist (Anglian Region)		
A Ferguson	Regional Biologist (Anglian Region)		
D Foster	Consents Scientist (Anglian Region)		
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Dissemination Status      Internal      **Restricted**      External      **Restricted**

### 2. Document Status and Intended Use

Details (should refer to where the document stands in relation to other documents and how it is to be used)

The report is a draft final report. It is to be reviewed by the above staff.

Detailed criteria for its assessment are presented on the attached Sign-Off form

### 3. Approval For Status and Use

Project Leader

*G. Miller*

Topic Leader

*M. Johnson*

Commissioner

Group Chairman<sup>1</sup>

Notes: <sup>1</sup>Signature of Chairman of Working Group if appropriate.

Date Output Sent **6 / 8 / 93**

This document may have been distributed prior to the end of research stage assessment and before any decision has been made concerning its implementation.

Approval for permanent project outputs will be required from Project Leader/Topic Leader/Commissioner/Group Chairman. Less signatures will be required for draft or interim outputs.

**SIGN OFF FORM****1. Project and Deliverable Details**

Project Title	Distribution of PCDDs and PCDFs in surface freshwater systems				
Project Leader	G Miller	Region	Anglian	Project Number	330
Deliverable	Draft Final Report			Reference	330/ 3/A

**2. Sign Off Instructions** (to be completed by the Project Leader)

	Reviewer	Region	Review and Sign Off Criteria
			<p>The reviewer is asked to consider:</p> <ul style="list-style-type: none"> <li>- the approach and scope of the survey undertaken</li> <li>- the levels of contaminants found in freshwater and sediment and implications for NRA management</li> <li>- conclusions drawn - are they appropriate / realistic / sufficiently soundly based / conservative <u>vs</u> exaggerated</li> <li>- recommendations for future work: which should NRA consider undertaking and are there others not presented</li> <li>- how NRA should now implement those recommendations</li> </ul>

Issued to Reviewer on ..6./8../93

To be returned by 3../9../93...

**3. Review Comments** (to be completed by the Reviewer)

I have reviewed the above deliverable on behalf of

(Department, Region, Function, Working Group)

The deliverable is:

☐  
☐  
☐

accepted;

accepted subject to the inclusion of the comments noted below; or

rejected for the reasons noted below.

Comments

Signed

Date



# MEMORANDUM



**To:** See distribution list.  
**From:** Geoff Brighty, Regional R&D Scientist, Anglian Region  
**Our ref:** 846/00/23  
**Your ref:**  
**Date:** 5 August 1993

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## **NATIONAL R&D PROJECT 330: PCDDs AND PCDFs IN SURFACE FRESHWATER SYSTEMS**

### **REVIEW OF DRAFT FINAL REPORT**

I enclose a copy of the above draft final report.

When the research was commissioned, the envisaged review panel was that associated with the Topic Area A6 "Chemical Contaminants". It is still appropriate that this report is appraised initially by these staff.

The report presents data on dioxin and difuran levels in freshwater and sediment from across England and Wales, and associated with various potential pollution sources. "Background" sites were also sampled. The data represent the first such survey within the UK. The report works on several levels: site-specific, industrial process types, catchment and the UK picture. I am sure that you will find it an interesting read.

Please can you return your comments, specifically addressing those criteria outlined on the attached "Sign-Off" form, to the Project Leader, Gordon Miller, at Peterborough by 3 September 1993. These will then be discussed with the Commissioner for Water Quality and an implementation plan will be developed with the WQ Business Groups as appropriate.

**DR G C BRIGHTY**  
**Regional R&D Scientist**

encs.

cc G Miller

## ANNEX 2 SITE INFORMATION

[illegible]

ANNEX 2 SITE INFORMATION - YORKSHIRE NRA

INDICATOR CHEMICAL	CONCENTRATION RANGE	SAMPLE POINT CODE	REASON CODE	NATIONAL GRID REFERENCE	DETERMINAND CODE	WATER TYPE	DISCHARGE/ POINT SOURCE? Y/N	ASSOCIATED INDUSTRY	DISTRICT CONTACT NAME/No.
V	2.8 - 177.3 mg/l	041911270		SE 684 283	9574	TIDAL FRESHWATER	Y	POWER STN	
CHLOROFORM	<0.1 - 45 µg/l	041941050		SE 532 255	0816	FRESHWATER	Y	POWER STN/ CHEMICAL WORKS	
BOD	1.8 - >30 mg/l	041941095		SE 381 285	0085	"	Y	SEWAGE WORKS	
As	<5 - 29 µg/l	042911240		SE 937 264	9260	ESTUARY	Y	NON-FERROUS METAL SMELTER	
COD	29 - 220 mg/l	043933010		SK 452 726	0092	FRESHWATER	Y	COAL CHEMICAL	
BOD	0.6 - 14.5 mg/l	043933200		SK 421 922	0085	"	Y	STW/STEEL IND./INCINERATOR	
PHENOLS	<15 - 734 µg/l	043933950		SK 425 905	9271	"	Y	CHEM. INDUSTRY/ SEWAGE WORKS	
DIELDRIN	<0.001 - 0.61 µg/l	044951700		SE 136 123	0511	"	Y	SEWAGE WORKS/ TEXTILE INDUSTRY	
BOD	3.2 - 24.3 mg/l	044952250		SE 189 205	0085	"	Y	SEWAGE WORKS/ CHEM. INDUSTRY	
MCP	0.6 - 250 µg/l	044952860		SE 231 205	9322	"	Y	PHENOL-ACETIC ACID MANUFACTURE	

Our ref GE/KD  
Your ref

Date 31 December 1991



National Rivers Authority  
North West Region

Mr. P.F. Ambridge  
Organic Analysis Section  
Analytical Sciences Centre  
AEA Environment and Energy  
B551 Harwell Laboratory  
PO Box 34  
Didcot  
Oxfordshire OX11 0RE

Dear Mr. Ambridge

DISTRIBUTION OF PCDDs AND PCDFs IN SURFACE FRESHWATER SYSTEMS

I refer to your letter dated 20 December in which you request information about suitable freshwater sites within the North West region to monitor as part of a national survey for polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs).

There are a number of industrial discharges within the region which fall into the categories identified in Annex 1 of your letter but in most cases direct aqueous discharges from these industries are to estuarine and coastal waters.

The only freshwater sites which may be useful to your study are those which are downstream of major sewage treatment works which are known to receive trade effluent discharges from the industrial sectors to which you refer. I therefore suggest the following sites, which are above the tidal limits of the major urbanised river systems, and are regularly monitored for the full suite of EC List I Dangerous substances (eg. pentachlorophenol, organochlorine pesticides etc.).

1. River Mersey and Howley Weir (NGR SJ 616 880)
2. River Alt at Altmouth (NGR SD 292 051)
3. River Weaver at Acton Swing Bridge (NGR SJ 601 761)

We would be able to collect samples on your behalf, if you decide to include these sites in your survey.

Since monitoring for dioxins has not been undertaken within the region I am unable to provide you with data concerning background concentrations of PCDDs or PCDFs present in inland waters.

If you require further information or have any queries then please do not hesitate to contact me on 0924 5399 Ext. 2643.

Yours sincerely,

Glyn Edwards

Quality Audit & Legislation Manager

P.O. Box 12 Richard Fairclough House Knutsford Road Warrington WA4 1HG Tel: (0925) 53999 Telex: 628425 Fax: (0925) 415961



# NRA ANGLIAN REGION

## ANNEX 2 SITE INFORMATION

INDICATOR CHEMICAL	CONCENTRATION RANGE	SAMPLE POINT CODE	REASON CODE	NATIONAL GRID REFERENCE	DETERMINAND CODE	WATER TYPE	DISCHARGE/ POINT SOURCE? Y/N	ASSOCIATED INDUSTRY	DISTRICT CONTACT NAME/No.
Range of Pesticides -	See (1) (inc. raw materials by products e.g. chlorophenils)	RO2LF29025		TL431527			Y	Manufacture of Agrochemicals	David Tester (0480) 414581
General Pesticide range	See WRC report Granta Catchment Study (PRS 1998-11)	RO2BF28103		TL561468			N	Pesticide usage in catchment	as above
Pesticides inc. PCP	See (4)	RO14DFYAR230		TG350440			Y	Manufacture of Agrochemicals	Dr. David King (0473) 727712
Organochlorine Insecticides + Fungicides	See (2)	RO3BFCA133		TF31854205			Y	Wood Preservatives	John Swain (0522) 513100
Pesticides inc. PCP	See (3)	RO2BF26131		TF394747			N	General pesticide usage in area	David Tester (0480) 414581
*	*	*	*	*	*	SURFACE WATER INTERCEPTION (A12, COPPOLE SURREY)	Y	ROAD RUNOFF	DAVID TAYLOR SENIOR QUALITY OFFICER (0473) 727712

\* - Site not regularly sampled - but should be of  
significant interest to the project.

## ANNEX 2 SITE INFORMATION

## THAMES

	INDICATOR CHEMICAL	CONCENTRATION RANGE (1990)	SAMPLE POINT CODE	REASON CODE	NATIONAL GRID REFERENCE	DETERMINAND CODE	WATER TYPE	DISCHARGE/ POINT SOURCE? Y/N	ASSOCIATED INDUSTRY	DISTRICT CONTACT NAME/No.
①	γ-HCH	0.004 → 0.027 µg/l	THAMES AT WATER INTAKE FARNBORO		SP4390 0640		FRESHWATER RIVER	N	—	MR. NIGEL MARSHALL 0734 311422
②	γ-HCH	0.004 → 0.044 µg/l	THAMES AT CAVERSHAM WEIR		SU7210 7420		FRESHWATER RIVER	N	—	(as above)
③	γ-HCH	0.008 → 0.052 µg/l	THAMES AT TEDDINGTON		TQ1700 7130		FRESHWATER RIVER	N	—	MR. P. LLOYD 081-310-5500
④	γ-HCH	0.005 → 0.031 µg/l	KENNET DOM. U/S THAMES		SU 7310 7380		FRESHWATER RIVER	N	COLTHROP PAPER MILL?	(MR. MARSHALL)
⑤	γ-HCH	0.054 → 0.137 µg/l	LEE AT LEABRIDGE WEIR		TQ 3570 8660		FRESHWATER RIVER	N	DEEDHAMS SEWAGE WORKS	MR. BOB WALKER 0992 645050

## ANNEX 2 SITE INFORMATION

## SEVERN TRENT

INDICATOR CHEMICAL	CONCENTRATION RANGE	SAMPLE POINT CODE	REASON CODE	NATIONAL GRID REFERENCE	DETERMINAND CODE <i>Specific to ST w/ archive</i>	WATER TYPE	DISCHARGE/ POINT SOURCE? Y/N	ASSOCIATED INDUSTRY	DISTRICT CONTACT NAME/No.
PCBs Total	0.19 µg/l	River Derwent- Church Wilne	Red List	SK452314	OCI	River	yes	Chemical Manufacture	K. Selby 0602-455-722
PCBs Total	1.78 µg/l 1.58 µg/l	Hallam Fiddle Stn Miltonhey Stn	Red List	SK483390 SK456462	OCI	Sewage Effluents River	yes	Drinking Chemical Wastewater Disposal	K. Selby
PCP	1.0 µg/l	River Amberd Ambergate	Red List routine	SK348517	OAD	River	yes	Drinking Chemical	K. Selby
PCP	2.6 µg/l	Leak Stn	Red List	ST981540	OAD	Sewage Effluents	yes	Drinking Chemical	A. Stanley 0523 444161
PAH Total	0.16 µg/l	Ffresen Brook at Kneeklas	Investigative	SO254743	OUY	River	yes	Tyre Fire	R. Harvey 0743 272 878
PCDFs/ PCDDs	NE limited detection	Cause Dyke at Geckling	Specific Survey	SK615431	Analysed by Warner Frings	River	yes	LA Incinerator	K. Selby
Oxyeno (chlorine + others)	0.05 µg HCH + others	R. Tame at Lee Marston	Routine	SP205 934	OWE	River	yes/No	Sewage Sludge Incinerator	A. Stanley
PCBs	High proportion of local to N. Sec	River Trent at Dunham	Red List	SK819744	OCI	River	yes/No	Sewage/Industry Post-generation	K. Selby

## ANNEX 2 SITE INFORMATION

WELSH

## N. AREA

INDICATOR CHEMICAL	CONCENTRATION RANGE	SAMPLE POINT CODE	REASON CODE	NATIONAL GRID REFERENCE	DETERMINAND CODE	WATER TYPE	DISCHARGE/ POINT SOURCE? Y/N	ASSOCIATED INDUSTRY	DISTRICT CONTACT NAME/No.
		27502	D/S STW Cefni	SH 4646 7370		River	Y	Pharmaceutical, Sewage works, Printing.	
		27505	U/S STW Cefni (control)	SH 4600 7560		River	Y		
	*	7048	STW final effluent Five Fords.	SS 3623 4837					

\* Five Fords treats a wide range of Trade Effluents - none specifically containing above but could be representative of an industrial area.

## ANNEX 2 SITE INFORMATION

WRSH

S.E. AREA

INDICATOR CHEMICAL	CONCENTRATION RANGE	SAMPLE POINT CODE	REASON CODE	NATIONAL GRID REFERENCE	DETERMINAND CODE	WATER TYPE	DISCHARGE/ POINT SOURCE? Y/N	ASSOCIATED INDUSTRY	DISTRICT CONTACT NAME/No.
<u>UPLAND RIVER SAMPLING POINTS.</u>									
		57102	U/s Major forestry	SN 853 526		R. Irfon @ Abergwesyn	N	Forestry	T. Whittaker
		50816	D/s Major forestry	SN 935 472		R. Irfon @ Llangannoch	N	Forestry	4
<u>LOWLAND AGRICULTURAL AREA SPT'S</u>									
		50075	Significant intensive horticulture + crops.	SO 3655 392		R. Frome @ Longworth	N	Agriculture	4

## **APPENDIX B**

## **SITE DESCRIPTIONS**

### **B.1 Thames Region**

The questionnaire response indicated that there was no known point source of PCDD/Fs in this Region, and so the following sites represent general urban inputs and a background site. Samples were taken in July 1992. Weather conditions had been dry prior to sampling although it rained whilst sampling at Caversham Weir. Conditions were dry following this.

R. Thames at Caversham Weir (Reading), Fig. B1.1: Deposited sediment was located in a slow moving part of the river above the weir. Emergent macrophytes were present along the river edge, helping to trap sediment. Cores were taken using the Gilson corer with pole attachment.

R. Thames at Teddington, West London, Fig B1.2: No sediment was located at the original weir site, and some difficulty was encountered locating any deposited sediment. A site was located on the west bank in a slow-moving inlet near a leisure/outdoor pursuits centre. The sediments were soft but fairly sandy. Ducks and Canadian geese were present at the site. Cores were taken using the Gilson corer with pole attachment.

R. Thames at Cricklade, Fig. B1.3: This was selected as a background site. The Thames was narrow and wadeable with clear water. The river was fast flowing and sediments were sampled from small pockets where obstacles (e.g. vegetation) had slowed the flow and allowed sediment to accumulate. Cores were taken manually.

### **B.2 Anglian Region**

Of the six possible sites identified by the questionnaire, three were selected for sampling; a point source, a diffuse source and a background site. Samples were taken in July 1992 and weather conditions were warm and calm. Rivers were at low flow.

R. Cam at Hauxton, Fig. B2.1: Schering Agrochemicals had been identified as a potential point source for this region. Samples were taken above and below the effluent pipe (and also above and below a road runoff pipe). The samples above the effluent pipe were taken from a slow-moving part of the river above a weir. The sediment collected was fine-grained and muddy. Cores were taken using the Gilson corer with pole attachment. Emergent and submergent macrophytes were present, and fish, some large, were observed. Anglers were fishing here. The river channel below the effluent pipe was narrow and wadeable with a largely gravely bed. Some pockets of accumulating sediment were located where the river had slowed on bends or by vegetation. The surface accumulating sediments were fine with sand lower down. Cores were taken manually. The banks were steep making access in and out of the river difficult. Small fish and swans were observed.

R. Granta at Hildersham, Fig B2.2: The site originally suggested was at Linton, chosen as pesticides are used in the catchment. No sediments were found at this location, but about 3 km further downstream at Hildersham, sediments were located near a ford. The river was at low flow and wadeable, and fine-grained sediments had accumulated along the sides of the river, probably to a maximum depth of 6-7 cm. Cores were taken manually. An NRA representative was of the opinion that a sewage treatment works upstream contributed

significantly to the water volume at low flow conditions. The water was clear with small fish present.

New River at Wicken Fen, Fig. B2.3: This location, at an NRA gauging station site, was taken to represent background conditions. This is a Grade 1 clean site, although surrounded by agricultural land with possible pesticide runoff. The water was slightly cloudy due to the chalk bedrock. The sediment was up to 50 cm deep and fine with some sand layers. Cores were taken manually. Many shrimp-like invertebrates were present.

### **B.3 North West Region**

The questionnaire reply indicated that there were no known potential point sources in the region, but three locations were suggested to represent diffuse urban inputs. A forth site was chosen as a background site. Weather conditions over the sampling period (end July 1992) were dry and sunny although heavy rain had fallen prior to sampling.

R. Alt at Altmouth, Fig. B3.1: This site was on Ministry of Defence land near an NRA pumping station which controls flow. The river was wide and deep, and flow varied during sampling due to the pumping station. This change in flow may have disturbed the top layers of sediment. Underneath a fine accumulating material was thick mud indicative of bank material. Cores were taken manually.

R. Mersey at Howley Weir, Warrington, Fig. B3.2: Some difficulty was encountered locating suitable points of access to the Mersey. However, a site of accumulating muddy sediment was located upstream of the weir at the back of a new housing and industrial estate. The sediment was accumulating near the bank where the flow was slowed by vegetation. Cores were taken manually.

R. Weaver at Acton swing bridge, Fig. B3.3: The river split into two under the bridge, one side being navigable. We sampled from the non-navigable side. Very soft mud made sampling dangerous away from the bank. Cores were collected manually.

R. Dane at Hugbridge, Fig. B3.4: This site was upstream of a pumping station. The river was of variable depth and fast flowing so location of sediment was difficult. One area located where sediments were very soft with a large fraction being decaying plant material. Sampling disturbed elvers and small fish. Cows were grazing in fields either side and obvious drinking areas were avoided.

### **B.4 Yorkshire Region**

The seven rivers sampled in central and south Yorkshire were either background sites or had potential point sources located nearby. The sites were sampled in August 1992 and the weather conditions were generally dry and breezy with some sunny spells with the exception of Fleet Weir where it rained. Heavy rain and thunder preceded sampling at Mag Brook.

Mag Brook (or R. Hall Dike) at Honley, Fig. B4.1: The potential point source identified here was a textiles industry whose effluent discharged into a sewage treatment works (STW). Above the point source a water sample only was taken as no accumulating sediment could be located, even at slower parts of the river (e.g. above weirs). Below the point source, soft





accumulating sediment was found above a small weir at a site overhung with trees. The sediments had a high water content with some air bubbles. Cores were taken manually.

R. Calder at Mirfield Fig. B4.2: The potential point source here was a chemical industry and STW. The river bank was steep and overgrown and access above the point source was limited to fishing bays. Aquatic macrophytes such as duckweed were plentiful. Sediments were not easy to locate, but patches were found near the bank. Cores were taken using the Gilson corer with pole attachment. Water samples were taken further upstream due to disturbance of sediment whilst getting into the river, and the amount of floating weed. Below the point source, sediments were located above a weir. Again there was little sediment, and what was located was sandy with a low water content. Woodlouse-type invertebrates were observed on rocks and the sediment surface. Cores were taken using the Gilson corer with pole attachment.

R. Aire at Castleford and Beal Fig. B4.3: Samples were collected above and below a chemical works/STW and a power station. Above the point source at Castleford, sediments were taken above a weir. They were fairly sandy but contained slightly more fine material than the previous site. Water fleas (*Daphnia*?) and the woodlouse-type bottom dwellers were present. Cores were taken using the Gilson corer with pole attachment. Below the point source at Beal, samples were taken in a navigable stretch of the river above a weir. Sediments were variable from fine sand to mud and clay. Blanket weed and other aquatic flora were present, also some fry. Care was taken to avoid an animal drinking area. Cores were taken using the Gilson corer with pole attachment.

R. Aire at Fleet Weir, Fig. B4.4: A STW was the potential point source investigated, and samples above the STW were taken from an island (site of Thwaites Mill) between the navigation channel and river, on the river side. Samples were collected using the Gilson corer with pole attachment. Sediments were difficult to locate even though the river was slow moving. Those collected had a high sand content. The woodlouse-type invertebrates were again present on the sediment surface. Below the point source, sediment was located above a weir and above the outlet from the navigation channel. Many aquatic macrophytes were present, and the sediment was very soft although still sandy. Cores were taken using the Gilson corer with pole attachment. Angling bays were evident.

R. Spenn at Dewsbury and Oakenshaw, Fig. B4.5: The point source investigated was a chemical works producing phenoxy-acetic acid, and associated STW. About two weeks before sampling, a fire had broken out at a second chemical works in the catchment. The chemical content of the water used to put out the fire would have damaged the STW, so the works were by-passed and the water went directly into the Spenn. Life in the river was severely damaged by this incident. No sediment was located upstream of the source, even at slower moving parts of the river. Below the source, sediment was black and smelly. A light, fluffy floc with a high water content extended down several centimetres. Cores were taken manually.

R. Don at Rotherham, Fig. B4.6: Sediments were taken above and below a steel works and STW. Above this source, sediment was located at a difficult access point down an overgrown bank. Anglers nearby had observed several species of fish in this stretch of river. Water



samples were taken from an easier access point. Cores were taken using the Gilson corer with pole attachment. Downstream of the source, samples were taken near a railway bridge at a site previously sampled by the NRA. Debris from the STW was evident, along with rat prints and droppings. Sediments were mostly muddy with some sandy patches. Cores were taken manually.

R. Loxley near Sheffield, Fig. B4.7: This was a background site. The river was flowing quite quickly but some sediment was accumulating near the edges around trees and vegetation. The sediment was soft and fluffy with a high water content. Cores were collected manually.

### **B.5. Severn Trent Region**

From the Severn Trent Region, five potential point sources, one diffuse source and two background sites were identified for sampling. Sampling in this region took place in July and August 1992 where conditions were generally dry and sunny. The River Tame was sampled in October 1992 when it rained heavily after a fair spell.

R. Amber at Ambergate, Fig. B5.1: Sources of interest here were a textiles industry, colliery and associated STW. The river receives a relatively large amount of effluent compared to the size of the catchment. Upstream, muddy sediment samples were taken using the Gilson corer with pole attachment, from a grassy, overgrown bank. A water rat was observed. Downstream, access to the river was easy. The water was shallow at the edges where sediment was accumulating, but the bed shelved steeply further out. Sediment was muddy and was sampled manually.

R. Derwent at Derby and Church Wilne, Fig. B5.2: Samples were taken above and below a textile industry which produces acetate and has dealt with speciality chemicals e.g. flame retardants, and a STW. Above this point source, the river was wide with fine grained sediment deposited near the banks. Cores were taken manually. Submerged macrophytes (e.g. *Elodea*) were present and the site was overhung by trees. Small fish were observed. Downstream, soft sediment was difficult to find, but an area was located above a small weir near an NRA gauging station. Cores were taken manually. Small fish were observed, and anglers were fishing further downstream.

R. Derwent at Belper, Fig. B5.3: The STW at Belper receives effluent from a lubricating oils manufacturer. Above this point source, samples were taken near a garden centre where the car park came close to the river. The sediment was fine grained with air trapped, which was released as air bubbles on sampling. This disturbed the sediment in the core tube so sampling was not ideal. Cores were taken manually. Large fish, ducks and geese were observed. Below the point source, fine silty mud was located at a site down a steep wooded path off the main road. Cores were taken manually. Some small fish were observed.

R. Erewash at Eastwood, Fig. B5.4: The potential point source here was a textiles industry/STW. The discharges have a toxic effect on the biota of the river, and there is an NRA biological monitoring point in the locality. Upstream, the river was quite narrow and accumulating sediment was found on a bend. Cores were taken manually. The river was accessed down a farm track. Downstream, a site was located near a small road bridge where the river runs close to the canal. Access to the river was difficult due to steep, overgrown

banks. Sediment was difficult to find in this stretch of the river with a largely stoney bed, and when located, it was composed of both clayey and fine mud.

R. Lathkill at Alport, Fig. B5.5: This was a background site, where an old mill and weir were slowing the flow of the river, which had widened at this point. Sediment from this pond-type feature had been cleared some years ago, but one corner of deep, muddy sediment still remained. Cores were taken using the Gilson corer with pole attachment. The water was very clear and large trout, water invertebrates and ducks were present.

R. Derwent at Froggatt, Fig. B5.6: This was selected as a background site on the Derwent. Muddy sediment was easy to find above a weir and bridge. Cores were taken using the Gilson corer with pole attachment.

Pressbrook at Ogston, Fig. B5.7: This site was suggested by Severn Trent as a possible diffuse source due to the local burial of rubble from an explosion at the Coalite plant. The site was upstream of the confluence with the R. Amber and of Severn Trent water works pipes. The water was clear and shallow and the stream easily accessed. Light brown, fluffy accumulating sediment was sampled manually.

R. Tame at Lea Marston, Fig. B5.8: This is the site of a series of water purification lakes, receiving discharges from STWs from the Birmingham and Black Country area. The river flowing into the lakes is 90% treated sewage discharge, and suspended particulates settle out into the lakes. The sediment is then dredged from the lakes and incinerated, so there is a large incinerator nearby. The Tame downstream of the lakes was sampled first, and as might be expected, sediment was not easy to locate. Patches were located at a slower part of the river but the sediment was a mixture of fine and sandy particles. Cores were collected manually. Above the lakes, the Tame was at medium flow and not easy to sample. Accumulating sediment was found near a bridge and sampled using the Gilson corer with pole attachment. Again sediments were a mixture of fine-grained and sand particles.

#### **B.6. Welsh Region**

Two types of land use were identified as possible diffuse sources. Samples were taken above and below an upland area of major forestry, and one sample was taken in a lowland area of intensive agriculture. Weather conditions during sampling in October 1992 were, cold and clear with overnight frosts.

R. Irfon at Abergwesyn and Llangammarch Wells, Fig. B6.1: The site at Abergwesyn was chosen as upstream of the afforested area and also as a background site. The river was clear and fast flowing with a rocky bed and no accumulating sediment. Water samples only were taken. At Llangammarch Wells, again no sediment was located after many access points were investigated. Again, water samples only were taken.

R. Lugg at Hereford, Fig. B6.2: This site was chosen after no sediment could be located at the original site suggested (R. Frome) which was fast flowing and stoney. The sediment sampled was soft and largely fine grained with some sand particles. Aquatic invertebrates were observed in the sediment.

# Key

Sample site

Bridge



River / watercourse



Motorway



Trunk road and main road ('A' road)



Secondary road ('B' road)



Minor road



Railway

Station



Church  
or  
Chapel

with tower

with spire

without tower or spire

Sch

School

Hospl

Hospital

Resr

Reservoir



Golf course

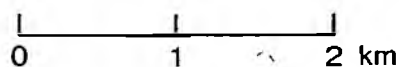


Windmill

STW

Sewage treatment works

Scale



2 cm = 1 km

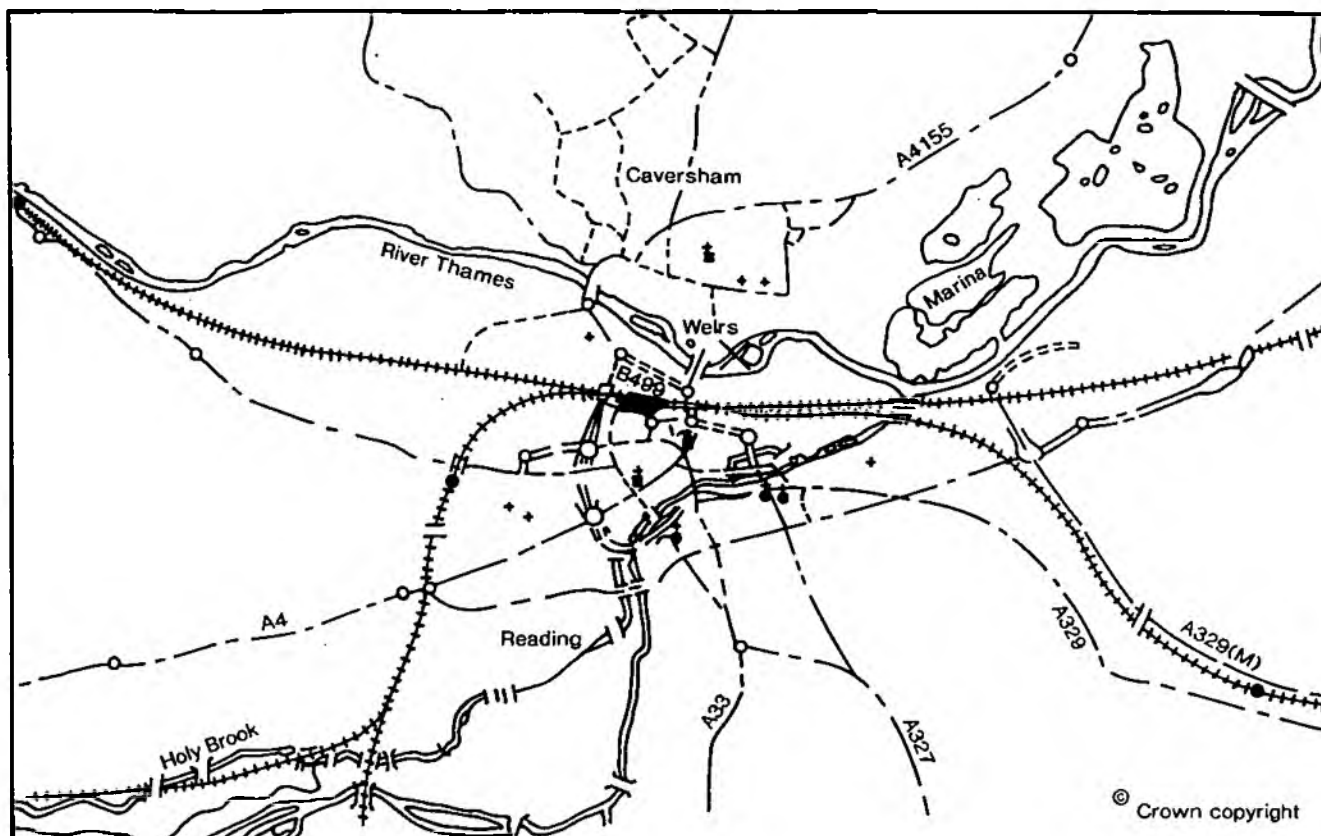


Figure B1.1 River Thames at Caversham Weir

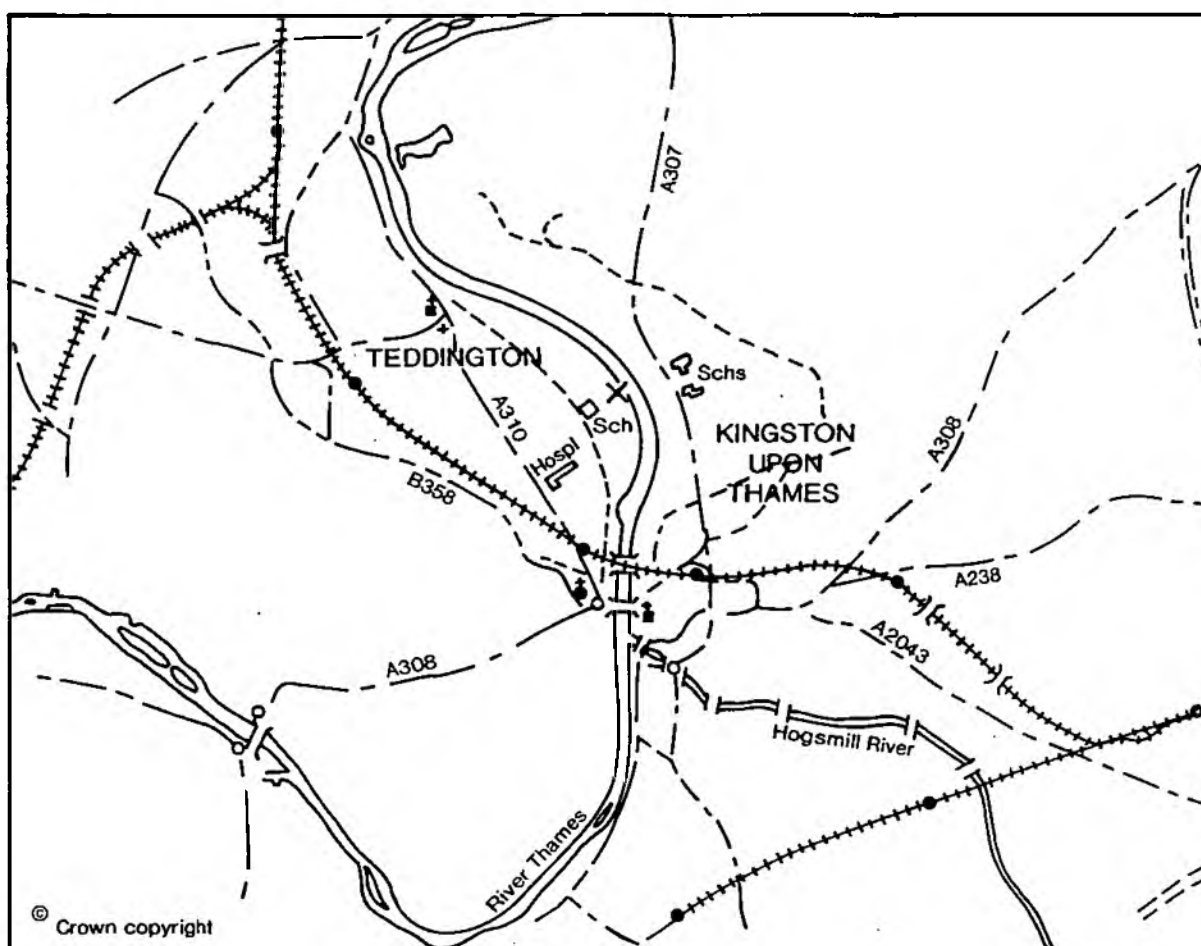


Figure B1.2 River Thames at Teddington

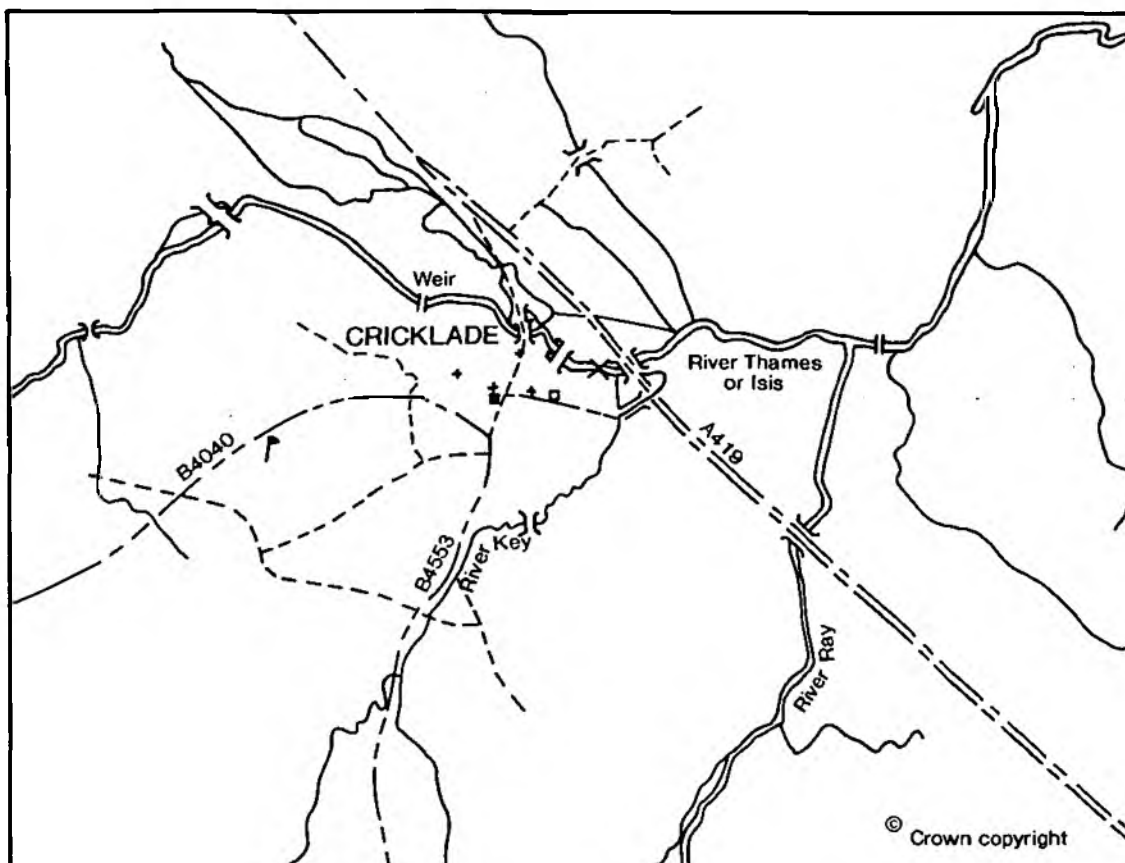


Figure B1.3 River Thames at Cricklade



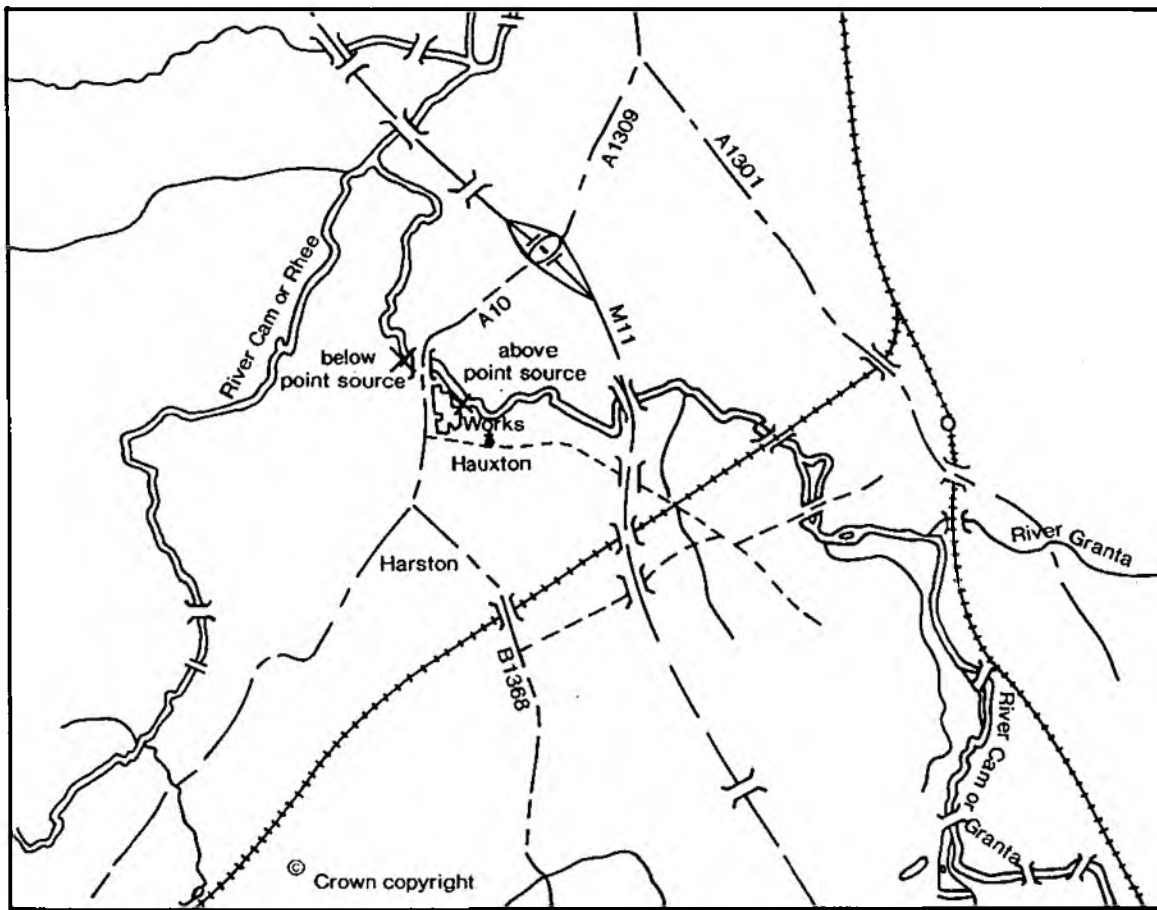


Figure B2.1 River Cam at Hauxton

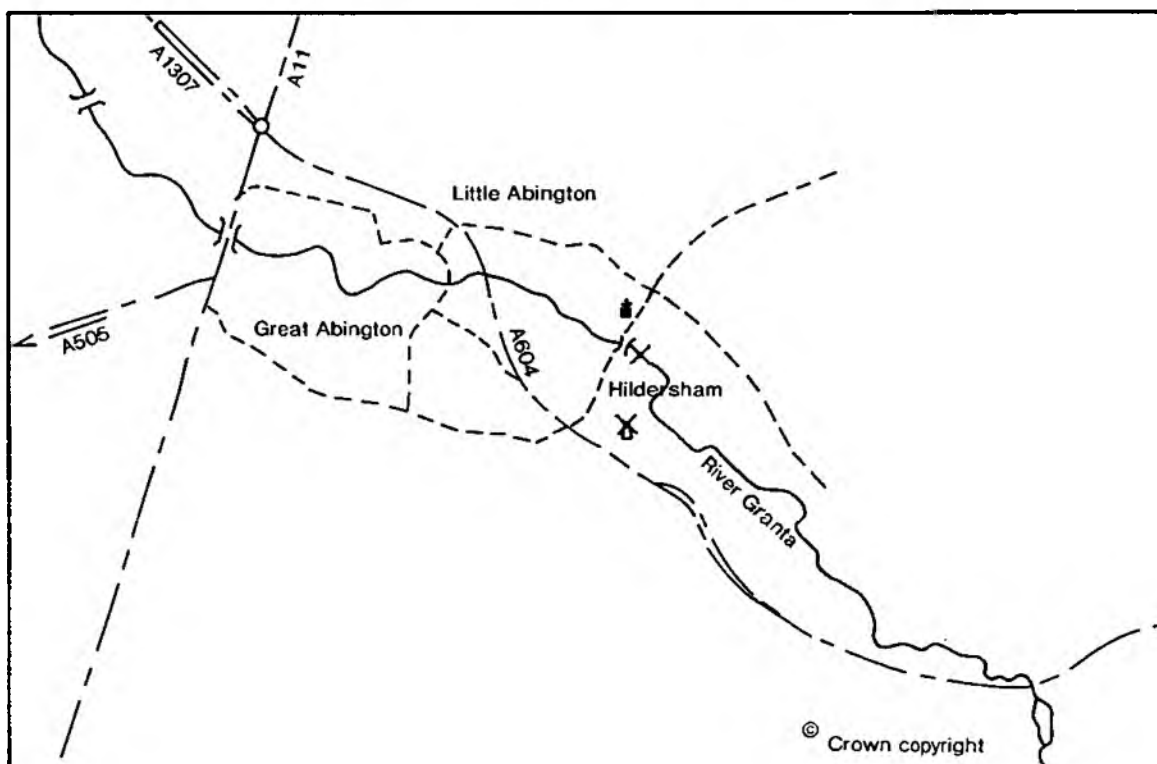


Figure B2.2 River Granta at Hildersham

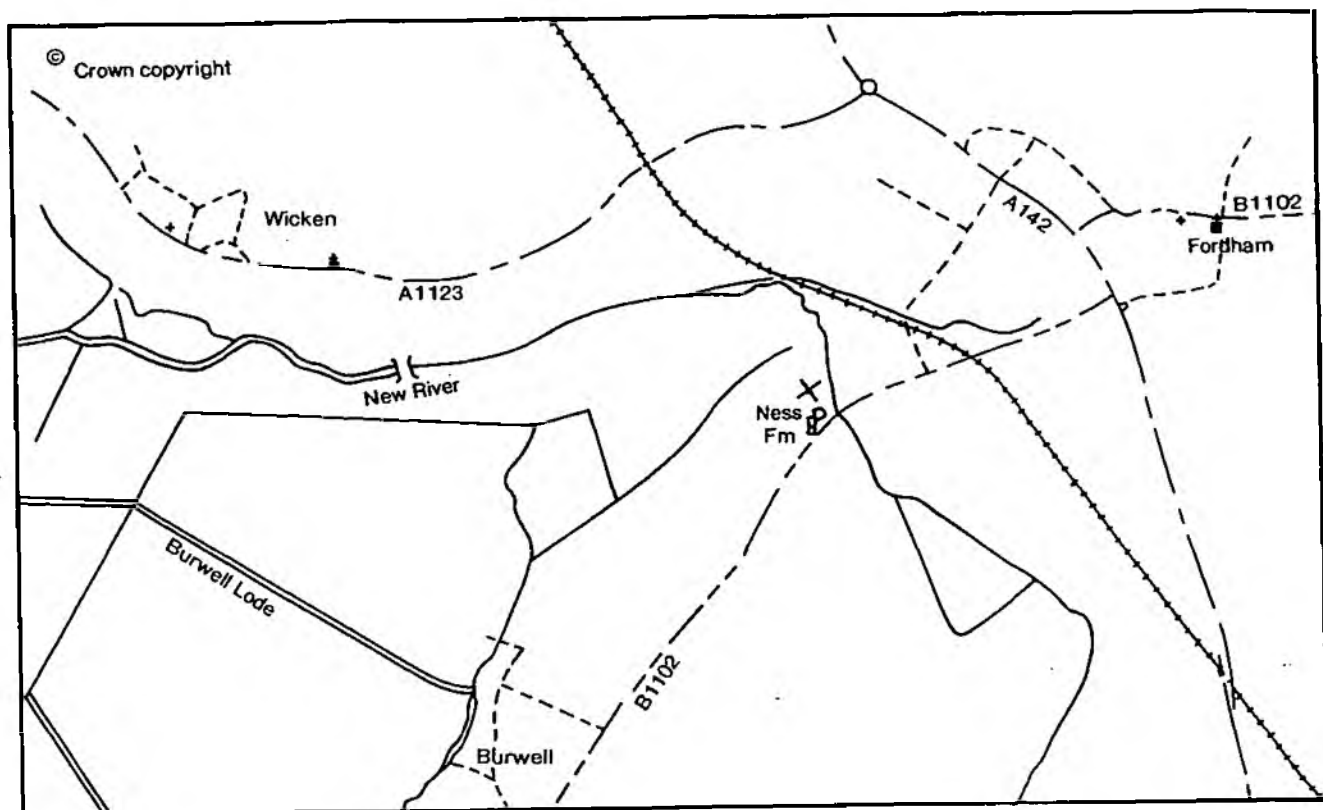


Figure B2.3 New River at Wicken Farm

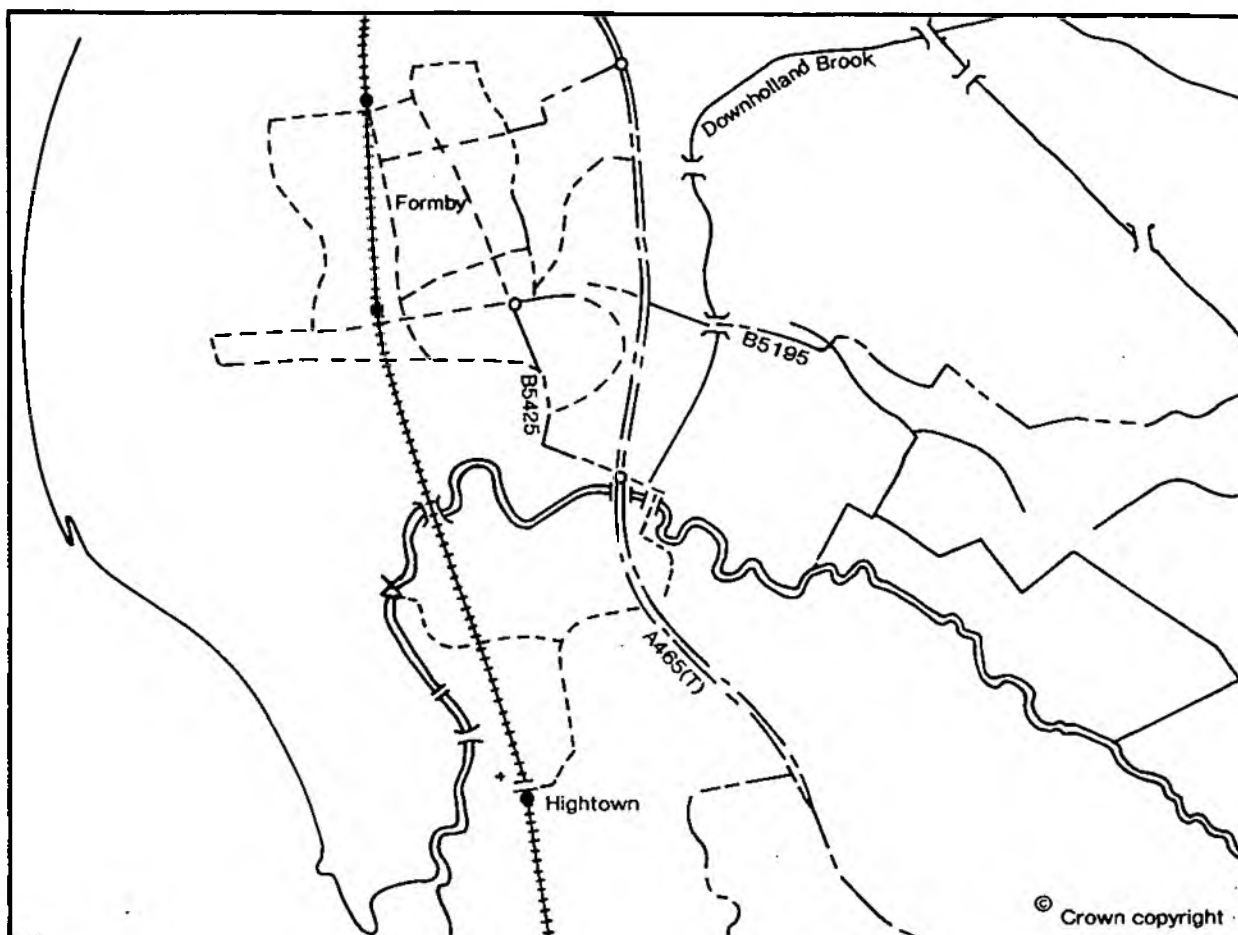


Figure B3.1 River Alt at Altmouth

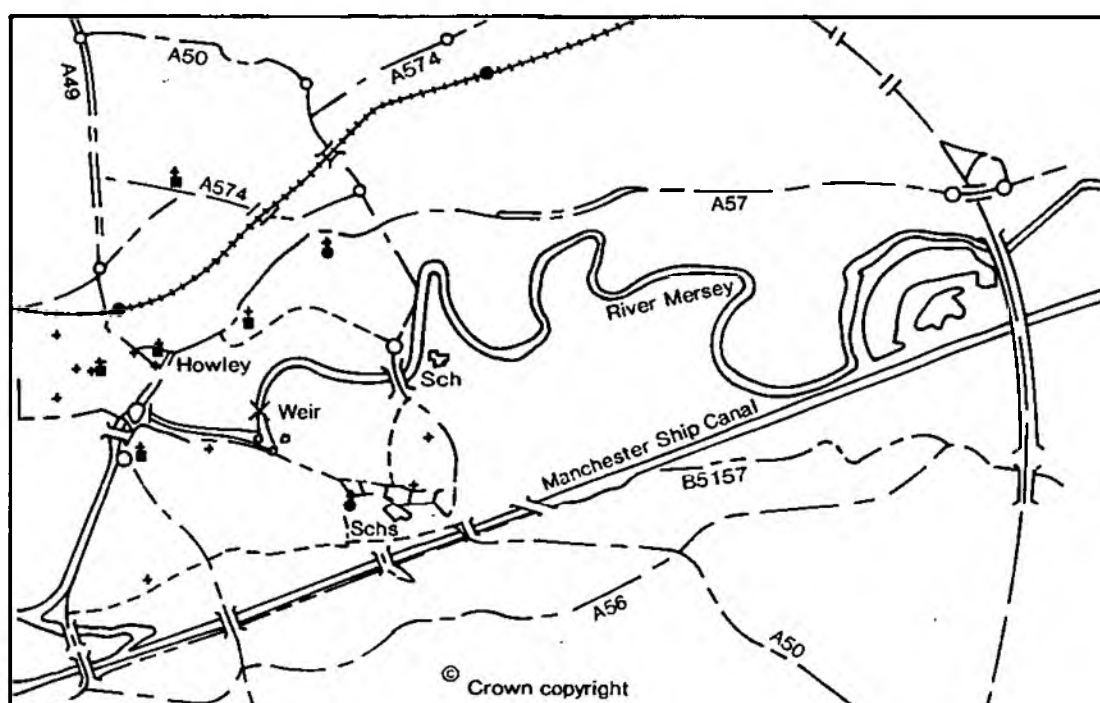


Figure B3.2 River Mersey at Howley Weir

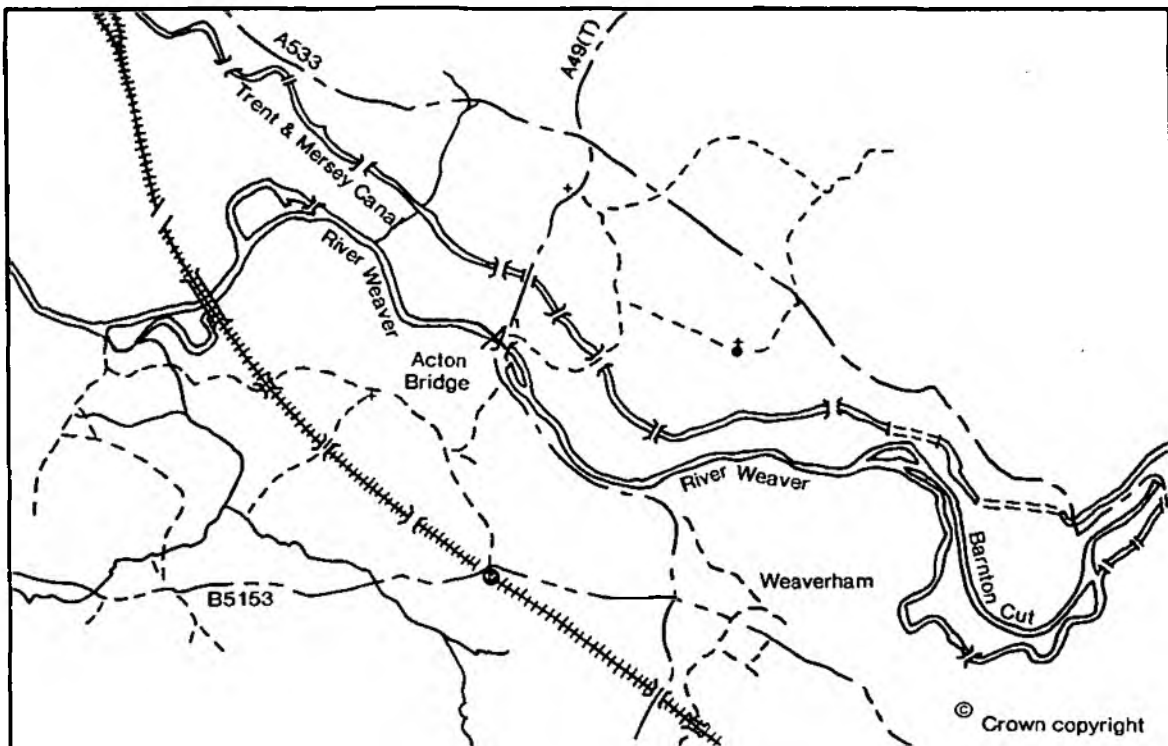


Figure B3.3 River Weaver at Acton Swing Bridge

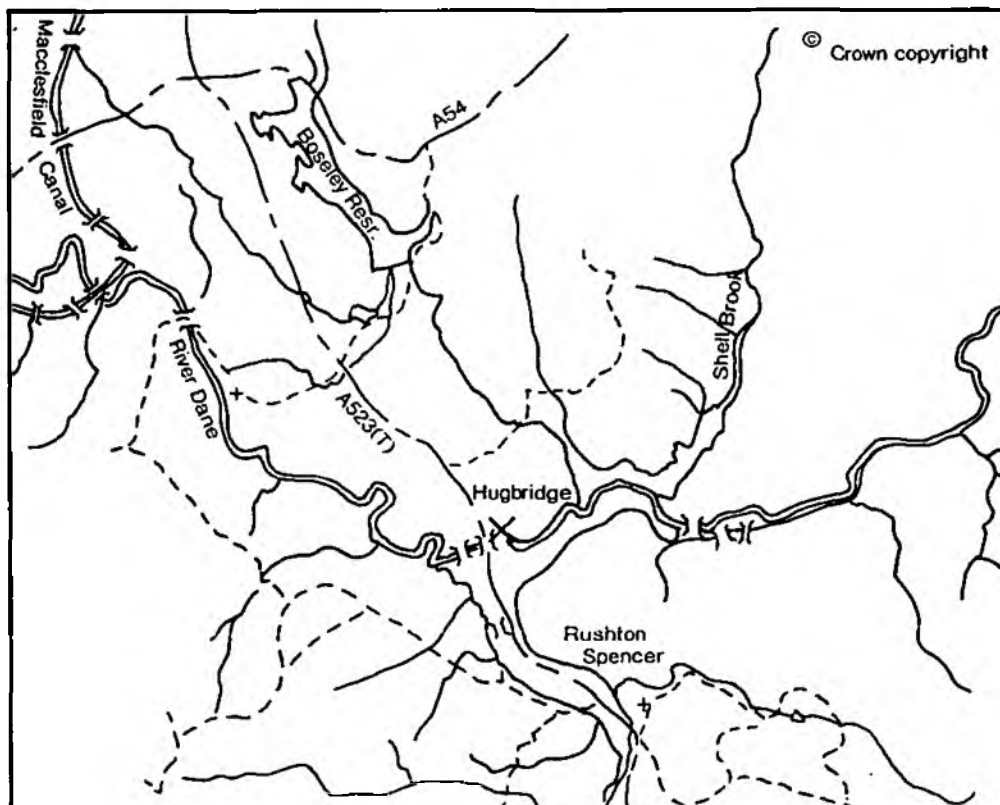


Figure B3.4 River Dane at Hugbridge

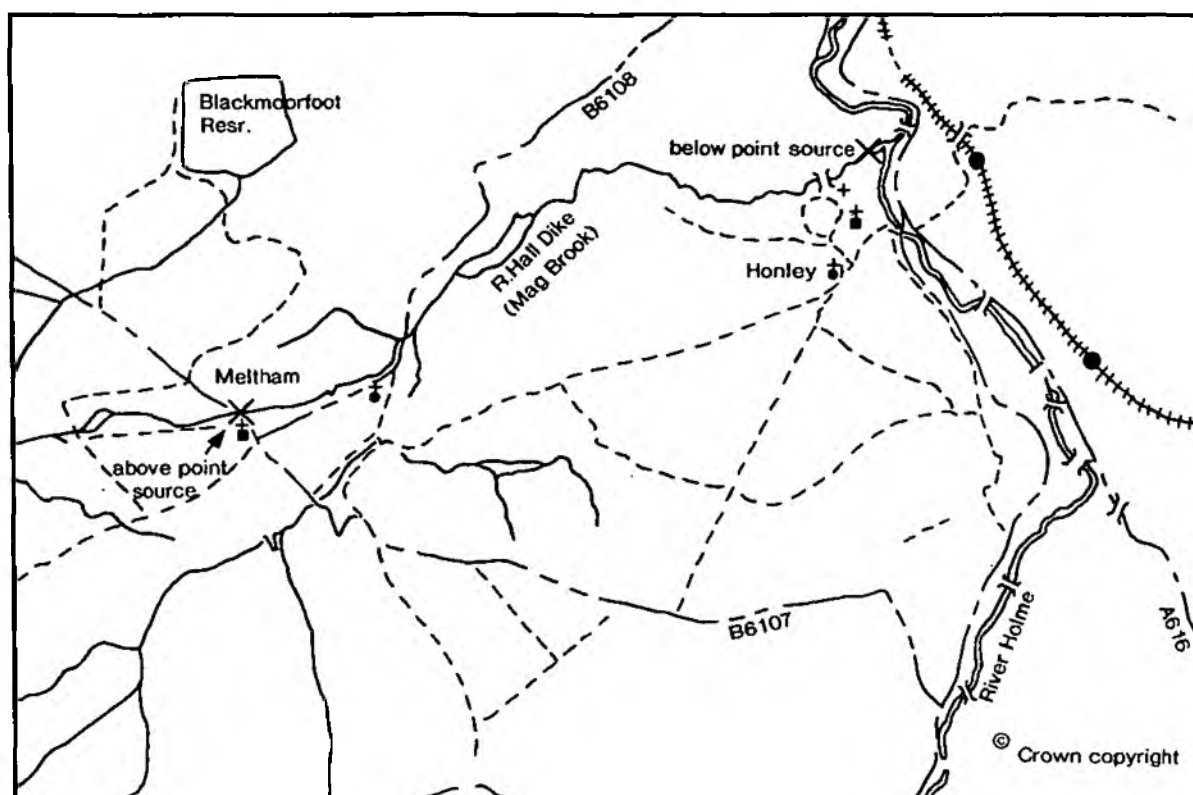


Figure B4.1 Mag Brook at Honley

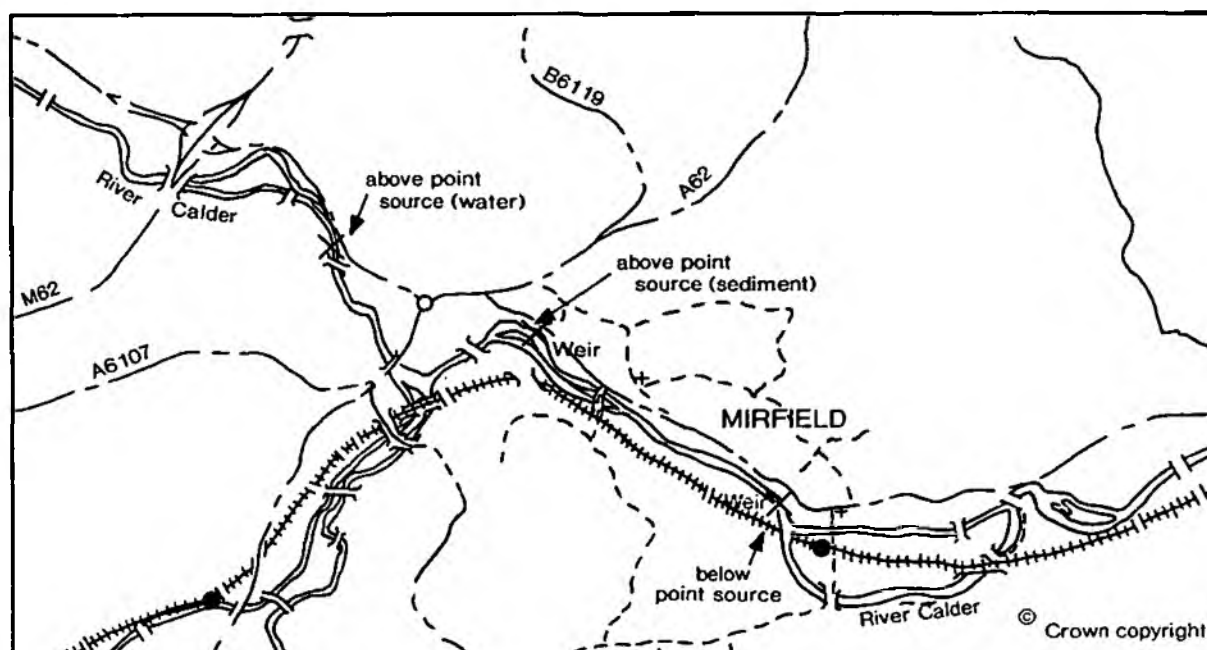


Figure B4.2 River Calder at Mirfield

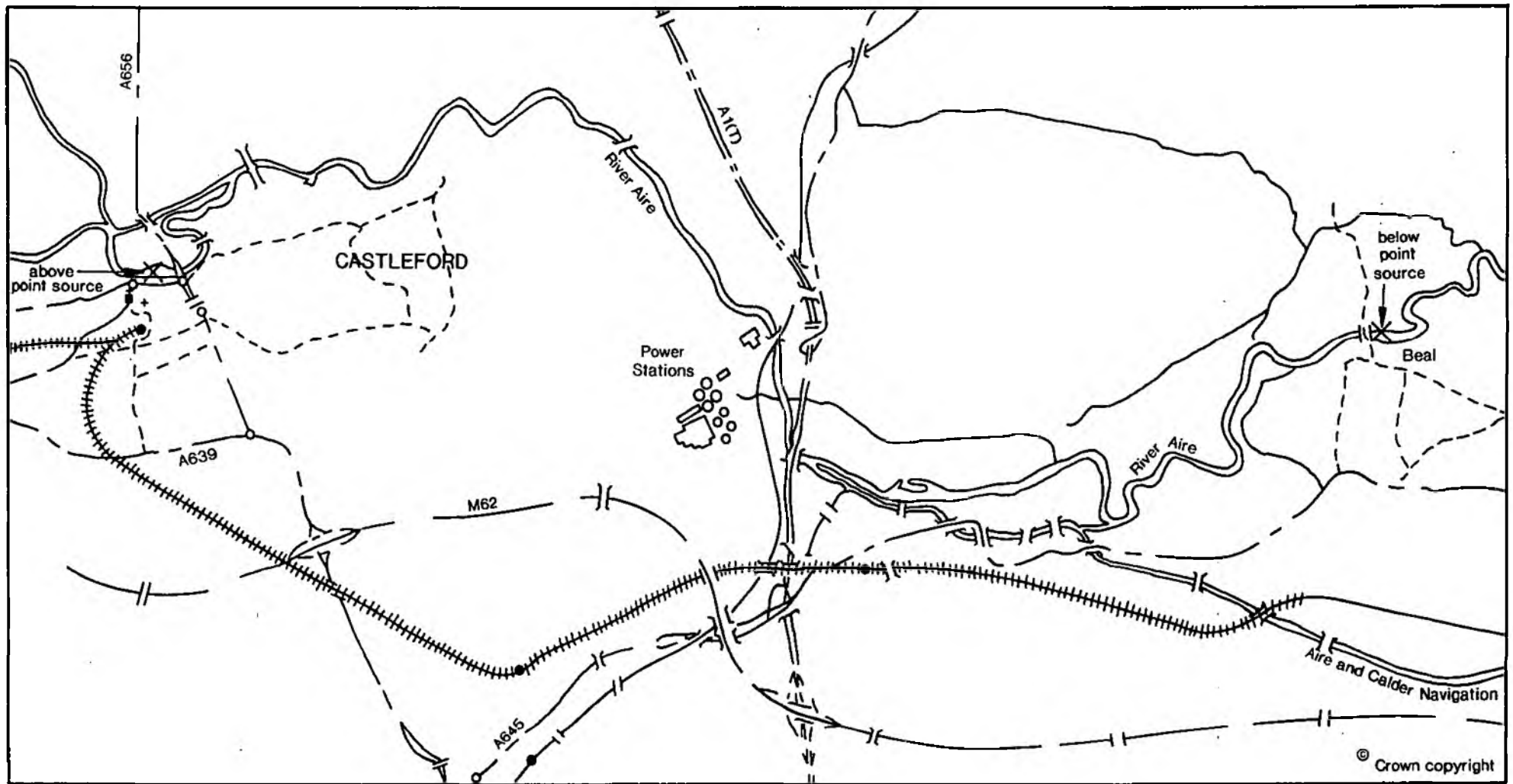


Figure B4.3 River Aire at Castleford and Beal

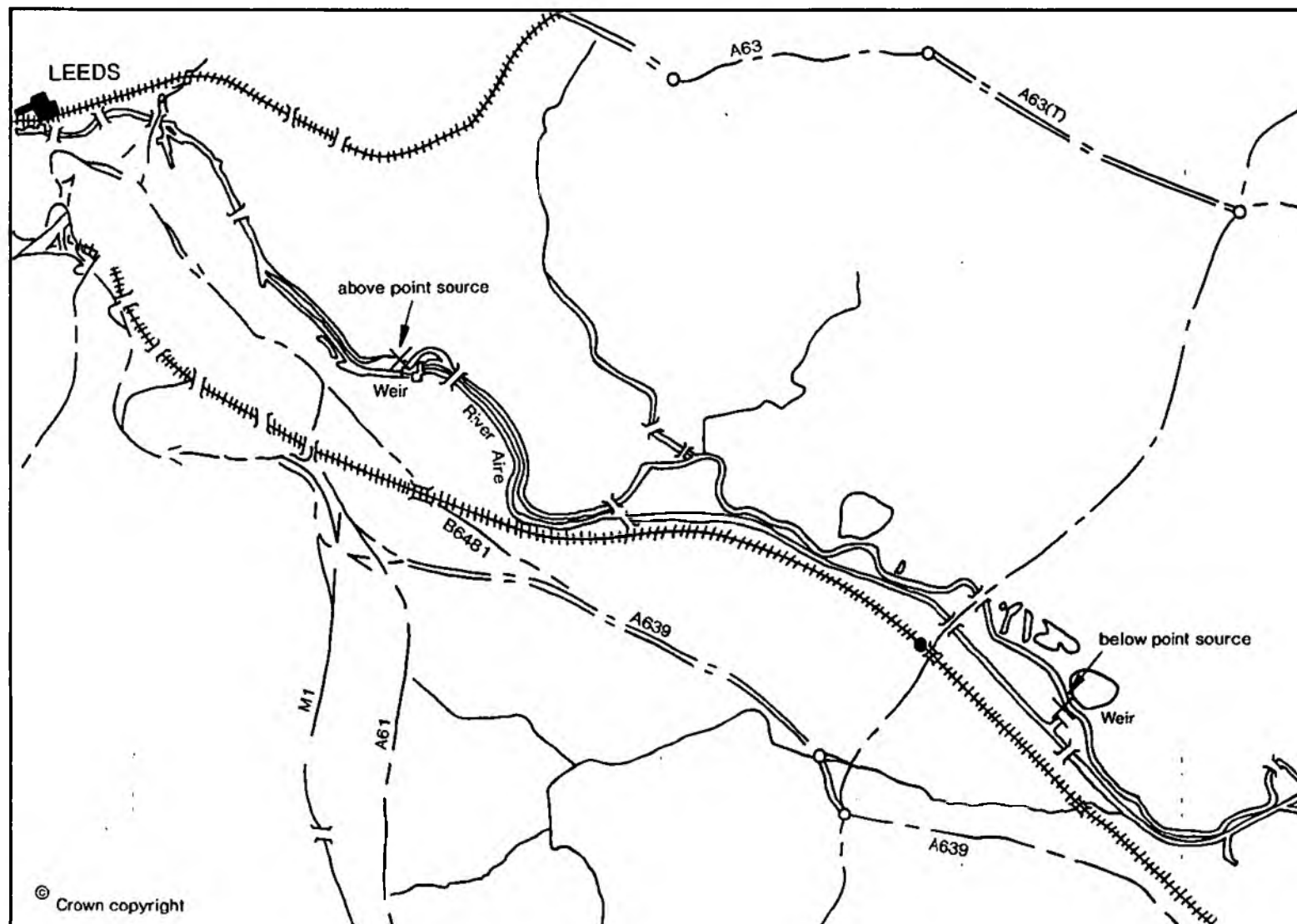


Figure B4.4 River Aire at Fleet Weir



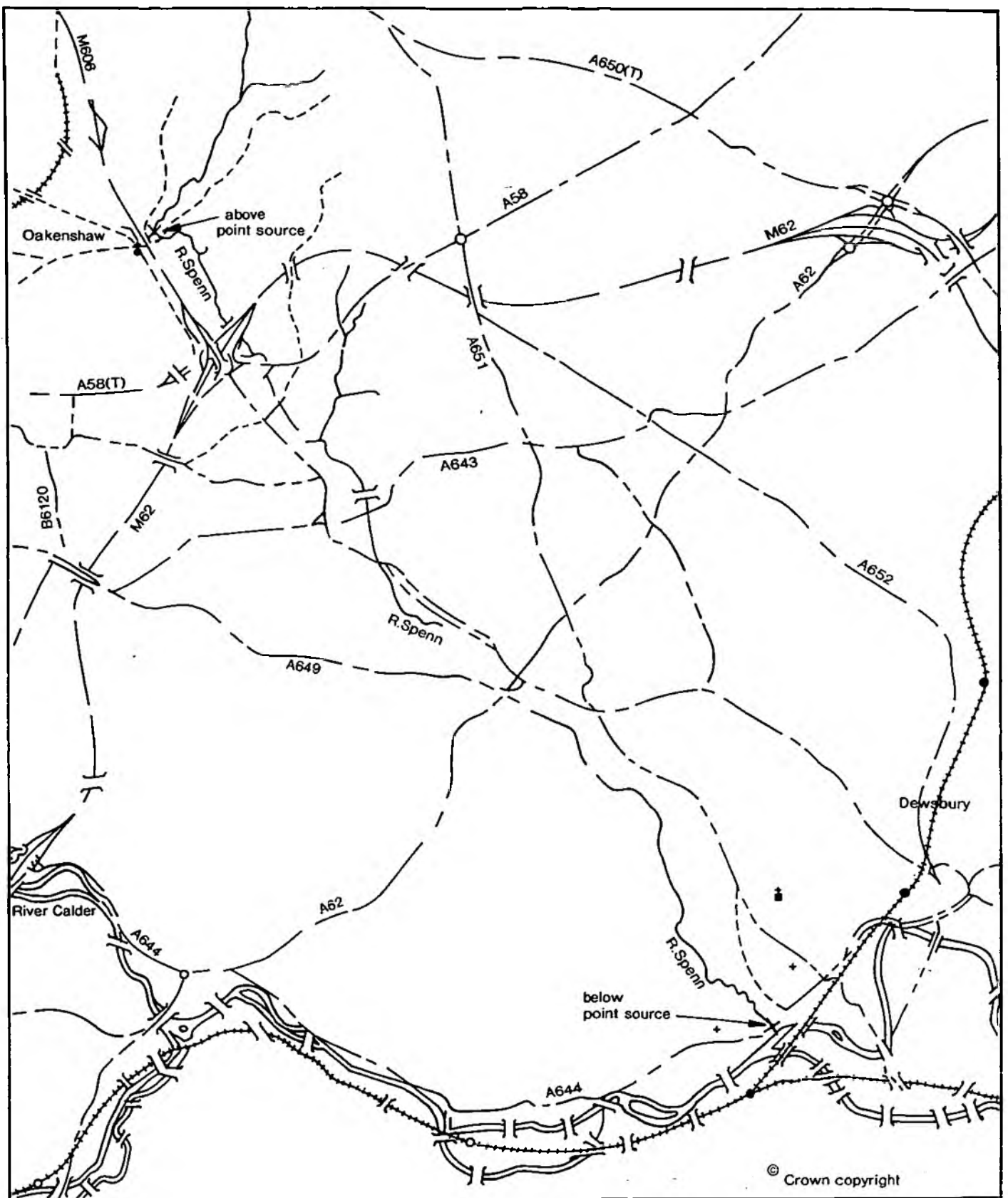


Figure B4.5 River Spenn at Dewsbury and Oakenshaw



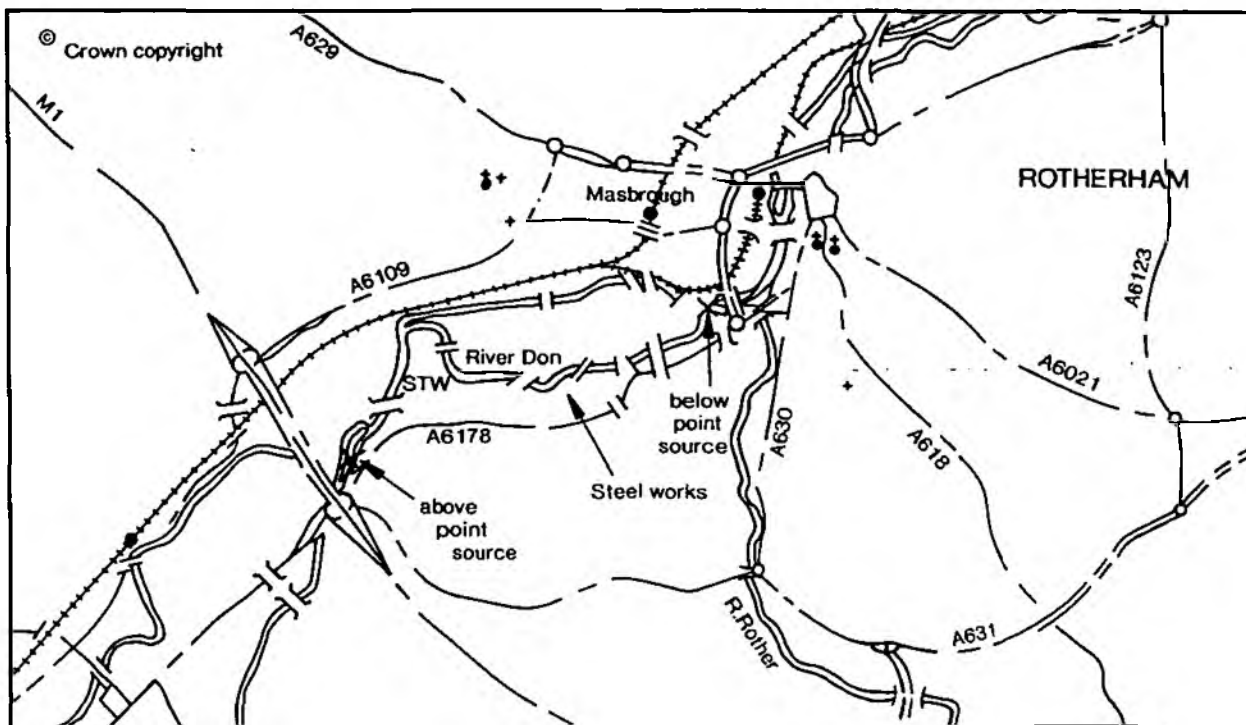


Figure B4.6 River Don at Rotherham

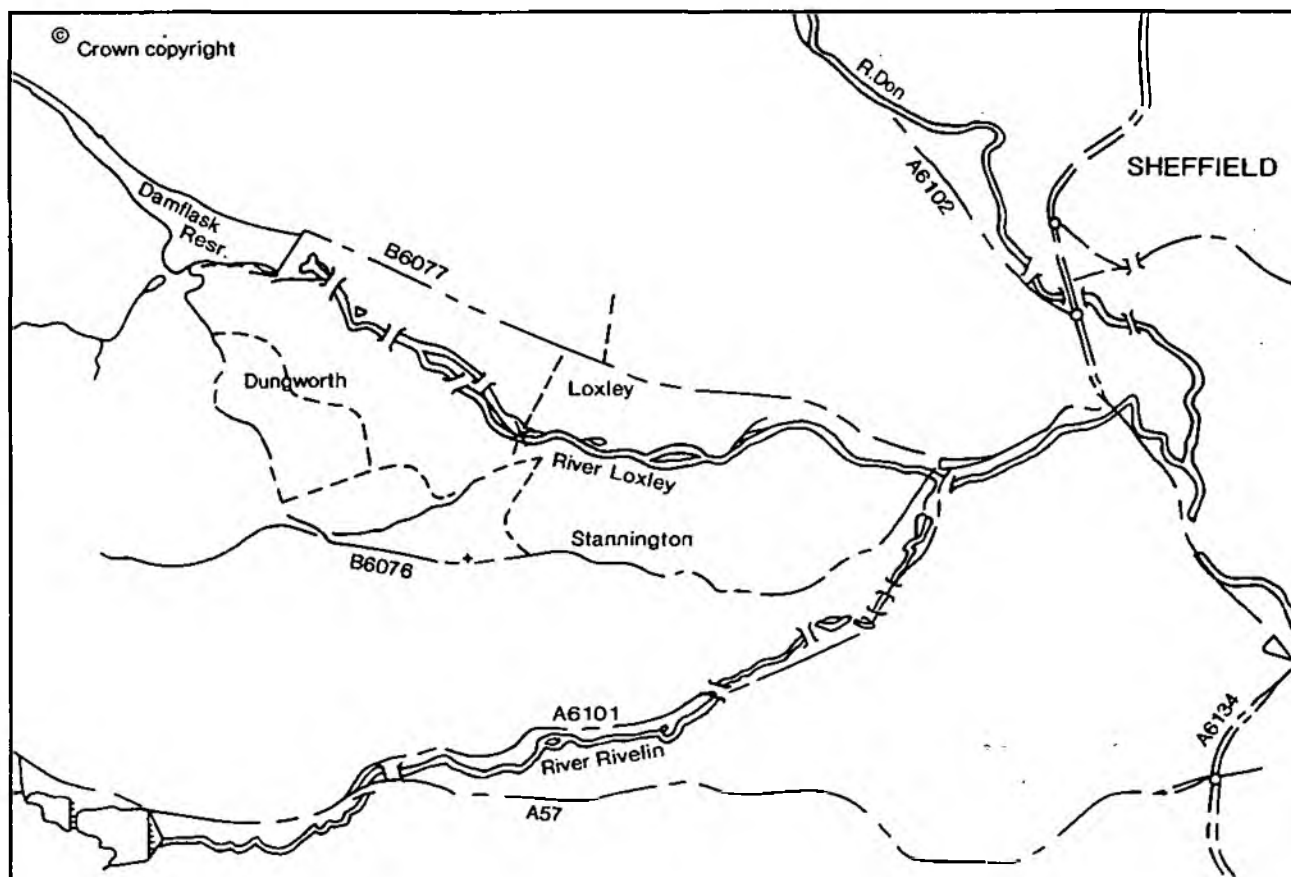


Figure B4.7 River Loxley at Sheffield

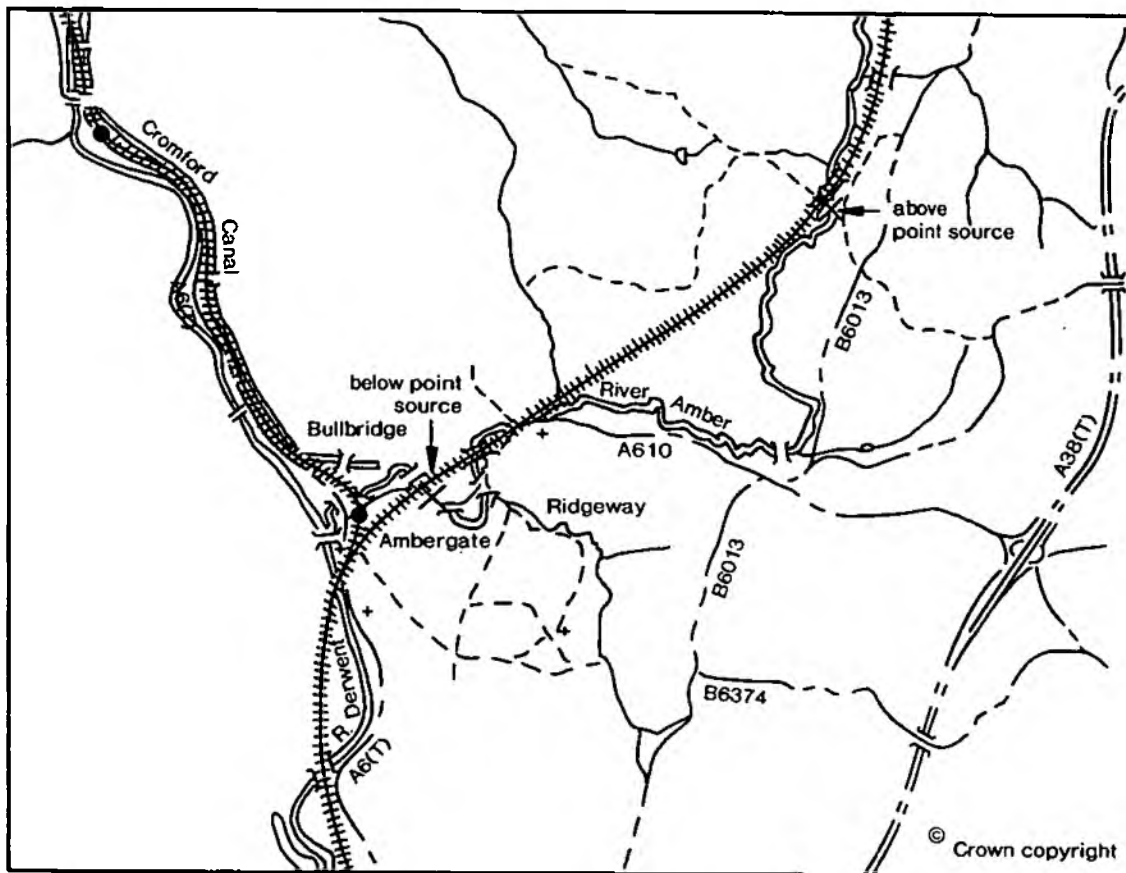


Figure B5.1 River amber at Ambergate

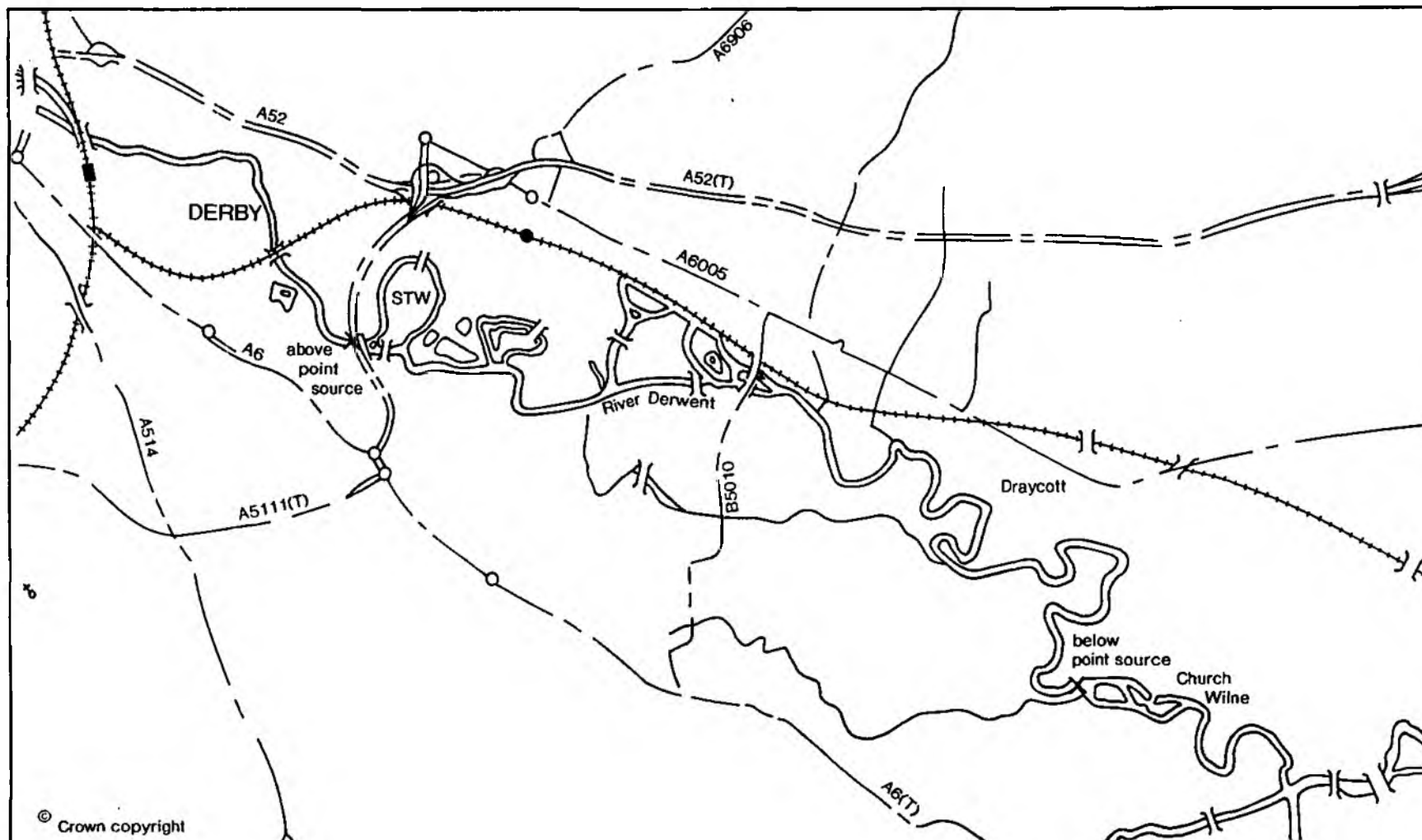


Figure B5.2 River Derwent at Derby and Church Wilne

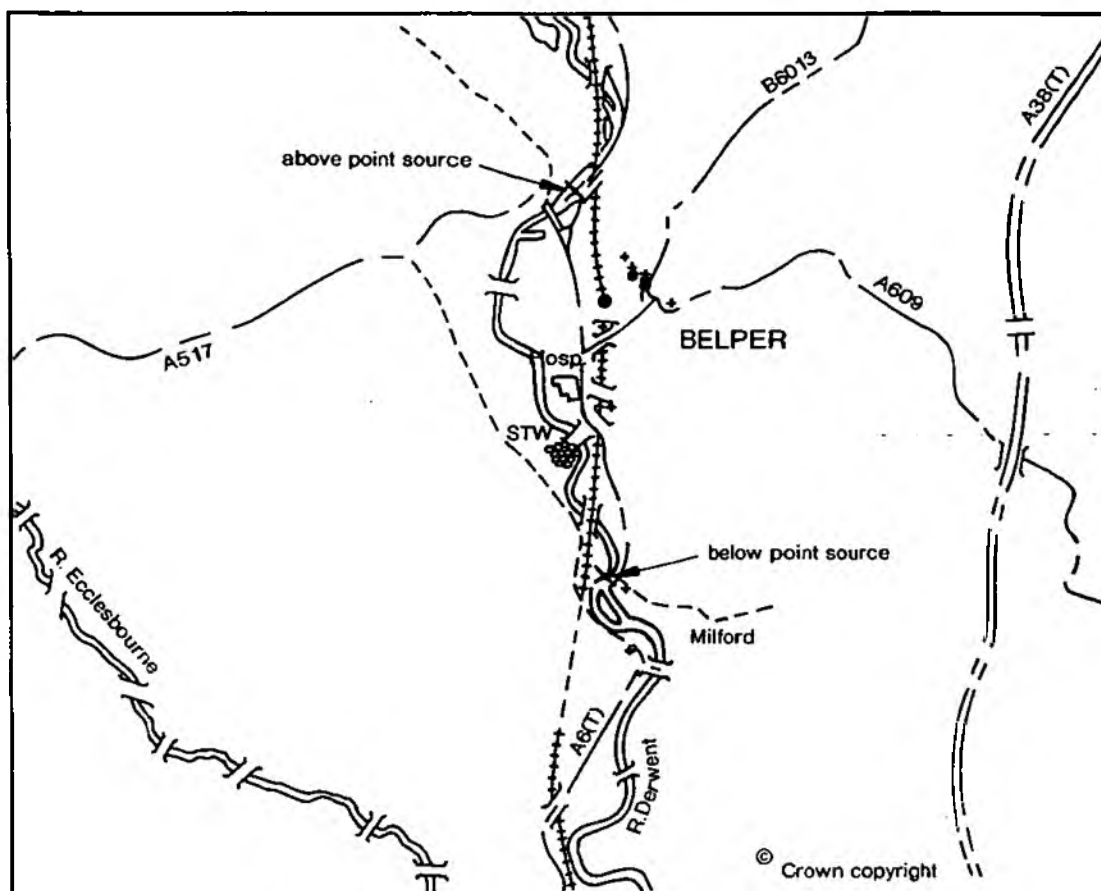


Figure B5.3 River Derwent at Belper

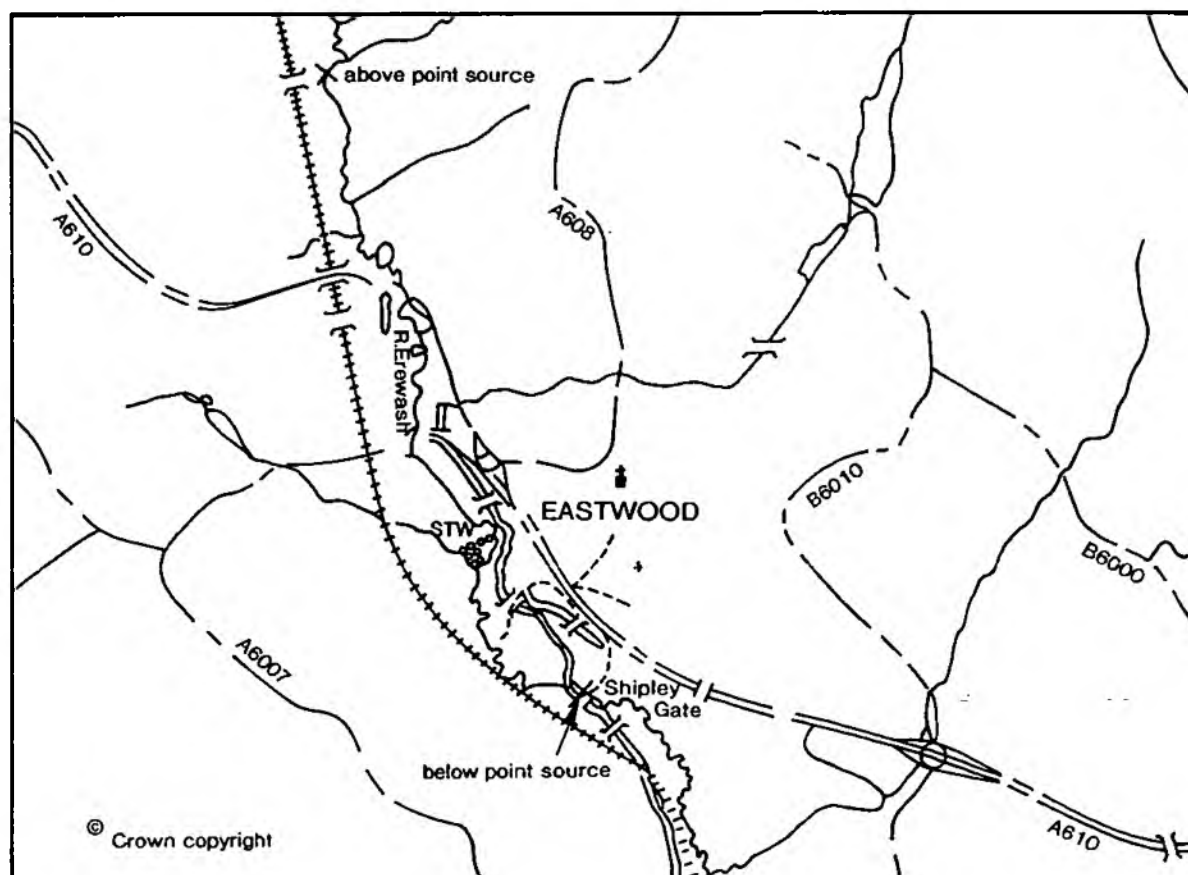


Figure B5.4 River Erewash at Eastwood

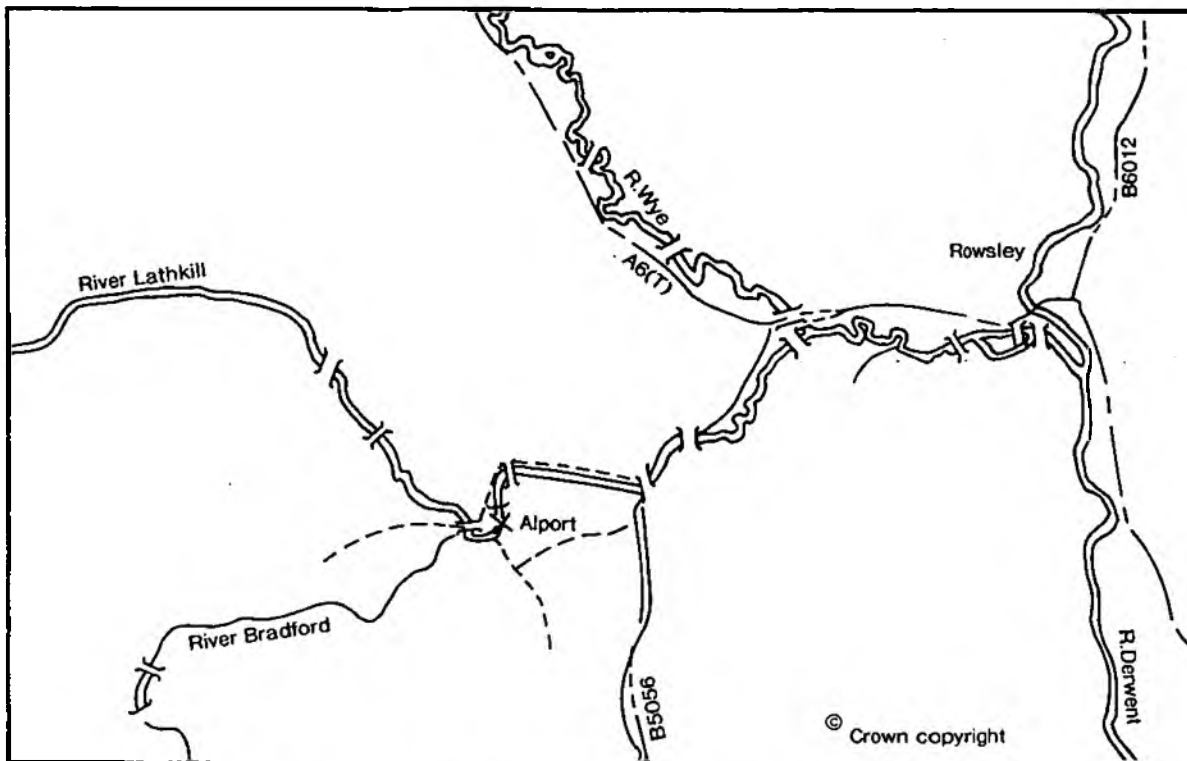


Figure B5.5 River Lathkill at Alport

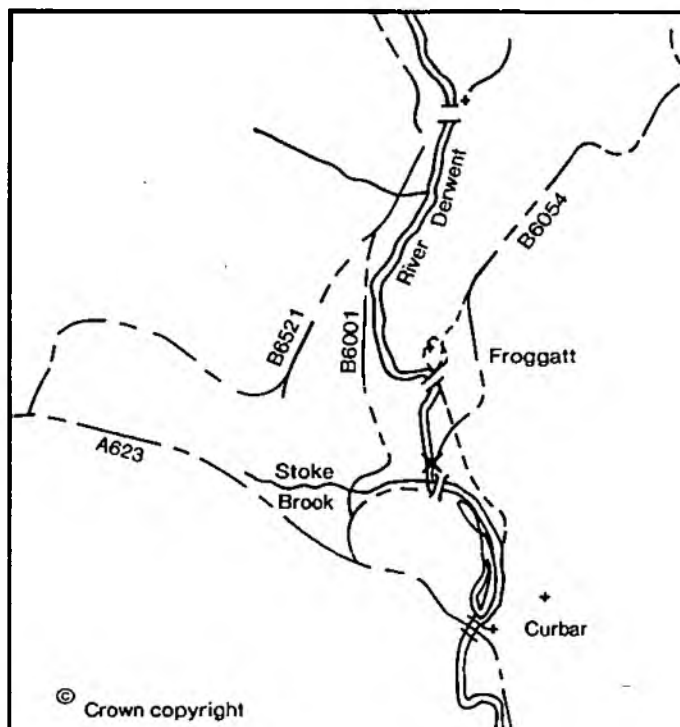


Figure B5.6 River Derwent at Froggatt

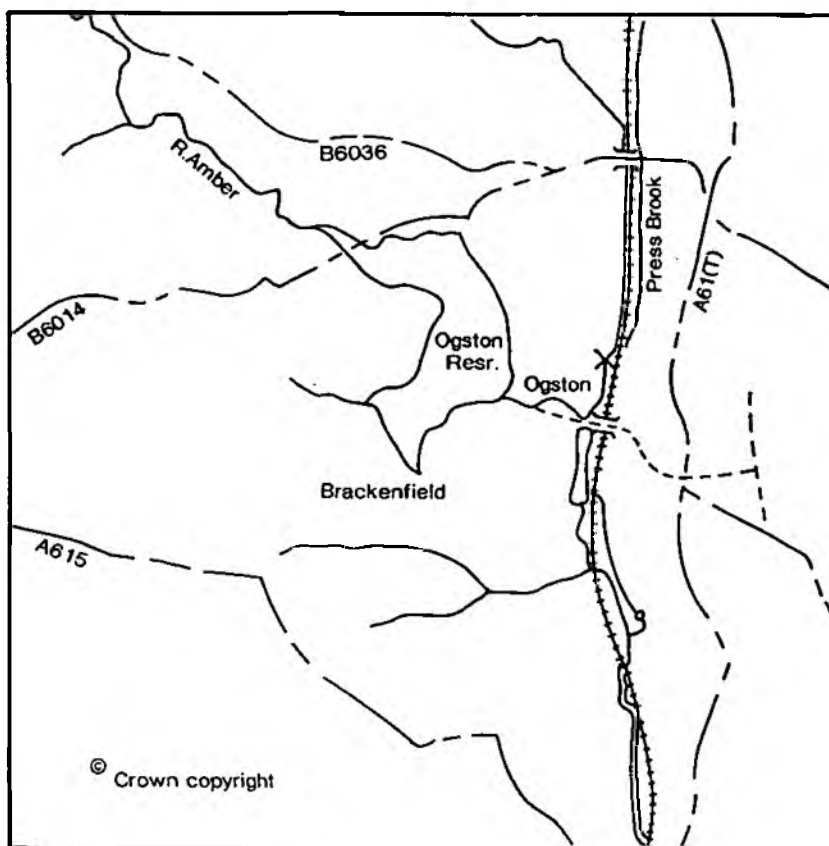


Figure B5.7 Pressbrook at Ogston

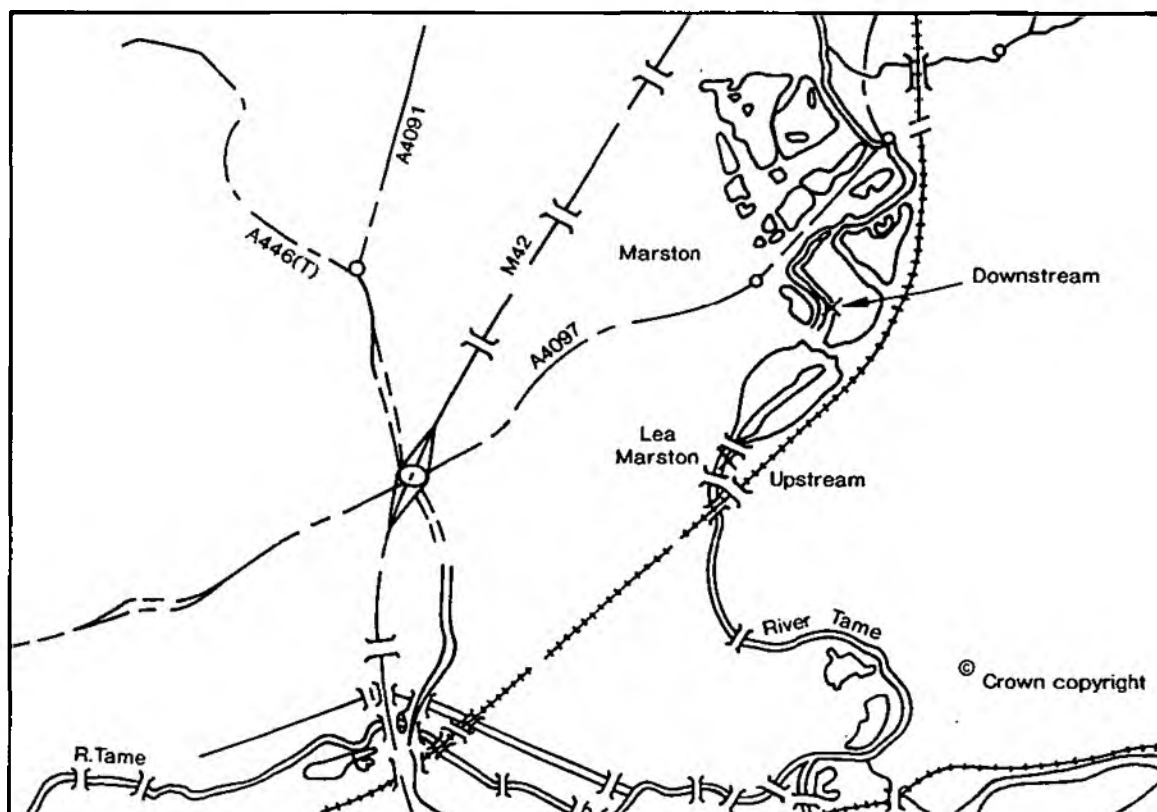


Figure B5.8 River Tame at Lea Marston

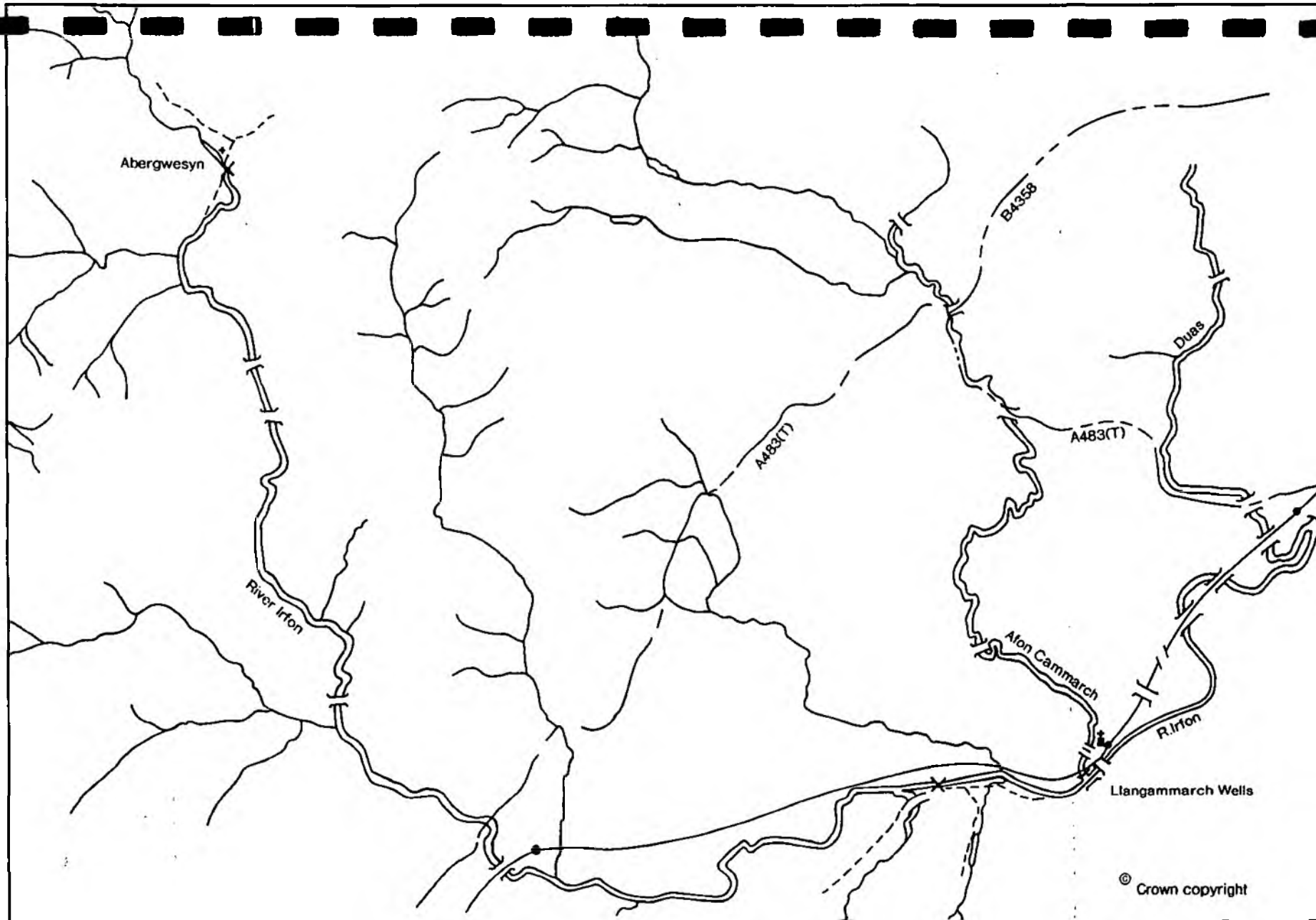


Figure B6.1 River Irfon at Abergwesyn and Llangammarch Wells

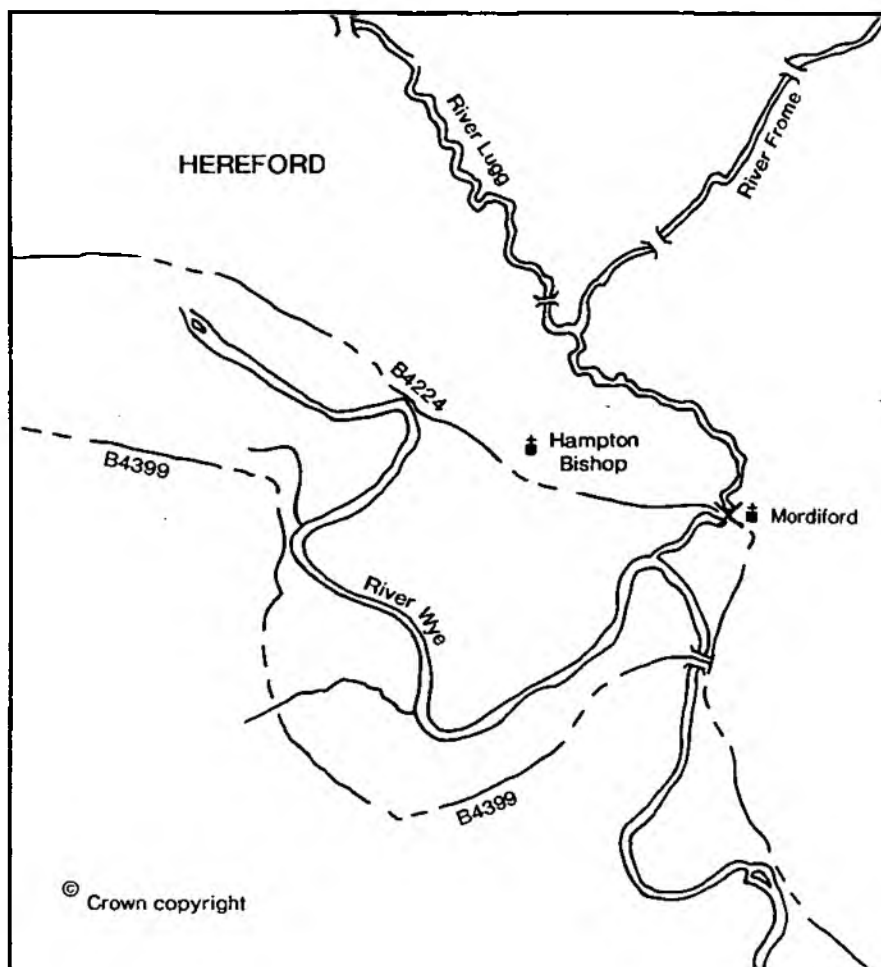


Figure B6.2 River Lugg at Hereford



## APPENDIX C

## **SAMPLING PROTOCOL FOR THE COLLECTION OF RIVER WATER AND SEDIMENTS FOR PCDD/F ANALYSIS**

1. Prepare thoroughly - wash and prepare collecting bottles as necessary, check all equipment.
2. If site has not been visited before, spend time locating a site with easy access and with accumulating sediment.
3. Label collecting bottles before samples are taken.
4. Take water samples as follows. Collect the samples in hexane-washed amber glass bottles. When sampling, the lids of the bottles should be removed and recapped submerged beneath the water and the bottles should be rinsed twice with river water before the final sample are collected. On return to the river bank, a hexane-rinsed aluminium foil lid insert should be put in place to prevent contamination by the lid of the bottle.
5. Collect sediment as follows. Where the river water is deep, or sampling has to be carried out from the river bank, sediments should be collected using a Gilson corer. Where the river is easily accessed, and it is possible to wade into the water, sediment cores can be removed using the Gilson corer with pole attachment. Where the river bank is sheer, the pole can be lowered into the water from the bank. Where the river is shallow and the core tubes can be manually inserted into the sediment, the corer will not be needed. Both these methods allow the recovery of samples with an intact sediment-water interface.

Once a sediment core had been extracted, the surface 3 cm of sediment is sliced off and placed into a 1 l hexane-washed amber glass bottle. Additional cores (10-15) should collected, and this method repeated until the bottle has been filled. Cores that have 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, should be discarded.
6. Ensure equipment is clean, sample bottles are sealed, take field notes/photographs before moving to next site.

## APPENDIX D

**Table D.1 Particulate loading of water samples**

NRA Region/River	Site Location	Particulate load (mg l <sup>-1</sup> )
<b>Anglian</b>		
R. Cam	Hauxton (above)	2.7
	(below)	3.1
R. Granta	Hildersham	7.9
New River	Wicken	6.7
<b>North West</b>		
R. Alt	Altmouth	2.9
R. Mersey	Howley Weir	7.0
R. Weaver	Acton	17.7
R. Dane	Hugbridge	2.0
<b>Yorkshire (Central)</b>		
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
<b>Yorkshire (South)</b>		
R. Don	Rotherham (above)	3.5
	(below)	6.1
R. Loxley	near Sheffield	12.4
<b>Severn Trent</b>		
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
<b>Welsh</b>		
R. Irfon	Abergwesyn	0.5
R. Irfon	Llangammarch Wells	31.3
R. Lugg	Hereford	4.5

**Table D.2. Results of total organic carbon (TOC), dissolved organic carbon (DOC), particulate organic carbon (POC) and DOC:POC ratio**

NRA Region/River	Site Location		TOC <sup>a</sup> (mg l <sup>-1</sup> )	DOC <sup>a</sup> (mg l <sup>-1</sup> )	POC <sup>b</sup> (mg l <sup>-1</sup> )	DOC:POC
<b>Thames</b>						
R. Thames	Caversham Weir		6.3	5.4	0.9	6.0
R. Thames	Teddington		6.5	6.2	0.3	20.7
R. Thames	Cricklade		4.9	4.6	0.3	15.3
<b>Anglian</b>						
R. Cam	Hauxton	(above)	6.9	6.5	0.4	16.3
		(below)	6.9	6.6	0.3	22.0
R. Granta	Hildersham		5.2	5.0	0.2	25.0
New River	Wicken		1.8	1.7	0.1	17.0
<b>North West</b>						
R. Alt	Altmouth		16.8	14.8	2.0	7.4
R. Mersey	Howley Weir		12.4	11.5	0.9	12.8
R. Weaver	Acton		9.8	8.0	1.8	4.4
R. Dane	Hugbridge		6.0	5.9	0.1	59.0
<b>Yorkshire (Central)</b>						
Mag Brook (or R. Hall Dike)	Honley	(above)	2.3	2.3	0	
		(below)	18.0	16.9	1.1	15.4
R. Calder	Mirfield	(above)	7.9	7.1	0.8	8.9
		(below)	25.2	22.6	2.6	8.7
R. Aire	Beale	(above)	14.2	12.7	1.5	8.5
		(below)	15.0	13.5	1.5	9.0
R. Aire	Fleet Weir	(above)	10.4	9.6	0.8	12.0
		(below)	13.6	12.5	1.1	11.4
R. Spenn	Dewsbury	(above)	21.1	20.1	1.0	20.1
		(below)	20.2	18.3	1.9	9.6
<b>Yorkshire (South)</b>						
R. Don	Rotherham	(above)	7.5	6.7	0.8	8.4
		(below)	9.6	8.4	1.2	7.0
R. Loxley	near Sheffield		5.0	3.5	1.5	2.3
<b>Severn Trent</b>						
R. Amber	Ambergate	(above)	6.9	5.9	1.0	5.9
		(below)	7.1	5.8	1.3	4.5
R. Derwent	Church Wilne	(above)	3.2	2.8	0.4	7.0
		(below)	6.4	5.9	0.5	11.8
R. Derwent	Belper	(above)	5.4	2.1	3.3	0.6
		(below)	2.8	2.0	0.8	2.5
R. Erewash	Eastwood	(above)	12.9	11.7	1.2	9.8
		(below)	12.4	*		
R. Lathkill	Alport		1.6	1.5	0.1	15.0
R. Derwent	Froggatt		2.8	2.7	0.1	27.0
Pressbrook	Ogston		8.1	7.5	0.6	12.5
R. Tame	Lea Marston	(above)	12.1	9.9	2.2	4.5
		(below)	12.0	9.7	2.3	4.2
<b>Welsh</b>						
R. Irfon	Abergwesyn		1.5	1.5	0	
R. Irfon	Llangammarch Wells		1.8	1.8	0	
R. Lugg	Hereford		2.5	2.3	0.2	11.5

<sup>a</sup> measured, <sup>b</sup> calculated

\* Sample broken in transit

**Table D.3      Results of dry weight, loss on ignition and particle size determinations**

NRA Region/River	Site Location		Dry weight (%)	LOI (%)	Sediment <63 μm (%)
Thames					
R. Thames	Caversham Weir		14.0	17.5	52
R. Thames	Teddington		44.7	5.8	17
R. Thames	Cricklade		12.5	20.0	70
Anglian					
R. Cam	Hauxton	(above)	21.2	17.0	46
		(below)	15.3	16.4	71
R. Granta	Hildersham		18.9	14.1	53
New River	Wicken		30.8	23.1	29
North West					
R. Alt	Altmouth		49.5	8.9	44
R. Mersey	Howley Weir		39.1	17.1	58
R. Weaver	Acton		37.5	10.7	56
R. Dane	Hugbridge		18.3	34.2	56
Yorkshire (Central)					
Mag Brook (or R. Hall Dike)	Honley	(below)	6.9	35.1	55
R. Calder	Mirfield	(above)	29.8	15.8	36
		(below)	68.0	3.2	4
R. Aire	Beale	(above)	42.1	10.8	12
		(below)	21.3	22.3	66
R. Aire	Fleet Weir	(above)	55.4	10.9	14
		(below)	47.2	10.4	26
R. Spenn	Dewsbury	(below)	5.9	42.0	69
Yorkshire (South)					
R. Don	Rotherham	(above)	17.0	25.5	67
		(below)	39.9	19.4	26
R. Loxley	near Sheffield		8.4	24.0	76
Severn Trent					
R. Amber	Ambergate	(above)	42.6	8.8	49
		(below)	17.4	17.8	55
R. Derwent	Church Wilne	(above)	38.7	11.6	45
		(below)	27.6	12.1	51
R. Derwent	Belper	(above)	21.2	18.2	71
		(below)	27.4	13.6	47
R. Erewash	Eastwood	(above)	29.9	25.0	60
		(below)	39.5	22.6	70
R. Lathkill	Alport		32.7	11.4	50
R. Derwent	Froggatt		37.8	11.9	30
Pressbrook	Ogston		16.5	16.4	85
R. Tame	Lea Marston	(above)	31.2	16.8	44
		(below)	49.4	9.0	19
Welsh					
R. Lugg	Hereford		33.8	7.5	70

## **APPENDIX E**

Table E.1

**The composition of internal quantitation standard for PCDD/F analysis on water and sediment samples.**

<sup>13</sup> C <sub>12</sub> -labelled 2378 congener	standard for water samples <sup>a</sup> concentration (pg µl <sup>-1</sup> )	standard for sediment samples <sup>b</sup> concentration (pg µl <sup>-1</sup> )
2378-TCDD	48	96
12378-PeCDD	52	104
123678-HxCDD	52	104
1234678-HpCDD	48	96
OCDD	36	72
2378-TCDF	52	104
12378-PeCDF	54	108
123478-HxCDF	58	116
1234678-HpCDF	46	92
OCDF	48	96

a 2x50 µl added to the sample prior to extraction

b 50 µl added to the sample prior to extraction



Table E.2

**Limit of detection for PCDD and PCDF analysis of water samples**  
(ng l<sup>-1</sup>, ppt)

Congener		Concentration	xTEF
2,3,7,8	TCDD	<0.01	<0.01
Total	TCDD	<0.1	
1,2,3,7,8	PeCDD	<0.02	<0.01
Total	PeCDD	<0.2	
1,2,3,4,7,8	HxCDD	<0.05	<0.005
1,2,3,6,7,8	HxCDD	<0.05	<0.005
1,2,3,7,8,9	HxCDD	<0.05	<0.005
Total	HxCDD	<0.5	
1,2,3,4,6,7,8	HpCDD	<0.4	<0.004
Total	HpCDD	<1.0	
	OCDD	<1.0	<0.001
2,3,7,8	TCDF	<0.01	<0.001
Total	TCDF	<0.1	
1,2,3,7,8	PeCDF	<0.02	<0.01
2,3,4,7,8	PeCDF	<0.02	<0.001
Total	PeCDF	<0.2	
1,2,3,4,7,8	HxCDF	<0.03	<0.003
1,2,3,6,7,8	HxCDF	<0.03	<0.003
1,2,3,7,8,9	HxCDF	<0.03	<0.003
2,3,4,6,7,8	HxCDF	<0.03	<0.003
Total	HxCDF	<0.3	
1,2,3,4,6,7,8	HpCDF	<0.05	<0.0005
1,2,3,4,7,8,9	HpCDF	<0.05	<0.0005
Total	HpCDF	<0.5	
	OCDF	<2.0	<0.002
PCDD/F		<5.9	
NATO I-TEQ			<0.067

Table E.3

**PCDD and PCDF Concentrations in River Thames Sediment  
at Caversham Weir and Teddington**  
(ng kg<sup>-1</sup> dry weight, ppt)

		R. Thames, Caversham Weir		R. Thames, Teddington	
Congener		Concentration	xTEF	Concentration	xTEF
2,3,7,8	TCDD	0.3	0.3	0.5	0.5
Total	TCDD	55		31	
1,2,3,7,8	PeCDD	1.5	0.75	0.5	0.25
Total	PeCDD	57		31	
1,2,3,4,7,8	HxCDD	1.7	0.17	<0.5	0.05
1,2,3,6,7,8	HxCDD	5.6	0.56	<0.5	0.05
1,2,3,7,8,9	HxCDD	2.9	0.29	<0.5	0.05
Total	HxCDD	81		43	
1,2,3,4,6,7,8	HpCDD	220	2.2	160	1.6
Total	HpCDD	390		330	
	OCDD	500	0.5	2100	2.1
2,3,7,8	TCDF	7.6	0.76	3.3	0.33
Total	TCDF	120		63	
1,2,3,7,8	PeCDF	2.4	0.12	0.8	0.04
2,3,4,7,8	PeCDF	3.5	1.75	0.9	0.45
Total	PeCDF	100		74	
1,2,3,4,7,8	HxCDF	49	4.9	62	6.2
1,2,3,6,7,8	HxCDF	2.6	0.26	<0.5	0.05
1,2,3,7,8,9	HxCDF	<0.3	0.03	<0.5	0.05
2,3,4,6,7,8	HxCDF	2.8	0.28	1.5	0.15
Total	HxCDF	130		130	
1,2,3,4,6,7,8	HpCDF	30	0.3	30	0.3
1,2,3,4,7,8,9	HpCDF	<0.7	0.007	<1.0	0.01
Total	HpCDF	54		73	
	OCDF	<50	0.05	<100	0.1
ΣPCDD/F		1537		2975	
NATO I-TEQ			13.227		12.28

**Table E.4 PCDD and PCDF Concentrations in River Thames Sediment  
at Cricklade**  
(ng kg<sup>-1</sup> dry weight, ppt)

		Cricklade	
Congener		Concentration	xTEF
2,3,7,8	TCDD	0.3	0.3
Total	TCDD	32	
1,2,3,7,8	PeCDD	<0.1	0.05
Total	PeCDD	42	
1,2,3,4,7,8	HxCDD	<0.1	0.01
1,2,3,6,7,8	HxCDD	4.1	0.41
1,2,3,7,8,9	HxCDD	<0.1	0.01
Total	HxCDD	100	
1,2,3,4,6,7,8	HpCDD	23	0.23
Total	HpCDD	95	
	OCDD	79	0.079
2,3,7,8	TCDF	6.7	0.67
Total	TCDF	130	
1,2,3,7,8	PeCDF	0.4	0.02
2,3,4,7,8	PeCDF	0.7	0.35
Total	PeCDF	180	
1,2,3,4,7,8	HxCDF	34	3.4
1,2,3,6,7,8	HxCDF	<0.4	0.04
1,2,3,7,8,9	HxCDF	<0.2	0.02
2,3,4,6,7,8	HxCDF	<0.3	0.03
Total	HxCDF	120	
1,2,3,4,6,7,8	HpCDF	16	0.16
1,2,3,4,7,8,9	HpCDF	0.5	0.005
Total	HpCDF	32	
	OCDF	<2.0	0.05
ΣPCDD/F		860	
NATO I-TEQ			5.834

Table E.5

**PCDD and PCDF Concentrations in River Cam Sediments  
at Hauxton, above and below the potential point source  
(ng kg<sup>-1</sup> dry weight, ppt)**

		R. Cam, Hauxton (above)		R. Cam, Hauxton (below)	
Congener		Concentration	xTEF	Concentration	xTEF
2,3,7,8	TCDD	0.9	0.9	2.3	2.3
Total	TCDD	240		920.	
1,2,3,7,8	PeCDD	2.8	1.4	<1.0	0.5
Total	PeCDD	150		96.	
1,2,3,4,7,8	HxCDD	3.7	0.37	3.6	0.36
1,2,3,6,7,8	HxCDD	12	1.2	<1.0	0.1
1,2,3,7,8,9	HxCDD	3.6	0.36	<1.0	0.1
Total	HxCDD	140		59.0	
1,2,3,4,6,7,8	HpCDD	350	3.5	120.	1.223
Total	HpCDD	840		310.	
	OCDD	1400	1.4	<50.	0.05
2,3,7,8	TCDF	14	1.4	16.	1.59
Total	TCDF	200		1600.	
1,2,3,7,8	PeCDF	3.6	0.18	<1.0	0.05
2,3,4,7,8	PeCDF	3.8	1.9	<1.0	0.5
Total	PeCDF	220		250.	
1,2,3,4,7,8	HxCDF	120	12	<2.0	0.2
1,2,3,6,7,8	HxCDF	2.6	0.26	<2.0	0.2
1,2,3,7,8,9	HxCDF	<0.5	0.05	<2.0	0.2
2,3,4,6,7,8	HxCDF	5.3	0.53	<2.0	0.2
Total	HxCDF	280		180.	
1,2,3,4,6,7,8	HpCDF	44	0.44	13.0	0.135
1,2,3,4,7,8,9	HpCDF	<1.0	0.01	<2.0	0.02
Total	HpCDF	76		26	
	OCDF	<100	0.1	<50	0.05
ΣPCDD/F		3646		3541	
NATO I-TEQ			26		7.778

Table E.6

**PCDD and PCDF Concentrations in River Granta Sediments  
at Hildersham and New River Sediments at Wicken**  
(ng kg<sup>-1</sup> dry weight, ppt)

		R. Granta, Hildersham		New River, Wicken	
Congener		Concentration	xTEF	Concentration	xTEF
2,3,7,8	TCDD	0.4	0.4	12	12
Total	TCDD	34		270	
1,2,3,7,8	PeCDD	0.6	0.3	53	26.5
Total	PeCDD	38		700	
1,2,3,4,7,8	HxCDD	0.5	0.05	41	4.1
1,2,3,6,7,8	HxCDD	2.6	0.26	71	7.1
1,2,3,7,8,9	HxCDD	<0.5	0.05	44	4.4
Total	HxCDD	45		1600	
1,2,3,4,6,7,8	HpCDD	98	0.98	840	8.4
Total	HpCDD	190		3000	
	OCDD	330	0.33	630	0.63
2,3,7,8	TCDF	3.3	0.33	3.0	0.3
Total	TCDF	63		49	
1,2,3,7,8	PeCDF	1.0	0.05	1.7	0.085
2,3,4,7,8	PeCDF	1.5	0.75	0.4	0.2
Total	PeCDF	74		70	
1,2,3,4,7,8	HxCDF	38	3.8	87	8.7
1,2,3,6,7,8	HxCDF	0.8	0.08	2.5	0.25
1,2,3,7,8,9	HxCDF	<0.5	0.05	<0.5	0.05
2,3,4,6,7,8	HxCDF	1.1	0.11	<0.5	0.05
Total	HxCDF	86		190	
1,2,3,4,6,7,8	HpCDF	22	0.22	18	0.18
1,2,3,4,7,8,9	HpCDF	<1.0	0.01	<1.0	0.01
Total	HpCDF	42		34	
	OCDF	<50	0.05	<50	0.05
ΣPCDD/F		952		6593	
NATO I-TEQ			7.82		73.005

Table E.7

**PCDD and PCDF Concentrations in River Alt Sediments  
at Altmouth and River Mersey Sediments at Howley Weir  
(ng kg<sup>-1</sup> dry weight, ppt)**

		R. Alt, Altmouth		R. Mersey, Howley Weir	
Congener		Concentration	xTEF	Concentration	xTEF
2,3,7,8	TCDD	2.7	2.7	1.2	1.2
Total	TCDD	170		450	
1,2,3,7,8	PeCDD	7.1	3.55	21	10.5
Total	PeCDD	210		520	
1,2,3,4,7,8	HxCDD	6.5	0.65	12	1.2
1,2,3,6,7,8	HxCDD	39	3.9	56	5.6
1,2,3,7,8,9	HxCDD	5.5	0.55	7.9	0.79
Total	HxCDD	450		730	
1,2,3,4,6,7,8	HpCDD	1700	17	960	9.6
Total	HpCDD	3300		1800	
	OCDD	9300	9.3	3000	3
2,3,7,8	TCDF	25	2.5	66	6.6
Total	TCDF	340		880	
1,2,3,7,8	PeCDF	6.9	0.345	32	1.6
2,3,4,7,8	PeCDF	9.8	4.9	11	5.5
Total	PeCDF	490		440	
1,2,3,4,7,8	HxCDF	730	73	440	44
1,2,3,6,7,8	HxCDF	12	1.2	56	5.6
1,2,3,7,8,9	HxCDF	1.0	0.1	1.2	0.12
2,3,4,6,7,8	HxCDF	11	1.1	22	2.2
Total	HxCDF	1200		910	
1,2,3,4,6,7,8	HpCDF	190	1.9	380	3.8
1,2,3,4,7,8,9	HpCDF	< 1.0	0.01	10	0.1
Total	HpCDF	410		480	
	OCDF	< 100	0.1	< 100	0.1
ΣPCDD/F		15970		9310	
NATO I-TEQ			122.805		101.51

**Table E.8** **PCDD and PCDF Concentrations in River Weaver Sediments  
at Acton and River Dane Sediments at Hugbridge**  
(ng kg<sup>-1</sup> dry weight, ppt)

		R. Weaver, Acton		R. Dane, Hugbridge	
Congener		Concentration	xTEF	Concentration	xTEF
2,3,7,8	TCDD	0.7	0.7	0.3	0.3
Total	TCDD	68		36	
1,2,3,7,8	PeCDD	1.1	0.55	0.9	0.45
Total	PeCDD	46		41	
1,2,3,4,7,8	HxCDD	2.1	0.21	1.2	0.12
1,2,3,6,7,8	HxCDD	4.6	0.46	2.3	0.23
1,2,3,7,8,9	HxCDD	1.1	0.11	<1.0	0.1
Total	HxCDD	68		28	
1,2,3,4,6,7,8	HpCDD	75	0.75	21	0.21
Total	HpCDD	160		48	
	OCDD	260	0.26	58	0.058
2,3,7,8	TCDF	23	2.3	3.3	0.33
Total	TCDF			68	
1,2,3,7,8	PeCDF	13	0.65	2.0	0.1
2,3,4,7,8	PeCDF	13	6.5	2.2	1.1
Total	PeCDF	220		60	
1,2,3,4,7,8	HxCDF	43	4.3	2.5	0.25
1,2,3,6,7,8	HxCDF	7.2	0.72	6.8	0.68
1,2,3,7,8,9	HxCDF	<0.5	0.05	<0.5	0.05
2,3,4,6,7,8	HxCDF	3.6	0.36	0.6	0.06
Total	HxCDF	130		40	
1,2,3,4,6,7,8	HpCDF	42	0.42	11	0.11
1,2,3,4,7,8,9	HpCDF	<1.0	0.01	<1.0	0.01
Total	HpCDF	55		17	
	OCDF	<50	0.05	<50	0.05
ΣPCDD/F		1527		446	
NATO I-TEQ			18.4		4.208

Table E.9

**PCDD and PCDF Concentrations in Mag Brook Sediments  
at Honley and River Spenn Sediments at Dewsbury, below  
potential point source  
(ng kg<sup>-1</sup> dry weight, ppt)**

Congener	Mag Brook, Honley, below		R. Spenn, Dewsbury, below	
	Concentration	xTEF	Concentration	xTEF
2,3,7,8 TCDD	<1.0	1	1.1	1.1
Total TCDD	1700		950	
1,2,3,7,8 PeCDD	<1.0	0.5	25	12.5
Total PeCDD	690		430	
1,2,3,4,7,8 HxCDD	9.5	0.95	5.4	0.54
1,2,3,6,7,8 HxCDD	40	4	14	1.4
1,2,3,7,8,9 HxCDD	12	1.2	4.8	0.48
Total HxCDD	390		450	
1,2,3,4,6,7,8 HpCDD	1000	10	940	9.4
Total HpCDD	2100		2000	
OCDD	4900	4.9	2600	2.6
2,3,7,8 TCDF	56	5.6	44	4.4
Total TCDF	830		1400	
1,2,3,7,8 PeCDF	<2.0	0.1	11	0.55
2,3,4,7,8 PeCDF	31	15.5	20	10
Total PeCDF	430		570	
1,2,3,4,7,8 HxCDF	19	1.9	23	2.3
1,2,3,6,7,8 HxCDF	18	1.8	14	1.4
1,2,3,7,8,9 HxCDF	<1.0	0.1	<0.5	0.05
2,3,4,6,7,8 HxCDF	<1.0	0.1	<0.5	0.05
Total HxCDF	570		630	
1,2,3,4,6,7,8 HpCDF	320	3.2	170	1.7
1,2,3,4,7,8,9 HpCDF	<0.5	0.005	<0.5	0.005
Total HpCDF	550		400	
OCDF	<250	0.25	260	0.26
ΣPCDD/F	12410		9690	
NATO I-TEQ		51.105		48.735



Table E.10

**PCDD and PCDF Concentrations in River Calder Sediments  
at Mirfield, above and below a potential point source  
(ng kg<sup>-1</sup> dry weight, ppt)**

		R. Calder, Mirfield, above		R. Calder, Mirfield, below	
Congener		Concentration	xTEF	Concentration	xTEF
2,3,7,8 TCDD	TCDD	1.5	1.5	<0.5	0.5
Total	TCDD	200		65	
1,2,3,7,8 PeCDD	PeCDD	21	10.5	<0.5	0.25
Total	PeCDD	220		49	
1,2,3,4,7,8 HxCDD	HxCDD	8.3	0.83	<0.5	0.05
1,2,3,6,7,8 HxCDD	HxCDD	20	2	5.7	0.57
1,2,3,7,8,9 HxCDD	HxCDD	3.8	0.38	<0.5	0.05
Total	HxCDD	220		210	
1,2,3,4,6,7,8 HpCDD	HpCDD	610	6.1	130	1.3
Total	HpCDD	1300		300	
	OCDD	1400	1.4	350	0.35
2,3,7,8 TCDF	TCDF	100	10	4.8	0.48
Total	TCDF	320		110	
1,2,3,7,8 PeCDF	PeCDF	8.0	0.4	1.2	0.06
2,3,4,7,8 PeCDF	PeCDF	11	5.5	3.0	1.5
Total	PeCDF	350		82	
1,2,3,4,7,8 HxCDF	HxCDF	19	1.9	3.9	0.39
1,2,3,6,7,8 HxCDF	HxCDF	23	2.3	2.9	0.29
1,2,3,7,8,9 HxCDF	HxCDF	<0.5	0.05	<0.5	0.05
2,3,4,6,7,8 HxCDF	HxCDF	1.4	0.14	<0.5	0.05
Total	HxCDF	360		110	
1,2,3,4,6,7,8 HpCDF	HpCDF	110	1.1	45	0.45
1,2,3,4,7,8,9 HpCDF	HpCDF	<0.5	0.005	<0.5	0.005
Total	HpCDF	160		73	
	OCDF	<100	0.1	<100	0.1
SPCDD/F		4450		1449	
NATO I-TEQ			44.205		6.445

Table E.11

**PCDD and PCDF Concentrations in River Aire Sediments  
at Beal, above and below a potential point source  
(ng kg<sup>-1</sup> dry weight, ppt)**

		R. Aire, Beal, above		R. Aire, Beal, below	
Congener		Concentration	xTEF	Concentration	xTEF
2,3,7,8	TCDD	2.3	2.3	6.0	6
Total	TCDD	150		430	
1,2,3,7,8	PeCDD	<0.5	0.25	2.8	1.4
Total	PeCDD	110		290	
1,2,3,4,7,8	HxCDD	5.6	0.56	7.1	0.71
1,2,3,6,7,8	HxCDD	17	1.7	18	1.8
1,2,3,7,8,9	HxCDD	4.7	0.47	4.4	0.44
Total	HxCDD	280		490	
1,2,3,4,6,7,8	HpCDD	550	5.5	690	6.9
Total	HpCDD	1300		1500	
	OCDD	2100	2.1	2500	2.5
2,3,7,8	TCDF	21	2.1	21	2.1
Total	TCDF	330		550	
1,2,3,7,8	PeCDF	7.7	0.385	11	0.55
2,3,4,7,8	PeCDF	7.7	3.85	15	7.5
Total	PeCDF	310		570	
1,2,3,4,7,8	HxCDF	15	1.5	21	2.1
1,2,3,6,7,8	HxCDF	11	1.1	11	1.1
1,2,3,7,8,9	HxCDF	<0.5	0.05	1.4	0.14
2,3,4,6,7,8	HxCDF	<0.5	0.05	1.4	0.14
Total	HxCDF	290		480	
1,2,3,4,6,7,8	HpCDF	130	1.3	170	1.7
1,2,3,4,7,8,9	HpCDF	<0.5	0.005	<0.5	0.005
Total	HpCDF	190		310	
	OCDF	<100	0.1	270	0.27
SPCDD/F		5160		7390	
NATO I-TEQ			23.32		35.355

Table E.12

**PCDD and PCDF Concentrations in River Aire Sediments  
at Fleet Weir above and below a potential point source  
(ng kg<sup>-1</sup> dry weight, ppt)**

		R. Aire, Fleet Weir, above		R. Aire, Fleet Weir, below	
Congener		Concentration	xTEF	Concentration	xTEF
2,3,7,8 TCDD	TCDD	0.9	0.9	0.6	0.6
Total TCDD	TCDD	53		110	
1,2,3,7,8 PeCDD	PeCDD	3.9	1.95	<1.0	0.5
Total PeCDD	PeCDD	120		110	
1,2,3,4,7,8 HxCDD	HxCDD	<1.0	0.1	3.3	0.33
1,2,3,6,7,8 HxCDD	HxCDD	16	1.6	17	1.7
1,2,3,7,8,9 HxCDD	HxCDD	1.9	0.19	2.7	0.27
Total HxCDD	HxCDD	180		170	
1,2,3,4,6,7,8 HpCDD	HpCDD	590	5.9	540	5.4
Total HpCDD	HpCDD	1200		1100	
	OCDD	3900	3.9	1800	1.8
2,3,7,8 TCDF	TCDF	28	2.8	8.8	0.88
Total TCDF	TCDF	440		290	
1,2,3,7,8 PeCDF	PeCDF	5.1	0.255	1.2	0.06
2,3,4,7,8 PeCDF	PeCDF	7.9	3.95	<0.2	0.1
Total PeCDF	PeCDF	300		300	
1,2,3,4,7,8 HxCDF	HxCDF	11	1.1	4.2	0.42
1,2,3,6,7,8 HxCDF	HxCDF	5.3	0.53	4.5	0.45
1,2,3,7,8,9 HxCDF	HxCDF	<0.2	0.02	<0.2	0.02
2,3,4,6,7,8 HxCDF	HxCDF	<0.2	0.02	<0.2	0.02
Total HxCDF	HxCDF	290		240	
1,2,3,4,6,7,8 HpCDF	HpCDF	88	0.88	69	0.69
1,2,3,4,7,8,9 HpCDF	HpCDF	<0.5	0.005	<0.5	0.005
Total HpCDF	HpCDF	180		130	
	OCDF	<100	0.1	<250	0.25
ΣPCDD/F		6763		4500	
NATO I-TEQ			24.2		13.495

**Table E.13      PCDD and PCDF Concentrations in River Don Sediments**  
**at Rotherham, above and below a potential point source**  
**(ng kg<sup>-1</sup> dry weight, ppt)**

		R. Don, Rotherham, above		R. Don, Rotherham, below	
Congener		Concentration	xTEF	Concentration	xTEF
2,3,7,8 TCDD		2.9	2.9	<0.5	0.5
Total TCDD		670		260	
1,2,3,7,8 PeCDD		7.1	3.55	<0.5	0.25
Total PeCDD		320		130	
1,2,3,4,7,8 HxCDD		5.2	0.52	5.5	0.55
1,2,3,6,7,8 HxCDD		26	2.6	5.4	0.54
1,2,3,7,8,9 HxCDD		12	1.2	<0.5	0.05
Total HxCDD		390		170	
1,2,3,4,6,7,8 HpCDD		740	7.4	340	3.4
Total HpCDD		1600		720	
OCDD		1400	1.4	1400	1.4
2,3,7,8 TCDF		33	3.3	18	1.8
Total TCDF		960		390	
1,2,3,7,8 PeCDF		18	0.9	14	0.7
2,3,4,7,8 PeCDF		35	17.5	21	10.5
Total PeCDF		580		280	
1,2,3,4,7,8 HxCDF		38	3.8	25	2.5
1,2,3,6,7,8 HxCDF		31	3.1	19	1.9
1,2,3,7,8,9 HxCDF		<0.5	0.05	<0.5	0.05
2,3,4,6,7,8 HxCDF		<0.5	0.05	<0.5	0.05
Total HxCDF		570		290	
1,2,3,4,6,7,8 HpCDF		240	2.4	120	1.2
1,2,3,4,7,8,9 HpCDF		<0.5	0.005	<0.5	0.005
Total HpCDF		310		180	
OCDF		<250	0.25	<250	0.25
SPCDD/F		7050		4070	
NATO I-TEQ			50.925		25.645

**Table E.14** **PCDD and PCDF Concentrations in River Loxley Sediments near Sheffield**  
(ng kg<sup>-1</sup> dryweight, ppt)

		R. Loxley, near Sheffield	
Congener		Concentration	xTEF
2,3,7,8 TCDD		<1.0	1
Total TCDD		81	
1,2,3,7,8 PeCDD		<1.0	0.5
Total PeCDD		100	
1,2,3,4,7,8 HxCDD		<1.0	0.1
1,2,3,6,7,8 HxCDD		10	1
1,2,3,7,8,9 HxCDD		<1.0	0.1
Total HxCDD		99	
1,2,3,4,6,7,8 HpCDD		230	2.3
Total HpCDD		540	
	OCDD	820	0.82
2,3,7,8 TCDF		6.5	0.65
Total TCDF		210	
1,2,3,7,8 PeCDF		8.6	0.43
2,3,4,7,8 PeCDF		11	5.5
Total PeCDF		210	
1,2,3,4,7,8 HxCDF		9.1	0.91
1,2,3,6,7,8 HxCDF		9.0	0.9
1,2,3,7,8,9 HxCDF		<1.0	0.1
2,3,4,6,7,8 HxCDF		<1.0	0.1
Total HxCDF		270	
1,2,3,4,6,7,8 HpCDF		43	0.43
1,2,3,4,7,8,9 HpCDF		<0.5	0.005
Total HpCDF		100	
	OCDF	<100	0.1
ΣPCDD/F		2530	
NATO I-TEQ			14.945

Table E.15

**PCDD and PCDF Concentrations in River Amber Sediments  
at Ambergate, above and below a potential point source  
(ng kg<sup>-1</sup> dry weight, ppt)**

		R. Amber, Ambergate, above		R. Amber, Ambergate, below	
Congener		Concentration	xTEF	Concentration	xTEF
2,3,7,8	TCDD	0.7	0.7	4.2	4.2
Total	TCDD	100		600	
1,2,3,7,8	PeCDD	1.5	0.75	13	6.5
Total	PeCDD	59		290	
1,2,3,4,7,8	HxCDD	2.1	0.21	63	6.3
1,2,3,6,7,8	HxCDD	4.6	0.46	40	4
1,2,3,7,8,9	HxCDD	1.4	0.14	73	7.3
Total	HxCDD	69		1300	
1,2,3,4,6,7,8	HpCDD	88	0.88	1300	13
Total	HpCDD	190		3900	
	OCDD	230	0.23	2600	2.6
2,3,7,8	TCDF	5.3	0.53	11	1.1
Total	TCDF	170		390	
1,2,3,7,8	PeCDF	1.1	0.055	6.7	0.335
2,3,4,7,8	PeCDF	3.1	1.55	13	6.5
Total	PeCDF	160		460	
1,2,3,4,7,8	HxCDF	29	2.9	280	28
1,2,3,6,7,8	HxCDF	2.4	0.24	<0.5	0.05
1,2,3,7,8,9	HxCDF	<0.5	0.05	<0.5	0.05
2,3,4,6,7,8	HxCDF	<0.5	0.05	<0.5	0.05
Total	HxCDF	95		550	
1,2,3,4,6,7,8	HpCDF	15	0.15	90	0.9
1,2,3,4,7,8,9	HpCDF	<1.0	0.01	<1.0	0.01
Total	HpCDF	24		200	
	OCDF	<50	0.05	<100	0.1
ΣPCDD/F		1147		10390	
NATO I-TEQ			8.955		80.995

Table E.16

**PCDD and PCDF Concentrations in River Derwent Sediments at  
Church Wilne, above and below a potential point source  
(ng kg<sup>-1</sup> dry weight, ppt)**

		R. Derwent, Church Wilne, above		R. Derwent, Church Wilne, below	
Congener		Concentration	xTEF	Concentration	xTEF
2,3,7,8	TCDD	2.7	2.7	1.2	1.2
Total	TCDD	280		140	
1,2,3,7,8	PeCDD	26	13	4.6	2.3
Total	PeCDD	580		120	
1,2,3,4,7,8	HxCDD	85	8.5	1.4	0.14
1,2,3,6,7,8	HxCDD	53	5.3	9.1	0.91
1,2,3,7,8,9	HxCDD	99	9.9	2.5	0.25
Total	HxCDD	1900		160	
1,2,3,4,6,7,8	HpCDD	1300	13	420	4.2
Total	HpCDD	4200		840	
	OCDD	1700	1.7	1300	1.3
2,3,7,8	TCDF	9.9	0.99	7.0	0.7
Total	TCDF	210		200	
1,2,3,7,8	PeCDF	4.2	0.21	3.3	0.165
2,3,4,7,8	PeCDF	3.3	1.65	6.0	3
Total	PeCDF	230		170	
1,2,3,4,7,8	HxCDF	110	11	13	1.3
1,2,3,6,7,8	HxCDF	12	1.2	4.1	0.41
1,2,3,7,8,9	HxCDF	<1.0	0.1	<0.2	0.02
2,3,4,6,7,8	HxCDF	0.7	0.07	<0.2	0.02
Total	HxCDF	310		190	
1,2,3,4,6,7,8	HpCDF	73	0.73	56	0.56
1,2,3,4,7,8,9	HpCDF	<1.0	0.01	<0.5	0.005
Total	HpCDF	170		88	
	OCDF	<50	0.05	<50	0.05
SPCDD/F		9630		2088	
NATO I-TEQ			70.11		16.53

Table E.17

**PCDD and PCDF Concentrations in River Derwent Sediments  
at Belper, above and below a potential point source  
(ng kg<sup>-1</sup> dry weight, ppt)**

		R. Derwent, Belper, above		R. Derwent, Belper, below	
Congener		Concentration	xTEF	Concentration	xTEF
2,3,7,8	TCDD	0.8	0.8	0.6	0.6
Total	TCDD	140		70	
1,2,3,7,8	PeCDD	2.5	1.25	3.5	1.75
Total	PeCDD	120		57	
1,2,3,4,7,8	HxCDD	2.6	0.26	1.8	0.18
1,2,3,6,7,8	HxCDD	12	1.2	7.5	0.75
1,2,3,7,8,9	HxCDD	1.3	0.13	1.5	0.15
Total	HxCDD	130		87	
1,2,3,4,6,7,8	HpCDD	470	4.7	260	2.6
Total	HpCDD	980		530	
	OCDD	2200	2.2	1300	1.3
2,3,7,8	TCDF	7.7	0.77	6.0	0.6
Total	TCDF	270		130	
1,2,3,7,8	PeCDF	4.6	0.23	3.0	0.15
2,3,4,7,8	PeCDF	9.8	4.9	4.1	2.05
Total	PeCDF	220		120	
1,2,3,4,7,8	HxCDF	17	1.7	27	2.7
1,2,3,6,7,8	HxCDF	7.8	0.78	3.9	0.39
1,2,3,7,8,9	HxCDF	<0.2	0.02	<0.2	0.02
2,3,4,6,7,8	HxCDF	<0.2	0.02	<0.2	0.02
Total	HxCDF	250		140	
1,2,3,4,6,7,8	HpCDF	75	0.75	42	0.42
1,2,3,4,7,8,9	HpCDF	<0.5	0.005	<0.5	0.005
Total	HpCDF	110		72	
	OCDF	<50	0.05	<50	0.05
ΣPCDD/F		4470		2556	
NATO I-TEQ			19.765		13.735



Table E.18

**PCDD and PCDF Concentrations in River Erewash Sediments**  
**at Eastwood, above and below a potential point source**  
**(ng kg<sup>-1</sup> dry weight, ppt)**

		R. Erewash, Eastwood, above		R. Erewash, Eastwood, below	
Congener		Concentration	xTEF	Concentration	xTEF
2,3,7,8	TCDD	<0.2	0.2	<0.5	0.5
Total	TCDD	190		110	
1,2,3,7,8	PeCDD	<0.5	0.25	1.5	0.75
Total	PeCDD	57		62	
1,2,3,4,7,8	HxCDD	<0.5	0.05	1.0	0.1
1,2,3,6,7,8	HxCDD	4.2	0.42	6.0	0.6
1,2,3,7,8,9	HxCDD	0.7	0.07	1.0	0.1
Total	HxCDD	90		77	
1,2,3,4,6,7,8	HpCDD	180	1.8	220	2.2
Total	HpCDD	440		480	
	OCDD	750	0.75	1200	1.2
2,3,7,8	TCDF	11	1.1	5.8	0.58
Total	TCDF	210		130	
1,2,3,7,8	PeCDF	4.8	0.24	2.2	0.11
2,3,4,7,8	PeCDF	4.4	2.2	4.0	2
Total	PeCDF	180		110	
1,2,3,4,7,8	HxCDF	3.6	0.36	25	2.5
1,2,3,6,7,8	HxCDF	4.3	0.43	2.5	0.25
1,2,3,7,8,9	HxCDF	<0.2	0.02	<0.2	0.02
2,3,4,6,7,8	HxCDF	<0.2	0.02	<0.2	0.02
Total	HxCDF	98		140	
1,2,3,4,6,7,8	HpCDF	37	0.37	100	1
1,2,3,4,7,8,9	HpCDF	<0.5	0.005	<0.5	0.005
Total	HpCDF	65		140	
	OCDF	<100	0.1	<50	0.05
ΣPCDD/F		2180		2499	
NATO I-TEQ			8.385		11.985

**Table E.19** **PCDD and PCDF Concentrations in River Lathkill Sediments at Alport, and River Derwent Sediments at Froggatt**  
(ng kg<sup>-1</sup> dry weight, ppt)

		R. Lathkill, Alport		R. Derwent, Froggatt	
Congener		Concentration	xTEF	Concentration	xTEF
2,3,7,8	TCDD	<0.2	0.2	<0.5	0.5
Total	TCDD	18		28	
1,2,3,7,8	PeCDD	<0.2	0.1	0.7	0.35
Total	PeCDD	18		27	
1,2,3,4,7,8	HxCDD	<1.0	0.1	<0.5	0.05
1,2,3,6,7,8	HxCDD	<1.0	0.1	2.9	0.29
1,2,3,7,8,9	HxCDD	<1.0	0.1	1.1	0.11
Total	HxCDD	16		36	
1,2,3,4,6,7,8	HpCDD	31	0.31	53	0.53
Total	HpCDD	58		120	
	OCDD	79	0.079	220	0.22
2,3,7,8	TCDF	1.4	0.14	4.4	0.44
Total	TCDF	40		62	
1,2,3,7,8	PeCDF	1.5	0.075	2.6	0.13
2,3,4,7,8	PeCDF	2.0	1	3.7	1.85
Total	PeCDF	29		33	
1,2,3,4,7,8	HxCDF	1.7	0.17	6.1	0.61
1,2,3,6,7,8	HxCDF	1.4	0.14	2.8	0.28
1,2,3,7,8,9	HxCDF	<0.5	0.05	<0.2	0.02
2,3,4,6,7,8	HxCDF	<0.5	0.05	<0.2	0.02
Total	HxCDF	19		36	
1,2,3,4,6,7,8	HpCDF	8.4	0.084	15	0.15
1,2,3,4,7,8,9	HpCDF	<0.5	0.005	<0.5	0.005
Total	HpCDF	8.4		19	
	OCDF	<50	0.05	<50	0.05
ΣPCDD/F		335		631	
NATO I-TEQ			2.753		5.605

**Table E.20 PCDD and PCDF Concentrations in Pressbrook  
Sediments at Ogston (ng kg<sup>-1</sup> dry weight, ppt)**

		Pressbrook, Ogston	
Congener		Concentration	xTEF
2,3,7,8 TCDD		0.5	0.5
Total TCDD		140	
1,2,3,7,8 PeCDD		1.4	0.7
Total PeCDD		74	
1,2,3,4,7,8 HxCDD		1.6	0.16
1,2,3,6,7,8 HxCDD		5.8	0.58
1,2,3,7,8,9 HxCDD		2.2	0.22
Total HxCDD		68	
1,2,3,4,6,7,8 HpCDD		100	1
Total HpCDD		250	
	OCDD	450	0.45
2,3,7,8 TCDF		6.4	0.64
Total TCDF		320	
1,2,3,7,8 PeCDF		3.5	0.175
2,3,4,7,8 PeCDF		5.6	2.8
Total PeCDF		210	
1,2,3,4,7,8 HxCDF		11	1.1
1,2,3,6,7,8 HxCDF		3.8	0.38
1,2,3,7,8,9 HxCDF		<0.2	0.02
2,3,4,6,7,8 HxCDF		<0.2	0.02
Total HxCDF		84	
1,2,3,4,6,7,8 HpCDF		26	0.26
1,2,3,4,7,8,9 HpCDF		<0.5	0.005
Total HpCDF		32	
	OCDF	<50	0.05
ΣPCDD/F		1678	
NATO I-TEQ			9.06

Table E.21

**PCDD and PCDF Concentrations in River Tame Sediments  
at Lea Marston above and below a water purification lake  
(ng kg<sup>-1</sup> dry weight, ppt)**

		T. Tame, Lea Marston, below		R. Tame, Lea Marston, above	
Congener		Concentration	xTEF	Concentration	xTEF
2,3,7,8	TCDD	<1.0	1	10	10
Total	TCDD	300		1600	
1,2,3,7,8	PeCDD	3.1	1.55	2.9	1.45
Total	PeCDD	220		190	
1,2,3,4,7,8	HxCDD	<1.0	0.1	2.9	0.29
1,2,3,6,7,8	HxCDD	8.6	0.86	13	1.3
1,2,3,7,8,9	HxCDD	<1.0	0.1	<1.0	0.1
Total	HxCDD	130		170	
1,2,3,4,6,7,8	HpCDD	200	2	250	2.5
Total	HpCDD	480		540	
	OCDD	470	0.47	1100	1.1
2,3,7,8	TCDF	8.5	0.85	10	1
Total	TCDF	330		1400	
1,2,3,7,8	PeCDF	6.6	0.33	12	0.6
2,3,4,7,8	PeCDF	12	6	17	8.5
Total	PeCDF	230		850	
1,2,3,4,7,8	HxCDF	12	1.2	16	1.6
1,2,3,6,7,8	HxCDF	10	1	14	1.4
1,2,3,7,8,9	HxCDF	<0.5	0.05	<0.5	0.05
2,3,4,6,7,8	HxCDF	<0.5	0.05	<0.5	0.05
Total	HxCDF	190		370	
1,2,3,4,6,7,8	HpCDF	110	1.1	190	1.9
1,2,3,4,7,8,9	HpCDF	<0.5	0.005	<0.5	0.005
Total	HpCDF	130		220	
	OCDF	<100	0.1	<250	0.25
ΣPCDD/F		2580		6690	
NATO I-TEQ			16.765		32.095

**Table E.22** PCDD and PCDF Concentrations in River Lugg Sediments at Hereford (ng kg<sup>-1</sup> dry weight, ppt)

		R. Lugg, Hereford	
Congener		Concentration	xTEF
2,3,7,8	TCDD	0.3	0.3
Total	TCDD	7.4	
1,2,3,7,8	PeCDD	<0.2	0.1
Total	PeCDD	6.5	
1,2,3,4,7,8	HxCDD	<0.2	0.02
1,2,3,6,7,8	HxCDD	0.6	0.06
1,2,3,7,8,9	HxCDD	<0.2	0.02
Total	HxCDD	8.9	
1,2,3,4,6,7,8	HpCDD	16	0.16
Total	HpCDD	33	
	OCDD	80	0.08
2,3,7,8	TCDF	1.7	0.17
Total	TCDF	37	
1,2,3,7,8	PeCDF	0.4	0.02
2,3,4,7,8	PeCDF	0.9	0.45
Total	PeCDF	34	
1,2,3,4,7,8	HxCDF	4.0	0.4
1,2,3,6,7,8	HxCDF	0.6	0.06
1,2,3,7,8,9	HxCDF	<0.2	0.02
2,3,4,6,7,8	HxCDF	<0.2	0.02
Total	HxCDF	15	
1,2,3,4,6,7,8	HpCDF	5.0	0.05
1,2,3,4,7,8,9	HpCDF	<0.5	0.005
Total	HpCDF	8.5	
	OCDF	<50	0.05
ΣPCDD/F		281	
NATO I-TEQ			1.985