

# Occurrence and mobility of the insecticide permethrin in rivers in the Southern Humber catchment, UK

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**Abstract:** The synthetic pyrethroid insecticides *cis*- and *trans*-permethrin are widely used, particularly in sheep-dips and for mothproofing within the textile industry. This study aims to establish the concentrations and mobility of permethrin within rivers in the Humber catchment, which contain some of the highest densities of wool-scouring activity in the world. Our approach was to utilise three different surveys: (a) weekly and storm-responsive sampling of 'whole waters' in the rivers Aire, Ouse, Don, Trent and Calder; (b) intensive sampling of 'whole waters' and suspended sediments in the rivers Aire (0.5 h) and Calder (1 h); (c) a bed-sediment survey of the River Calder. Sediments were extracted by supercritical fluid extraction and all samples were analysed by gas chromatography with mass spectrometry.

Results demonstrated the presence of permethrin in 'whole waters' and sediments, particularly in the rivers Aire and Calder, and at concentrations in the bed-sediment likely to cause ecotoxicological effects to benthic macro-invertebrates. Mass-balance calculations indicated some loss of permethrin from the water column during transport, with the greatest losses at low river-discharge. Isomer ratios (*trans*:*cis*) give retention times of permethrin in different components of the system as 'whole water' < suspended sediments < bed-sediments, with estimates of 4–26 days for suspended sediments and a maximum of 103–125 days for surface bed-sediments.

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**Keywords:** permethrin; Humber; river sediments; River Aire; River Calder; sorption; degradation

## 1 INTRODUCTION

Permethrin (3-phenoxybenzyl (1*RS*)-*cis-trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate), a widely used pyrethroid insecticide, is a contact insecticide active against a wide range of pests.<sup>1</sup> It is relatively non-toxic to mammals (LD<sub>50</sub> of 430–4000 mg kg<sup>-1</sup>) but is very toxic to aquatic life, with a proposed Environmental Quality Standard<sup>2</sup> in the UK of 0.01 µg dm<sup>-3</sup>. It is also a List II substance classified under the Dangerous Substance Directive (74/464/EEC). There have been recordings of concentrations >0.01 µg dm<sup>-3</sup> in surface waters, particularly in the Midlands and North-East regions of England where discharges from textile finishing factories and sewage treatment works are major contributors.<sup>2–4</sup> In 1996, 25.5% of Environment Agency monitored sites failed the Environmental Quality Standard for permethrin in surface waters and 47.6% of monitored sites failed for another synthetic pyrethroid, cypermethrin.<sup>2</sup> Permethrin has also been detected at mean concentrations of 11 000 µg kg<sup>-1</sup> (dry weight) in sewage sludge.<sup>5</sup> The present study focuses on the Humber catchment in the North-East region. The chemistry, biology and hydrology of the catchment have recently been studied in detail

as part of the Land Ocean Interaction Study (LOIS)<sup>6</sup> alongside a geographic description of the region,<sup>7</sup> and a survey of permethrin in the Humber estuary.<sup>8</sup>

There are currently few published data on the occurrence of synthetic pyrethroids in the environment, and particularly on how they are transported in rivers to the estuary. Research using artificial ponds has indicated the slower degradation of permethrin in sediments compared with that in the overlying water, with detection of permethrin in the bottom sediments more than a year after application.<sup>9</sup> Permethrin is also known to be more persistent in sediments of low pH and at low redox potential,<sup>10</sup> which are often found in slow-flowing rivers. This paper aims to establish concentrations of permethrin, including isomer ratios, in the Humber catchment and to explore the role of sediments in permethrin mobility for the rivers Aire and Calder, which contain some of the highest concentrations of wool-scouring activity in the world.<sup>11,12</sup>

## 2 METHODS

### 2.1 Field sites

Weekly and storm-water sampling was part of the

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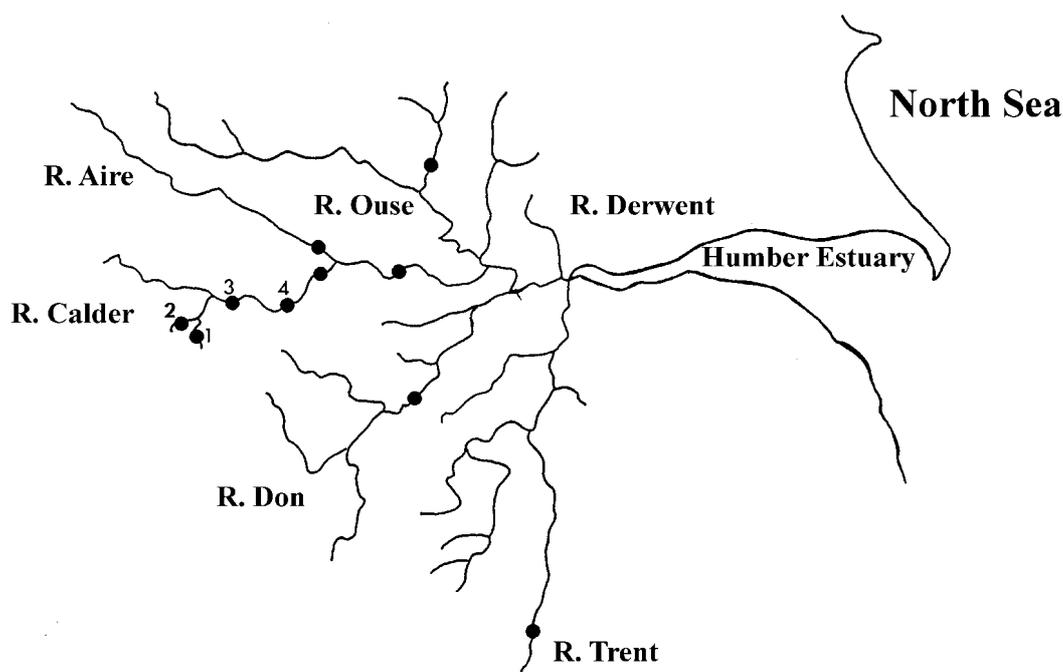


Figure 1. Location of the main rivers surveyed and sampling stations.

Land Ocean Interaction Study (LOIS) of the rivers delivering to the Humber estuary.<sup>6</sup> The sampling sites were at the Environment Agency gauging stations at the tidal limits of the rivers Aire, Ouse, Don and Trent, with further sites on the River Calder near its confluence with the River Aire, and on the River Aire at Allerton Bywater before its confluence with the River Calder (Fig 1). The locations of the sites and monitoring periods are shown in Table 1.

Intensive monitoring campaigns to measure permethrin in river water and suspended solids were conducted on the two rivers with the highest concentrations of permethrin: the River Aire at the tidal limit, and at the weekly monitoring site on the River Calder (Table 1). Additional studies were completed on the

River Calder to investigate the distribution of permethrin in the river bed-sediments. The sites were chosen from the headwaters at Meltham to the confluence of the river with the River Aire (Fig 1).

2.2 Sampling

2.2.1 Weekly and storm sampling of river waters

Sampling was done on a weekly basis and also during storm events. The samples were collected in 500-ml borosilicate glass bottles with PTFE caps. A control blank containing HPLC grade water, and after March 1995 ultrapure water (Elgastat UHQ-PS), was included in each batch of samples. Each week a sample from one of the rivers in rotation was spiked with a standard containing *cis*- and *trans*-permethrin. Stirred

Site name	Location	Type of sampling <sup>a</sup>	Date(s)
R Aire at Beal	SE534255	W	25 Oct 1994–16 Dec 1996
R Calder at Methley	SE409258	W	25 Oct 1994–16 Dec 1996
R Don	SE538014	W	25 Oct 1994–16 Dec 1996
R Trent	SK807612	W	25 Oct 1994–16 Dec 1996
R Ouse	SE594445	W	25 Oct 1994–16 Dec 1996
R Aire at Allerton	SE417274	W	7 Nov 1995–16 Dec 1996
R Aire at Beal	SE534255	I	20 Nov 1996–21 Nov 1996
R Calder, Methley	SE409258	I	16 Jan 1997–17 Jan 1997
R Calder, Metham Mills	SE116105	S1	20 Aug 1997
R Calder, Hall Dike	SE125124	S2	20 Aug 1997
R Calder, Huddersfield (1) <sup>b</sup>	SE169188	S3	20 Aug 1997
R Calder, Huddersfield (2) <sup>b</sup>	SE169188	S3	20 Aug 1997
R Calder, Healey	SE270192	S4	20 Aug 1997
R Calder, Methley	SE409258	S	20 Aug 1997

<sup>a</sup> W, weekly and storm sampling; I, intensive sampling, S, bed-sediment sampling (numbers indicating location on map in Fig 1).

<sup>b</sup> Sites (1) and (2) at Huddersfield are upstream and downstream of effluent treatment works respectively.

Table 1. Location of sampling sites

samples were extracted by solid-phase-extraction (SPE) within one day of collection and transported overnight from the field station to the Institute of Freshwater Ecology's laboratory at Wareham in Dorset for immediate processing.

The field samples were not pre-filtered but passed through a 70-ml reservoir containing a 20- $\mu\text{m}$  frit to an SPE-bonded silica (C18 (EC), ISOLUTE) and are referred to as 'whole water' samples. The sample bottle was washed with 10 ml of ethyl acetate to extract adsorbed permethrin<sup>13</sup> and the washings were placed in a 12-ml vial which was closed with a PTFE cap. The reservoir with suspended matter, ethyl acetate bottle wash and SPE column were stored in the dark at 4°C prior to transportation. The washings were then dried using 0.3 g of anhydrous sodium sulphate and the samples eluted with 5 ml of ethyl acetate from the bottle wash. The suspended solids, frit and SPE column were allowed to soak in the remaining bottle wash for 2 h before final elution. The bottle wash vial was finally rinsed with a further 2 ml of ethyl acetate, with the washings added to the reservoir. The combined extract was approximately 12 ml and this was evaporated under dry nitrogen at 35°C to *c* 2 ml and then dried by passing through a column of anhydrous sodium sulphate.

### 2.2.2 Intensive campaigns

Water samples were collected at 0.5 h (River Aire) or 1 h (River Calder) intervals by an automatic sampler (EPIC model 1011) with PTFE sample tubes to the river and delivered to 500-ml borosilicate bottles. These were extracted on-site with approximately 100 ml of dichloromethane. On return to the laboratory, the dichloromethane was separated, dried with anhydrous sodium sulphate and concentrated to approximately 1.5 ml in a Kuderna-Danish concentrator. The extract was then evaporated with dry nitrogen and reconstituted in approximately 1.5 ml of ethyl acetate.

Suspended matter was collected on site over periods of 3 h by continuous-flow centrifugation. River water was pumped at about 30.0 cm<sup>3</sup> s<sup>-1</sup> and the solids collected in a stainless-steel bowl. At the end of each period the contents of the bowl were emptied into a glass jar and the bowl rinsed with ultra-pure water. The collection bowl was then rinsed with solvent and the continuous centrifugation continued.

On return to the laboratory the sediments were extracted by supercritical-fluid extraction (Dionex-703/703M; Jun-Air 18-50 compressor) using carbon dioxide modified with 10 mol% of methanol. The extraction cells were packed with the sample, acid-washed sand and with copper granules at the outlet. The cells were held at 50°C at an initial pressure of 200 atm (0–5 min) with subsequent ramping to 400 atm (5–15 min) and 600 atm for 45 min. Sample blanks with no sediments were included in each sample batch. The efficiency of the extraction method was measured by spiking two different river sediments

(organic matter content of 3.5% and 1.5%) with 0.5  $\mu\text{g}$  of *cis*- and *trans*-permethrin.

### 2.2.3 Bed-sediment survey

Bed-sediment was collected by 'hoovering' the river bed for approximately 10 min. The method involves sweeping a 2-mm sieve, attached to the inlet tube of the continuous-flow centrifuge, across the surface of a river bed. In this manner a composite sample of the top few centimetres of river bed-sediment was obtained from the local area, the sweeping action of 'hoovering' ensuring that samples were collected from an area of approximately 5 m<sup>2</sup>. The length of the attached pole (about 2 m) also allowed for sediment to be taken from the centre of the river bed, thus producing samples that were as representative as possible of the river channel. This method also prevents the sampling of suspended sediment, the 'hoover' being passed directly over the surface of the sediment. The sediments were transferred from the centrifuge bowl to glass jars, transported to the laboratory, air dried and extracted by supercritical fluid as described above.

## 2.3 Chromatography

All samples were analysed by gas chromatography with mass-spectrometer detection (GC/MS: Hewlett Packard 5971A). The GC operated with split/splitless injection using a fused silica capillary column (25 m and 0.2 mm ID, 0.33  $\mu\text{m}$  film thickness, HP-5). The analysis was conducted in single-ion mode (SIM), with quantification from the abundance of the base ion (183 amu) and confirmation by one qualifier ion (163 amu) at a specified relative retention time with respect to an internal standard, decachlorobiphenol. Some samples were analysed to determine the relative abundance of the major mass-fragments (183, 163, 165, 184, 168, 181, 255, 390 amu) to compare with standard samples of permethrin. The limit of determination of the method was 0.01  $\mu\text{g dm}^{-3}$  for aqueous samples and 0.5  $\mu\text{g kg}^{-1}$  (dry weight) for sediment.

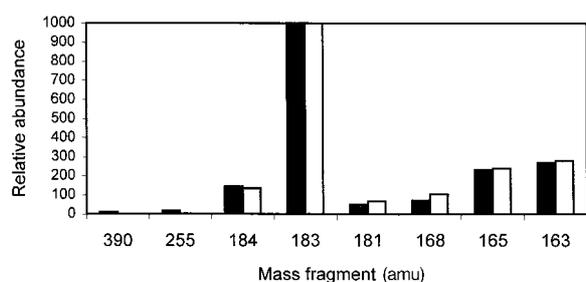
## 2.4 Sediment analysis

Specific surface area was determined on a Coulter SA 3100 instrument outgassing the sample (about 3 g) at 60°C for 12 h, and the adsorption results analysed using the BET equation.<sup>14</sup> The particle sizes were characterised using a Coulter analyser after dispersing in 10 g litre<sup>-1</sup> Calgon. Total organic carbon was measured by wet titration.<sup>15</sup>

## 3 RESULTS AND DISCUSSION

### 3.1 Extraction recoveries

The recovery of permethrin from spiked weekly and storm samples was variable. Samples of 500 ml containing high concentrations of suspended solids blocked the pre-filter and could not be extracted in their entirety. As the samples were continually stirred throughout the extraction, the residual sample volume was determined by weight. Permethrin recoveries were



**Figure 2.** Comparison of (□) the relative abundance of ion-fragments from a GC/MS analysis of an ethyl acetate extract of a 'whole water' sample from the River Aire with (■) the relative ion abundance calculated from a NIST library database.

calculated as a percentage of the initial amount added to the sample and, if only part of the sample was used, the recovery was calculated from the volume of sample extracted. This led to recoveries of total permethrin of 75 ( $\pm 20$ )% with the figure in brackets the standard deviation of 50 determinations. It is likely that the method underestimates permethrin associated with the particulates, ie the solvent is only in contact with the solids at room temperature for 2h so that a more rigorous extraction by isolation of solids and extraction is needed. This is impractical for the scale of monitoring reported here because of the size of sample needed and complexity of the process.

Recoveries of permethrin from sediments by SFE was good with values in the range 54–93% for different bed-sediments that have been tested.<sup>16</sup> The method has also been found to give satisfactory recoveries for a range of synthetic pyrethroids such as fenvalerate and cypermethrin.

### 3.2 Weekly and storm sampling

Permethrin was mainly detected in the rivers Aire and Calder during the weekly and storm sampling. An example of the relative abundance of major ion-fragments for *cis*-permethrin is shown in Fig 2 for a sample extracted from the River Aire collected on 5 November 1996. This is in good agreement with the pattern of abundance normalised on the 183 amu ion given in a standard library apart from the lower abundance of the higher mass ion-fragments (255 amu and the molecular ion, 390 amu). Taken

together with the coincidence of the relative retention times with respect to the internal standard for the samples and standards, this is good confirmation for the identification of permethrin.

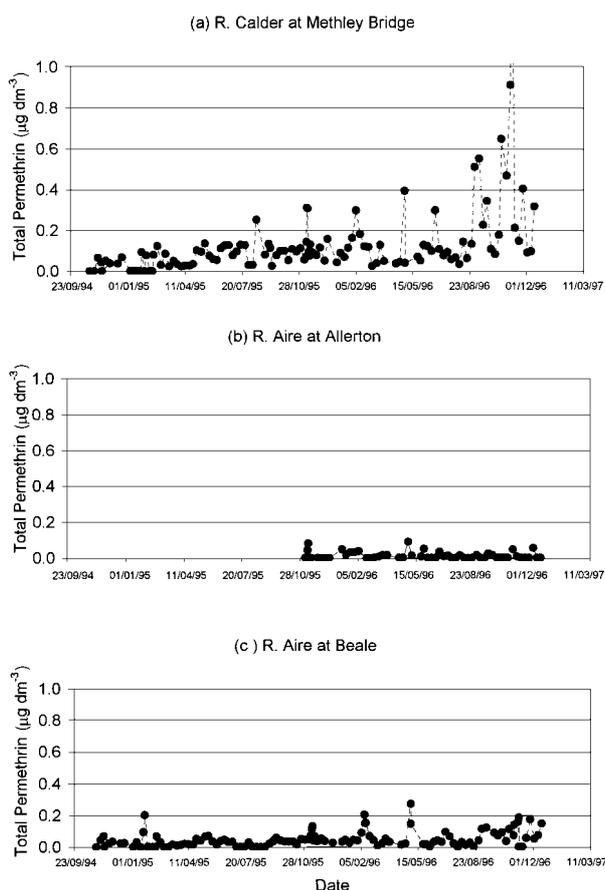
The occurrence in the other rivers, Don, Trent and Ouse was relatively infrequent, with all concentrations determined  $< 0.1 \mu\text{g dm}^{-3}$  (Table 2). The River Calder generally contained the highest concentration of permethrin, with maximum values of 1.39 and  $2.11 \mu\text{g dm}^{-3}$  for the *cis* and *trans* isomers respectively measured in November 1996. This is in agreement with previous studies of the occurrence of permethrin in the Humber catchment between March 1994 and November 1994. For example, permethrin was not detected in river water from the Swale, Ure, Nidd or Derwent during this period but was detected in the rivers Aire and Calder at between 0.02 and  $0.25 \mu\text{g dm}^{-3}$ , which compares with the results shown in Fig 3.<sup>17</sup>

A comparison of the concentrations of total permethrin (*cis* + *trans* isomers) in the River Calder and the two River Aire sites is shown in Fig 3. Sampling at Allerton Bywater was started later than at the other sites. The site at Methley is about 2 km from the confluence with the River Aire, whereas the site at Allerton is about 1.5 km from the confluence. The site at Beal is downstream of the confluence (see Fig 1). The results show higher concentrations of permethrin in the Calder compared with the Aire at Allerton. In principle a mass-balance may be constructed to predict the concentrations of total permethrin downstream of the confluence assuming conservative behaviour during transport through this river section. The mean daily river discharge over the study period was  $13.6 \text{ m}^3 \text{ s}^{-1}$  at Allerton,  $23.3 \text{ m}^3 \text{ s}^{-1}$  at Methley and  $37.7 \text{ m}^3 \text{ s}^{-1}$  at Beal. The concentration of permethrin at Beal may be predicted at each sampling occasion from the river discharge and concentration data before the confluence and the river discharge at Beal. The results of this calculation are shown in Fig 4 for dates when sampling was done at all three sites. On some occasions the concentrations at Beal were consistent with the conservative transport, with agreement between the predicted and measured values. However, most of the data ( $\approx 70\%$ ) indicate a predicted concentration greater than the measured value and

**Table 2.** Occurrence and concentrations of permethrin isomers in major rivers delivering to the Humber

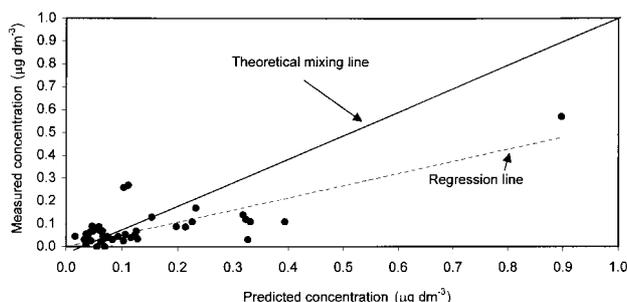
River	<i>Cis</i> -permethrin			<i>Trans</i> -permethrin		
	Occurrence	Mean ( $\mu\text{g dm}^{-3}$ )	Maximum ( $\mu\text{g dm}^{-3}$ )	Occurrence	Mean ( $\mu\text{g dm}^{-3}$ )	Maximum ( $\mu\text{g dm}^{-3}$ )
Don	6	0.014	0.022	20	0.024	0.061
Trent	6	0.023	0.039	5	0.013	0.017
Ouse	1	0.024		11	0.02	0.092
Aire (1) <sup>a</sup>	17	0.011	0.028	23	0.023	0.062
Aire (2) <sup>a</sup>	94	0.026	0.113	96	0.036	0.177
Calder	107	0.067	1.39	109	0.097	2.11

<sup>a</sup> (1) River Aire at Allerton Bywater, upstream of the confluence with the River Calder, sampled between 7 November 1995 and 16 December 1996. (2) River Aire at Beal at the intertidal limit. All rivers apart from the Aire at Bywater were sampled between 24 October 1994 and 16 December 1996.



**Figure 3.** Concentration of total permethrin (*cis*+*trans* isomer) in the rivers Calder (a) and Aire (b) and (c). Allerton (b) is on the River Aire at a location upstream of the confluence with the River Calder, and Beal (c) is at the tidal limit on the River Aire.

hence a loss of permethrin from the system during transport downstream. The greatest losses occurred at relatively low discharge, ie  $<20\text{ m}^3\text{ s}^{-1}$ , but there was an occasion when a high loss occurred at a flow of  $c\ 60\text{ m}^3\text{ s}^{-1}$  at Beal. A similar calculation for suspended solids at the three sites shows conservative behaviour, apart from during major storms when flooding led to overbank-flow and large losses of suspended material. Hence the loss of permethrin at other times must be a result of a change in the composition of the suspended



**Figure 4.** Comparison of the measured concentrations of permethrin in 'whole water' samples with values predicted assuming conservative mixing. The full line is the theoretical mixing line and the dotted line is the regression line through the data.

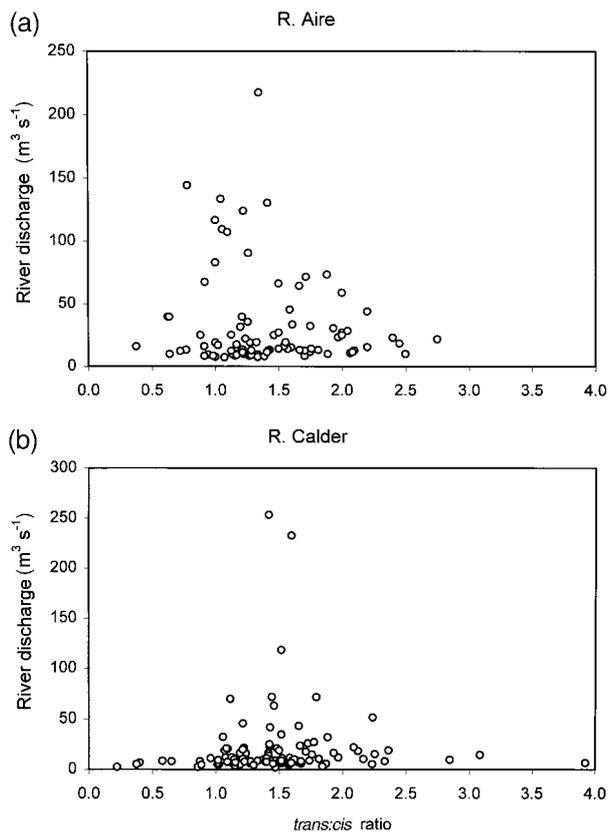
matter that affected the interaction with permethrin eg particle-size distribution or organic carbon content, possibly combined with kinetic effects through uptake to either bed or suspended material or degradation.

The ratios of the occurrence of the two permethrin isomers (*trans*:*cis*) were found to be similar for the rivers Aire and Calder, with values of  $1.48 (\pm 0.79)$  (SD) and  $1.48 (\pm 0.57)$  respectively. The mean ratio for samples from Allerton Bywater was  $2.29 (\pm 1.22)$ , but as it has based on the analysis of 15 samples it was not significantly different (*t*-test, 95% confidence limit) from the results for the other sites. Ratios close to the mean were measured for both rivers at the highest river discharge with a wide range of values at lower discharge. This may reflect the lower frequency of high discharge conditions that were measured, or the effects of greater retention of permethrin in the river during periods of low flow. During such periods it is expected that permethrin discharged to the river will exchange with in-stream components, particularly sediments, and lead to a range of isomer ratios depending on the history of the particles in the water. This is because the *trans* isomer is more rapidly degraded than the *cis* isomer in both oxic and anoxic conditions and therefore a decrease in the *trans*:*cis* ratio is expected as the retention in the river increases.<sup>18–21</sup> Isomerization of the *trans* isomer to the *cis* isomer also occurs by photolysis.<sup>9</sup> Most degradation half-lives have been measured in soil, and values reported vary from 6 to 105 days.<sup>22</sup> Jordan *et al*<sup>19</sup> also found a strong temperature-dependence, with degradation half-lives in a sandy loam soil of 55 days and 14 days for the *cis* and *trans* isomers respectively at  $10^\circ\text{C}$ . As the *trans*:*cis* ratio of commercial products ranges from 0.8 to 3.0,<sup>23</sup> and cover the measured range (Fig 5), it is not possible to draw any definite conclusions about the effects of residence on the measured ratios in the bulk river-water without a more detailed survey of sources in the Aire and Calder catchments.

There is some evidence for the mobilisation of permethrin during storm events from the concentration-discharge relationships for the River Aire, but this is not so evident for the River Calder (Fig 6). Contaminants from point-sources in the catchment usually show an inverse relationship between their concentration and river discharge as the contaminants are diluted with surface and sub-surface run-off containing little or none of the contaminant. In the River Aire, discharges  $>50\text{ m}^3\text{ s}^{-1}$  led to the highest concentrations of permethrin (Fig 6), suggesting the mobilisation of contaminated sediments in the Aire system or storm inputs.

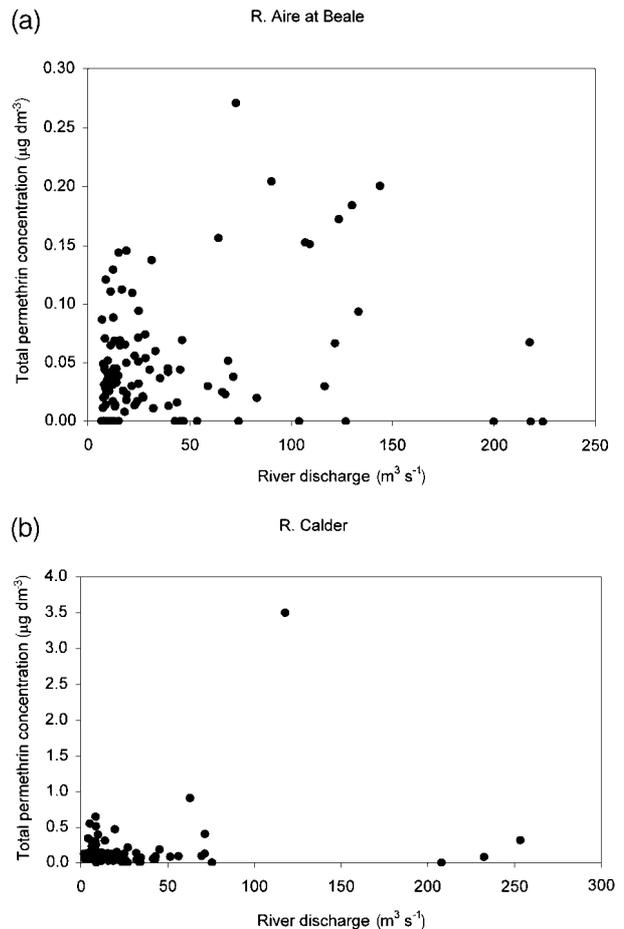
### 3.3 Intensive campaigns

The results from the weekly and storm sampling indicated periods when concentrations in the river water changed rapidly between sampling dates (Fig 3). This was also found during the intensive campaign on the River Aire (Table 1) when the concentrations



**Figure 5.** Comparison of the distribution of the *trans:cis* ratios of permethrin in 'whole water' samples collected during the weekly and storm sampling with values of river discharge for the Aire (a) and Calder (b).

changed markedly during the steepest part of the falling hydrograph and then settled at values  $<0.1 \mu\text{g dm}^{-3}$  (Fig 7). Peak values greater than  $0.6 \mu\text{g dm}^{-3}$  occurred twice during the campaign. These peaks did not coincide with an increase in the concentration of permethrin associated with suspended solids, as there was a monotonic decrease in suspended solids concentration from  $c 30 \text{ mg dm}^{-3}$  to  $9 \text{ mg dm}^{-3}$  during the sampling (see Fig 7). A comparison of the 3-hourly averaged data for permethrin in 'whole water' with that associated with suspended sediment in the water, the latter calculated from the average suspended solid concentration and concentration of permethrin on suspended sediment, revealed large variations in the contribution of suspended sediment to the transport of permethrin. This is shown in Table 3, with the greatest contributions of 30–90% at the lowest flows during the latter part of the sampling period. This implies that the peaks in concentration measured in the 'whole water' samples at 3–6h and 9–12h are caused by increases in dissolved or colloid-bound permethrin in the water, possibly as a result of a point discharge of dissolved or colloid-bound material. This result is also supported by previous research on the River Aire in which the calculated contribution of suspended solids to the transport of permethrin varies between 0.1% and 30%.<sup>4</sup> Similar calculations for the published data for the River Calder give contributions between 3% and



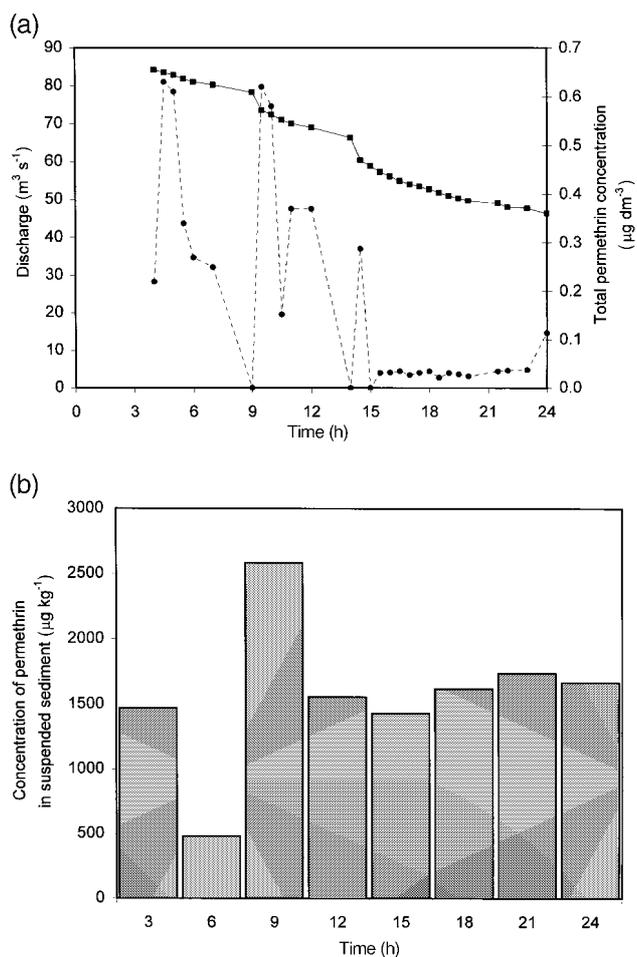
**Figure 6.** Relationship between river discharge and total permethrin concentration in 'whole water' samples collected during the weekly and storm sampling of the rivers Aire (a) and Calder (b).

21% during quarterly sampling over 1 year in 1995/96.<sup>4</sup>

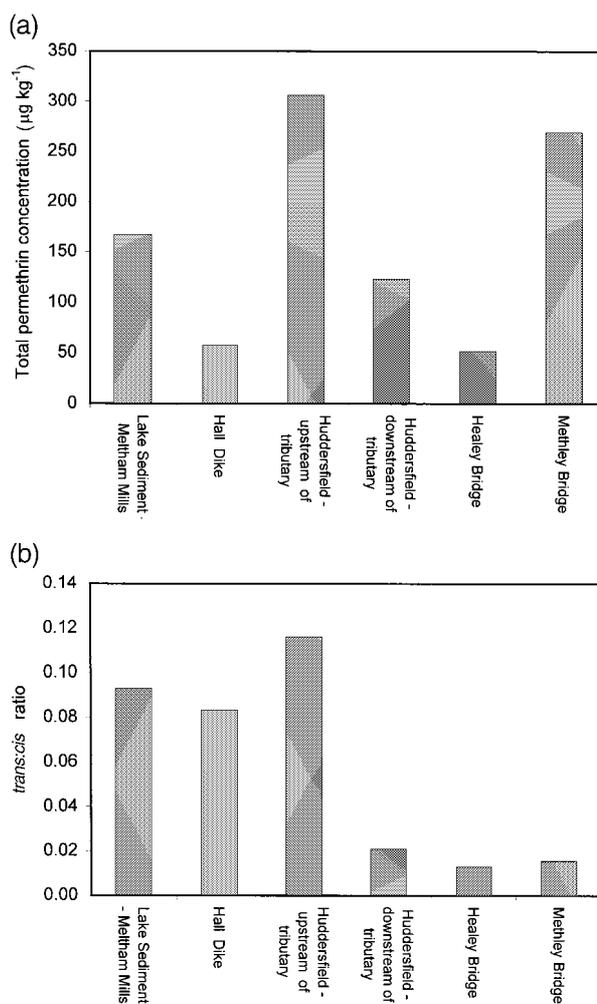
Previous research has shown that, under the conditions of sampling employed here, the continuous-flow centrifuge collects sediment particles of size typically  $>3 \mu\text{m}$ .<sup>24</sup> Hence finer sediments and colloids (defined as  $<1 \mu\text{m}$  in size<sup>25</sup>) are extracted in the 'whole water' together with dissolved permethrin. Although no measurements of organic or clay colloids were made during the period, values of dissolved organic carbon (DOC) from the LOIS monitoring programme were in the range of  $7.8\text{--}11.2 \text{ mg dm}^{-3}$  during the weekly sampling in November 1996.<sup>26</sup> When combined with the high distribution coefficient for organic colloids expected for permethrin,<sup>27</sup> ie  $>50\,000 \text{ dm}^{-3} \text{ kg}^{-1}$ , this range in concentration of DOC is sufficient to account for the non-sediment-bound fraction of permethrin in the samples.

### 3.4 Bed-sediment surveys

Concentrations of total permethrin in surface sediments varied between  $c 50$  and  $300 \mu\text{g kg}^{-1}$  at sites on the River Calder (Fig 8). The concentration at Methley Bridge, near the confluence with the River Aire, was lower than that previously measured<sup>4</sup> possibly reflecting temporal or seasonal changes. As



**Figure 7.** Intensive measurements of the occurrence of permethrin in the River Calder on 16–17 January 1997. (a) Changes in river discharge (—■—) and concentrations of total permethrin (---●---) measured in ‘whole water’ samples. (b) Concentrations measured in the suspended solids isolated by continuous-flow centrifugation over consecutive periods of 3 h.



**Figure 8.** Comparison of the occurrence of total permethrin (a) and the *trans:cis* isomer ratio (b) in surface bed-sediments from the River Calder catchment (see Fig 1 for site locations). Total concentrations are expressed relative to dry weight of sediment.

the sediment ‘hoovering’ technique integrates samples from a relatively large area of bed (approximately 5 m<sup>2</sup>), a comparison of values along the catchment is possible. As shown in Fig 8, there is no systematic trend in concentrations along the river. The *trans:cis* ratio does, however, decrease down the catchment to 0.02 at Methley bridge. The values found in the bed-sediment are in contrast to those found for permethrin

in ‘whole water’ samples. The weekly and storm sampling data give values of 1.48 (±0.57) for the River Calder, and this contrasts with 0.79 (±0.05) for suspended sediments extracted during the intensive campaign. The general decrease in the isomer ratio for permethrin in the order: ‘whole water’ > suspended sediment > bed-sediment, is consistent with the more rapid degradation and photolysis of the *trans* isomer

**Table 3.** Contribution of suspended solids to the transport of total permethrin, ie *cis+trans* isomers: All values are 3-hourly averages and solids masses are expressed as dry weight.

Time (h)	Concentration in SS <sup>a</sup> (µg kg <sup>-1</sup> )	Concentration in ‘whole-water’ (µg dm <sup>-3</sup> )	SS concentration (mg dm <sup>-3</sup> )	Permethrin associated with SS (%)
0–3	1471	—	—	—
3–6	480	0.41	26.8	3
6–9	2586	0.17	20.4	41
9–12	1557	0.35	18.4	9
12–15	1432	0.17	13.9	15
15–18	1621	0.026	12.3	87
18–21	1738	0.029	10.9	74
21–24	1666	0.055	9.8	32

<sup>a</sup> SS: suspended solids.

compared with the *cis*, and differences in retention time of permethrin in different parts of the system. Permethrin dissolved in fresh water or associated with natural colloids is expected to be retained for a shorter period in the river compared with permethrin on suspended solids or settled in the bed-sediment.<sup>28</sup> As the retention of permethrin increases, the difference in persistence of the isomers leads to the observed changes in the isomer ratio.

This can be further explored if it is assumed that the isomer ratio in the whole water samples reflect the initial ratios prior to retention, ie 1.48 ( $\pm 0.57$ ) for the River Calder. It is then possible to estimate the retention time of the compound in the river using first-order degradation rates measured in soils at 10 °C by Jordan *et al*<sup>19</sup> using the equation:

$$\frac{c_{\text{tran}}}{c_{\text{cis}}} = \frac{c_{0(\text{tran})}}{c_{0(\text{cis})}} \exp[t(k_{\text{cis}} - k_{\text{tran}})]$$

where  $c_{\text{tran}}$  and  $c_{\text{cis}}$  the isomer concentrations after a residence time  $t$ , starting with concentrations of  $C_0$ , and  $k_{\text{cis}}$  and  $k_{\text{tran}}$  are the rate constants of 0.0126 day<sup>-1</sup> and 0.049 day<sup>-1</sup> for *cis*- and *trans*-permethrin respectively. This choice of rate constants is also consistent with the changes isomer ratio measured for permethrin in a pond sediment, ie changing from 1.27 to 0.19 over 35 to 70 days and reducing to zero after 323 days.<sup>9</sup> This approach leads to estimates of the retention time of permethrin associated with suspended sediments of 4–26 days ( $c_{\text{tran}}/c_{\text{cis}} = 0.79$ ). The bed-sediment retentions were estimated from the ratios given in Fig 8 for the highest value found at the upstream site, ie 0.1, and the lowest value at Methley Bridge at the downstream site, ie 0.02. These figures lead to retention times of 60–82 days and 103–125 days respectively.

Multiple regression analysis showed that mineral composition, specific surface area and total organic content of the sediment had little influence on the total permethrin content of the sediment (Table 4). This is surprising considering the strong affinity of permethrin with organic matter ( $\log K_{\text{ow}} = 6.2$ ). Another complication is the strong affinity of permethrin for algal cells and invertebrates in sediments.<sup>28,29</sup> Even for sediments with the lowest organic carbon, eg 0.63% at the upstream site at Meltham, it is likely that high-energy

sorption sites on the sediment are in excess and do not limit the sorption of permethrin.

### 3.5 Toxicological effects

Permethrin dissolved in water is known to be extremely toxic to a wide range of invertebrates.<sup>1</sup> The many studies that have been reported are difficult to compare because of the wide range of physical and chemical variables in the experimental design and because experiments have covered a wide time scale. A wide range of aquatic invertebrates show ecotoxicological responses at concentrations  $< 2 \mu\text{g dm}^{-3}$ . Behavioural changes can have larger long-term effects on population densities than single organism mortality. This has been demonstrated by the immobilisation of invertebrates after exposure to permethrin and their subsequent drift with the flow of water, eg *Ephemeroptera*, *Trichoptera*, *Plecoptera*, *Diptera* and *Amphipoda*.<sup>30</sup> The length of the exposure is also crucial to the ecotoxicological effects observed. For example, *Brachycentrus* had a  $\text{LC}_{90-95}$  value of  $1.0 \mu\text{g dm}^{-3}$  but a concentration of  $0.02 \mu\text{g dm}^{-3}$ , although showing no immediate toxic effect, resulted in 55% mortality after 28 days exposure.<sup>31</sup>

The toxicity of sediment-associated permethrin is relatively poorly studied. It depends on the partition between the aqueous and solid phases as well as on the total concentration in the sediment. Toxicity tests with both artificial and natural sediments with *Chironomus riparius* larvae have shown that the results are sensitive to both the concentration of permethrin used in the test and the type of sediment employed. All sediments showed a reduction in the number of emerged adults at nominal test concentrations of  $200 \mu\text{g kg}^{-1}$  (dry weight) compared with a control vessel without permethrin.<sup>32</sup> Hence adverse ecotoxicological effects are expected at the bed-sediment concentrations listed for Huddersfield and Methley (Table 4).

The impact on benthic invertebrates of a pulse application to streams, eg accidental spillage or drift of spray during applications to crops, has been found to be severe when peak concentrations of  $0.3\text{--}2 \mu\text{g dm}^{-3}$  occurred<sup>33,34</sup> but recolonisation was rapid with full restoration of the communities in 6 weeks after impact.<sup>34</sup> However, the situation is different when the exposure is continuous, as in the rivers Aire and Calder (Fig 3), rising above known ecotoxicological

Site <sup>a</sup>	Total permethrin concentration ( $\mu\text{g kg}^{-1}$ dry wt)	Specific surface area ( $\text{m}^2 \text{g}^{-1}$ )	Total organic carbon (%)	Clay (%)	Silt (%)	Sand (%)
Meltham (1)	167	10.9	0.63	1.4	42.1	55.4
Hall Dike (2)	56	8.0	8.53	2.9	55.4	41.2
Huddersfield (3.1)	305	3.2	0.97	3.0	42.7	55.4
Huddersfield (3.2)	122	7.3	2.39	4.1	61.2	36.2
Healey (4)	51	1.3	1.45	2.1	52.7	46.2
Methley	268	8.7	8.67	3.7	45.3	53.0

**Table 4.** Characterisation of sediments from the River Calder.

<sup>a</sup> Number in brackets indicates site number in Fig. 1.

effect concentrations for sensitive organisms such as crustaceans.<sup>35</sup> Also, the sediments in slower flowing rivers are less mobile than in small streams that are invariably used in impact studies, and so retain their sediments and associated contaminants for longer.

#### 4 CONCLUSIONS

- 1 Permethrin was frequently detected in 'whole water' and sediment samples from the rivers Aire and Calder and rarely in the other rivers, the Don, Trent or Ouse. This reflects the industrial usage of the insecticide in the Aire and Calder catchments, particularly in relation to textile processing and manufacture.
- 2 Concentrations of permethrin found in bed-sediment are likely to give rise to ecotoxicological effects in the benthic macro-invertebrate community.
- 3 Mass-balance calculations indicate losses of permethrin from the water column during transport. Permethrin-sediment associations can be very significant, particularly at low-flow when up to 90% of the total permethrin in the water column may be suspended-sediment bound, (particles >c 3 µm).
- 4 An examination of isomer ratios (*trans:cis*) allows an appreciation of retention times for permethrin in different components of the systems. It was found that retention times increased in the order bed-sediment > suspended sediment > 'whole water', with estimates of 4–26 days for suspended sediment and a maximum of 103–125 days for surface bed-sediments.

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