Institute of Freshwater Ecology

Transportation of Pesticides by Colloids
Final Report

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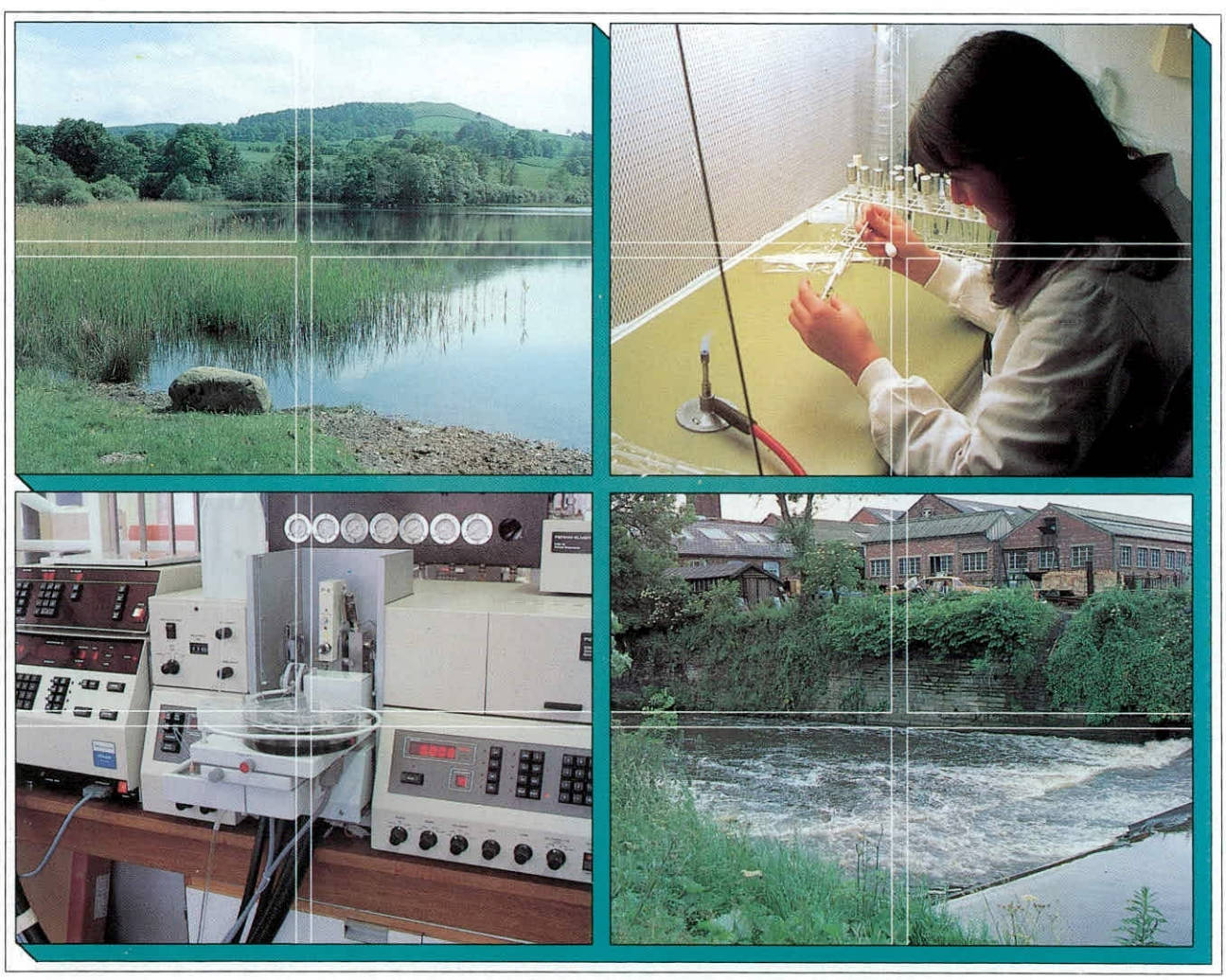

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CONTENTS

GLOSSARY

C_{coll}: Concentration of pesticide associated with colloids
C_f: Concentration of pesticide in the filtrate
C_p: Concentration of pesticide associated with suspended solids
C_s: Concentration of pesticide in the supernatant
C_{sol}: Concentration of pesticide "free" in solution
C_{tot}: Total concentration of pesticide in the sample
C_w: Concentration of pesticide in water in resin experiments
CFC: Continuous-Flow-Centrifugation
CV%: Coefficient of variation in percentage
DOC: Dissolved Organic Carbon
EA: Environment Agency, UK.
EC: End-Capped
EtAc: Ethyl acetate
IFE: Institute of Freshwater Ecology - component Institute of NERC
k_d: Distribution coefficient
k_{doc}: Distribution coefficient for dissolved organic carbon.
k_{oc}: Distribution coefficient for organic carbon component of sediment, soil or colloid.
k_{om}: Distribution coefficient for organic matter component of sediment or soil.
k_b: Distribution coefficient for bottle in resin experiments
k_r: Distribution coefficient for resin
K_A: Acid dissociation constant
K_B: Base dissociation constant
K_{ow}: Octanol - water partition coefficient
L_{rc}: Adsorption of pesticide to resin
LOIS: Land Ocean Interaction Study - a thematic programme of NERC
NERC: Natural Environment Research Council
NOM Natural Organic Matter
NPD: Nitrogen Phosphorus Detector (GC)
OC: Organic Carbon
PTV: Programmable Temperature Vapouriser injector (GC)
SFE: Supercritical Fluid Extraction
SOP: Standard Operating Procedure
spe: Solid-phase extraction
SS: Suspended Sediment concentration in mg dm^{-3}
UFC: Ultra-Filtration Cell

EXECUTIVE SUMMARY

Colloids are naturally occurring particles or large polymer molecules in the size range of 1-1000 nm, i.e. < 1 μm in diameter, which do not settle from fresh waters on standing. Larger particles are generally considered to be suspended in water and are kept in this state by the movement of the water. Colloids are generally more mobile in the environment compared with sediments and behave in a similar way to chemicals which are dissolved in water. Some pesticides, such as the synthetic pyrethroids which are extremely toxic to aquatic organisms, are only very slightly soluble in water but are very strongly bound to sediment particles and colloids. The association of such compounds with colloids has important implications for their translocation in the environment and movement from rivers to lakes and estuaries, and through the soil to groundwater. The current research was aimed at obtaining more information about the role of colloids in the fate and behaviour of pesticides and the development of practical methods to assess their relative importance. The methods developed will be of value in the assessment of the importance of colloid transport in the environmental fate of pesticides considered for registration purposes.

Routine analysis of natural waters for pesticides normally involves filtration of the samples prior to analysis and therefore neglects the contributions of suspended solids and a large fraction of the colloid component to the pesticide content of the sample. When samples are not filtered but treated as "whole water" samples, depending on the method used to extract the pesticides from the sample, some part of the colloid and sediment associated pesticides will be measured. The alternative method of separating the colloids and sediments from the water, and extracting these independently of the water sample, is a complex procedure, very time consuming and is impractical on a routine basis. Future development of analytical techniques to ensure that pesticides associated with suspended clays and other colloids are include in the reported concentrations to the appropriate regulators is needed. **This study shows that the analysis of "whole water" samples is essential if the pesticides which are bound to colloids and suspended material are to be determined. The analysis of filtered water samples will produce a very incomplete picture of the occurrence of pesticides in rivers and fate of pesticides applied in agriculture.**

This project examines in detail the interaction of selected pesticides with three major groups of colloids (a) clay particles, (b) macromolecules of humic/fulvic acid, i.e. part of the organic colloids and (c) inorganic colloids consisting of predominantly mineral particles. The study shows the importance of organic colloids in transporting a range of pesticides in rivers. Even relatively weakly adsorbed herbicides such as simazine, have a relatively strong affinity with organic colloids when compared with their affinity to organic carbon in soils. In view of the complex nature of colloids and sediments, a pragmatic approach is suggested in which routine water quality measurements are used to estimate the transport of pesticides with colloids and other particulates in rivers. Suspended solids measurements by filtration of the sample through a 0.45 μm membrane include clay and mineral colloids with the larger sediment particles. **Standard field measurements of the suspended solids concentration and dissolved organic carbon content may then be used with the appropriate distribution coefficients, to estimate the relative amounts of bound pesticide.**

SPECIFIC ADVANCES

- An automated ultra-filtration system has been developed and used to measure the distribution of a range of triazine and organophosphorus pesticides between the dissolved phase and organic colloids in river water.

- Organic colloids were found to interact strongly with a range of pesticides. Measurement of the distribution coefficients using the ultra-filtration cell containing fresh waters from the Humber rivers (Aire, Calder, Trent, Don and Swale) with atrazine, simazine, propazine, prometryn, desmetryn, terbutryn, cyanazine, parathion, fenitrothion and malathion, gave high distribution coefficients in the range of 7900 to 36,000 ml g^{-1} , normalised with respect to dissolved organic carbon. **Differences in the sorption affinities between the pesticides were generally in accordance with their octanol-water partition coefficients .**
- Field data from the rivers Aire (2 sites), Calder, Ouse, Trent and Don, from samples collected during storms and weekly monitoring, showed the presence of a wide range of pesticides including simazine, atrazine, prometryn, desmetryn, terbutryn, malathion, parathion and fenitrothion, *cis* and *trans* permethrin, dieldrin and lindane, e.g. over 90 % of the samples from the R. Calder contained lindane, permethrin and simazine at concentrations greater than 0.01 μg dm^{-3}. **The data were consistent with the mobilisation of permethrin and dieldrin with suspended sediments during storms and the strong affinity of permethrin with suspended sediments.**
- The importance of organic colloids in the transport of triazine and organophosphorus pesticides in the R. Aire was estimated using the distribution coefficients measured with the ultra-filtration cell together with field data of dissolved organic carbon and suspended sediments from the NERC LOIS (Land Ocean Interaction Study). The majority of the bound material was predicted to be with organic colloids measured as dissolved organic carbon, leading to maximum concentrations in periods of low-flow. **Up to 20 % of the triazine load was transported with colloids and suspended matter compared with up to 30 % for the selected organophosphorus compounds.**
- The good relationship between the distribution coefficients and the octanol-water partition coefficients for the triazines, organophosphorus compounds and literature data for polyaromatic hydrocarbons and DDT, permitted an estimate of the appropriate distribution coefficients. **This led to a prediction of between 70 and 90 % of permethrin and dieldrin in the R. Aire water associated with organic colloids and suspended sediments - with the majority sorbed to organic matter. The predictions for lindane were similar to the values obtained for the organophosphorus compounds.**
- Suspended sediments in the rivers Aire, Ouse and Swale were mainly composed of material of less than 900 μm diameter with the clay fraction, < 2 μm, generally < 10 % by volume but up to 30 % by mass. The R. Aire sediment was mainly clays such as montmorillonite, kaolinite, chlorite and illite. The majority of this material was separated during centrifugation leaving only the organic colloids in the centrifugate. The interaction of selected pesticides with clay colloids was exothermic and the isotherms linear at low concentrations. The specific interactions of flutriafol with clay colloids was investigated using molecular modelling. The interaction was found to be dominated by hydration and hydrogen bonding with a possibility for acid-base interactions with surface hydroxyl groups on the clay. The herbicide is unlikely to enter the interlayer spacing of the expandable clays such as montmorillonite. Sorption was not found to be strongly dependent on salinity with the greatest increase between 0.001 and 0.01 M NaCl, e.g. rainwater to hard water. Subsequent increases in dissolved solids to sea water concentrations, had a very small effect on sorption but such increases are expected to lead to particle aggregation in the water column. **It is concluded that molecular modelling is a powerful tool to gain insight to the binding mechanisms between surfaces and pesticides.**

1.0 PROJECT DESCRIPTION

Colloids are small particles and macromolecules which because of their chemical structure and high specific surface area, have a high affinity for pesticides. However, unlike suspended sediments, colloids are usually very mobile and are transported easily with fresh water and ground water without sedimenting. As a result, pesticides which are often considered as insoluble in water, are mobilised by their interaction with colloids and transported with water until they flocculate or degrade.

The majority of contaminants entering surface waters and discharging to the sea, regardless of their source, do not remain dissolved in the water but become adsorbed onto suspended solids and may at some stage sediment out. They may also be associated with colloids which are unlikely to sediment out. Consequently, movement of most contaminants from the source of inputs is a complex process and is a only loosely related to major water movement patterns. Understanding the movement and partitioning of contaminants is important in assessing their impact in surface waters and loading to the sea. The project seeks to improve the understanding of the role of colloids in the long-range transportation of contaminants, and in particular of pesticides.

2.0 PROGRAMME OF WORK

The objectives are:

- To measure the affinity between pesticides and natural colloids over a range of colloid and pesticide concentrations; also to assess the influence of salinity on this affinity.
- To determine the physical and chemical characteristics of the colloid which determine their interaction with selected pesticides.
- To evaluate the flux of colloid bound pesticides to an estuary of a selected river.
- To assess potential problems associated with flocculation of colloid bound pesticides in saline waters.

3.0 INTRODUCTION

Colloids are finely divided particulates which exhibit properties of specifically "colloidal character" i.e. are relatively stable compared to particle suspensions and are maintained in this state by Brownian motion; the dimensions in the dispersed phase lie in the range of 1-1000 nm, i.e. diameter up to 1 μm (Everett, 1992). These limits are not rigid and very often some dimension of the particle is outside the colloid range, e.g. some naturally occurring fibrils - typically 2-20 nm in diameter but sometimes greater than 1 μm in length (Leppard, 1997). In aquatic chemistry, the upper limit is conveniently taken as 0.45 μm or 0.70 μm, the membrane filter sizes usually used to separate the dissolved and particulate phases. It is also recognised that this cut-off is arbitrary because, in practise, the filtration properties of the membrane will be partly determined by the particulate-bed which forms on the filter surface once filtration starts. This in turn is determined by the size-distribution, density and suspended solids concentration of the sample being filtered. Surprisingly, there has been little work to document colloid sizes passing through membranes and how this depends on the sediment concentration in the sample (Hermans *et al.*, 1992)

The isolation and chemical characterisation of natural dissolved organic carbon (DOC) and colloids has been reviewed by Aiken and Leenheer (1993) and is an area of rapidly growing interest where new analytical and separation techniques are needed to understand the complex mixtures present in most environmental samples.

Natural colloids may be divided into the following groups:
1. Clay particles or aggregates with associated surface coatings of other minerals such as calcium carbonate/phosphates, iron or manganese oxyhydroxides or "organic" material (Zhou *et al.*, 1994; Murphy *et al.*, 1992). The mechanisms of interaction of clay minerals with pesticides has been reviewed by House (1998).

2. Macromolecules of humic or fulvic acid derived from humic substances (MacCarthy and Suffet, 1989). These may also be considered to be dissolved and measured as dissolved organic carbon (DOC). Mid- to high molecular constituents fall within the colloid range, e.g. a spherical colloid 2 nm in size with a density of 1.07 g ml^{-1} corresponds to an organic molecule of approximately 2500 Daltons (Dean, 1948). The mechanisms of interaction of humic substances with pesticides as been reviewed by Senesi (1992).

3. Inorganic colloids such as silica, hematite and calcium carbonate minerals - these are common components of natural colloidal mixtures (Higgo *et al.*, 1993; Tipping *et al*, 1993a; Lieser *et al.*, 1990) and may also have surface coatings similar to clay particles (House, 1998).

4. Organic fibrils composed of predominantly acid and neutral polysaccharides and other extra cellular polymers such as mucopolysaccharides. The polysaccharide chemistry varies according to the source of the material, biological speciation and environmental factors (Leppard, 1997).

Colloid mobilisation and transport in groundwater has been addressed in a recent review (Ryan and Elimelech, 1996). Mobilisation necessitates that the contaminants must be associated with colloid material, colloids must be present or generated in the system and pathways for colloid movement within the groundwater must be present. Although the transport of colloids may be modelled in such systems, there is little information available from natural systems to test and validate these models (Ryan and Elimelech, 1996; Higgo *et al*, 1993). At the moment only information about the association of contaminants with colloids is available for a limited number of systems (mainly radionuclides rather than micro-organic compounds) (Bachus *et al.*, 1993). Current knowledge about the mechanisms controlling the generation of colloids and transport is inadequate to predict these processes in natural systems. The main obstacle to progress in this field is the heterogeneity of natural sediments and their associated colloids (Ryan and Elimelech, 1996). For example, chemical perturbations such as decreasing ionic strength, increasing pH and increasing concentrations of surfactants and dissolved organic matter can mobilise colloids but these effects will depend on the surface chemistry of the sediment components. Physical effects such as colloid mobilisation through hydrodynamic shear in sediment/rock fractures and macropores very much depend on site specific data concerning the morphology and mineral composition of sediments. Much the same is true for river and lake colloids which are mobilised through chemical or physical perturbations such as the movement of contaminant plumes, storm waters changing the ionic

composition of the water or re-suspension of bed-sediments under increased bed-shear during high-flow events in a river.

In rivers both point and diffuse inputs of colloids are likely to be important. Diffuse inputs arise from natural processes such as the erosion of peat and associated humic substances in uplands (Tipping *et al.*, 1997), or mobilisation of soil colloids in agriculture, e.g. through surface or sub-surface runoff after ploughing or tilling the land. Although point-inputs to rivers and lakes are easily identified, the range of materials is likely to be large as it depends on sewage inputs, sewage treatment processes, local industry and river-water chemistry. In-stream or riverine generation of colloids is also likely to be important although, as yet, there is no information comparing the fluxes with other inputs. Riverine processes include, for example, the decay of vegetation and benthic biofilms (Leadbeater and Callow, 1992) bacterial and invertebrate extrudates - organic fibrils and polysaccaharides (Leppard, 1997), desegregation of faecal material and inorganic deposits and resuspension of fine particulates in riverine "dead zones" (Tipping *et al.*, 1993b; Carling *et al.*, 1994). Each of these processes is expected to have some seasonal variability and will again depend on the particular characteristics of the river, e.g. algal biofilms generally require a stable substrate to colonise and will not form easily on unstable bed-sediments in rivers which are subject to frequent spates.

Colloids are abundant in seawater with material between 0.4 and 1.0 μm recorded at concentrations of 10^7 particles ml^{-1} in near shore and pelagic waters (Koike *et al.*, 1994). Smaller colloids in the size range of 5 - 200 nm have also been measured at higher concentrations, e.g. > 10^9 particles ml^{-1} at various locations and depths in the North Atlantic, (Wells and Goldberg, 1994). In the latter study the morphology of the colloids collected from different locations and depths was very similar. The < 30 nm size colloids tended to be irregular in shape whilst the larger colloids (30 - 60 nm in diameter) were approximately spherical and often composed of small granules of 2 - 5 nm in size. Although there were no direct measurements in this study, the composition of the colloids is thought to be dominated by aggregates of relatively low molecular weight organic molecules of approximately 2,500 Daltons. Other work supports this proposal, e.g. the study of Benner *et al.* (1992) used tangential-flow-centrifugation to collect colloids from the North Pacific Ocean and found that high molecular weight polysaccharides composed an important part of the material. The sources of this organic material may be cellular material or exudates from phytoplankton and heterotrophic bacterial, egestion or excretion by invertebrate grazers, metabolic wastes from protozoans and cell lysis of algae or bacteria. Many of these sources also occur in rivers although, because of the greater influences of bottom sediments in many rivers, biological and chemical processes in the bottom sediments are likely to play a greater role in the generation of colloids, e.g. the production of polysaccharide exudates by algal and bacterial biofilms. Resuspensions of materials from the sea-bed has also been noted during episodic "storms" producing high energy near-bed flows which entrain colloid material into the overlying water (Gross *et al.*, 1988).

There is a vast literature on the characterisation of humic materials - see for example Suffet and MacCarthy (1989); Aiken and Leenheer (1993). Recent advances using field-flow fractionation and electron microscopy preparation techniques, have enabled much more

detailed information about the morphology and size-distribution of humic colloids and the effects of such factors as pH and ionic strength on the molecular configuration in aqueous solutions (Schimpf and Petteys, 1997; Contado *et al.*, 1997, Perret *et al.*, 1991). Using field-flow fractionation methods Schimpf and Petteys (1997), measured unimodal molecular weight distributions for a range of humic substances including Suwannee River fulvic acid and a soil humic. The peak molecular weights varied between 980 g mol^{-1} for the fulvic acid to 1350 g mol^{-1} for the soil humic with the humic acid having a greater portion of high molecular weight molecules. Decreasing the pH of the fulvic acid from 8.5 to 5.0 resulted in a shift of the distribution to smaller diameters, presumably as a result of the neutralisation of the molecular charge and subsequent compaction of the molecules. In contrast, the humic acid showed clear evidence for molecular aggregation as the pH was lowered. The effects of changes in solution ionic strength were dramatic, with the development of a bi-model distribution in the humic acid samples as the dissolved calcium concentration was raised to 4 mmol dm^{-3}. The results were consistent with the aggregation of molecules as the ionic strength increased followed by collapse of the aggregates at 15 mmol dm^{-3} . This is consistent with the formation of intra-molecular micelles and more compact structure (Senesi *et al*, 1997). Fulvic acid also undergoes similar changes in colloid size-distribution with increases in calcium concentration from 0 to 3 mmol dm^{-3} The distribution broadens indicating both increased aggregation and hydrodynamic collapse of unaggregated material (Schimpf and Petteys, 1997). In contrast, in solutions of NaCl (0- 32 mmol dm^{-3}), the shapes of the fulvic acid size-distributions did not change very much which probably indicates the less specific nature of the interaction of Na^{+} with the fulvic acid molecule compared with Ca^{2+}.

4.0 COMPOUNDS STUDIED

The pesticides studied in the present work cover a range of compounds commonly found in UK surface waters (Environment Agency, 1997), and monitored as part of the Land Ocean Interaction Study (LOIS) of the Humber catchment (House *et al.*, 1997; Long *et al.*, 1998; Meharg *et al.*, 1998). They encompass both very water soluble compounds, which are weakly adsorbed to surfaces, to extremely lipophilic and sparingly soluble compounds, such as the pyrethroid, permethrin, which are strongly adsorbed to surfaces by a predominantly hydrophobic interaction. The compounds include organochlorine insecticides such as lindane and dieldrin, the modern insecticides - synthetic pyrethroids, *cis/trans* permethrin, organophosphorus insecticides such as parathion and malathion, and a wide range of triazine herbicides as well as fungicides such as flutriafol.

Atrazine
2-chloro-4-ethylamino-6-isopropylamino-S-triazine, $C_8H_{14}ClN_5$, CAS: 1912-24-9
Molecular weight= 215.69
Use: Selective pre- and post emergence herbicide formulated as wettable powder, dispersible liquid and granules.
Sorption coefficients, k_{oc}: 57 - 174 ml g^{-1}

Simazine
2-chloro-6,6-bis(ethylamino)-S-triazine, $C_7H_{12}ClN_5$, CAS: 122-34-9
Molecular weight= 201.66

Use: Selective pre-emergence herbicide recommended for the control of broad-leaved and grass weeds in deep-rooted crops. It is formulated as wettable powder, dispersible liquid and granules.
Sorption coefficients, k_{oc}: 4 - 2200 ml g^{-1}

Desmetryn
2-isopropylamino-4-methylamino-6-methylthio-1,3,5-triazine, $C_8H_{15}N_5S$
Molecular weight= 213.3
Use: Selective post-emergence herbicide.
Sorption coefficients, k_{oc}: range not known.

Prometryn
N,N'-bis(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine, $C_{10}H_{19}N_5S$,CAS: 7287-19-6
Molecular weight= 241.4
Use: Selective pre- and post-emergence herbicide recommended for vegetables. It is formulated as a dispersible.
Sorption coefficients, k_{oc}: 150 - 2381 ml g^{-1}

Terbutryn
2-tert-butylamino-4-ethylamino-6-methylthio-S-triazine, $C_{10}H_{19}N_5S$, CAS: 886-50-0
Molecular weight= 241.4
Use: Selective pre-emergence herbicide recommended for winter cereals. It is formulated as wettable powder, dispersible liquid and granules.
Sorption coefficients, k_{oc}: 700 - 15600 ml g^{-1}

Fenitrothion
O,O-dimethyl O-4-nitro-m-tolyl phosphorothioate, $C_9H_{12}NO_5PS$, CAS: 122-14-5
Molecular weight= 277.2
Use: Contact insecticide. It is formulated as wettable powder, dispersible powder and emulsifiable concentrate.
Sorption coefficients, k_{oc}: 424- 14500 ml g^{-1}

Malathion
diethyl (dimethoxyphosphinothioyl)thiobutanediote, $C_{10}H_{19}O_6PS_2$, CAS: 121-75-5
Molecular weight= 330.3
Use: Non-systemic insecticide and acaricide. It is formulated as wettable powder, emulsifiable concentrate, oil solution and dust..
Sorption coefficients, k_{oc}: 93 - 1800 ml g^{-1}

Cyanazine
2[[4-chloro-6-(ethylamino)-S-triazin-2-yl]amino]-2-methyl propionitrile, $C_9H_{13}ClN_6$, CAS: 21725-46-2
Molecular weight= 240.7
Use: pre- and post- emergent herbicide for general weed control. It is formulated as wettable powder, dispersible liquid and dispersable granules.
Sorption coefficients, k_{oc}: 116 - 500 ml g^{-1}

Parathion
O,O-diethyl O-4-nitrophenyl phosphorothioate, $C_{10}H_{14}NO_5PS$, CAS: 56-38-2
Molecular weight= 291.27
Use: Non-systemic insecticide and acaricide. It is formulated as wettable powder, emulsifiable concentrate.
Sorption coefficients, k_{oc}: 350 - 34674 ml g^{-1}

Dieldrin
(1R,4S,4aS,5R,6R,7S,8S,8aR)-1,2,3,4,10,10-hexachloro1,4,4a,5,6,7,8,8a-octahydro-6,7-epoxy-1,4:5,8-dimethanonapthalene, $C_{12}H_8Cl_6O$, CAS: 60-57-1
Molecular weight= 380.9
Use: Non-systemic insecticide and acaricide. It is formulated as wettable powder, emulsifiable concentrate and granules.
Sorption coefficients, k_{oc}: 3982 - 50000 ml g^{-1}

Lindane
1,2,3,4,5,6-hexachlorocyclohexane (BHC- γ-isomer), $C_6H_6Cl_6$, CAS: 58-89-9
Molecular weight= 290.85
Use: Insecticide used in agriculture and timber preservation. It is formulated as wettable powder and emulsifiable concentrate.
Sorption coefficients, k_{oc}: 686 - 12400 ml g^{-1}

Permethrin
3-(phenoxyphenyl)methyl(1RS)-cis,trans-3 (2,2-dichloroethenyl)-2,2-dimethylcyclopropane carboxylate, C21H20Cl2O3, CAS: 52645-53-1.
Molecular weight= 391.30
Use: Contact insecticide. It is formulated as wettable powder, emulsifiable concentrate and granules.
Sorption coefficients, k_{oc}: 33300 - 134000 ml g^{-1}

Flutriafol
(RS)-2,4'-difluoro-a-(1H-1,2,4-triazol-1-ylmethyl)-benzhydryl alcohol, $C_{16}H_{13}F_2N_3O$, CAS: 76674-21-0.
Molecular weight= 301.3
Use: Systemic fungicide used as a spray on cereals.
Sorption coefficients, k_{oc}: range not known.

Propiconazol
1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]-1H-1,2,4-triazole, $C_{15}H_{17}Cl_2N_3O_2$, CAS: 60207-90-1
Molecular weight= 342.2
Use: Systemic foliar fungicide used on cereals. It is formulated as an emulsifiable concentrate.
Sorption coefficients, k_{oc}: 387 - 16897 ml g^{-1}

Trifluralin
2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)benzenamin, $C_{13}H_{16}F_3N_3O_4$, CAS: 1582-09-8
Molecular weight= 335.28
Use: Pre-emergent herbicide. It is formulated as an emulsifiable and granules
Sorption coefficients, k_{oc}: 1200 - 13700 ml g^{-1}

Isoproturon
3-(4-isopropylphenyl)-1,1-dimethylurea, $C_{12}H_{18}N_2O$, CAS: 34123-59-6
Molecular weight= 206.3
Use: Herbicide for control of annual grasses.
Sorption coefficients, k_{oc}:

Data source: A.G. Hornsby, R.D. Wauchope, A. E. Herner, (1996). Pesticide Properties in the Environment, Springer, New York.

TABLE 4.1 *List of the compounds included in the study with their associated physicochemical properties*

Name	Solubility /mg dm^{-3}	Half-Life /d	Soil sorption k_{oc}/ ml g^{-1} OC	Vapour pressure /mm Hg	Base pK_B
atrazine	33	60	100	$2.89x10^{-7}$	12.32
simazine	6.2	60	130	$2.21x10^{-8}$	12.35
desmetryn	580	-	-	$9.9x10^{-7}$	
prometryn	33	60	400	$1.238x10^{-6}$	9.95
terbutryn	22	42	2000	$2.1x10^{-6}$	9.7
fenitrothion	30	4	2000	$1x10^{-6}$ E	
malathion	130	1	1800	$8x10^{-6}$	
cyanazine	170	14	190	$1.6x10^{-9}$	12.9
parathion	24	14	5000E	$5x10^{-6}$	
dieldrin	0.2	1000E	12000E	$3x10^{-6}$	
lindane	7	400	1100	$3.3x10^{-5}$	
permethrin	0.006	30	100000	$1.3x10^{-8}$	
flutriafol	130	-	-	$3.0x10^{-9}$	
propiconazol	110	110	650	$4.2x10^{-7}$	
trifluralin	0.3	60	8000	$1.1x10^{-4}$	
isoproturon	55	-	-	$2.5x10^{-8}$	

KEY: E: *Estimated because of the diverse range of values found in the literature; OC: Organic Carbon.*

5.0 ULTRA-FILTRATION CELL

5.1 Development of an automated ultra-filtration unit

No apparatus is commercially available to enable measurements of the distribution of micro-organic compounds in true solution and in naturally occurring colloids. Previous research at

IFE has shown that the dialysis method of measuring the distribution of pesticides between solution and colloids is limited because of the large volume of solution/colloid needed for the analysis at the low concentrations of the pesticide found in natural waters. One method to solve this problem is to use large diameter ultra-filtration membranes (76 mm) installed in a 500 ml stirred cell and perform the separation of the dissolved and colloidal material by the application of high pressure (*ca* 4 atm) above the colloid to collect the filtrate. An analysis of the supernatant and filtrate for pesticides content then enables the concentration of the pesticides associated with the colloids to be calculated. If the concentration of colloids in known or can be measured, the appropriate distribution coefficient may be calculated.

Ultra-filtration is a technique for the separation of dissolved, colloid and suspended matter on the basis of size and molecular scale (Benner, 1991; Brownawell, 1991). The separation in ultra-filtration involves particles in a size range of 0.001 μm to 0.01 μm (10 - 100 Angstrom) or organic colloids in the range of 500 to 1,000,000 Dalton. Conventional membrane filters are available in the size range of 0.01 μm to 0.45 μm and above. Ultra-filters have an anisotropic surface structure allowing the retention of substances to take place on the membrane surface rather than within the filter structure.

The following points were considered in the design of the ultra-filtration unit:

1. The volume of ultra-filtration unit must be sufficient to enable multiple samples to be taken for pesticide analysis.

2. The cell must be stirred to reduce the risk of blockage of the membrane.

3. Facilities to enable the temperature control of the cell must be included, i.e. 5 ^{0}C to 25 ^{0}C.

4. It is essential that some degree of automation be incorporated to permit: (a) control of the colloid pH by the addition of CO_2/N_2 gas, (b) automatic addition of designated aliquots of pesticide stock solution to measure sorption isotherms, (c) automatic control of the air pressure above the colloid so that filtrates may be collected at pre-defined intervals.

5. Some facility for automatic sample collection co-ordinated with the control of the ultra-filtration cell to enable filtrates to be collected at predefined times, e.g. in kinetic studies with one-shot addition of pesticide or for isotherm measurements with multiple-shot addition of the pesticide stock solution.

6. Contact of the aqueous solutions in the cell with the walls, tubing and seals should not lead to contamination of the solution or excessive sorption of the pesticides to the components.

Previous studies in this laboratory have used an automated adsorption cell incorporating membrane filters such as GF/F glass micro-fibre or cellulose nitrate 0.01 to 0.45 μm pore size, and a syringe pump to remove filtrate for chemical analysis. This system is connected to a gas line (CO_2/N_2) and autoburette for the addition of the adsorbate with a suspension maintained by a stainless steel paddle stirrer mounted about 2 mm above the membrane. This system works very well and has been used extensively in studies of the interaction various micro-organic compounds

with minerals and natural river sediments, e.g. House and Farr (1989); Marchesi *et al.* (1991). However, it is not suitable for experiments with high concentrations of colloids, e.g. clays such as illite and montmorillonite or natural organic matter (NOM) of colloid size. With these materials, the membrane filter either blocks or the flow rate decreases to such an extent that the collection of sufficient volumes of filtrate is impracticable. The maximum differential pressure across the membrane is about 1 atm by suction. Even with the smallest size membrane filter (0.01 μm), judged by the sample colour, the filtrates from most natural samples contain appreciable amounts of dissolved organic material.

The ultra-filtration cell used is a commercially available CHEMLAB cell, with connectors modified to accept tubing from a autoburette (Radiometer ABU80/TTT80 titrator), CO_2/N_2 gas line, air pressure line and sample collector. The various inlets and outlets are controlled using solenoid operated valves in the configuration shown in Appendix 1. The software developed here for the automated adsorption cell was extensively modified to control the ultra-filtration unit through a PC386/25 MHz and the PC-LabCard series interface boards. The modifications to the software are summarised in Appendix 1. In fully automated mode, the system permits the automatic addition of pesticide stock solution and removal of filtrate at predefined intervals with control of valves to enable CO_2/N_2 purging between sampling and purge of the sampling tube after sampling. In addition, software was written to permit the manual operation of the unit, *viz* collection of a filtrate fraction, addition of a stock solution from the autoburette or a combination of stock addition and filtrate collection. Initial tests showed that it is essential to incorporate a valve on the sampling line because of the slow depressurisation of the ultra-filtration cell, and also to allow time for the depressurisation of the cell before opening the gas purge line.

5.2 Tests of performance of the ultra-filtration unit with PM series membranes of 10,000 Dalton size (PM10)

Initial tests were done using the PM series membranes. These are high-flow membranes made of inert, non-ionic polymer. The experiments were designed to test the performance of the automated unit and evaluate the sorption of pesticides to the internal components.

5.2.1 Preconditioning the ultra-filter membranes

New membranes were pre-conditioned to remove preservative agents and to clean the filters before use in the ultra-filtration unit. The treatment was as follows:

(a) Rinse in 1.5 litre of 5 % NaCl solution for 30 min with continual stirring.
(b) Rinse in 1.5 litre of ultra-pure water (Purite HP grade, 18 Mohm) for 1 h with continual stirring.
(c) Repeat of (b) in fresh ultra-pure water.

The membrane was rinsed with ultra-pure water between each step in the conditioning. After completion of the conditioning stages, the membrane was cut to the correct size and installed in the ultra-filtration cell. The membrane was not allowed to dry out at any time and was stored in a bottle of ultra-pure water between experiments.

5.2.2 Tests of performance in the absence of colloids and no recirculation

Initial test were done using aqueous solutions of 2 mM $CaCl_2$ containing a mixture of pesticides: simazine, atrazine, propazine, desmetryn, prometryn, terbutryn and parathion. The stock multi-pesticide solution was made by the addition of 2 ml of 0.5 μg ml^{-1} in ethyl acetate (EtAc) to a 500 ml volumetric and evaporation of the solvent before the addition of the $CaCl_2$ solution. This was mixed for 3 h prior to use to produce a nominal concentration of 2 μg dm^{-3} of each compound in the $CaCl_2$ solution.

Approximately 300 ml of ultra-pure water was passed through the ultra-filter. 250 ml of the spiked $CaCl_2$ solution was placed in the ultra-filtration cell and left stirring for 2.5 h. The first 10 ml of filtrate was discarded and a further 100 ml collected for pesticide analysis. Immediately after this, a 100 ml volume of the solution inside the ultra-filtration cell was removed using a PTFE 8 mm tube connected to a 50 ml syringe. The syringe was subsequently used as the reservoir on the solid-phase-extraction (spe) manifold thus minimising the difference in treatment of the two solutions prior to pesticide extraction. Another sample of 100 ml was taken from the spiked $CaCl_2$ solution; this sample had no contact with the ultra-filtration cell. The ultra-filtration unit was operated by the computer but in manual mode, i.e. using the program "MSAMPLE", Appendix 1.

The pesticides were extracted using IFE, River Laboratory SOP: 9/13.08.92. This is available to DoE on request. In brief the extraction is with 500 mg C18 (silica bonded phase), with pre-conditioning with methanol and elution with EtAc with the C18 column placed above a drying column of Na_2SO_4. The 2 ml EtAc eluate was collected using a vacuum manifold and injected directly into a capillary GC with a programmable temperature vapouriser (PTV) injector and detection with a nitrogen-phosphorus detector (NPD) ceramic bead. The chromatograms were processed using a Perkin Elmer 1020 integrator and quantified for simazine, atrazine, propazine and parathion. Typical analyte recoveries by this method are > 95% with standard deviations < 8 %. The results of the GC analysis are shown in Table 5.1. They indicate that pesticide concentrations in the $CaCl_2$ solution are < 2 μg dm^{-3} and therefore more time is needed during the dissolution stage to ensure the compounds are dissolved. In addition there is a difference between the pesticide concentrations in the filtrate and supernatant. The most likely reason for this is the sorption of the compounds from solution on the PM10 membrane.

TABLE 5.1 *Results of trial experiment in the absence of colloids and no re-circulation. UFC: ultra-filtration cell*

compound	pesticide concentration in solution / μg dm^{-3}		
	not exposed to UFC	filtrate	supernatant
simazine	1.44	0.49	0.75
atrazine	1.45	0.34	0.68
propazine	1.60	0.34	0.81
parathion	0.80	0.025	0.073

5.2.3 Test of performance of ultra-filtration cell in the absence of colloid but with re-circulation.

The procedure above was repeated with the PM10 membrane but with the following modifications:

(a) The $CaCl_2$ solution was mixed with the pesticide residues overnight and then filtered through a 0.45 μm membrane filter before use in the ultra-filtration cell.
(b) The concentration of compounds in the solution was increased to approximately 10 μg dm^{-3}.
(c) The solution in the ultra-filtration cell was re-circulated using the "AUTOUFC" (Appendix 1) program by connecting the autoburette to the filtrate collection vessel. The volume of the cell was replaced 2.5 times during the re-circulation over a period of 3 h. The results of the GC analysis of the stock solution, filtrate and supernatant are shown in Table 5.2.

TABLE 5.2 *Results of trial experiment in the absence of colloids and with re-circulation. UFC: Ultra-Filtration Cell*

compound	pesticide concentration in solution / μg dm^{-3}		
	not exposed to UFC	filtrate	supernatant
simazine	10.51	4.29	3.80
atrazine	9.58	4.24	4.20
propazine	9.68	4.41	4.70
desmetryn	8.13	3.86	3.58
prometryn	8.19	2.40	2.30
terbutryn	7.96	1.22	1.35
parathion	10.06	9.18	10.65

The results show better agreement of the measured concentrations with the nominal value (10 μg dm^{-3}) and general agreement between the filtrate and supernatant concentrations of all the pesticides. Hence although there is a loss of pesticides to the cell components, the re-circulation procedure is sufficient to allow a steady-state to be established. During these experiments the ultra-filtration cell was found to operate satisfactory and able to perform the main functions for which it was designed.

5.2.4 Test of the performance of the ultra-filtration cell in the presence of colloids and with re-circulation.

A preliminary test of the performance of the apparatus was completed using a sample of natural water from the river Ouse (Naburn Lock, York, NGR: SE594445). A 50 l quantity of this water was continuous-flow-centrifuged. One litre of the water was placed through the ultra-filtration unit and the supernatant reduced to *ca* 100 ml using the autoburette to deliver the centrifuged water to the cell. The filtrate was collected for UV absorbance measurements. 100 ml of the stock $CaCl_2$ solution was then added to the cell and mixed. This was then circulated through the cell using the

autoburette to deliver the filtrate to the ultra-filtration cell (16 x 25 ml to give 2 volume replacements). Samples of the filtrate and supernatant were taken as described above, extracted and analysed by GC. The results in Table 5.3 show that in samples of this type a further concentration of the colloid component, separated with the 10,000 PM10 ultra-filter, is needed to measure k_{oc}s (see Appendix 2 for the definition of distribution coefficients) as low as 1000.

The application of the automated UFC has been extended with deployment of a 500 Dalton membrane. The membrane was tested by circulating a solution of 2 mM $CaCl_2$ containing a multi-standard pesticide mixture of simazine, atrazine, propazine, desmetryn, prometryn, fenitrothion, cyanazine and parathion. The results shown in Table 5.4, indicate the satisfactory performance of the membrane in the absence of colloids for all of the compounds apart from prometryn.

TABLE 5.3 *Results of the trial experiment with R. Ouse water after continuous-flow-centrifugation. The distribution coefficients are normalised with respect to organic carbon (DOC=7.9 mg dm^{-3}); see equation (5) in Appendix 2. UFC: ultra-filtration cell.*

compound	concentration of pesticide / μg dm^{-3}		
	filtrate	supernatant	k_{oc} / ml g^{-1}
simazine	2.11	2.14	1119
atrazine	1.76	1.80	3042
propazine	2.03	2.11	5200
desmetryn	2.62	2.72	5011
prometryn	1.19	1.17	-
terbutryn	0.71	0.90	33253
parathion	0.14	0.16	20588

TABLE 5.4 *Comparison of the concentrations of a range of pesticides in the filtrate and supernatant of the UFC (500 Dalton). Results are shown for duplicate determinations.*

Pesticide	F, mean concentration in filtrate/ μg dm^{-3}	S, mean concentration in supernatant/ μg dm^{-3}	ratio of concentrations (S/F)
simazine	5.70	5.83	1.02
atrazine	5.88	6.18	1.05
propazine	6.21	6.52	1.05
desmetryn	11.79	10.62	0.90
prometryn	10.82	12.67	1.17
fenitrothion	1.51	1.36	0.90
cyanazine	3.03	3.24	1.07
parathion	0.37	0.39	1.05

5.3 Ultra-filtration experiments with Humber river waters

Experiments were performed with: (a) R. Ouse water after continuous-flow-centrifugation (b) concentrated R. Swale water, (c) R. Calder water and (d) R. Aire water. The dates of sampling are given in Table 5.5.

(a) Colloids in the R. Ouse sample were concentrated by 10 fold using a 1000 Dalton membrane. A multi-pesticide mixture was added to the cell and the contents re-circulated to obtain a two-volume change. Samples of the filtrate and supernatant were retained for DOC analysis. The distribution for the colloid material (here normalised with respect the DOC) was then calculated from the equation:

$$k_{doc} = \frac{10^6}{DOC} * [(C_s / C_f) - 1] \qquad (5.1)$$

where DOC is the concentration of dissolved organic carbon (mg dm^{-3}) and C_s and C_f are the concentrations of the pesticide in the supernatant and filtrate respectively. Hence it is assumed that:

$$C_s = C_f + C_{coll} \qquad (5.2)$$

where C_{coll} is the concentration of the pesticide on the colloid material. The distribution coefficient is in units of ml g^{-1} or dm^3 kg^{-1}. The factor of 10^6 accounts for the change in units allowing the DOC concentration to be in mg dm^{-3}.

The results of the calculation of the distribution coefficient, normalised with respect to DOC, are shown in Table 5.5 and compared with the previous results for the R. Ouse obtained using a 10,000 Dalton membrane. A comparison of the results using the different size membranes suggests that the colloidal material between 1000 and 10,000 Dalton is an important fraction influencing pesticide interactions in this sample.

(b) A sample from the R. Swale (sampled on 16.9.94) was concentrated by 6.3 fold using a 1000 Dalton membrane. The concentrate was stored at 6 ^{0}C in the dark prior to the experiments. The UFC experiment was conducted using a similar procedure as described in (a) above with a two-volume change. The results of the calculation of the distribution coefficient are shown in Table 5.5. In this instance, the k_{doc}s are lower than those calculated for the R. Ouse sample with the same size of membrane in the UFC.

(c) A sample from the R. Calder was collected on 3/7/95 from Methley bridge (SE409258) in a 10 l container. This was transported to the River Laboratory and stored at 5 ^{0}C in the dark prior to use. One litre of this water was filtered through a 0.45 μm membrane filter before adding the UFC. The UFC was used to determine the k_{doc} values for the multi-pesticide mixture. The distribution coefficients are higher than those obtained for the R. Ouse sample with the 10,000 Dalton membrane but smaller than the results from the 1000 Dalton membrane, e.g. for simazine and atrazine the k_{doc}s for the R. Calder water were 19.3 and 23.8 l g^{-1} respectively compared with 1.1 and 3.0 dm^3 g^{-1} respectively for the R. Ouse with the same porosity membrane.

(d) A sample of R. Aire water was collected on 24.8.95 from Beale (SE534255) near the Environment Agency, EA, gauging station at the tidal limit of the river. The initial experiments consisted of filtering the river water through a GF/F glass membrane pad and concentrating two-fold with a 1000 Dalton membrane in the UFC and then adjusting the volume with a multi-pesticide mixture. This was then re-circulated to produce a 1.4 volume changes before the filtrate and supernatant were separated for pesticides analysis. The results are shown in Table 5.5. A similar experiment was performed with the unfiltered R. Aire sample and the results are also shown in Table 5.5. The suspended solids content of the water was measured using the protocol (SOP: 36/16.5.1995) as 13.5 mg dm^{-3}. The distribution coefficients are similar to those calculated for the R. Calder water discussed above but generally much lower than the values shown in Table 5.5 for the R. Ouse. The distribution coefficients for the unfiltered water are generally higher than the filtered because of the presence of larger particulate matter (>0.45 μm) in the sample.

TABLE 5.5 *Summary of the k_{doc} values (in $dm^3\ g^{-1}$) that have been measured for river waters. The distribution coefficients are normalised with respect to the dissolved organic carbon values (DOC) measured or estimated from the visible absorbance at 340 nm. Sample Aire(2), was not pre-filtered. Mean values are calculated for the rivers Ouse (10,000 Dalton), Swale Aire and Calder KEY: CFC: continuous-flow centrifugation; GF/F: filtration with glass micro-fibre pad. CV % is coefficient of variation for 3 samples or more.* **To convert k_{doc} values to ml g^{-1}, multiply by 1000.***

	R. Ouse	R. Ouse	R. Swale	R. Aire(1)	R. Aire(2)	Mean	CV %
Sampling date	2.3.95	2.3.95	16.9.94	24.8.95	24.8.95		
Preparation	CFC	CFC	CFC	GF/F	none		
membrane.	1000	10,000	1000	1000	1000		
DOC/mg dm^{-3}	4.86	7.90	17.5	21.9	15.3		
simazine	19	1.1	5.3	9.5	12.4	8.8	89
atrazine	122	3.0	6.2	11.8	17.3	11.2	82
propazine	160	5.2	9.9	11.4	20.7	8.8	37
desmetryn	105	5.0	10.5	8.2	11.0	7.9	35
prometryn	150	-	32.9	6.4	5.4	19.7	-
terbutryn	-	33	8.5	6.1	-	15.9	94
fenitrothion	160	-	35.1	7.1	25.6	21	
malathion	-	-	36.0	-	74.9	36	
cyanazine	153	-	25.5	24.5	32.6	25	
parathion	51	21	77	3.6	10.6	33.9	113

The results for the series of compounds do show correlations with k_{oc}s from soil (Table 4.1), e.g. comparing mean k_{doc}s in Table 5.5 with k_{oc}s in Table 4.1, produces a correlation of r^2=0.48 (log k_{oc}(soil)=0.23logk_{doc}(colloid)+3.63), with the k_{doc} values greater by a factor of between 7 and 132 fold. However, the variability between samples (see the coefficients of variation in Table 5..5), combined with the wide range of k_{oc}s for soil which have been reported e.g. see section 4, means that such correlations should be treated with caution.

The relationships between the k_{doc} values (Table 5.5) and octanol - water coefficients (K_{ow}) were also investigated using linear regression analysis. The K_{ow}s for simazine, atrazine, propazine, prometryn, terbutryn, fenitrothion, malathion and parathion are 100, 363, 933, 2570, 3890, 2512, 776 and 2570 respectively. Reliable values for desmetryn and cyanazine are unavailable. The results of the analysis are shown in Table 5.6.

TABLE 5.6 *Comparison of the linear regression of the distribution coefficients, log k_{doc} (Table 5.5.) against the octanol - water partition coefficients, log K_{ow}*

sample	membrane	correlation	gradient	r^2
R. Ouse	1000	+	0.25	0.31
R. Ouse	10,000	+	0.41	0.41
R. Swale	1000	+	0.22	0.31
R. Aire	1000	-	0.21	0.41
R. Aire	1000	-	0.09	0.11

The samples from the rivers Ouse and Swale give reasonable positive correlation between the log k_{dos} and log K_{ow}, i.e. the distribution coefficients generally increase as the octanol - water partition coefficients. This is particularly evident for simazine, atrazine and propazine for which the K_{ow} increases from 100 to 933 (see Table 5.5). For the R. Aire samples, the correlation is negative indicating that the interaction with the colloids is different from the other samples. The reason for this difference is not clear; it may relate to interactions of the pesticides with colloidal clay particles detected by X-ray diffraction in these samples.

5.4 Estimation of the contribution of organic colloids to pesticide transport

The results from the UFC experiments indicate high values of k_{doc} in river waters when compared with k_{oc} values for soils and sediments. For example, the literature k_{oc} given in section 4 for atrazine and simazine are in the range of 4-2200 ml g^{-1} (0.004 - 2.2 dm^3 g^{-1}) which compare with k_{doc} values in Table 5.5 of between 1100-120,000 ml g^{-1}.

The relative contribution of DOC to pesticide movement may be estimated from a mass-balance:

$$C_{tot} = C_p + C_{coll} + C_{sol} \qquad (5.3)$$

where C_p is the pesticide concentration on suspended solids (μg dm^{-3}), C_{coll} the concentration on organic colloids and C_{sol}, the concentration that is "free" in solution - which can be equated to C_f in the UFC with a low molecular weight cut-off membrane. The concentration, C_p, may be calculated from:

$$C_p = C_{sol} SS \times k_d / 10^6 \qquad (5.4)$$

where SS is the concentration of suspended solids in mg dm^{-3} and k_d is the distribution coefficient for the pesticide on suspended solids (ml g^{-1}). Similarly, the concentration of pesticide associated with organic colloids is:

$$C_{coll} = C_{sol} \times DOC \times k_{doc} / 10^6 \qquad (5.5)$$

where DOC is the dissolved organic carbon content in mg dm^{-3} and k_{doc} is the distribution coefficient for the pesticide on organic colloids. These equations may be combined to give the concentration of "free" pesticide, C_{sol} :

$$C_{sol} = C_{tot}(1 + SS \times k_d / 10^6 + DOC \times k_{doc} / 10^6)^{-1} \qquad (5.6)$$

where C_{tot} is the total concentration of pesticide in the natural water, i.e is equivalent to the pesticide concentration in the "whole" water sample and includes the pesticide adsorbed to suspended sediments, and colloidal material such as clay and dissolved organic material. The analysis of "whole" water samples is usually done by extraction with a solvent such as dichloromethane or by solid-phase-extraction with precautions to separate the suspended material and extract that as part of the determination (see the LOIS method described in section 7).

The application of these equations may be demonstrated for the R. Aire in the following conditions (for details of the data, see section 8.2):

(a) Low-flow during the summer when the DOC concentrations are a maximum, *ca* 12 mg dm^{-3}, and suspended solid concentrations are low, *ca* 10 mg dm^{-3}.

(b) High-flow conditions in the late autumn or winter periods when the DOC concentrations are lower than in the summer because of the dilution effects of storm water entering the river. DOC concentrations are typically 4 mg dm^{-3}, and suspended solids at a maximum, *ca* 200 mg dm^{-3}, because of the re-suspension of river bed-sediments and particulate mobilisation in surface flow, i.e. that direct-flow from hard surfaces and fields.

As examples, calculations have been done for simazine and atrazine - which are amongst the most soluble and least adsorbed pesticides. A more extensive discussion of the results is given in section 8.3. A value of the distribution coefficient, k_d, was chosen appropriate for simazine or atrazine (for a review, see section 4), k_d=4 ml g^{-1}, and the concentration of pesticide "not free", i.e. concentration which is associated with organic colloids and suspended matter, was calculated for a range of k_{doc} values encompassing those found in this work (Table 5.5). Association of the herbicides with DOC was found to be more important than with suspended sediments and this resulted in an increase in the percentage material carried with DOC relative to "free" compounds in the low-flow during the summer (Figure 5.1). Although increases in river flow during the winter resulted in large increases in suspended material, because the DOC was diluted, the transport of the herbicides in "free" form was greater than in low-flow conditions. Generally the relative contributions of compounds adsorbed to suspended material, i.e. that material not passing through 0.45 μm membranes, and to DOC, will be determined by the relative magnitudes of k_d and k_{doc} respectively. Examples are given in Figures 5.1 and 5.2 of the calculated "bound" pesticide, i.e. that associated with SS or DOC, for a range of k_ds (4 - 800 ml g^{-1}) and k_{doc}s (1000 - 80,000 ml g^{-1}), for conditions typical for R. Aire in low- and high-flow.

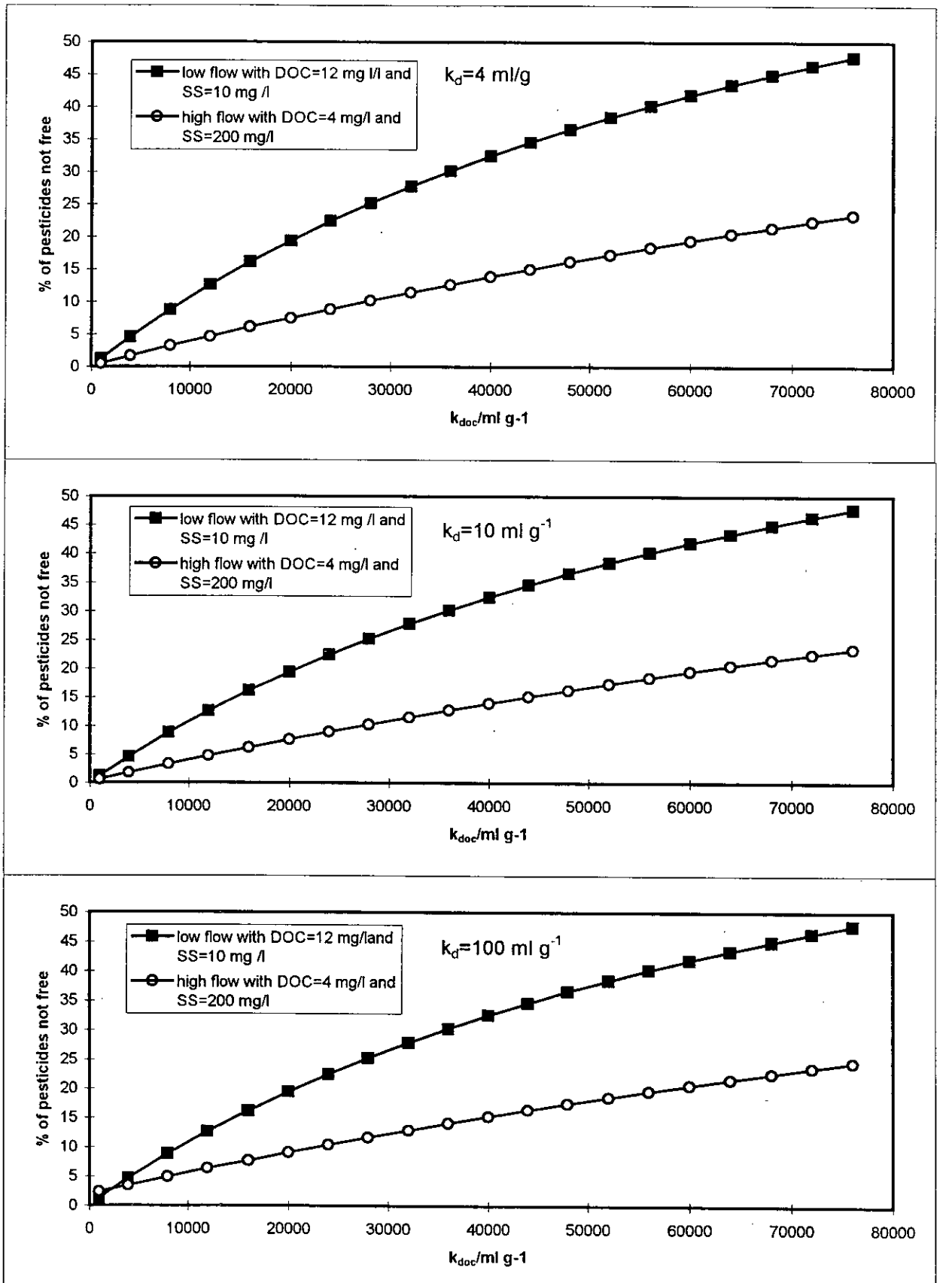


Figure 5.1 Contribution of bound-pesticides to transport in conditions of low and high flow in the R. Aire for suspended sediment distributions coefficients in the range of 4 to 100 ml g^{-1}.

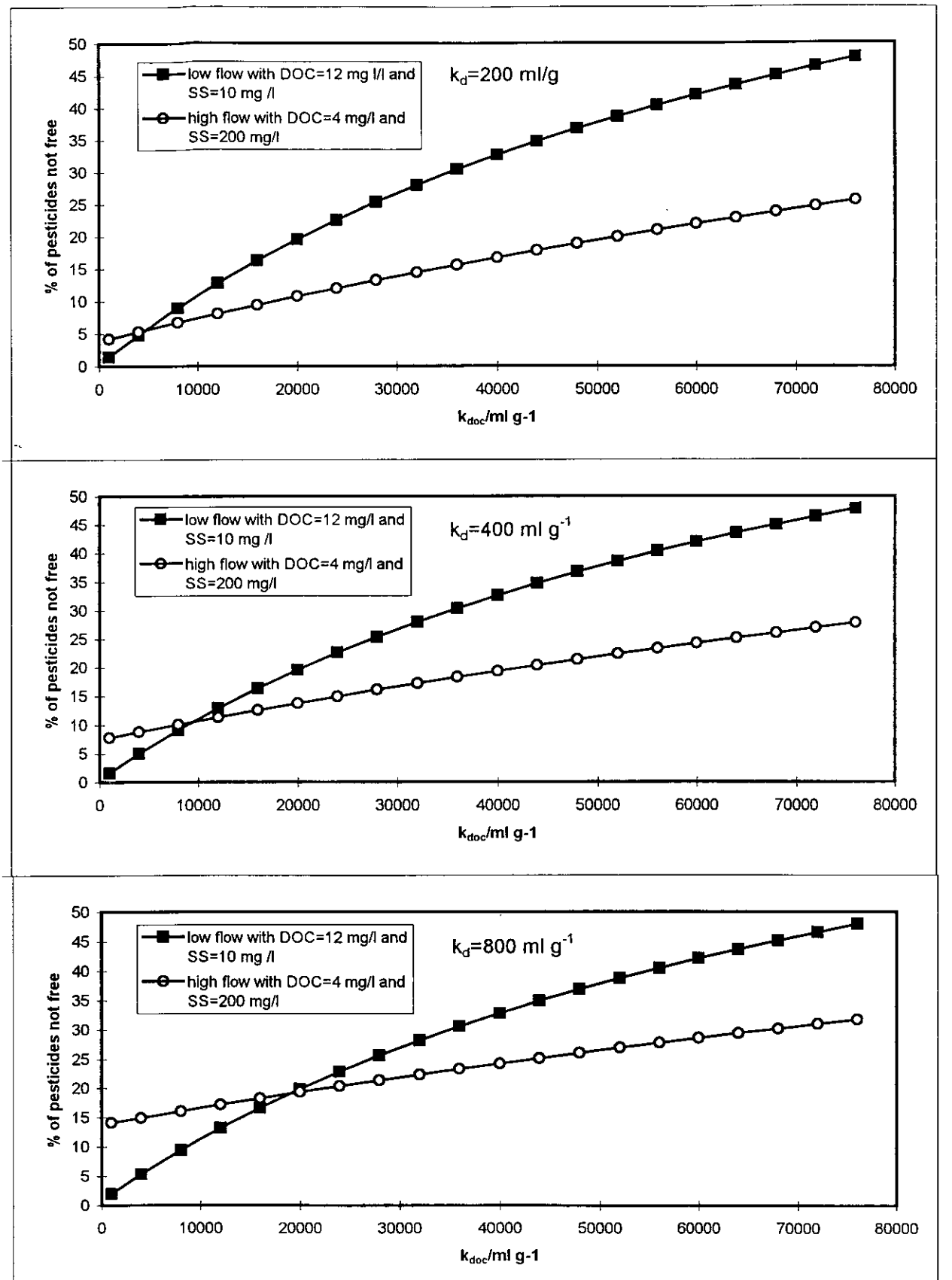


Figure 5.2 Contribution of bound-pesticides to transport in conditions of low and high flow in the R. Aire for suspended sediment distributions coefficients in the range of 200 to 800 ml g^{-1}.

6.0 RESIN EXCHANGE

6.1 Development of a competitive adsorption method

Although the automated ultra-filtration unit is available to enable the measurement of the distribution of micro-organic compounds in true solution and in naturally occurring colloids, a second method for making such measurements was desired to enable checks to be made on the values obtained. One alternative method is competitive adsorption, where the quantity of pesticide associated with a reference material is used to estimate the concentration of pesticides in true solution. For this method to work effectively the reference material must be uniform, easily added to and separated from the sample solutions, be able to adsorb a significant quantity of the pesticides yet allow the adsorbed pesticides to be recovered efficiently. Extensive work was required to study the interactions between the reference material and the pesticides both as a function of time and as a function of concentration.

6.2 Application of solid-phase-extraction (spe) techniques to the isolation of pesticides in organic colloids.

Three different types of solid-phase-extraction (spe) columns were investigated: (a) C18(EC) 1 g/ 6 ml (pore size 5.6nm; (b) Supelco ENVI graphitised non-porous carbon (0.5 g/ 6 ml) and (c) SAX (quaternaryamine) anion exchange (1 g/ 6 ml).

Previous work on this project used C18 (end-capped, EC) solid-phase-extraction (spe) columns to isolate the pesticides from solution. Although humic substances were clearly sorbed to the C18 matrix, some fractions eventually broke through the column and reached the effluent at the bottom of the column. If pesticides are bound to the humic substances, they may not interact effectively with the C18 bonded phase. One method to avoid breakthrough is to mount an anion exchanger on top of the C18 column. However, preliminary experiments indicated this to be ineffective at high humic concentrations (300 mg/l). Thus, although the anion exchanger retained more of the humic fraction than the C18 column, a more retentive matrix is needed for waters containing high organic carbon. The graphitised carbon column also permitted the penetration of the humic substances leading to breakthrough of the colloids in the effluent. The recoveries of the pesticides were also very variable; for this reason no further work was attempted with either the anion exchang or graphitised carbon columns.

The results from the extraction of a spiked solution of pesticides in distilled water and 300 mg dm^{-3} humic acid (Aldrich) on C18 (EC) are shown in Table 6.1. The humic acid solution was prepared by adding 0.3 g humic acid to 1 litre of 2 mM $CaCl_2$ and dissolving over 48 h, followed by filtration through a 0.7 μm GF/F glass fibre pad. A multi-pesticide mixture was prepared by adding 1 ml of 10 mg dm^{-3} EtAc solution of simazine, atrazine, propazine, desmetryn, prometryn, terbutryn, fenitrothion, malathion, cyanazine and parathion (multi-pesticide mixture) to a 1 litre volumetric flask, evaporating the EtAc with nitrogen, and dissolving overnight in 2 mM $CaCl_2$ solution. The multi-pesticide solution was then filtered through a GF/F glass fibre pad prior to use. The compounds were then extracted using the protocol, SOP: 9/13.08.92, and final elution with 2

ml of EtAc through the C18 (EC) column in-line with a sodium sulphate drying column. The results show that at this concentration of pesticide, there is no significant difference (t-test, 95 %) between the two sets of results. This indicates either that the majority of the pesticides are not associated with the humic material or that the interaction of the pesticides with the C18 matrix is greater than with the humic molecules.

TABLE 6.1 *Results of the comparison of the performance of the C18 (EC) spe columns for extracting pesticides from solutions with and without humic acid. The concentration of humic acid was 300 mg dm^{-3}. The figures are the pesticide concentrations in μg dm^{-3}*

compound	No humic acid				With humic acid		
replicates	1	2	3	mean	1	2	mean
simazine	5.42	5.25	4.77	5.15	4.87	5.00	4.94
atrazine	5.88	5.76	5.19	5.61	5.26	5.55	5.40
propazine	6.27	6.04	5.54	5.95	5.69	5.98	5.84
prometryn	6.06	7.26	6.84	6.72	6.85	6.66	6.75
terbutryn	6.51	8.07	7.64	7.41	7.62	7.33	7.47
fenitrothion	0.88	0.68	0.58	0.71	0.70	0.67	0.68
malathion	0.27	0.17	0.15	0.20	0.19	0.16	0.18
cyanazine	2.62	2.03	1.97	2.20	2.19	2.27	2.23
parathion	2.98	2.46	2.33	2.59	2.57	2.64	2.61

6.3 Selection of resin

Four resins were obtained with differing pore sizes and tested in initial selection experiments to identify which resin would provide appropriate levels of adsorption and could be easily added to and separated from the bulk of the sample. The four resins tested were Amberlite XAD-2, Amberlite XAD-4, Amberlite XAD-7, and Superlite DAX-8. Approximately 10 g of each resin was slurried with methanol, before being rinsed with three changes of ultra-pure water (Purite HP grade, 18 Mohm), being left to stand for 15 minutes and the excess water decanted off. The wet resins were then stored in sealed PTFE bottles. The water content of each wet resin was determined by weighing about 0.5 g of wet resin before and after drying in an oven at 100 °C for 1 hour.

A known weight (approximately 2 g) of each wet resin was shaken overnight at 10 °C with 100 ml of nominal 15 μg dm^{-3} pesticide multi-standard in PTFE bottles. A control bottle containing an equal volume of the multi-standard was incubated at the same time. The resins were then separated, and the pesticides remaining in the waters extracted by solid-phase-extraction and

analysed by GC-MS. As this stage no efficient method had been identified for extracting the pesticides from the collected resin, approximate k_r were calculated from the loss of free pesticides from solution; these are tabulated in Table 6.2. The k_r values obtained indicate that the 2 g of wet resin used was capable of adsorbing far more than 50 % of the pesticides from 100 ml of the 15 μg dm^{-3} solution used, and that future experiments should be based around smaller quantities of resin for the same type and quantity of pesticide solution.

At this stage it was noted that the resins were best separated from the liquid by a simple filtration step incorporated into the normal solid-phase extraction procedure. Due to variations in resin bead size XAD-2 and DAX-8 could be made to yield a small resin column from which efficient extraction could be expected, while XAD-4 and XAD-7 could only be separated in the form of a thin layer of material requiring the use of far greater volumes of solvent in later extraction steps; therefore the XAD-2 and DAX-8 resins were taken on to a further set of experiments.

To obtain better estimates of the distribution constants (k_r) for the pesticides and some measure of the recovery that could be obtained from the resins, a further screening experiment was performed. For each resin and pesticide, the mass of wet resin required to remove half of the pesticide from 100 ml of volume of 15 μg dm^{-3}pesticide solution was calculated. These were averaged to obtain M, the average mass of resin required to remove half of the pesticides from the solution. Four bottles were used for each resin containing 0 , 0.5 M, 1.5 M and 2 M of resin and a 100 ml of the pesticide solution. These were incubated for 48 hours before being filtered, the aqueous phases extracted and analysis performed by GC-NPD. Again k_r values were calculated based on the loss of free pesticide from solution and these are also shown in Table 6.2 below.

Two experimental extractions were performed on collected resins, this involved passing four 0.5 ml aliquots of ethyl acetate through the column of collected resin. The eluate from each set of resin was dried, and analysed by GC-NPD. The data from these extracts was used to calculate the recoveries shown in Table 6.3. The recoveries from the resin DAX-8 are in general far better than the recoveries from XAD-2. The result for dimethoate were unreliable because of the comparatively large uncertainties in the measurement of this particular pesticide at low concentrations. The resin DAX-8 was selected for further study as it gave reasonable recoveries from a simple extraction procedure which could be easily performed with only small modifications to the procedures.

TABLE 6.2 *Initial and second estimates of k_r values ($dm^3\ kg^{-1}$)*

	Initial values				Second estimates	
	XAD-2	XAD-4	XAD-7	DAX-8	XAD-2	DAX-8
trifluralin	966	899	215	1039	2453	2571
dimethoate	nd	nd	nd	nd	370	495
simazine	995	957	714	1343	3167	1506
atrazine	nd	nd	nd	nd	3244	1845
propazine	956	857	1437	1250	3265	2217
desmetryn	1086	1294	1323	1311	2250	1268
prometryn	1022	1092	1806	1473	2269	1762
terbutryn	1345	1436	2204	1811	3174	3092
fenitrothion	nd	nd	nd	nd	4303	4127
malathion	nd	nd	nd	nd	2479	3399
cyanazine	nd	nd	nd	nd	2453	1780
parathion	2052	2200	1399	1498	4832	4401

TABLE 6.3 *Pesticides recovered from resin as percentage of pesticide lost from solution*

	XAD 2	DAX 8
trifluralin	50	114
dimethoate	137	-
simazine	19	72
atrazine	21	73
propazine	21	133
desmetryn	28	99
prometryn	27	93
terbutryn	47	113
fenitrothion	40	99
malathion	35	96
cyanazine	23	95
parathion	30	93

6.4 Further studies on the adsorption of pesticides by DAX-8

Before competitive adsorption can be used as a method of estimating the concentration of free pesticides in solution, and hence as a method of calculating how much pesticide is associated with colloids in natural water samples, the interactions between the pesticides and the resin must be fully characterised. This includes both kinetics of the adsorption process (measurements of the time required for the distribution of pesticides between the various phases to settle to their final or "equilibrium" values), and the measurement of adsorption isotherms (the relationship between pesticide concentrations on the resin and in true solution).

The adsorption kinetics of the pesticides were studied first as they must be known before experiments to measure the adsorption isotherm can be designed. Five pairs of bottles were prepared, each pair consisting of a control containing no resin and an second bottle containing a known mass of resin (approximately 0.25 g wet resin per bottle). An aliquot of pesticide solution (50 ml nominally 15 $\mu g\ dm^{-3}$) was added to each bottle, and the pairs shaken at 10 °C for various lengths of time. The distribution coefficients were calculated for each pair, using the loss of pesticide from solution in each pair to estimate the uptake of pesticide onto the resins. This data was used to calculate the half-life of the adsorption interaction. Typical half-life values are tabulated below with predicted percent deviation from equilibrium at 24 hours (Table 6.4).

In most cases the distributions of the compounds are within 1 % of their equilibrium values within twenty four hours, of the resin being mixed with the liquid. Therefore the kinetics for the adsorption of the pesticide into the resin will not introduce large errors into the method if the samples are incubated for 24 hours or more.

TABLE 6.4 *Pesticides extracted from resin as percentage of pesticide lost from solution*

	Half-life (h)	% deviation from equilibrium at 24 h
trifluralin	2.1	0.04
dimethoate	8.9	15
simazine	2.8	0.24
atrazine	2.7	0.20
propazine	2.5	0.13
desmetryn	3.0	0.39
prometryn	4.3	1.99
terbutryn	2.2	0.05
fenitrothion	1.3	0.00
malathion	2.1	0.04
cyanazine	2.5	0.12
parathion	2.1	0.04

6.5 Modified method

A volume of sample was shaken in PTFE bottles with a quantity of resin (DAX-8) selected to reduce the concentration of pesticides present by approximately 50 %. After 24 h incubation at 10°C the contents of the bottles were poured into 70 ml reservoirs and any resin not transferred rinsed in to the reservoir with water out of the reservoir. The samples were then drawn through an empty 3 mm glass column fitted with a PTFE frit, which captures the resin, and a solid-phase extraction cartridge which had been pre-conditioned in the normal manner.

The pesticides isolated by the solid-phase extraction were eluted and prepared for GC analysis. Initially the columns were extracted using the normal procedure for a solid-phase extraction cartridge but it was found impossible to adequately control the elution rate, therefore the following modified elution procedure was adopted. A drying column, containing anhydrous sodium sulphate, was placed on a vacuum manifold with a valve and needle leading to a 2 ml collection vial. The glass column containing the resin was fitted on top of this, and 2 ml of ethyl acetate (EtAc) pipetted into it. The elution of the liquid was started, and about 1 ml of EtAc was drawn down out of the glass column. At this point the extraction was stopped using the valve, and an unused solid-phase extraction cartridge fitted to the top of the glass column. The extra air resistance provided by the extraction cartridge enables the extraction to continue in a controlled manner, and the extract to be collected efficiently. In the absence of the cartridge, extract is usually lost from the vials as a result of the high air flow through the resin

A series of experiments were performed to study the influence of specific effects on the competitive adsorption method. The pesticides reported are: simazine, atrazine, propazine, terbutryn, fenitrothion, malathion and parathion. These included experiments to confirm that the bottles did not significantly adsorb the pesticides. Measurements of the distribution of pesticide between the resin and the aqueous phase, (based on measurements of pesticides extracted from the resin rather than lost from solution). Initial tests were also performed with water from the R. Aire at Beale, and comparisons made with solutions containing Aldrich Humic acid.

6.6 Measurement of adsorption to containers.

Fourteen bottles containing various dilutions of stock pesticide solution were incubated for 24 h. Eight measurements were made of the concentration of the stock, and the average of these values used to obtain predicted concentrations for each of the bottles. The concentrations measured in the bottles after 24 h was plotted against the expected concentration, and regression statistics obtained. Distribution coefficients (k_b = amount adsorbed by bottle / concentration in solution or amount adsorbed by bottle per dm^2 / concentration in solution), were calculated from the regression gradients where possible and are summarised below. In a separate experiment eleven bottles were incubated for various times and the loss of pesticide was plotted as a function of time. It was noted that the bottles had reached equilibrium in under 24 h. Although these distribution coefficients appear small, there is significant loss of the compounds to the PTFE bottles amounting to 20-30 % at low concentrations.

TABLE 6.5 *Adsorption of two representative pesticides to PTFE bottles*

	unit	propazine	parathion
k_b	dm^3/bottle	0.005	0.008
Standard error of k_b	dm^3/bottle	0.004	0.005
k_b	dm^3/dm^2	0.009	0.015
Standard error of k_b	dm^3/dm^2	0.007	0.009
Predicted recovery	%	89	83

6.7 Confirmation of resin sorption properties

6.7.1 Adsorption kinetics on the resin

The initial experiments (sections 6.1 - 6.2) estimated the distribution of the pesticide (k_r) from the loss of pesticide measured in solution. The final method will rely on direct measurements of the pesticide sorbed on the resin, by extraction of the pesticides. The kinetics of the adsorption of the selected pesticides onto the resin DAX-8 was therefore reinvestigated. Twelve bottles were prepared each containing a known mass or pre-wetted resin. A fixed volume (50 ml) of stock pesticide solution (10 μg dm^{-3}nominal) was pipetted into each bottle, and incubated at 10°C for various time before being separated and extracted as described above. Two additional bottles were treated in the same way except that their contents were shaken and then immediately separated without incubation.

After GC/NPD analysis, the adsorption on the resin samples were calculated (amount of pesticide extracted / dry mass resin) and the concentrations in the water samples calculated (amount of pesticide extracted / volume water). The distribution coefficient for the resin in each bottle, (k_r), was then calculated and plotted against contact time. It was noted that all the pesticides showed a rapid rise in distribution coefficient prior to the first measurement. The distribution coefficients became unmeasurable after 48 h for all the pesticides because the concentrations in the aqueous phase dropped below the limit of determination of the method. It was also noted that although none of the pesticides appear to have reached adsorption equilibrium, simazine, atrazine, propazine and parathion appeared to be further from equilibrium than fenitrothion and malathion. For experimental convenience it was decided to set the incubation time at 24 h. Using linear fits to the kinetic data, the effect of uncertainty in the measurement of incubation time was assessed giving the values summarised below. In practice it has been found that the incubation time may be fixed at 24 h ± 15 min.

TABLE 6.6 *Percentage error in estimate of distribution coefficient associated with incubation for 24 ± 1 hours*

	Simazine	Atrazine	Propazine	Fenitrothion	Malathion	Parathion
Distribution coefficient	2996	3083	11861	1808	6949	14554
% error	17	16	17	8	15	17

6.7.2 Resin isotherms

The above estimates of the distribution coefficient after 24 h mixing were refined using a series of 10 bottles containing known masses of resin. Various dilutions of a stock (10 μg dm^{-3}nominal) pesticide solution were pipetted into the bottles which were incubated at 10°C for 24 h. After 24 h the contents of the bottles were separated, extracted and the extracts analysed. In a separate experiment over a week later two bottles were prepared, incubated and analysed in the same manner to check that the results obtained were reproducible. The adsorption on the resin were plotted against the concentrations in solution for each pesticide where more than 3 valid points were obtained in the main experiment - many points could not be plotted as the concentration of pesticide in the solution had dropped below the limit of determination. The plots for the three remaining pesticides (simazine atrazine and parathion) showed a large degree of scatter superimposed upon the expected trend of a straight line through the origin. Regression analysis was performed for a model line through the origin for the two sets of data separately. The results are summarised in Table 6.7. It was noted that there was no significant difference (95% confidence limit) between the two sets of estimates which were then pooled to obtain the third estimate values of k_r listed below.

TABLE 6.7 *Refined distribution coefficients for DAX-8*

	simazine	atrazine	parathion
k_r	1784	2962	23616
standard error of k_r	200	530	2692
Degrees freedom	6	4	4
k_r (2nd week)	1389	2483	22988
k_r (2nd week)	160	304	5425
Degrees freedom	1	1	1
Third estimate k_r	1727	2866	23490
pooled standard error	195	493	3418
Coefficient variation, CV %	11	17	15

6.8 Method tests

6.8.1 Initial test with a natural water from the R. Aire.

Four bottles containing known masses of resin, and various mixtures of filtered water from the R. Aire, (collected on 24.8.95 from the R. Aire at Beale, NGR: SE534255) and stock pesticide solution. (ratios: 9:1, 3:2, 2:3, 1:9) were incubated with the bottles used to measure the k_r and separated, extracted and analysed in the same way. In both of these bottles the proportion of the pesticides remaining in the liquid was increased suggesting that the method can detect the binding of pesticides by the colloids present in this natural water. Net distribution constants for simazine and atrazine were calculated for the colloids naturally occurring in the R. Aire water using the equation:

$$k_{doc}=10^6*[(C_w \,.\, k_r/ L_{rc})-1]/DOC \qquad (6.1)$$

where DOC is the concentration of DOC in mg dm^{-3}, C_w is the concentration of pesticides present in the water from the bottle in μg dm^{-3}, k_r is the distribution constant for the resin in dm^3 kg^{-1} and L_{rc} is the adsorption of pesticide on the resin in μg kg^{-1}.

TABLE 6.8 *Distribution coefficients estimated for the R. Aire sample using the resin exchange method.*

Example	bottle 1	bottle 2	UFC measurement
DOC concentration / mg dm^{-3}	2.19	8.76	21.9
simazine, k_{doc} / dm^3 g^{-1}	186	32	9.5
atrazine, k_{doc} / dm^3 g^{-1}	256	78	11.8

The values estimated by the competitive adsorption method are higher than those measured by the ultra-filtration cell (UFC). Unfortunately the experiments with the bottles with the highest DOC concentration used with the competitive adsorption method were unsuccessful because the extracts were accidentally spilled. The two results shown for the competitive method with low DOC concentrations indicate a dependence of k_{doc}, on the DOC concentration. This is very unlikely unless the DOC was partitioned in some way prior to dilution so that the bottles contained different size distributions of the colloids. It is more likely that the uncertainties in the measurement of the pesticides are such that the results shown are unreliable. The uncertainties are:

(a) There is some interaction between the resin and the colloid. Any tendency for the colloidal material to attach itself to the resin beads will result in a lowering of the k_{doc} value obtained with this effect being more significant at higher concentrations of colloid. If the variation is due to colloid resin interactions, then either the separation procedure would have to be modified to remove the colloid from the surface of the resin before extraction of either phase, or a number of experiments would have to be performed on each water and a more complex model fitted to the data in order to estimate the extent of each interaction.

(b) An alternative explanation is that as the concentration of colloids is reduced below that found in the natural water (and used in the UFC) experiment, interactions within the colloidal fraction are reduced and as a result the colloids present a greater surface area to the water. If this is the case then either additional experiments are required to quantify these effects, or all measurements will have to be performed using the natural concentration of colloids, i.e. without significant dilution or pre-concentration.

Values are not available for the other pesticides due to a combination of a lack of suitable k_r values for the pesticides on the resin, and the appearance of negative results for many of the substances as a result of uncertainty in the analytical measurements.

6.8.2 Tests with Aldrich humic acid

Ten bottles containing known masses of resin, various quantities of water and stock humic acid solution (100 mg dm^{-3} Aldrich Humic acid, sodium salt) together with 50 ml of stock pesticide solution (10 μg dm^{-3} nominal) to give 10 different humic acid concentrations in the range 0 - 10 mg dm^{-3} and a constant amount of pesticides in each bottle. These bottles were then incubated for 24 h, before being separated, extracted and analysed. Initially equation (6.1) was used to calculate the distribution of pesticide between the water and the humic acid (using the amount on the resin to predict the concentration of pesticide "free" in the water and obtaining the amount on the humic acid by subtraction). The results from this model were found to be variably, producing k_{doc} values fluctuating around zero. No trend in the k_{doc}s was found with increasing concentration of humic acid. The poor results are largely due to problems in the analytical method resulting in higher than normal scatter in the measured concentrations of the pesticides. The method relies on the determination of a difference between two quantities, i.e. the concentration of "free" pesticide predicted from the adsorption to the resin, and the concentration in the solution containing colloids. Hence absolute errors in the individual measurements are added to produce the absolute error in the amount adsorbed to the colloid. If the latter is small, the percentage error in the adsorption amount becomes excessive.

Further results have indicated an attachment of the colloids to the resins and difficulties in the analysis of the pesticide concentrations. Although the method still has potential, there was no further time to develop the approach.

7.0 COMPARISON OF METHODS

The analysis of "whole" water samples, i.e. natural waters without filtration, includes pesticides attached to solids and colloids, is generally done by two methods:

(a) Solvent extraction with dichloromethane (DCM), concentration by Kurduna-Danish apparatus and drying using sodium sulphate (House and Ou, 1992; House, 1994; House *et al.*, 1992; Long *et al.*, 1997; 1998)

(b) Solid-phase-extraction with bonded silica phases such as silica (Isolute, C18(EC), 1 g/ 6 ml). The method has been modified in the Land Ocean Interaction Study (LOIS) (House *et al.*, 1997) and includes a pre-filter reservoir placed on top of a C18 cartridge. The sediment collected in the pre-filter is eluted with EtAc after soaking for 2 hours. This method was also used in the work reported here so that the results can be compared with those from the LOIS.

The methods were compared on two occasions using samples 96/3 and 96/4 (see Table 8.1) and the results are shown in Table 7.1 below. The agreement between the two methods is better for sample 96/3, with the largest difference for simazine. The solvent extraction method is slightly more efficient in extracting the more hydrophobic compounds such as the synthetic pyrethroids.

TABLE 7.1 *Comparison of the analysis of "whole" water samples using DCM extraction and the LOIS method with solid-phase extraction (House et al., 1997). The percentage differences are calculated from the results obtained by the LOIS method.*

compound	96/3 DCM	96/3 LOIS	% difference	96/4 DCM	96/4 LOIS	% difference
simazine	0.011	0.028	61	0.134	0.128	4.7
atrazine	0.068	0.069	1.4	0.164	0.248	34
desmetryn	0.117	0.108	8.3	0.08	0.249	68
prometryn	3.45	3.60	4.2	-	-	-
terbutryn	-	-	-	0.068	0.069	1.4
fenitrothion	<0.01	-	-	<0.01	<0.01	-
malathion	<0.01	<0.01	-	<0.01	<0.01	-
cyanazine	<0.01	-	-	0.012	0.017	29
parathion	<0.01	-	-	<0.01	<0.01	-
cis-permethrin	0.01	<0.01	-	0.016	0.013	23
trans-permethrin	0.01	<0.01	-	0.023	0.018	28
cypermethrin	2.33	2.34	<1	0.971	0.906	7.2

8.0 FIELD STUDIES

Bulk water samples (50 dm^3) were collected from the R. Aire in Yorkshire on several occasions during the period of November (1996) to March (1997). A summary of the samples is given in Table 8.1 below. In addition, weekly samples from the rivers Aire, Calder, Ouse, Don and Trent were collected from June to the end of December 1997, and the pesticides isolated by solid-phase-extraction (spe) using the method employed in the Land Ocean Interaction Study (LOIS) described in section 7.0.

TABLE 8.1. *Summary of field sampling for the collection of whole water and particulate samples from the R. Aire at Beale*

date	time	code	SS/mg dm^{-3}	pH	conductivity/ µS cm^{-1} at 25 °C	temperature /°C	DO %
21.11.96	9.00	96/1	14.0	7.11	924	10.9	90
21.11.96	15.30	96/2	8.9	7.20	898	10.1	90
17.1.97	14.30	96/3	5.7	7.32	1087	9.3	70
15.2.97	11.30	96/4	17.8	8.26	578	-	77
15.3.97	11.00	96/5	-	-	-	-	-

The bulk water samples were collected and returned to the River Laboratory the next day. They were stored overnight in the dark in a cold room (6-8 °C) and the following day put

through a continuous-flow centrifuge operated at 11,000 rpm at 10 °C and 200 ml min^{-1}. The final volume of material collected in the centrifuge chamber was isolated by spinning to a small volume (< 50 ml) and this was then freeze-dried to isolate the sediment and colloid material from the water.

Samples of water were also retained for pesticide analysis as follows:

1. 1 litre of whole water was extracted with dichloromethane and evaporated to 2 ml and dried ready for GC/MS.

2. 500 ml of whole water was analysed using C18 solid-phase-extraction (spe) columns by the same method employed in the LOIS programme - sediments were retained as part of the analysis.

3. GF/F filtered samples were placed through the UFC using the procedures described in previous reports. The supernatant and filtrates were analysed using a HP prep-station with C18 SPE columns. Extracts from the GF/F filtrate were also extracted in the same way. Samples for DOC analysis uv/vis absorption were retained as appropriate.

The freeze-dried solids were extracted by supercritical-fluid-extraction with 10% methanol as modifier (Long *et al.*, 1997). The extracts were concentrated to 2 ml in EtAc at 35 °C under dry nitrogen gas and stored for GC/MS analysis. The last sample (96/5) was used to isolate very fine colloid material for more intensive studies. The solids were also used to measure particle-size distributions and clay mineralogy.

8.1 Characterisation of natural suspended sediments

8.1.1 Methods

Samples of river water (50 litre as "whole" water samples) were collected from selected Humber rivers (Aire, Ouse and Swale) as described above. Some of these waters were used in ultra-filtration experiments (Tables 5.5 and 8.1). In addition to these, samples were collected in February and June 1996 for characterisation.

In summary the methods used are as follows:

(a) Determination of the particle-size distribution by sedimentation

This follows the operating procedure: SOP: 26/20.7.94. The method was run without the addition of a deflocculation agent.

(b) Determination of the particle-size distribution by Laser granulometry.

This was done using a Coulter LS130 laser instrument to measure sizes in the range of 0.1 to 900 μm. The sample was suspended in tap water containing a small amount of dispersant and continually pumped through the cell. A beam of monochromatic light of wavelength 750 nm is used

in the instrument to form a 13 μm diameter beam passing through the sample cell. Light is diffracted by particles to an angle which is dependant on their size. The smaller the particle, the larger the angle of diffraction. The diffracted light passes through a Fourier lens to focus on a 126 photodiode detector. The lens ensures that the diffracted light is focused at a specific angle for that particle size independently of the position of the particles in the cell. The intensity of light at each detector is measured and the Fraunhofer model is used to determine the particle size distribution.

(c) The mineral composition of the suspended and colloidal sediment was measured by X-ray diffraction using a Philips PW 1380 horizontal goniometer with 1710 diffraction control. Measurements were made on the whole water sediment samples and also the clay fractions (i.e. < 2 μm in diameter).

8.1.2 Particle-size distributions

The results from laser granulometry are summarised in Table 8.2 for all the samples and in Figures 8.1 - 8.2 for samples 96/1, 96/3 and 96/4. The results for the samples collected from the R. Ouse, R. Swale (16.9.94) and R. Aire (13.12.95) are compared with those obtained by sedimentation in Table 8.3. The two sites on the R. Swale are at Catterick and about 57 km south at Crakehill near the confluence of the Swale with the Ure and Ouse. Both sites are adjacent to the Environmental Agency (EA) gauging stations. Typical river bank material was also collected from a site in the middle of the reach between Catterick and Crakehill near the village of Maunby. The R. Swale, in this section south of Catterick, is particularly susceptible to bank erosion during storm periods. The other two sites on the rivers Aire and Ouse are close to the EA gauging stations at the inter-tidal limits. The site at Naburn on the Ouse is south of York and the main STW input from York. The sediments from the R. Aire are very similar in composition.

The results show:

a) The suspended solids in these rivers are mainly in the size classification of 2-63 μm, i.e. the silt fraction.

b) The suspended solids from the rivers Aire and Ouse had a low sand content. In contrast, the R. Swale sediment contained more sand, probably as a results of the contributions from bank erosion. This is demonstrated from the results of the analysis of the river bank material from Maunby on the river Swale as shown in Table 8.2. The bank material contains approximately equal proportions of the sand and silt fractions.

c) There is negligible suspended material greater than 900 μm in diameter.

d) The clay contents of the suspended material is generally less than 12 % by volume by laser granulometry. However, the results in Table 8.3 indicate substantial differences between the laser granulometry and sedimentation results for the clay fraction (< 2 μm). For the rivers Aire and Ouse, the clay fraction amounts to 35 and 31 % by mass compared with 10 and 11 % by volume by laser granulometry. This implies that the particulates in this fraction are of high density and compact rather than low density organic material.

e) Apart from the river bank material, the particle-size distributions are all similar with medians between 10 and 20 μm. The R. Swale sediments do show some evidence of multiple peaks; for example the peak between 100 and 200 μm found in the sample collected from Crakehill on 1.5.96 is coincident with the second peak in the distribution of the river bank material.

TABLE 8.2 *Particle-size determination (% by volume) by laser granulometry for river suspended sediments isolated by continuous-flow centrifugation. The size-fractions are: < 2 μm, clay; 2-63 μm, silt; 63-2000 μm, sand. The size distribution of a river bank material collected from an eroded section of the R. Swale at Maunby is also shown.*

River	Site reference	Date	<2 μm	2-63 μm	63-900 μm	> 900 μm
Aire	Beale NGR: SE534255	21.6.96	5.55	90.36	4.09	0.0
Aire	Beale NGR: SE534255	13.12.95	10.07	85.92	4.01	0.0
Ouse	Naburn Lock NGR: SE594445	2.3.95	9.61	85.75	4.64	0.0
Swale	Catterick NGR: SE225994	16.9.94	10.66	76.16	13.18	0.0
Swale	Catterick NGR: SE225994	28.2.96	7.92	76.92	15.16	0.0
Swale	Crakehill NGR: SE425733	28.2.96	11.05	81.50	7.45	0.0
Swale	Catterick NGR: SE225994	1.5.96	5.49	71.84	22.67	0.0
Swale	Crakehill NGR: SE425733	1.5.96	6.88	72.48	20.64	0.01
Swale	Maunby bank material NGR: SE347862	28.2.96	7.82	45.50	46.68	0.0

TABLE 8.3 *Comparison of the results for the particle-size determination by laser granulometry and sedimentation. KEY to methods: lg: laser granulometry (% by volume) and s: sedimentation (% by mass).*

Site	Date	>20 μm	5-20 μm	2-5 μm	<2 μm
Ouse, Naburn (lg)	2.3.95	27	48	14	11
Ouse, Naburn (s)	2.3.95	9	42	17	31
Swale, Catterick (lg)	16.9.94	40	34	14	12
Swale, Catterick (s)	16.9.94	40	34	6	21
Aire, Beale (lg)	13.12.95	27	48	15	10
Aire, Beale (s)	13.12.95	10	31	24	35

8.1.3 Mineral characterisation

A brief introduction to the colloidal clay minerals and terminology is given below:
a) Kaolinite group. These are 1:1 type minerals composed of alternate tetrahedral silica and octahedral aluminium sheets producing a layer thickness of about 0.7 nm. Members of the group

include kaolinite, dickite, nacrite, serpentine and halloysite. The particles are usually 0.05-5 μm in size with a relatively low specific surface area (10-30 $m^2 g^{-1}$) and cation exchange capacity of 3-15 meq per 100g.

b) 2:1 type minerals (2 tetrahedral silicas and 1 octahedral aluminium sheet). These includes the expandable minerals (smectites) such as montmorillonite and vermiculities and also non-expanding fine-grained micas (illite). The smectite group is noted for interlayer expansion which is a result of swelling when wetted. Montmorillonite is the predominant member of this group although beidellite, nontronite and saponite are also found in soils. There is strong evidence that some polar pesticides can penetrate the interlayer spacing of the expandable clays and so become less labile. In illite, K^+ ions of low hydration usually balance the charge and produce a non-expanding mica layer of approximately 1.0 nm whereas in vermiculite, containing hydrated Mg^{2+} ions, the interlayer spacing is 0.498 nm corresponding to a bilayer of water between the sheets. The cation exchange capacity of montmorillonites is much greater than non-expanding minerals, usually in the range of 80-150 meq per 100 g of clay with specific surface areas of 70- 100 $m^2 g^{-1}$. Illite differs from micas in that the stacking of layers of illite is more random than mica, the particles are finer than in mica, small amounts of Ca and Mg are present in the interlayer of illites but not in micas and aluminium substitution in the tetrahedral sheets is much less than in true mica.

c) Chlorites are iron-magnesium silicates with some aluminium present. Typically, 2: 1 layers such as in the smectites, alternate with Mg-dominated trioctahedral sheets. Mg also dominates the trioctahedral sheets in the 2:1 layer and so the crystal contains two silica tetrahedral sheets and two Mg-dominated trioctahedral sheets.

d) Feldspars are mainly in two groups: alkali feldspars and plagioclase feldspars. The former includes K-feldspar ($KAlSi_3O_8$). The plagioclase feldspars comprise the series between $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$. They are both similar in structure to the polymorphs of SiO_2, consisting of an infinite network of SiO_4 as well as AlO_4 tetrahedra. The structure can be considered as a derivative of SiO_2 structures, by incorporation of Al into the tetrahedral network, and concomitant housing of Na^+ (or K^+ or Ca^{2+}) in available voids.

The "whole" sediment analysis revealed the presence of quartz (sand or silica) and mica in all the samples. Kaolinite was found to be a dominant mineral present in many samples. Calcite, was measured in trace quantities in all the rivers. Vivianite (see Table 8.4) is an iron phosphate ($Fe_3(PO4)_2$. $8H_2O$) mineral which is a weathering product of Fe-Mn-phosphates and rarely encountered in rivers. The clay analysis, Table 8.5, indicates the dominance of illite and kaolinite in all the samples. The clays from the river bank material (R. Swale) were similar in composition to the suspended sediment from that river. The expandable clays (an illite-smectite mixture) were also important in these rivers. A detailed comparison of the composition of the clay components in samples 96/1, 96/3 and 96/4 is shown in Figure 8.3. The compositions of the clay fractions are very similar.

8.2 Pesticide concentrations

The concentrations of pesticides in suspended sediments from the R. Aire (samples 96/1, 96/3 and 96/4) are shown in Figure 8.4 and for two samples from 96/5, in Figure 8.5. The mineral colloid fraction (96/5_2) was identified by X-ray diffraction as kaolinite and mica with traces of quartz and

calcite with particles of 0.1 μm in diameter . The colloid material was more adsorptive than the rest of the sediment minerals (see Figure 8.5). The distribution coefficients calculated for these samples were calculated from the measured aqueous and sediment concentrations with no correction for the pesticides associated with DOC. These are illustrated in Figure 8.6. The results reveal a lot of variability between the samples which cannot be related to particle-sizes and clay components because these are very similar for each of the samples.

TABLE 8.4 *Qualitative "whole" sample analysis by X-ray diffraction. The minerals present have been ranked as dominant (D), present (P) and trace (T).*

River	Date	mica	kaolinite	chlorite	quartz	K-feldspar	Plag. feldspar	calcite/ dolomite	vivianite
Aire, Beale	21.6.96	P			P			T	D
Aire, Beale	13.12.95	D	D		P	T	P		
Ouse, Naburn	2.3.95	P	D		D	T	T	T	
Swale, Catterick	16.9.94	P	D		P		T		
Swale, Catterick	28.2.96	P		D	D				
Swale, Crakehill	28.2.96	P	D		D		T	T	
Swale, Catterick	1.5.96	P	D		P			T	
Swale, Crakehill	1.5.96	P	D		P				

TABLE 8.5 *Semi-quantitative analysis of the clay fractions by X-ray diffraction (%). The expandable mineral is an illite-smectite mixed-layer of approximately equal proportions. Values of zero indicate a mineral is not identified as present.*

River	Date	illite	expandable	kaolinite	chlorite
Aire, Beale	21.6.96	40	19	32	9
Aire, Beale	13.12.95	55	14	28	3
Ouse, Naburn	2.3.95	41	19	35	5
Swale, Catterick	16.9.94	44	18	35	3
Swale, Catterick	28.2.96	45	9	45	1
Swale, Crakehill	28.2.96	43	13	37	7
Swale, Catterick	1.5.96	49	4	47	0
Swale, Crakehill	1.5.96	45	15	40	0

"Whole water" samples from the rivers Aire at Allerton Bywater (NGR: 417274), Calder at Methley Bridge (NGR: SE 409258), Aire at Beale Bridge (NGR: SE534255), Don at Sprotbrough

(NGR: SE570040), Trent at Cromwell Lock (NGR: SK 801601) and Ouse at Acaster near Naburn Lock (NGR:SE594445) were collected at weekly intervals from 4/6/96 to 16/12/96 by the LOIS team at the University of York. The samples were obtained at the mid-point of the rivers at a sampling depth of 1 m where possible. The pyrex sampling bottles were pre-rinsed with solvents and not with river water and sealed with a PTFE lined screw tops. The samples were extracted onto solid-phase-extraction (spe) columns immediately on return to the laboratory and the suspended material was retained separately on 50 μm frit located at the base of a 70 ml reservoir.

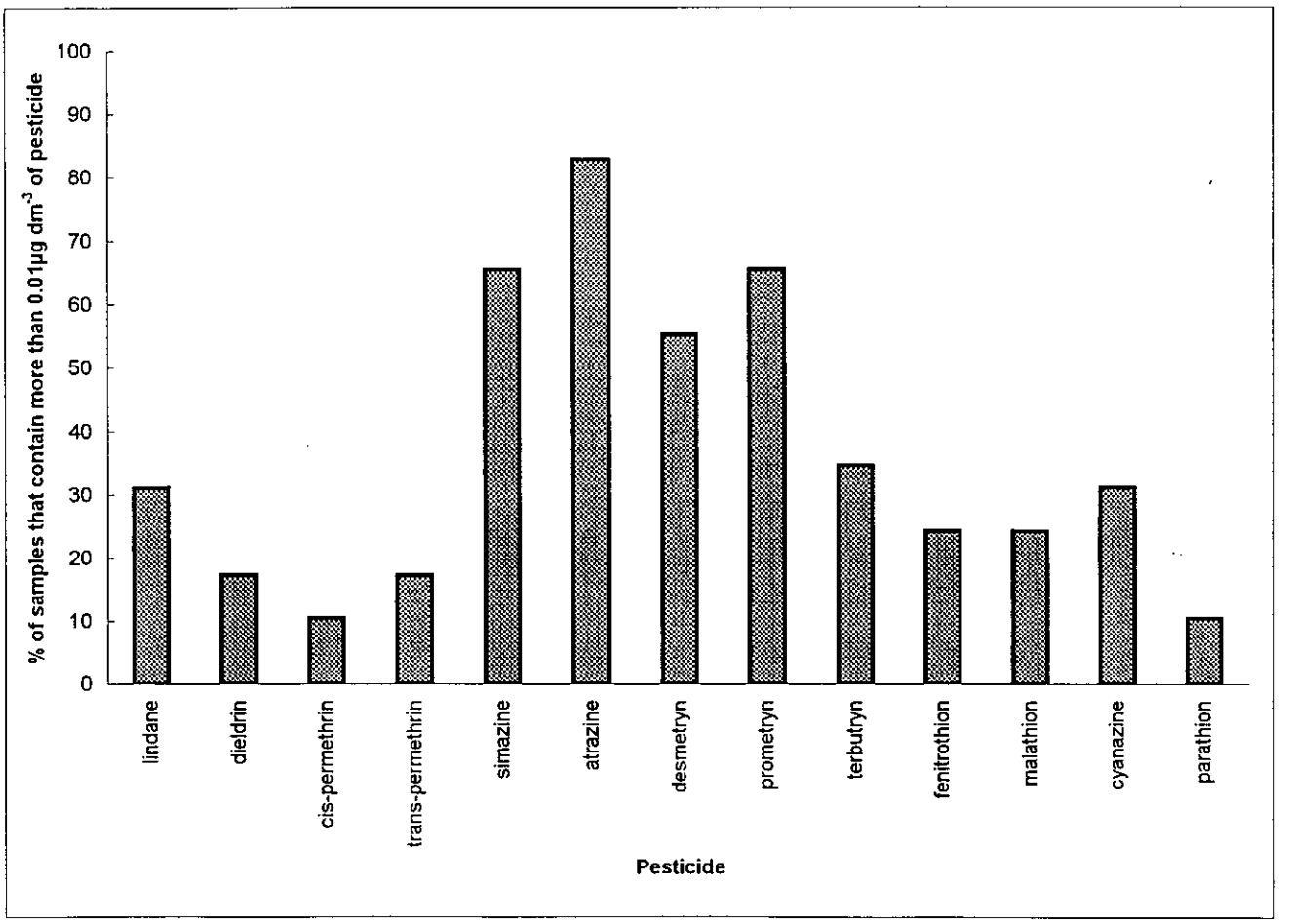
The spe column and reservoir were stored at *ca* 5 ^{0}C overnight before transportation to the River Laboratory in Dorset to arrive before 11.00 h the following day. The samples were then immediately extracted with EtAc and stored in the dark at *ca* 5 ^{0}C. The extraction involved eluting the suspended solids, frit and spe column with EtAc and leaving them in contact with EtAc for 2 hours before final elution. The eluate was collected in a 20 ml bottle and the final extract of 12 ml was then reduced to a volume of approximately 1 ml by evaporation with a stream of dry nitrogen and the vial walls rinsed to obtain a final volume of approximately 2 ml. This was then dried by passing through an anhydrous sodium sulphate column to yield a final volume of 2 ml. Sample blanks of hplc grade water were carried in the field and treated the same as the river samples. Each week, one of the rivers was spiked with a mixture of the target pesticides and extracted and analysed in the same way as the other samples - this information provided data on the recovery of pesticides from the samples during the programme.

The EtAc extracts were spiked with ametryn and decachlorobiphenyl (DCBP) as internal standards. These compounds were used to check the relative retention times of the target pesticides and in the quantification of the concentration of the compounds in the extracts. The triazines and organophosphorus compounds were measured using GC with detection by NPD and injection through a programmable vapouriser into a 30 m x 0.25 mm i.d. DB% (5% phenyl methylpolysiloxane), 0.25 μm film thickness, fused silica column. Dieldrin, lindane and *cis- trans*-permethrin were determined by GC/MS with the same column as above but with split/splitless injection and He carrier gas. Previous results using this procedure have been presented by House *et al.* (1997).

The results, shown in Tables 8.6 to 8.11 and Figures 8.7 to 8.30, indicate a widespread occurrence of many of the compounds in the region, particularly in the rivers Aire and Calder. The sites on the river Aire at Allerton Bywater and Calder at Methley Bridge are upstream of the confluence of the two rivers and Beale, on the Aire, is at the tidal limit. The occurrence of most of the compounds and particularly lindane, *cis* and *trans* permethrin and terbutryn, was greater in the R. Calder than in samples from the R. Aire at Allerton Bywater indicating that the R. Calder is the dominant source of the contaminants contributing to the occurrence downstream at Beale. Apart from the triazines: simazine, atrazine, desmetryn and prometryn, samples from the other rivers, the Don, Trent and Ouse, were less contaminated with the other compounds. The widespread occurrence of the triazine in the region, even after the ban on their use in non-agricultural applications, is surprising. The organochlorines and *cis* and *trans* permethrin were rarely measured in the rivers Trent and Ouse.

Table 8.6. The number of samples analysed from the R. Aire at Allerton Bywater, the number of samples in which the pesticides were detected and quantified, and the number of samples in which the pesticides were detected but not quantified i.e. at concentrations less than the limit of determination (LD) of 0.01µg dm^{-3}.

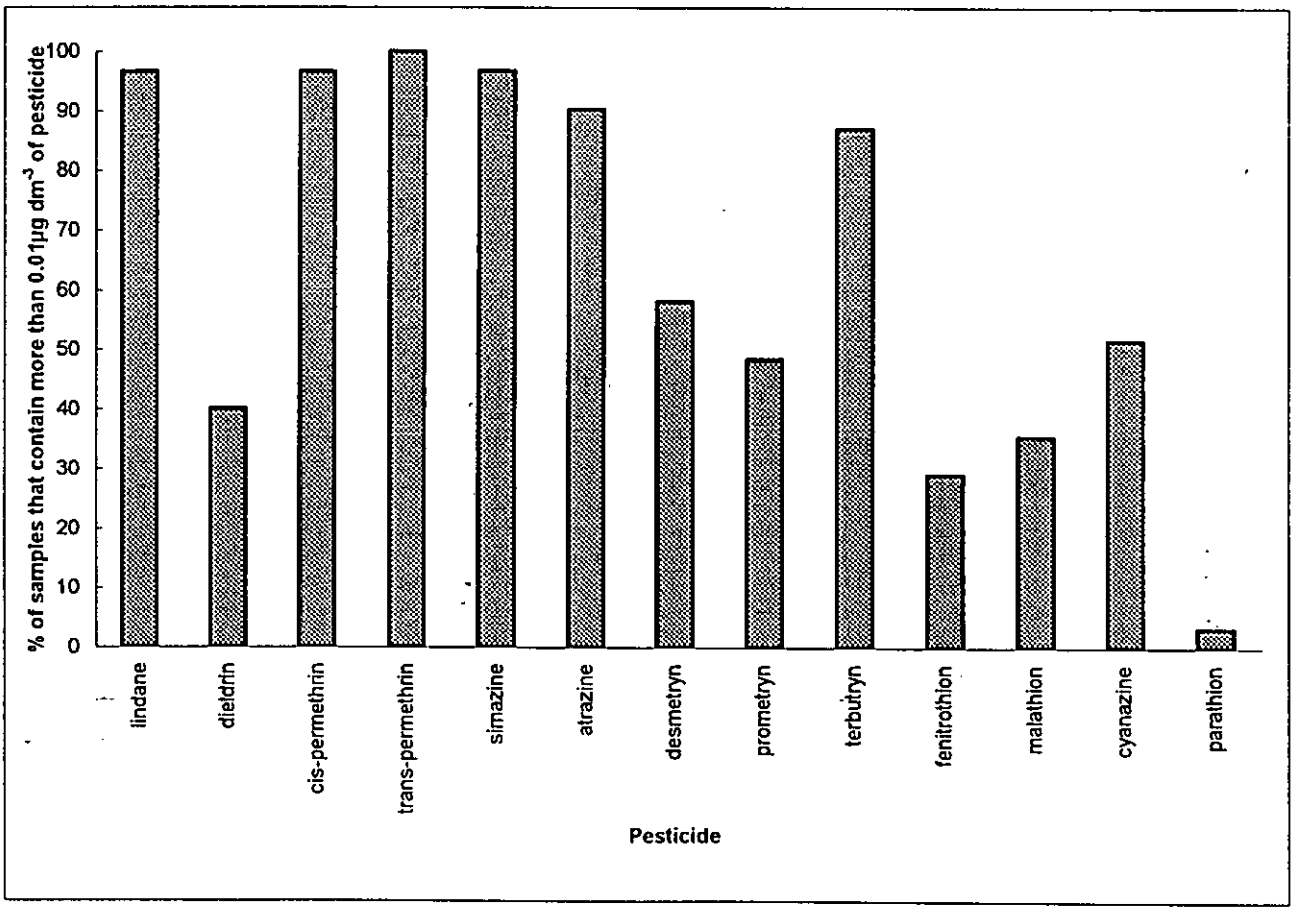
Compound	No. samples analysed	No. samples not detected	No. samples detected	No. samples less than LD
lindane	29	20	9	0
dieldrin	29	24	5	0
cis-permethrin	29	22	3	4
trans-permethrin	29	21	5	3
simazine	29	7	19	3
atrazine	29	1	24	4
desmetryn	29	13	16	0
prometryn	29	10	19	0
terbutryn	29	17	10	2
fenitrothion	29	4	7	18
malathion	29	3	7	19
cyanazine	29	18	9	2
parathion	29	10	3	16



The percentage of samples containing more than 0.01µg dm^{-3} of the pesticides.

Table 8.7. The number of samples analysed from the R. Calder at Methley Bridge, the number of samples in which the pesticides were detected and quantified, and the number of samples in which the pesticides were detected but not quantified i.e. at concentrations less than the limit of determination (LD) of 0.01µg dm^{-3}.

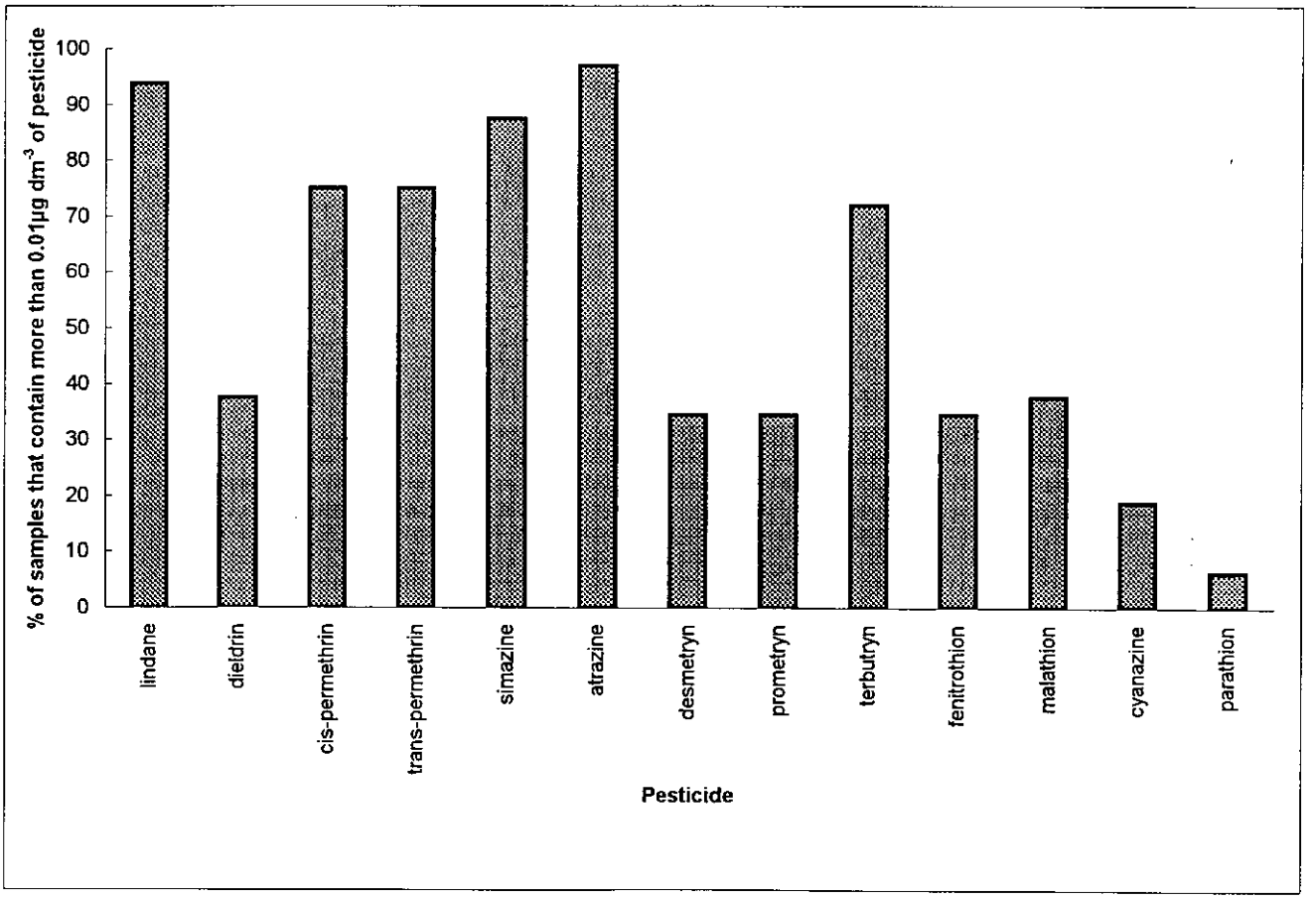
Compound	No. samples analysed	No. samples not detected	No. samples detected	No. samples less than LD
lindane	30	1	29	0
dieldrin	30	16	12	2
cis-permethrin	30	1	29	0
trans-permethrin	30	0	30	0
simazine	31	1	30	0
atrazine	31	3	28	0
desmetryn	31	11	18	2
prometryn	31	13	15	3
terbutryn	31	4	27	0
fenitrothion	31	2	9	20
malathion	31	6	11	14
cyanazine	31	11	16	4
parathion	31	4	1	26



The percentage of samples containing more than 0.01µg dm^{-3} of the pesticides.

Table 8.8. The number of samples analysed from the R. Aire at Beal Bridge, the number of samples in which the pesticides were detected and quantified, and the number of samples in which the pesticides were detected but not quantified i.e. at concentrations less than the limit of determination (LD) of 0.01µg dm^{-3}.

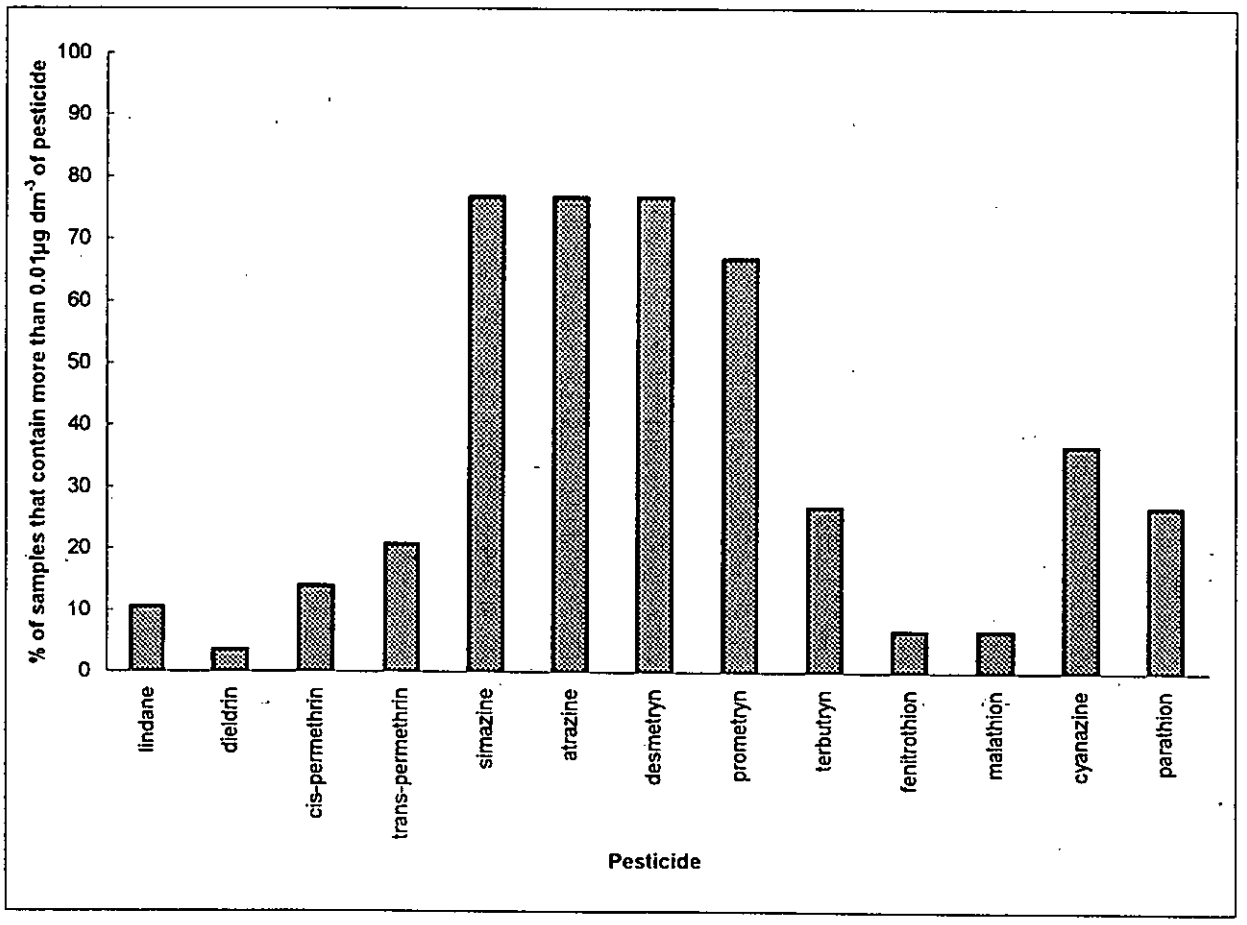
Compound	No. samples analysed	No. samples not detected	No. samples detected	No. samples less than LD
lindane	32	2	30	0
dieldrin	32	18	12	2
cis-permethrin	32	7	24	1
trans-permethrin	32	8	24	0
simazine	32	4	28	0
atrazine	32	1	31	0
desmetryn	32	20	11	1
prometryn	32	19	11	2
terbutryn	32	8	23	1
fenitrothion	32	8	11	13
malathion	32	9	12	11
cyanazine	32	22	6	4
parathion	32	11	2	19



The percentage of samples containing more than 0.01µg dm^{-3} of the pesticides.

Table 8.9. The number of samples analysed from the R. Don at Sprotbrough Bridge, the number of samples in which the pesticides were detected and quantified, and the number of samples in which the pesticides were detected but not quantified i.e. at concentrations less than the limit of determination (LD) of 0.01µg dm^{-3}.

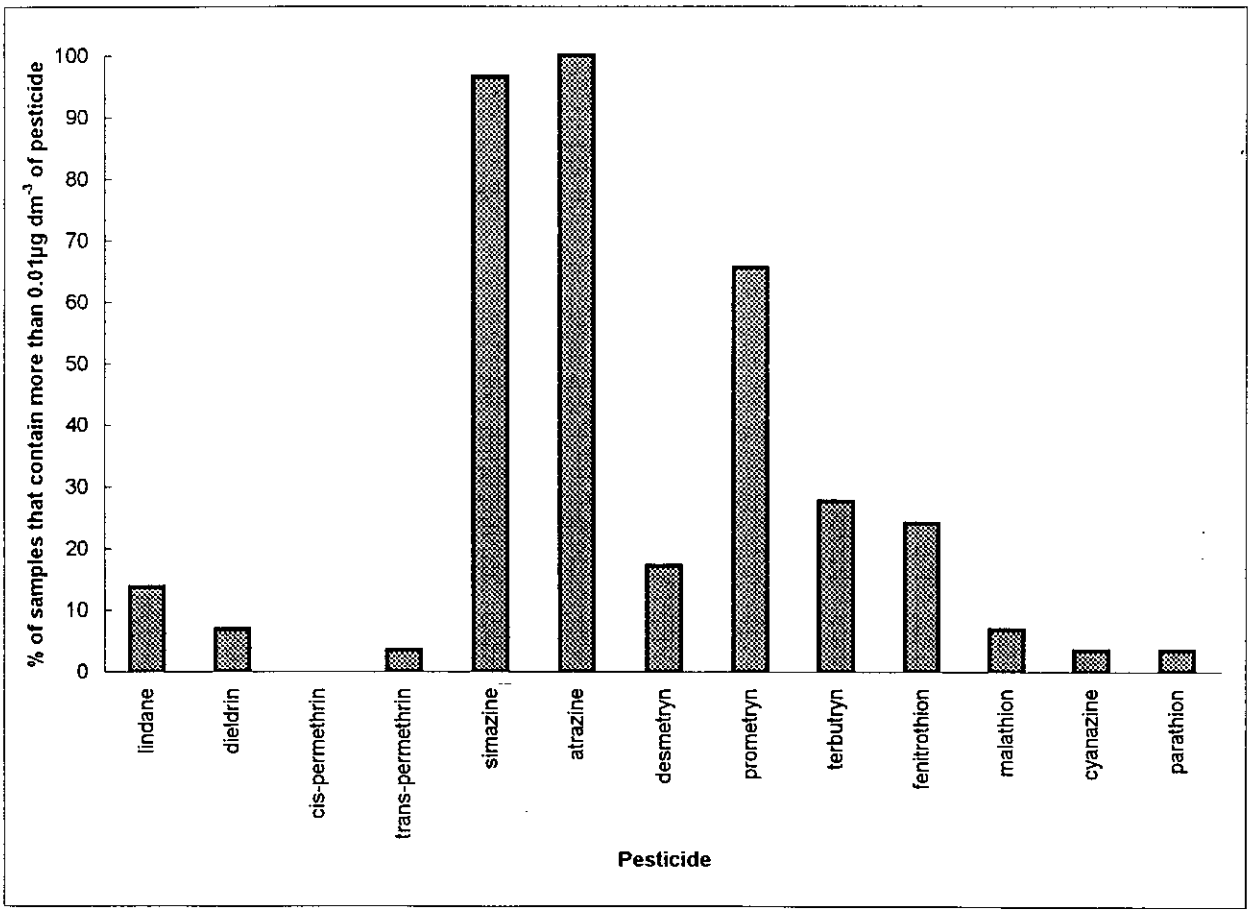
Compound	No. samples analysed	No. samples not detected	No. samples detected	No. samples less than LD
lindane	29	26	3	0
dieldrin	29	27	1	1
cis-permethrin	29	25	4	0
trans-permethrin	29	21	6	2
simazine	30	5	23	2
atrazine	30	5	23	2
desmetryn	30	7	23	0
prometryn	30	10	20	0
terbutryn	30	22	8	0
fenitrothion	30	6	2	22
malathion	30	10	2	18
cyanazine	30	16	11	3
parathion	30	22	8	0



The percentage of samples containing more than 0.01µg dm^{-3} of the pesticides.

Table 8.10. The number of samples analysed from the R. Trent at Cromwell Lock, the number of samples in which the pesticides were detected and quantified, and the number of samples in which the pesticides were detected but not quantified i.e. at concentrations less than the limit of determination (LD) of 0.01µg dm^{-3}.

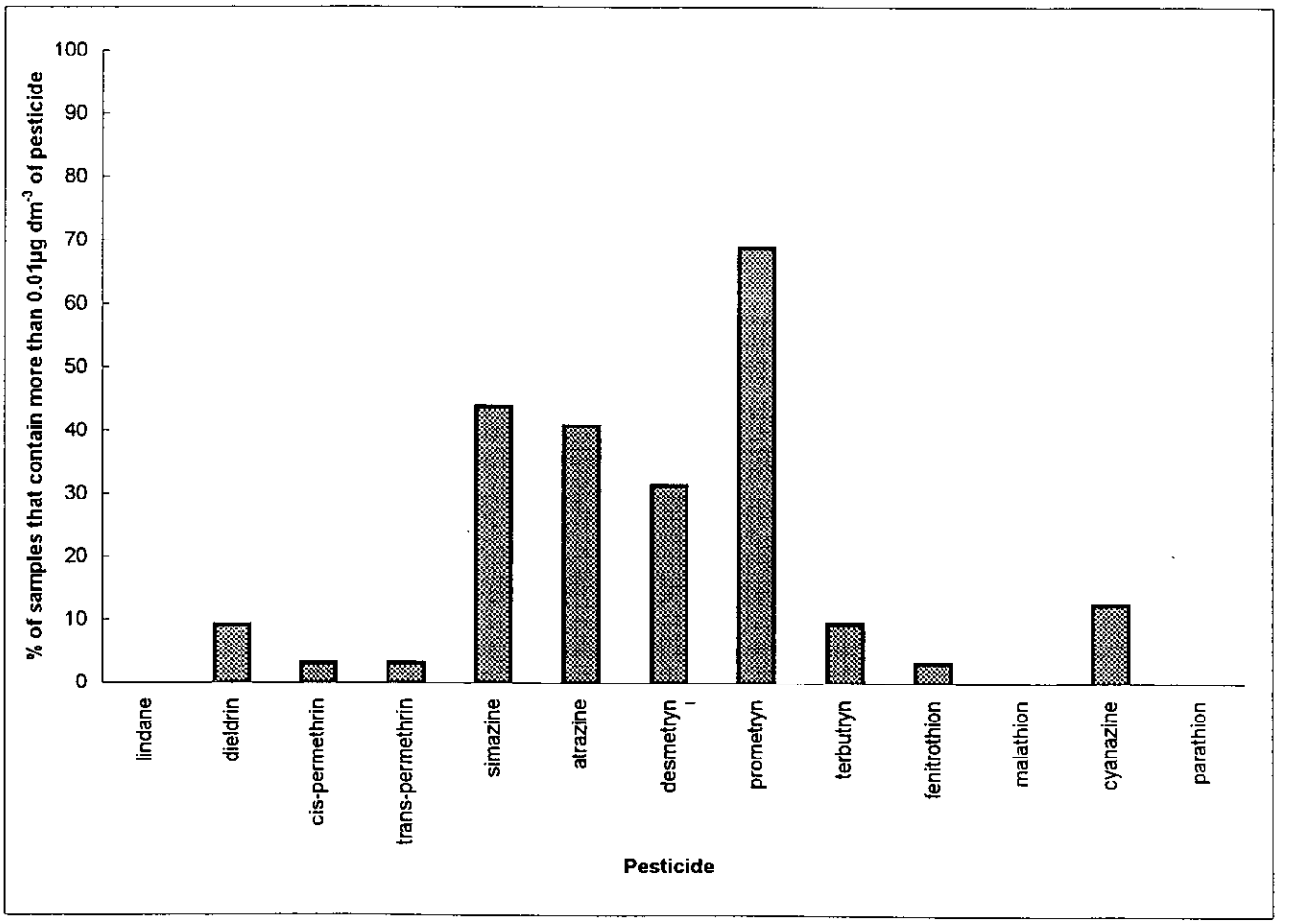
Compound	No. samples analysed	No. samples not detected	No. samples detected	No. samples less than LD
lindane	29	25	4	0
dieldrin	29	26	2	1
cis-permethrin	29	28	0	1
trans-permethrin	29	28	1	0
simazine	29	0	28	1
atrazine	29	0	29	0
desmetryn	29	24	5	0
prometryn	29	10	19	0
terbutryn	29	20	8	1
fenitrothion	29	1	7	21
malathion	29	16	2	11
cyanazine	29	26	1	2
parathion	29	14	1	14



The percentage of samples containing more than 0.01µg dm^{-3} of the pesticides.

Table 811. The number of samples analysed from the R. Ouse at Acaster (Naburn Lock), the number of samples in which the pesticides were detected and quantified, and the number of samples in which the pesticides were detected but not quantified i.e. at concentrations less than the limit of determination (LD) of 0.01µg dm^{-3}.

Compound	No. samples analysed	No. samples not detected	No. samples detected	No. samples less than LD
lindane	33	33	0	0
dieldrin	33	28	3	2
cis-permethrin	33	32	1	0
trans-permethrin	33	30	1	2
simazine	32	5	14	13
atrazine	32	3	13	16
desmetryn	32	20	10	2
prometryn	32	9	22	1
terbutryn	32	28	3	1
fenitrothion	32	13	1	18
malathion	32	17	0	15
cyanazine	32	26	4	2
parathion	32	19	0	13



The percentage of samples containing more than 0.01µg dm^{-3} of the pesticides.

River discharge data at the sampling points were provided by the EA and supplementary chemical data on the concentrations of suspended solids and DOC were obtained from the LOIS laboratory. The relationship between pesticide concentration and suspended solid concentrations or river discharge for *cis* and *trans* permethrin (Figures 8.7-8.12), lindane and dieldrin (Figures 8.13 - 8.18), simazine and atrazine (Figures 8.19-8.24) and desmetryn, prometryn and terbutryn (Figures 8.25- 8.30) show contrasting relationships. For *cis* and *trans* permethrin, the highest concentrations were measured during high-flow conditions when suspended solids concentrations were highest. This is consistent with the high concentrations of permethrin measured on suspended solids in the Humber rivers by Long *et al.* (1998). The triazines, in contrast, were found at their highest concentrations during periods of low-flow, e.g. Figure 8.21. Lindane and dieldrin, although less abundant than the other compounds, show a lot of variability with a tendency to high concentrations at low-flow (see Figure 8.14 for the R. Calder) but also evidence of mobilisation during high-flow in other rivers (see Figure 8.15 for dieldrin in the R. Aire at Beale).

As expected, there is a strong relationship between the suspended solids concentration and river discharge (see for example Figure 8.31 for the R. Aire), and also between DOC and river discharge. The latter follows an inverse relationship (Figure 8.32), indicating the dilution of DOC during high river-flows (see also Tipping *et al.*, 1997). Hence transport of pesticides with suspended solids and organic colloids, will vary according to river discharge. At low river-flows, suspended solid concentrations are low (typically < 20 mg dm^{-3}) and DOC concentrations are at their highest; in contrast, in high-flow conditions the DOC is diluted by storm run-off and suspended solids concentrations are high - reaching values of up to 2 g dm^{-3} in the Humber rivers (Wass *et al.*, 1997).

8.3 Transport by colloids and suspended matter

The percentage of pesticide transported with suspended solids and associated with DOC, (denoted by the variable: ass) may be calculated by re-arranging equation (5.6):

$$ass = 100 \times [1 - (1 + SS \times k_d / 10^6 + DOC \times k_{doc} / 10^6)^{-1} \qquad (8.1)$$

where SS is the concentration of suspended solids (mg dm^{-3}), DOC is the dissolved organic carbon content (mg dm^{-3}), k_d is the sediment distribution coefficient (ml g^{-1}) and k_{doc} is the distribution coefficient for pesticides associated with organic colloids (ml g^{-1}). This prediction does not depend on the concentration of the pesticides in the water. This may be expanded to take account of components within either the suspended solid or colloid fractions, e.g.

$$ass = 100 \times [1 - \sum_i SS_i \times k_{di} / 10^6 + \sum_j coll_j \times k_j / 10^6)^{-1} \qquad (8.2)$$

where i represents the sediment components and j the colloid (coll) components. The sediment components may be the different mineral and biological particles, and similarly the colloid fraction may be based on the categories outline in section 3. The problem with this approach is the lack of information about the distribution coefficients in natural systems and the effort needed to determine the relative amounts of the components within the sediment and colloid fractions. If this is coupled with the difficulties in monitoring temporal and spatial changes in these parameters, the approach becomes impracticable. Hence equation (8.1) is more viable in that the main variables are:

(a) SS: suspended solids, typically > 0.45 μm in diameter; this measurement is relatively simple and inexpensive to perform.

(b) DOC: dissolved organic carbon. This may be estimated from uv/visible absorbance or measured directly. The former method is relatively simple to perform without extensive sample processing.
(c) k_d: distribution coefficient for the suspended solids. This is likely to be variable between river catchments depending on the local geology, point-inputs and the importance of river bank erosion as well biological productivity in the river. A range of values may determined for a particular catchment or estimates found from the literature were available, see Table 8.12. The lack of turbidity in the filtered and centrifuged samples also suggest that the colloidal clay fraction was not carried into the filtrate but remained on the filter bed.

Equation (8.1) has been examined using the simazine concentration data from the R. Aire (at Beale, Figure 8.21). k_d was taken as 4 ml g^{-1} and k_{doc} as 8800 ml g^{-1} (mean value from the UFC experiments, Table 5.5). This leads to the percentage of simazine associated with sediments and colloids as shown in Figure 8.33. The equation predicts that under 10 % of the compound is bound to sediments or colloids with the majority associated with DOC rather than suspended sediment. Hence the maximum in Figure 8.33 occurs during low river-flows in the summer period when the concentrations of DOC are at a maximum and suspended solid concentrations are a minimum.

Similar calculations have been done for the other compounds for which k_{doc} values were measured (Table 5.5) and k_d data are available. k_ds were calculated from the values of k_{oc} given in Table 4.1 with the organic carbon content chosen as 10 % - a value typical for contaminated rivers. The k_{oc}s chosen are likely to be an underestimate as the limited data which are available indicates that sediment k_{oc}s are usually greater than those found in soils (House *et al.*, 1992. More detailed information on the distribution of micro-organic contaminants in river sediments, for the Aire, Calder, Trent, Don, Ouse and Swale, will be available on completion of the LOIS programme. The results of the calculation are shown in Figures 8.33 - 36. For all the compounds the interaction with organic colloids, expressed as DOC, is greater than with suspended sediments. Atrazine and simazine are the least bound with < 12 % associated with DOC or sediment; other compounds such as prometryn, terbutryn and fenitrothion, show greater interactions amounting to a maximum of approximately 20 % of the material adsorbed. This increases to approximately 30 % for parathion and malathion.

Independent measurements of k_{doc} have not been made for the other pesticides found in the R. Aire. However, values may be estimated from the relationship between K_{ow} and k_{doc} obtained in this work (mean values in Table 5.5), combined with data available from the literature for more hydrophobic compounds (Rav-Ach and Rebhun, 1992) - see Table 8.12 below. The sediment distribution coefficient for the *cis* and *trans* permethrins are similar to values calculated by House *et al.*, (1991) and Long *et al.*, (1998) for sediments from the R. Stour and R. Aire (February and May 1996) respectively, i.e for the R. Aire the range of $\log(k_d)$ was 2.09 to 2.64. The results of the calculation of the bound pesticide in the R.Aire for lindane, permethrin and dieldrin are shown in Figure 8.36 and 8.37. The more hydrophobic compounds such as dieldrin or permethrin (no distinction between *cis* and *trans* isomers) are very strongly adsorbed to sediments and colloids. Almost 90 % of the permethrin and dieldrin present in the "whole" water sample is predicted to be associated with DOC and suspended solids, with the majority interacting with organic colloids.

TABLE 8.12. *Values of distribution coefficients, K_{ow} and k_d selected from the literature to calculates the appropriate k_{doc} using the relationship:*
$\log k_{doc} = 0.4665 . \log K_{ow} + 2.8295$.

compound	log (K_{ow})	log (k_d)	log (k_{doc})
permethrin	6.2 [a]	2.59 [b]	5.72
lindane	3.7 [c]	3.4 [c]	4.56
dieldrin	6.2 [d]	2.65 [e]	5.72

a: Muir *et al.* (1985); b: Sharom and Solomon (1981); c: Saleh *et al.* (1982); d: Briggs (1981) and e: Sharom *et al.* (1980).

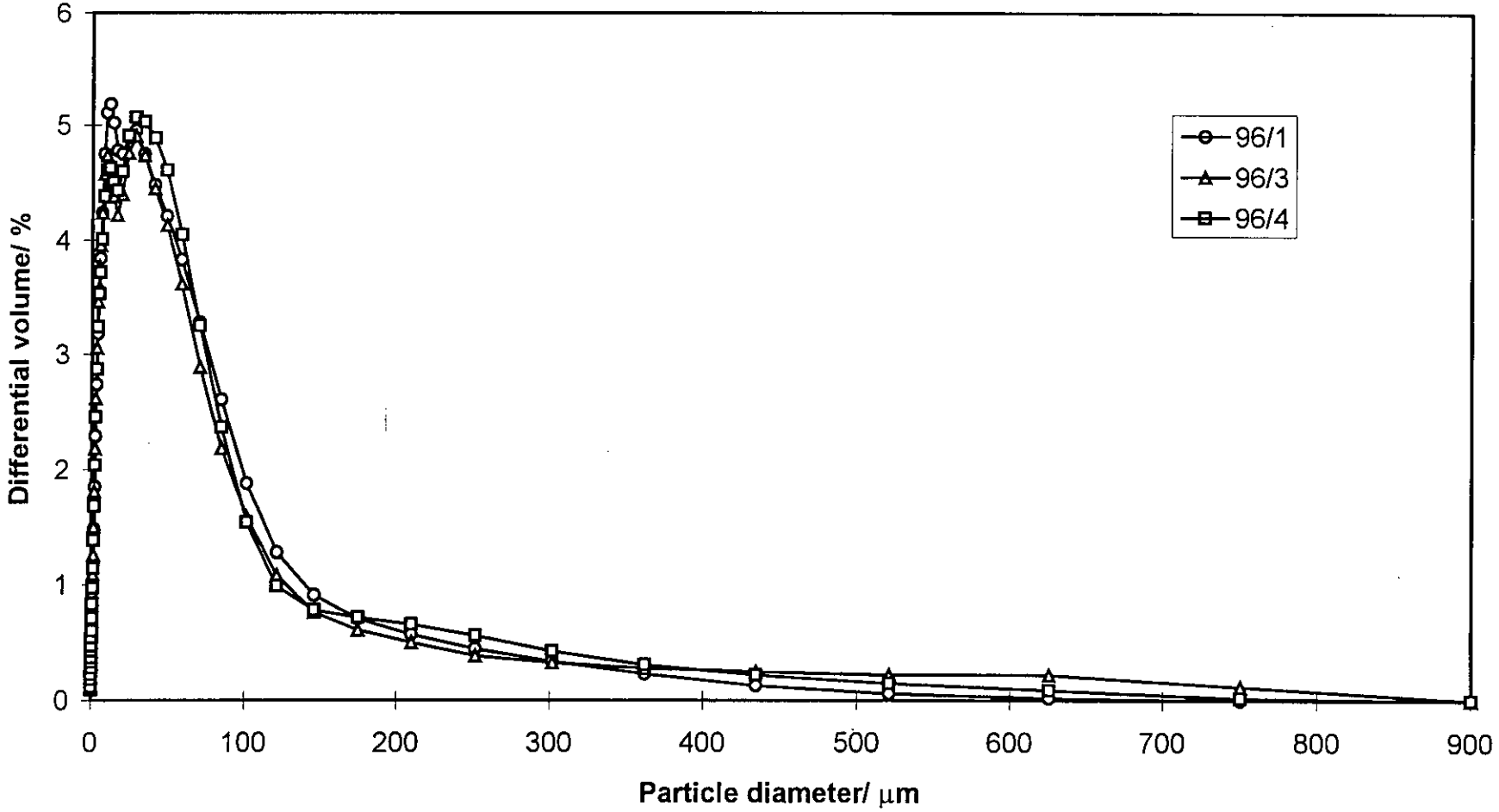


Figure 8.1 Comparison of the particle size distribution for diameters < 900 μm.

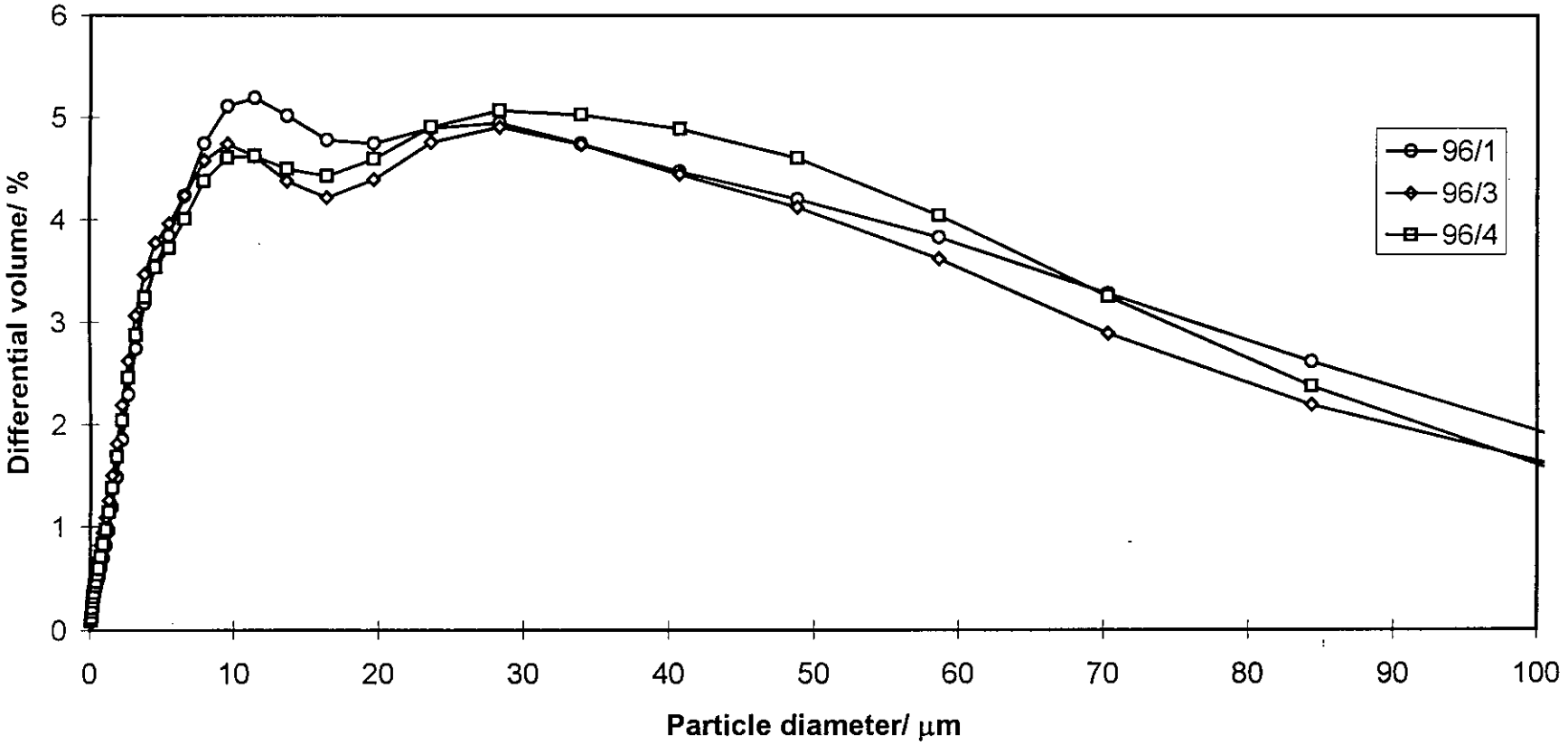


Figure 8.2 Comparison of the particle size distribution for diameters < 100 μm.

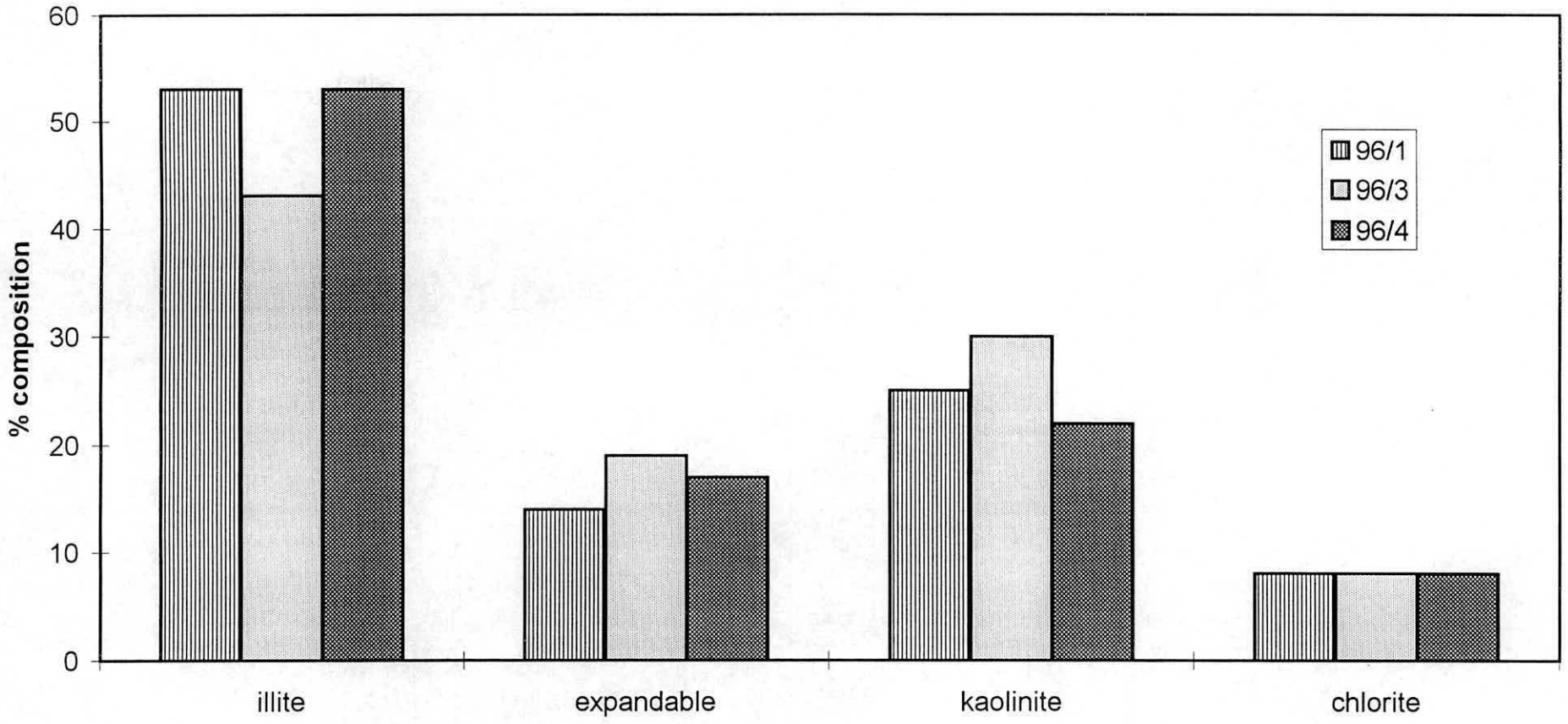


Figure 8.3 Comparison of the clay components after separation by CFC

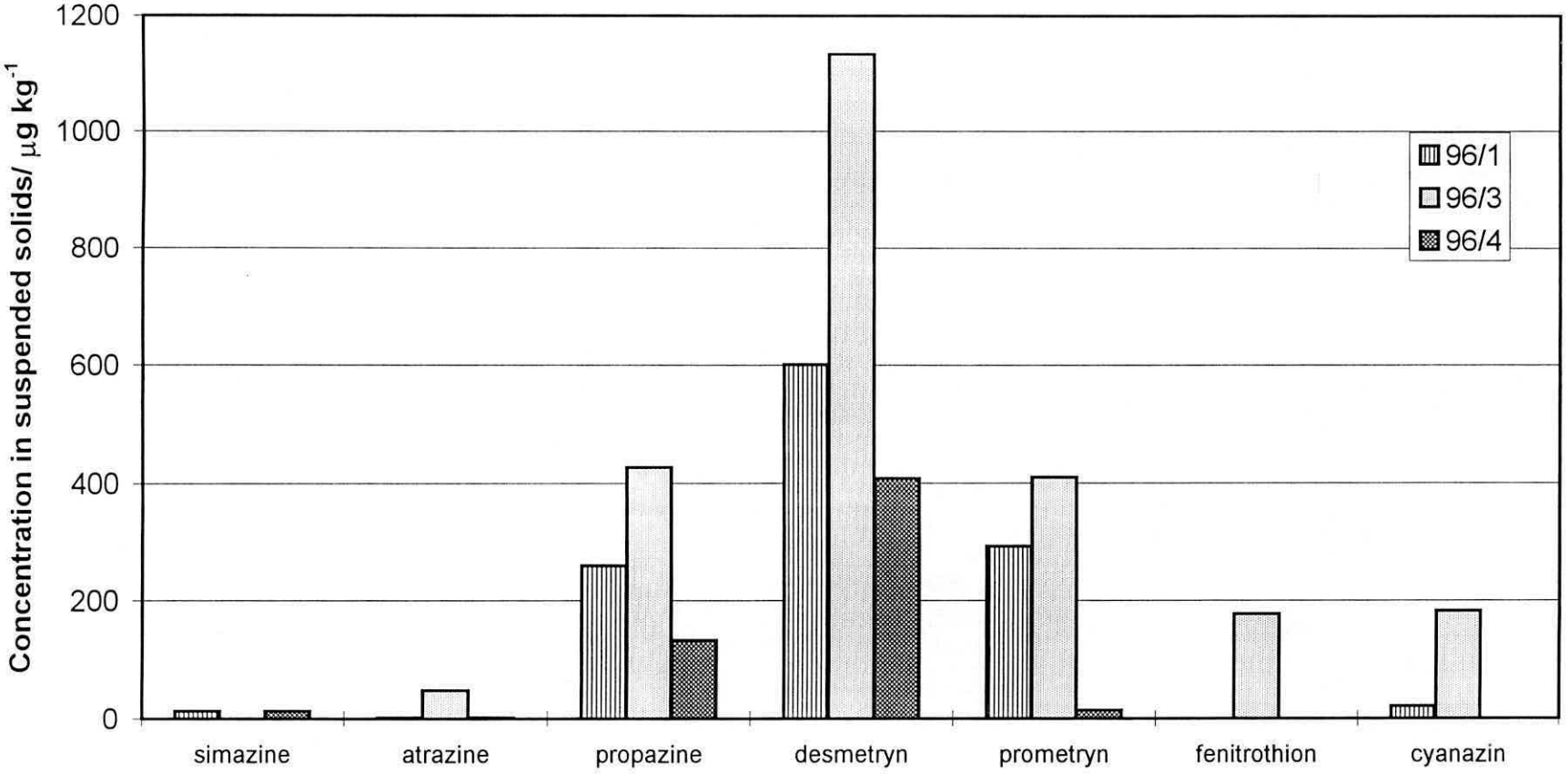


Figure 8.4 Concentration in suspended solids for samples 96/1- 96/4

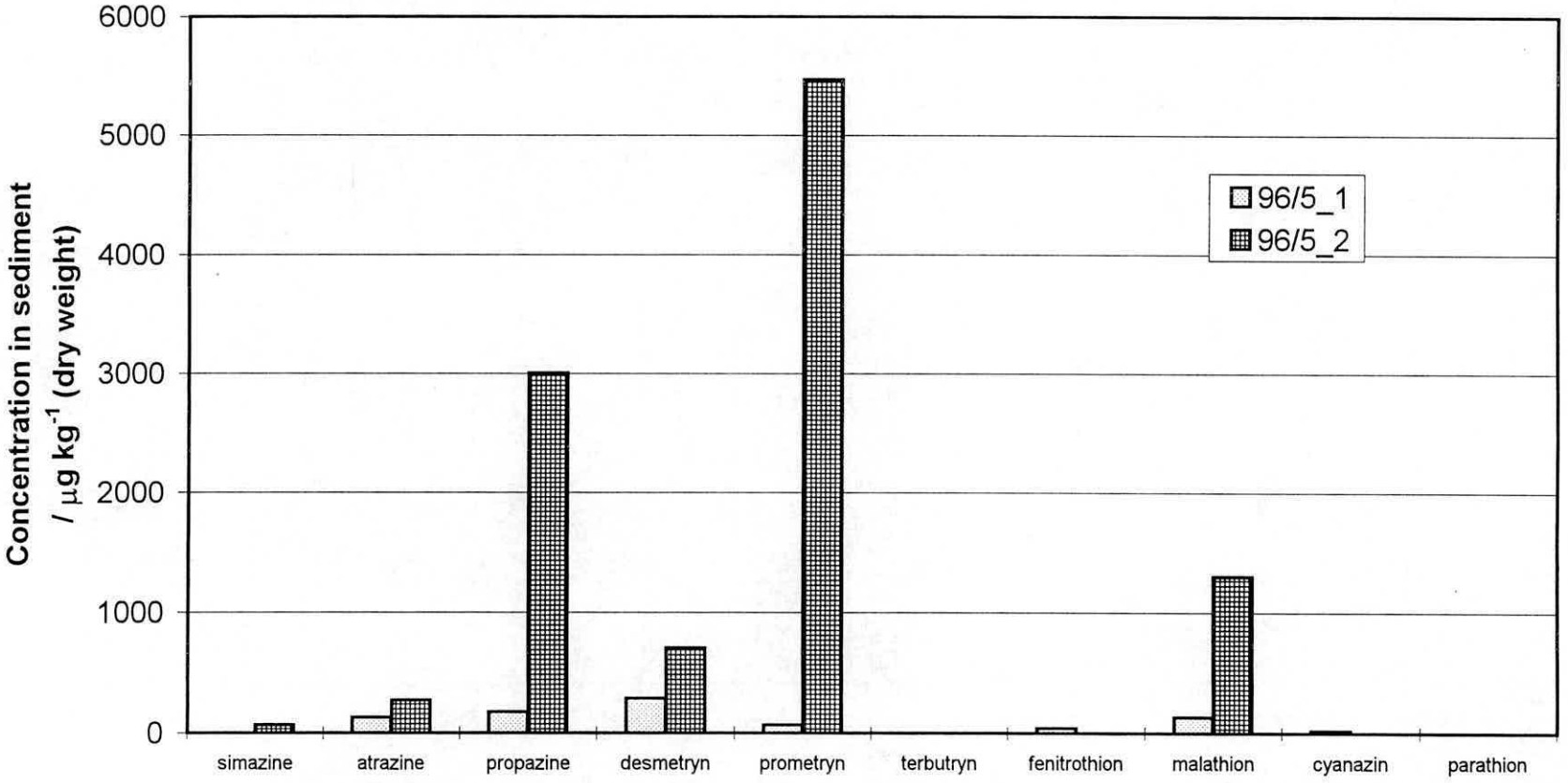


Figure 8.5 Comparison of the concentration of pesticides measured on the sediment (96/5_1) and colloids (96/5_2)

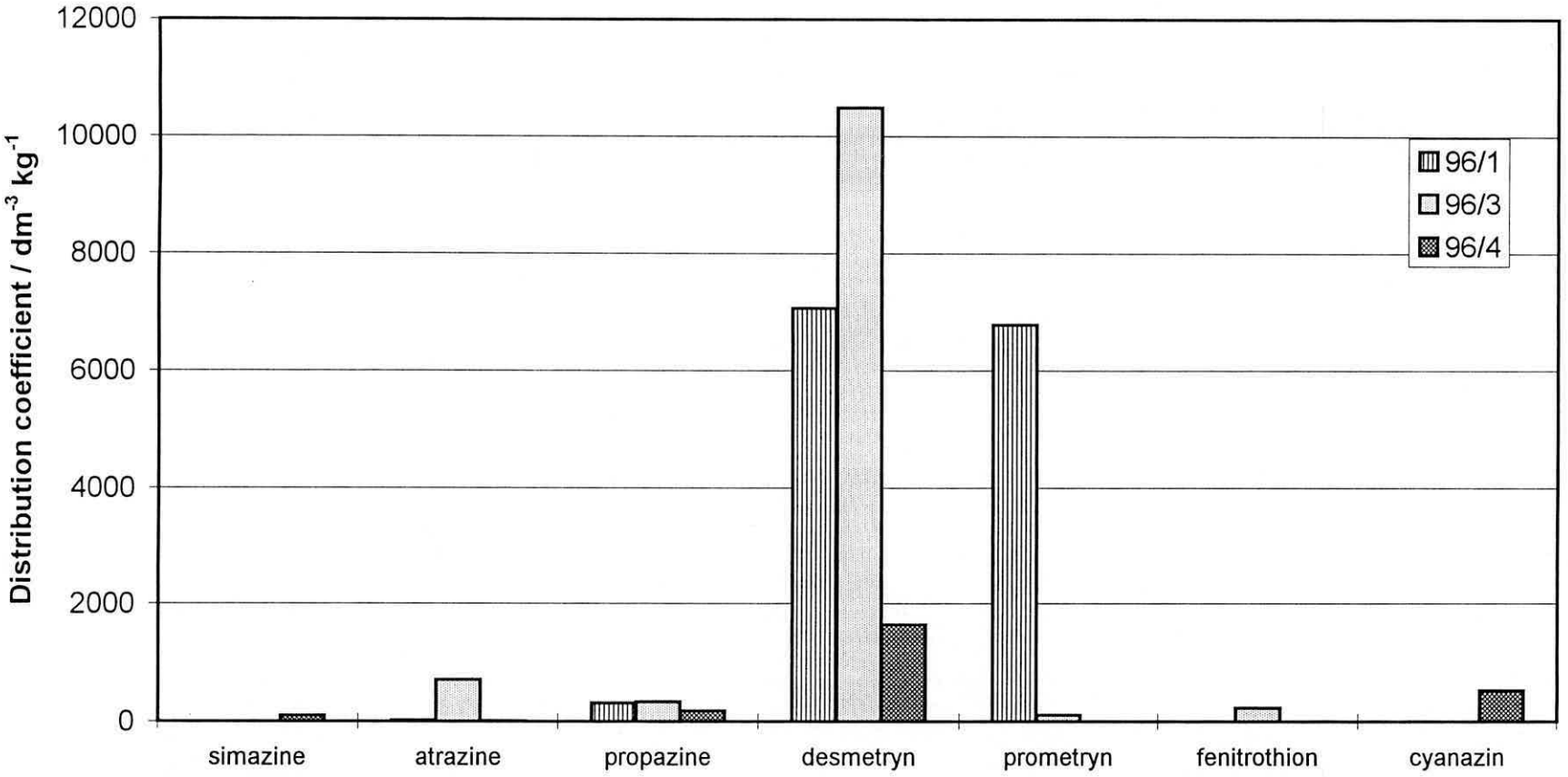


Figure 8.6 Comparison of the field distribution coefficients for samples 96/1- 96/4

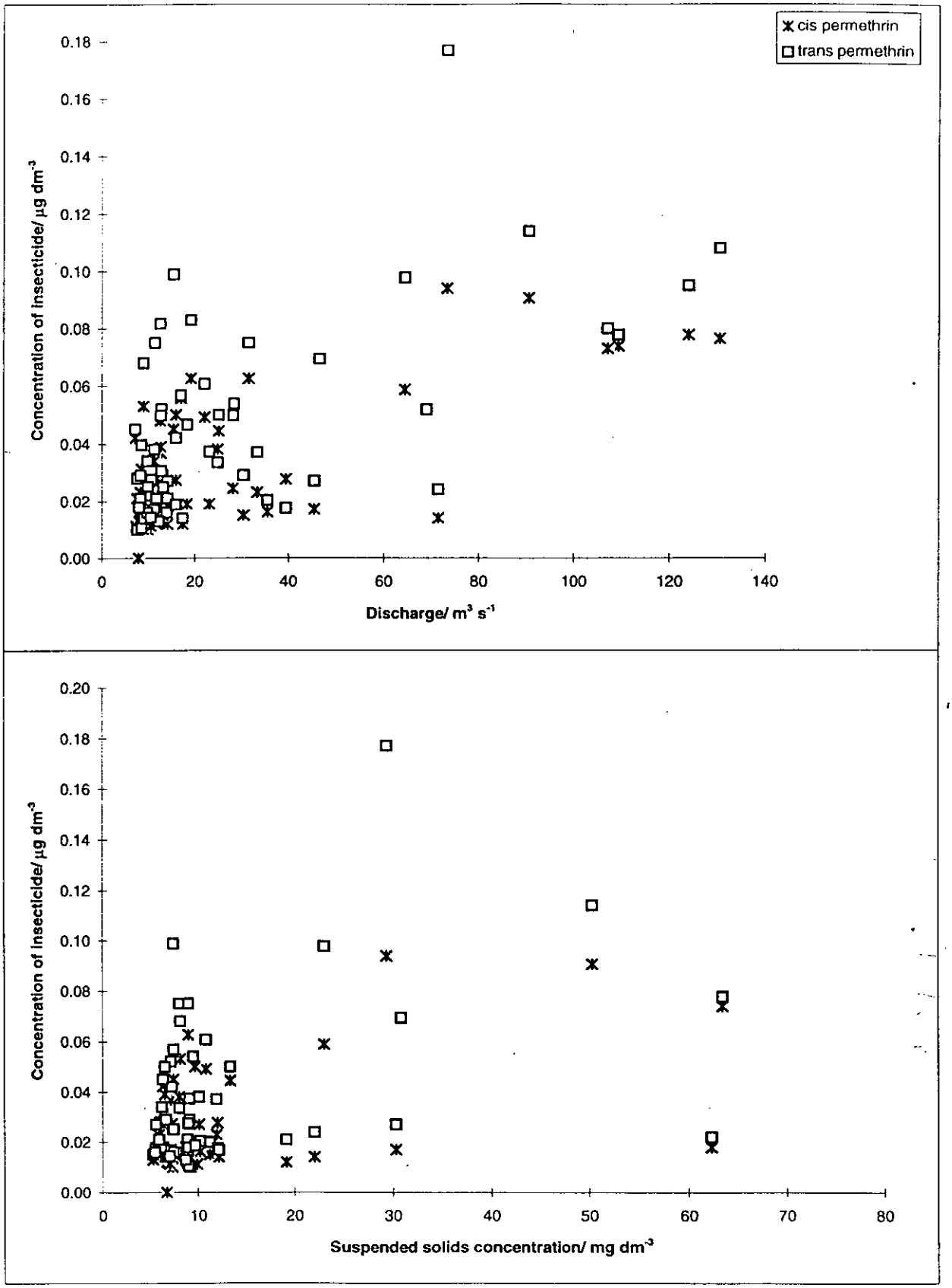


Figure 8.9. Relationship between river discharge, suspended solids concentration and concentrations of *cis* and *trans*-permethrin in the R. Aire at Beal Bridge.

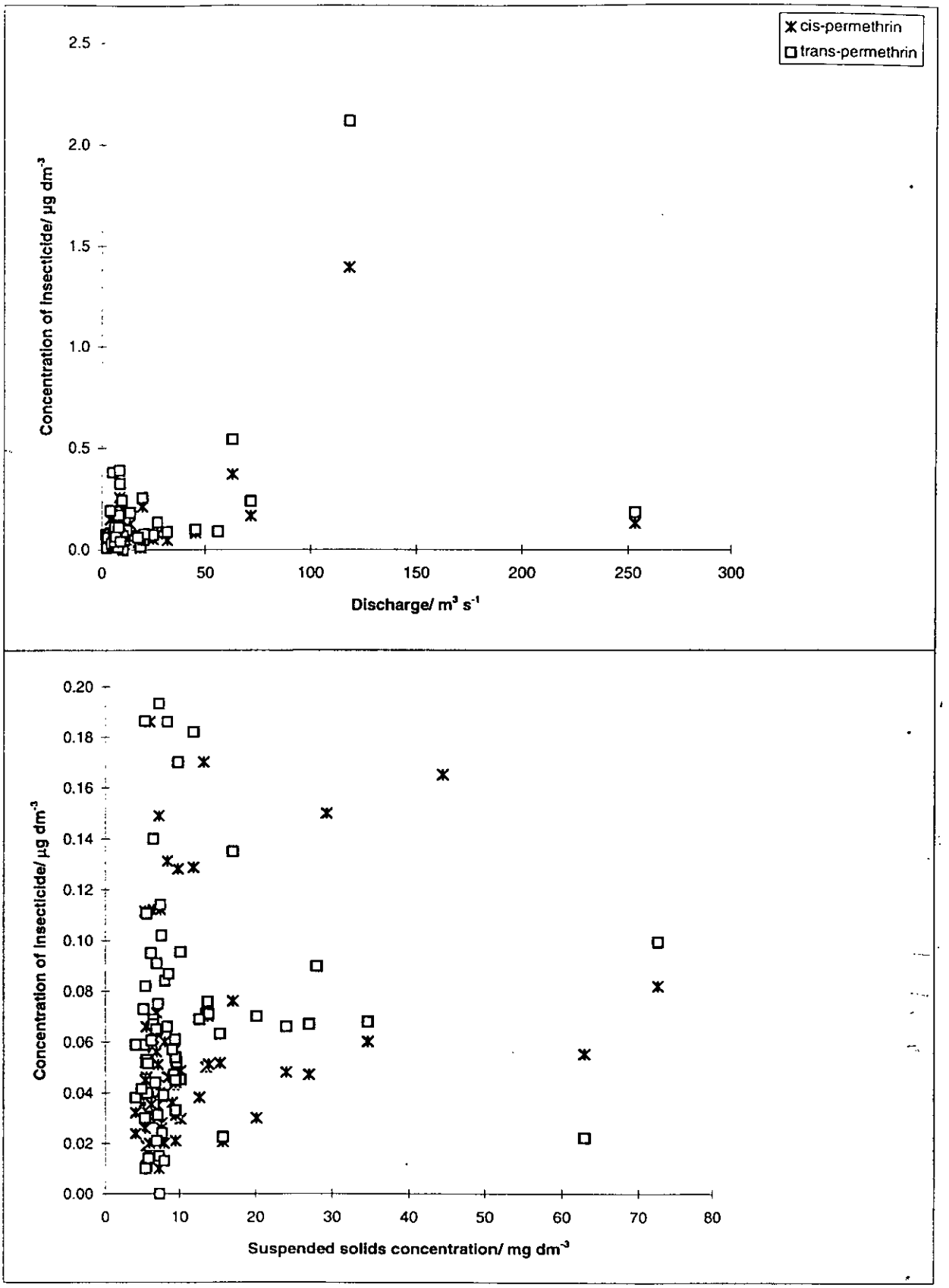


Figure 8.8. Relationship between river discharge, suspended solids concentration and concentrations of *cis* and *trans*-permethrin in the R. Calder at Methley Bridge.

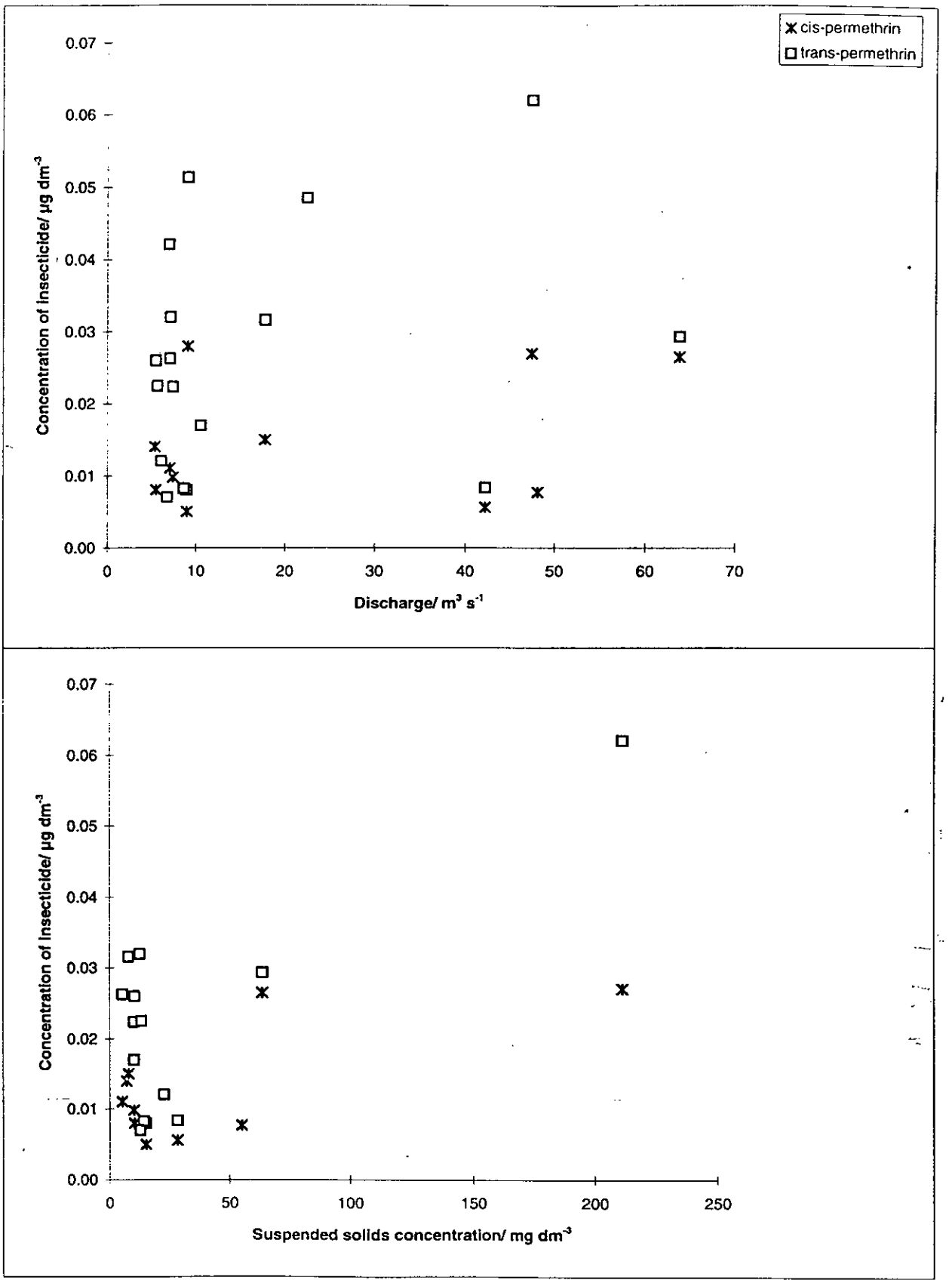


Figure 8.7. Relationship between river discharge, suspended solids concentration and concentrations of *cis* and *trans*-permethrin in the R. Aire at Allerton Bywater.

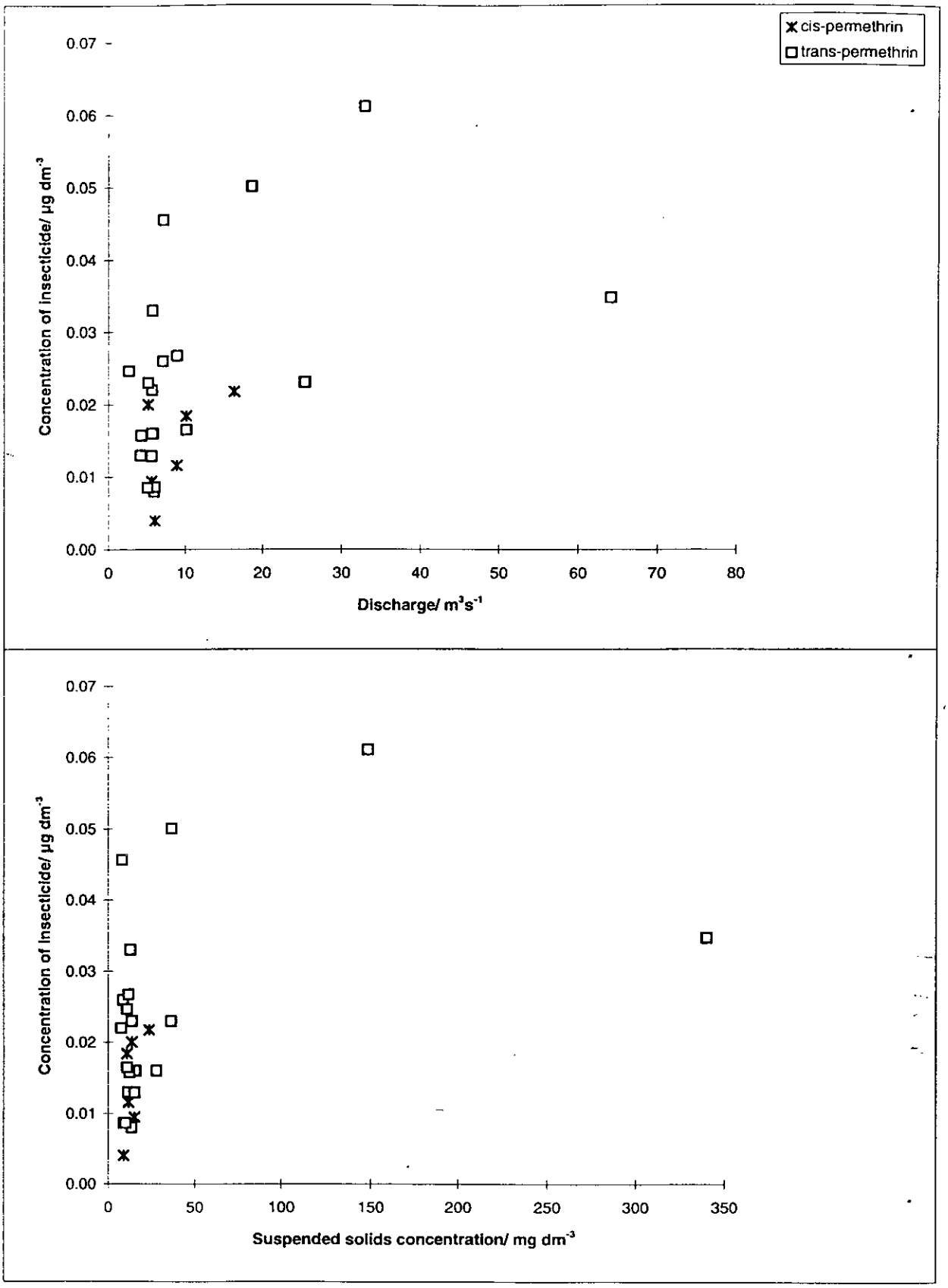


Figure 8.10. Relationship between river discharge, suspended solids concentration and concentrations of *cis* and *trans*-permethrinin in the R. Don at Sprotbrough Bridge.

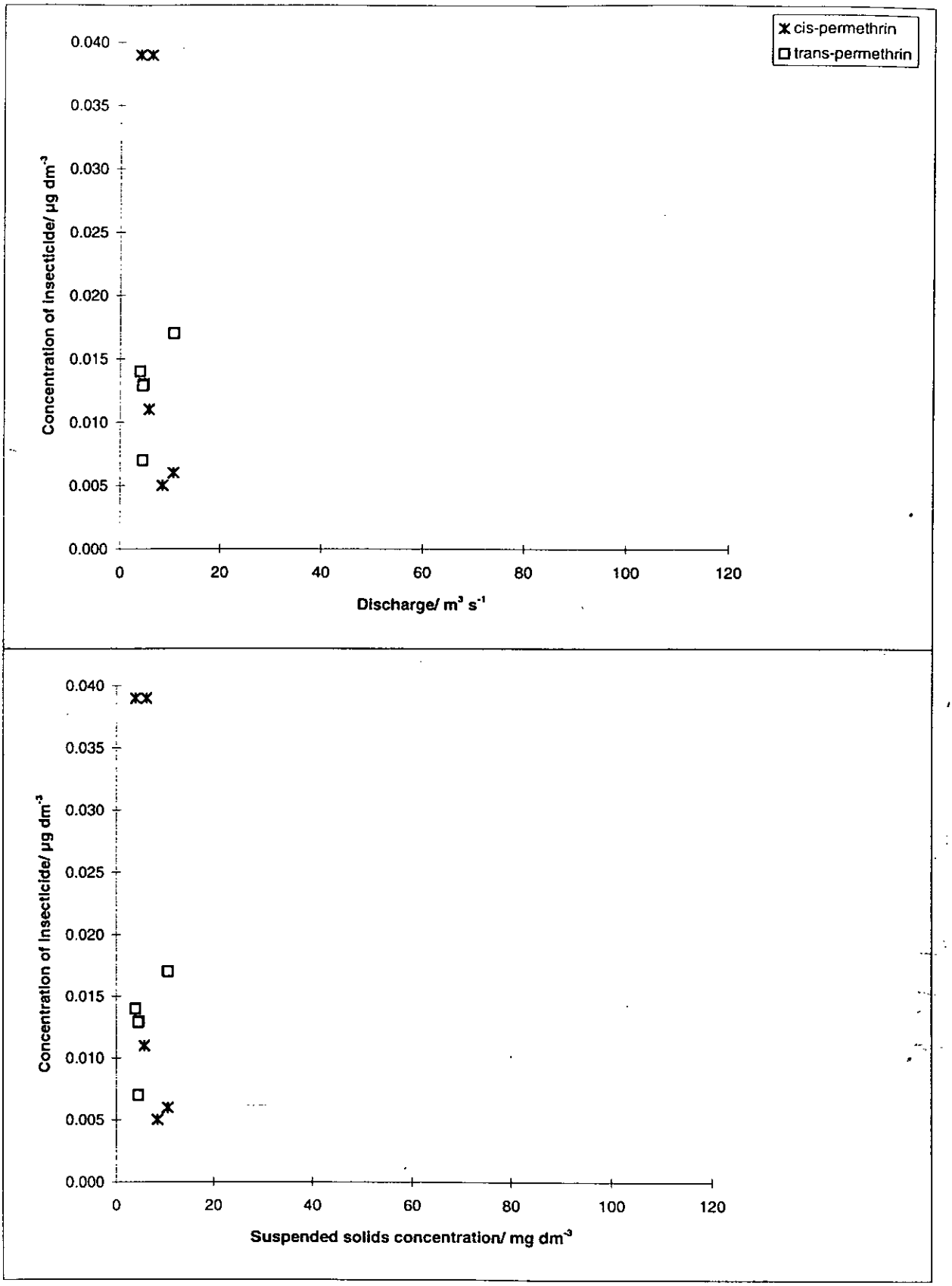


Figure 8.11. Relationship between river discharge, suspended solids concentration and concentrations of *cis* and *trans*-permethrin in the R. Trent at Cromwell Lock.

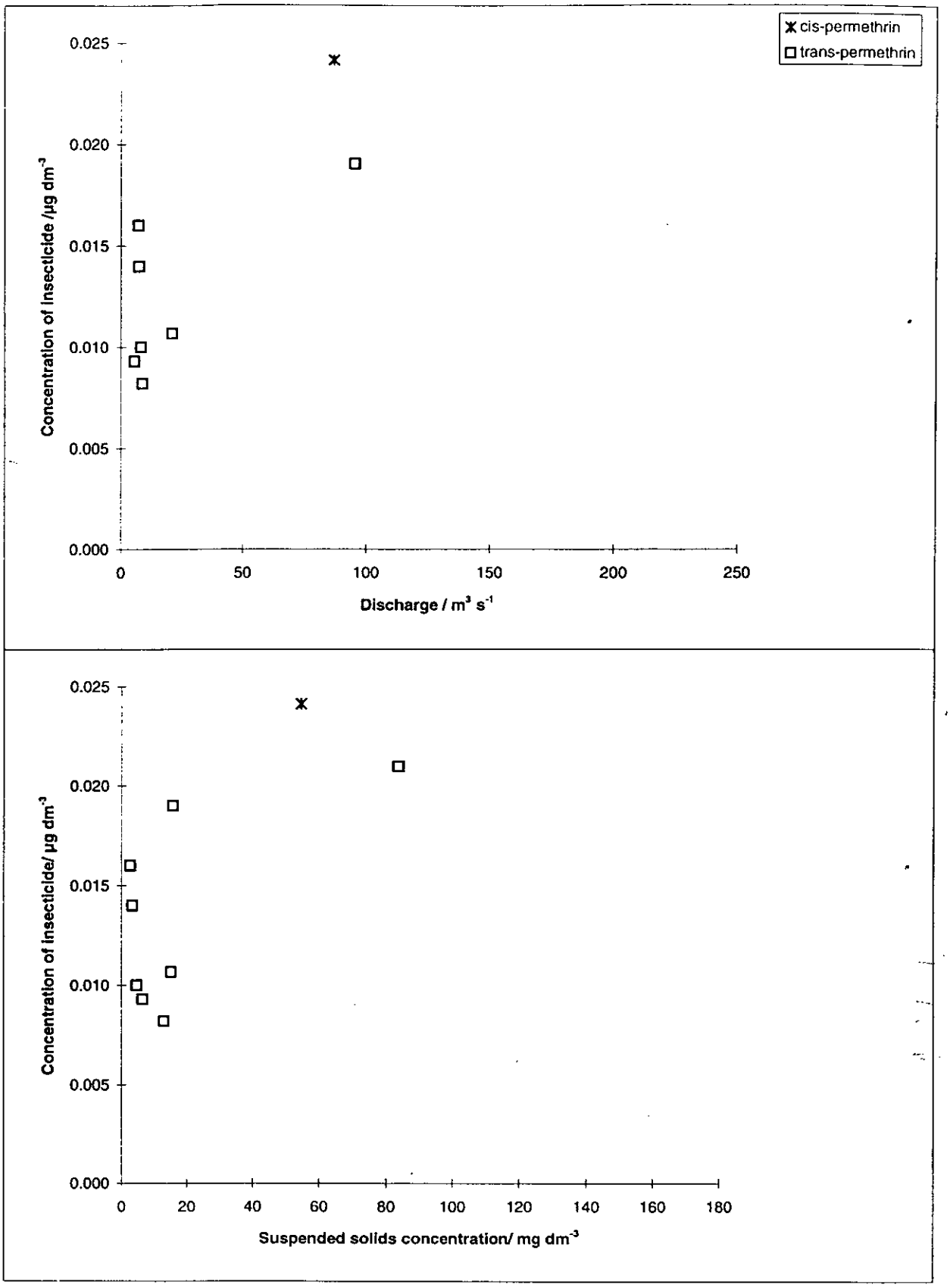


Figure 8.12. Relationship between river discharge, suspended solids concentration and concentrations of *cis* and *trans*-permethrin in the R. Ouse at Acaster (Naburn Lock).

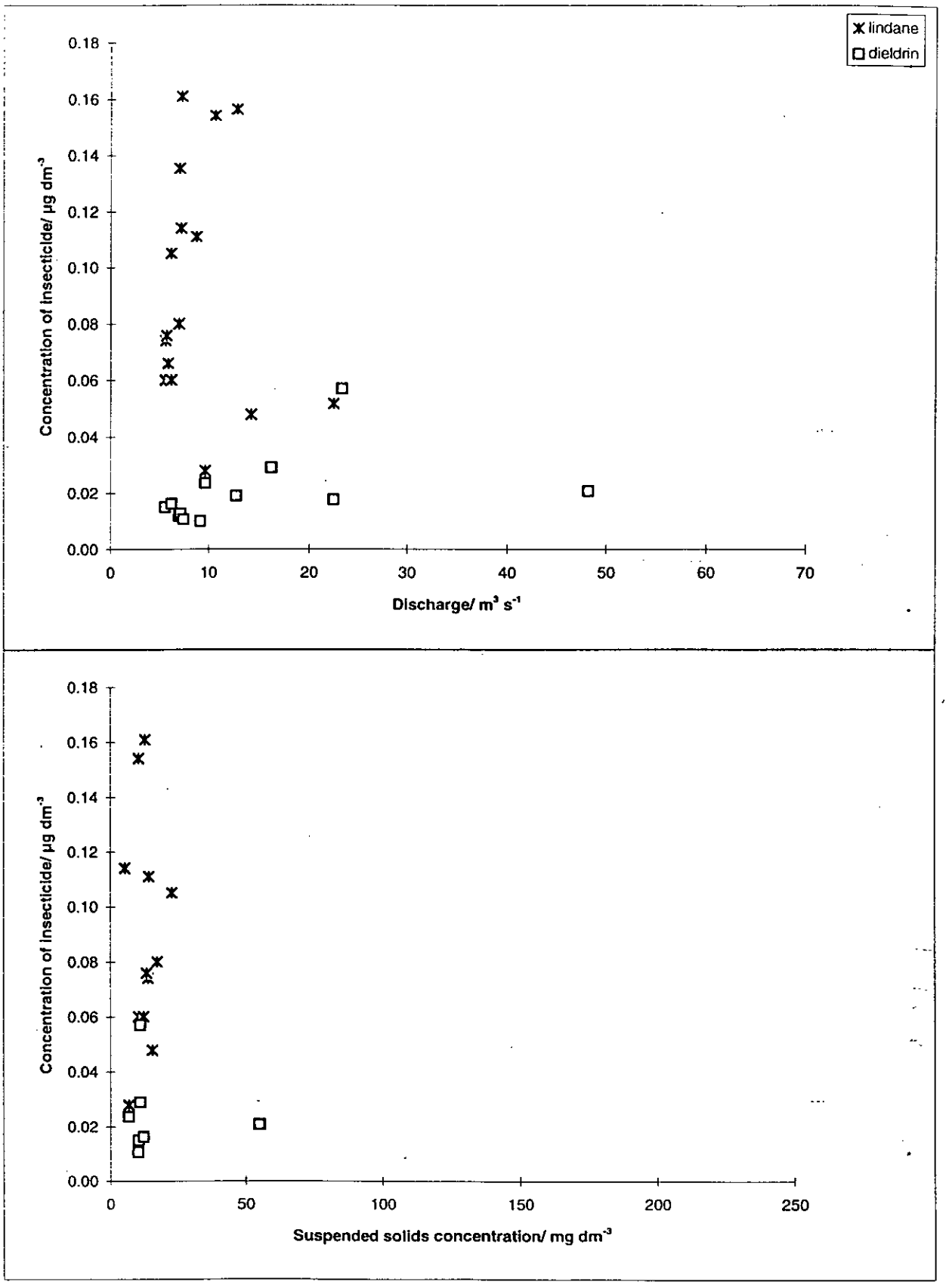


Figure 8.13. Relationship between river discharge, suspended solids concentration and concentrations of lindane and dieldrin in the R. Aire at Allerton Bywater.

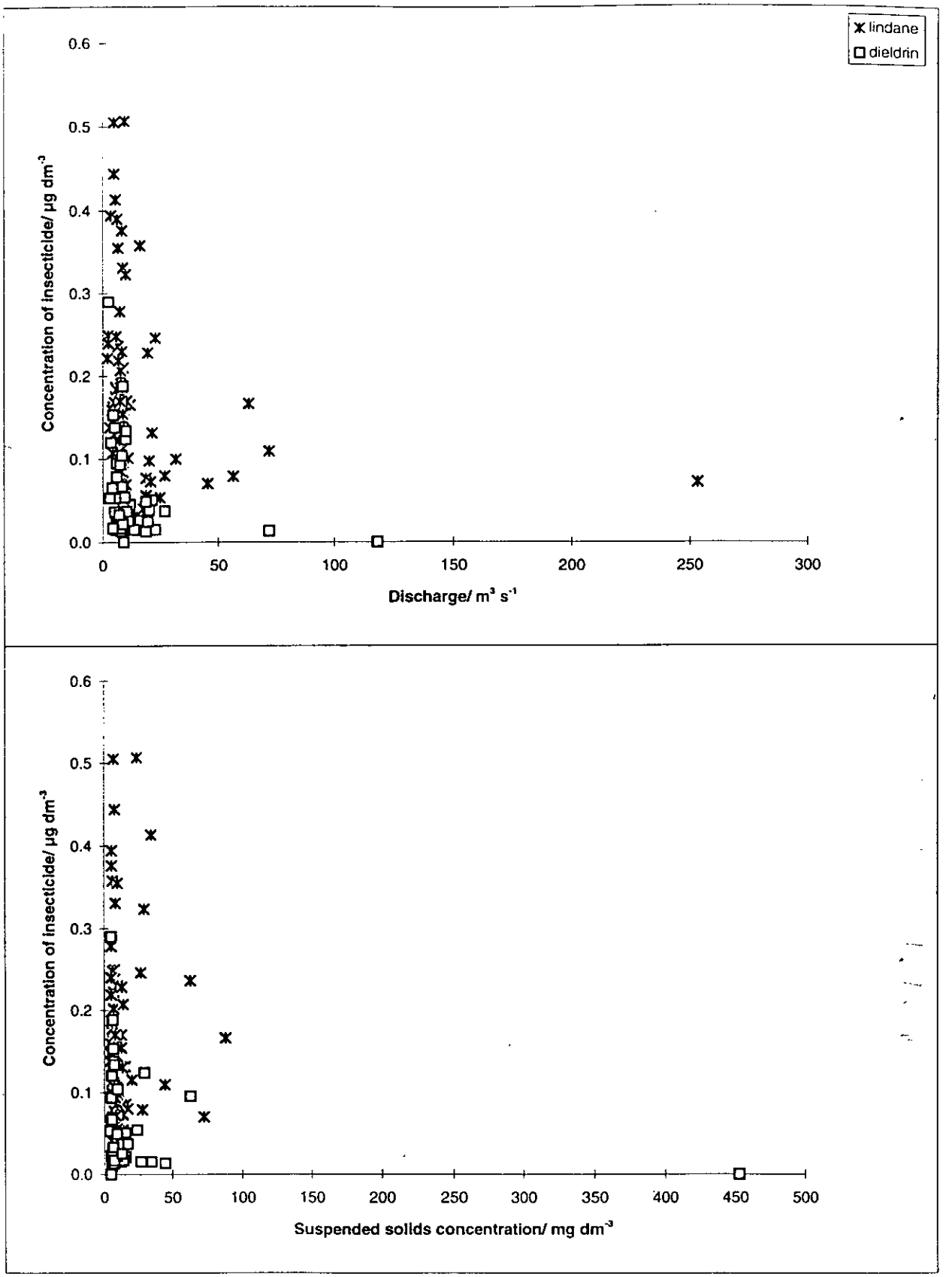


Figure 8.14. Relationship between river discharge, suspended solids concentration and concentrations of lindane and dieldrin in the R. Calder at Methley Bridge.

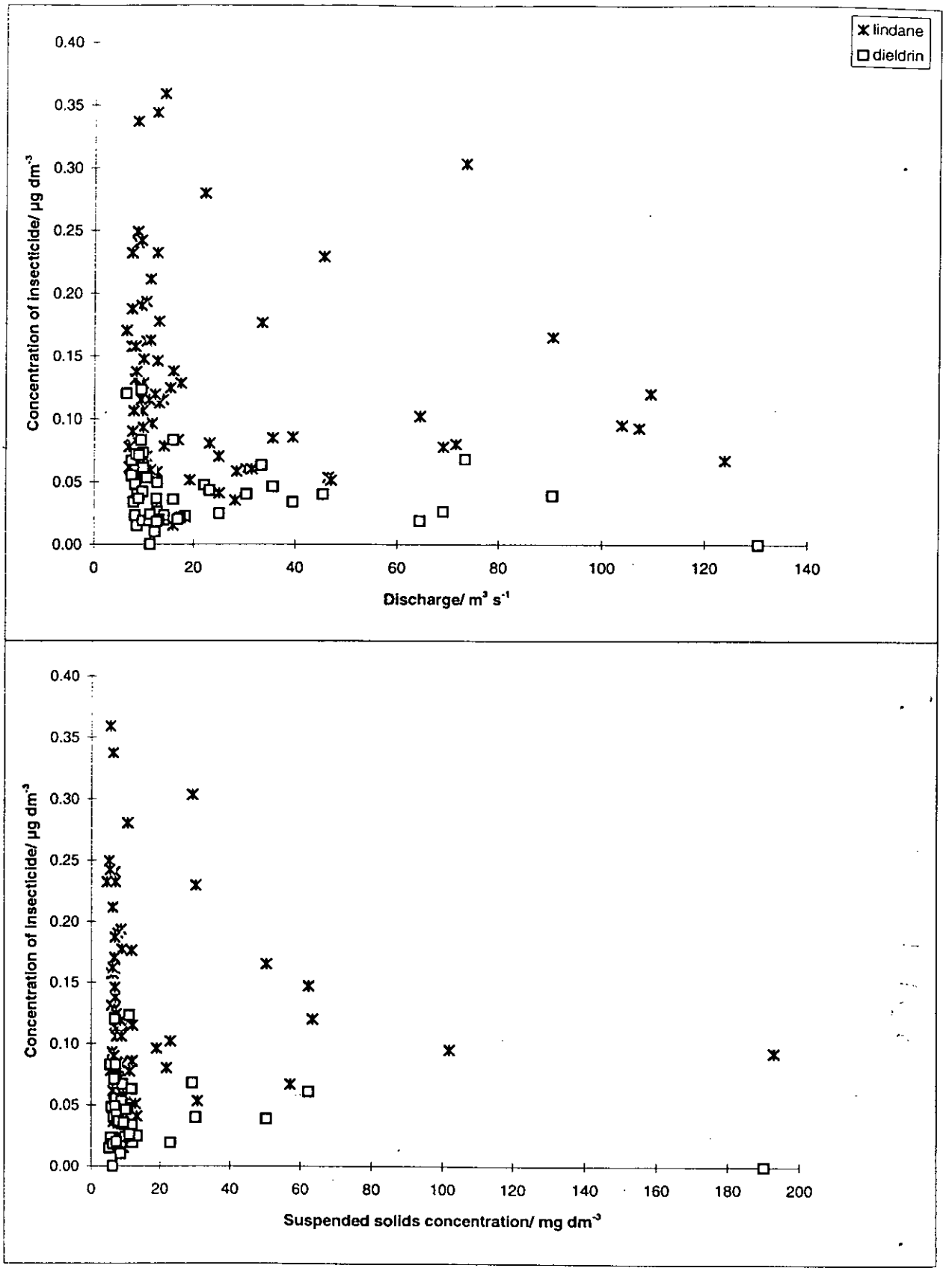


Figure 8.15. Relationship between river discharge, suspended solids concentration and concentrations of lindane and dieldrin in the R. Aire at Beal Bridge.

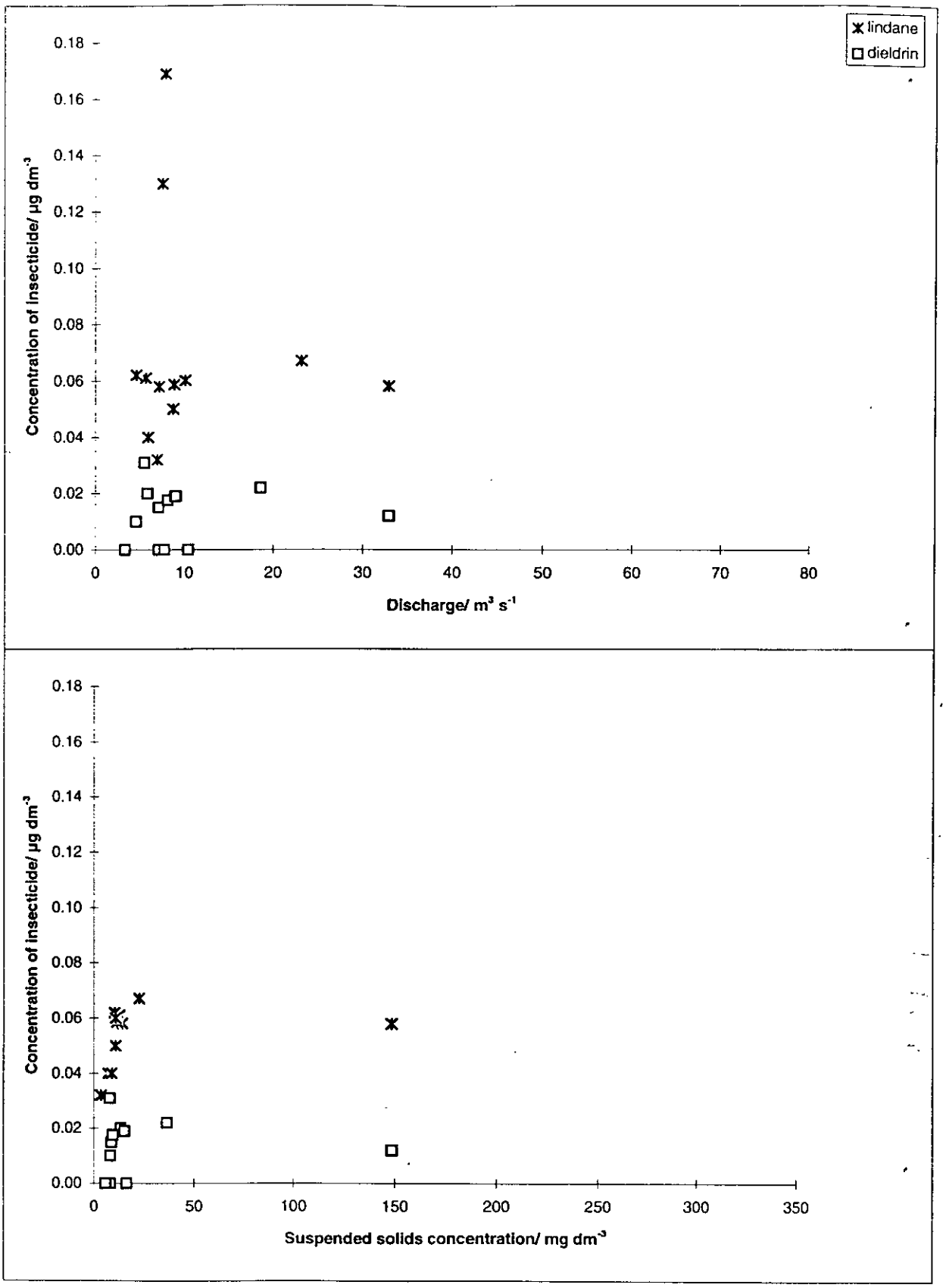


Figure 8.16. Relationship between river discharge, suspended solids concentration and concentrations of lindane and dieldrin in the R.Don at Sprotbrough Bridge.

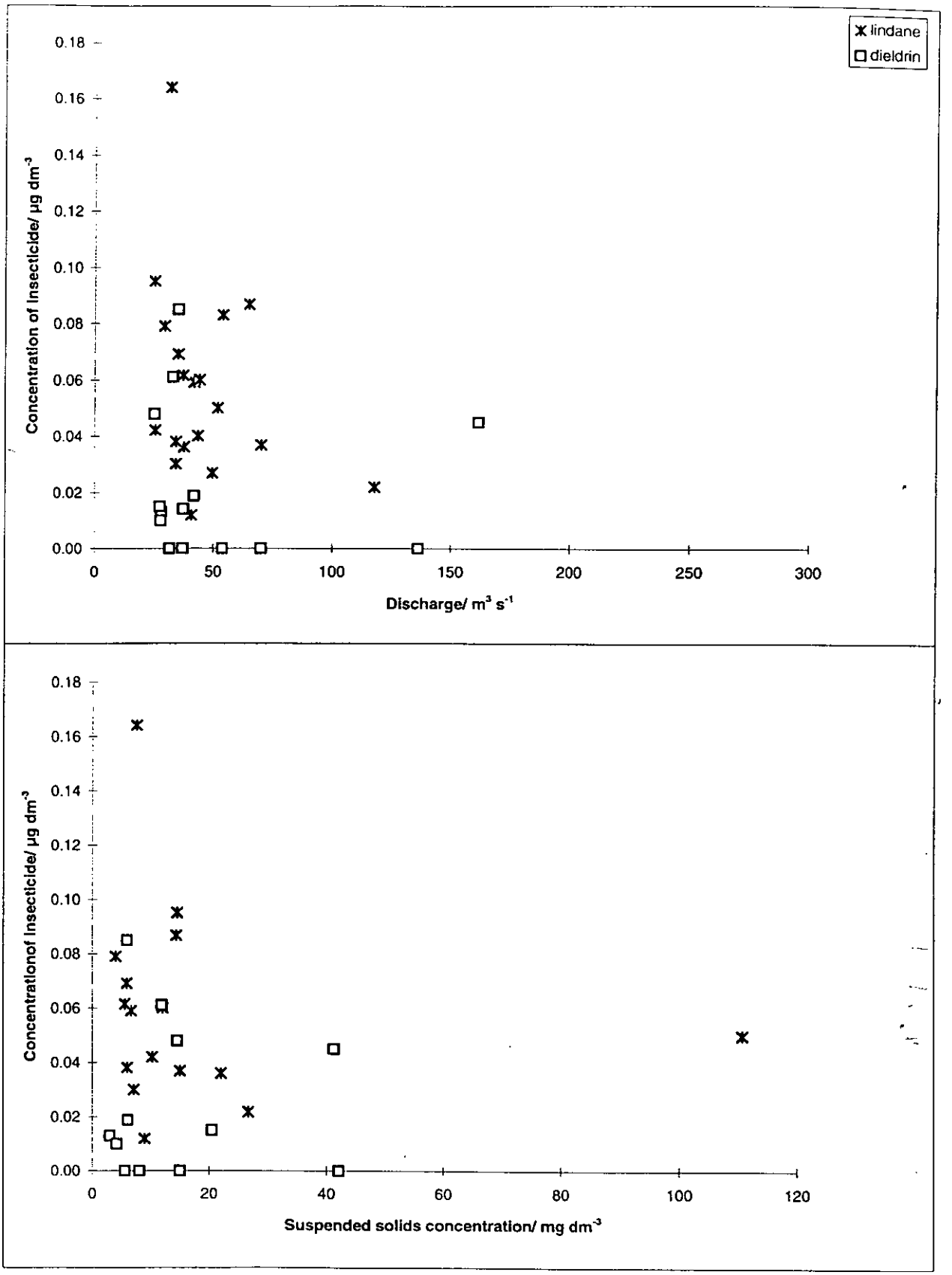


Figure 8.17. Relationship between river discharge, suspended solids concentration and concentrations of lindane and dieldrin in the R.Trent at Cromwell Lock.

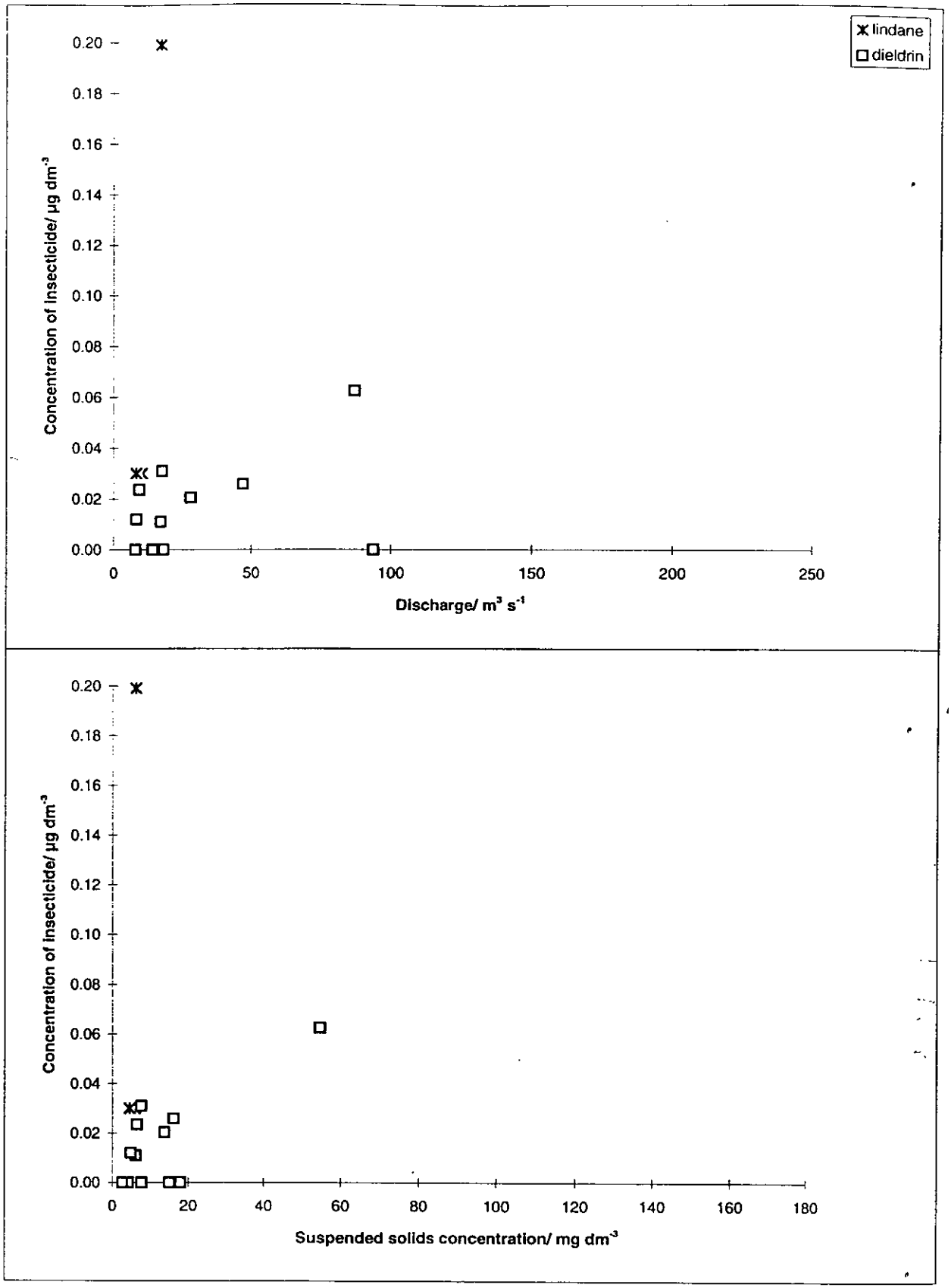


Figure 8.18. Relationship between river discharge, suspended solids concentration and concentrations of lindane and dieldrin in the R. Ouse at Acaster (Naburn Lock).

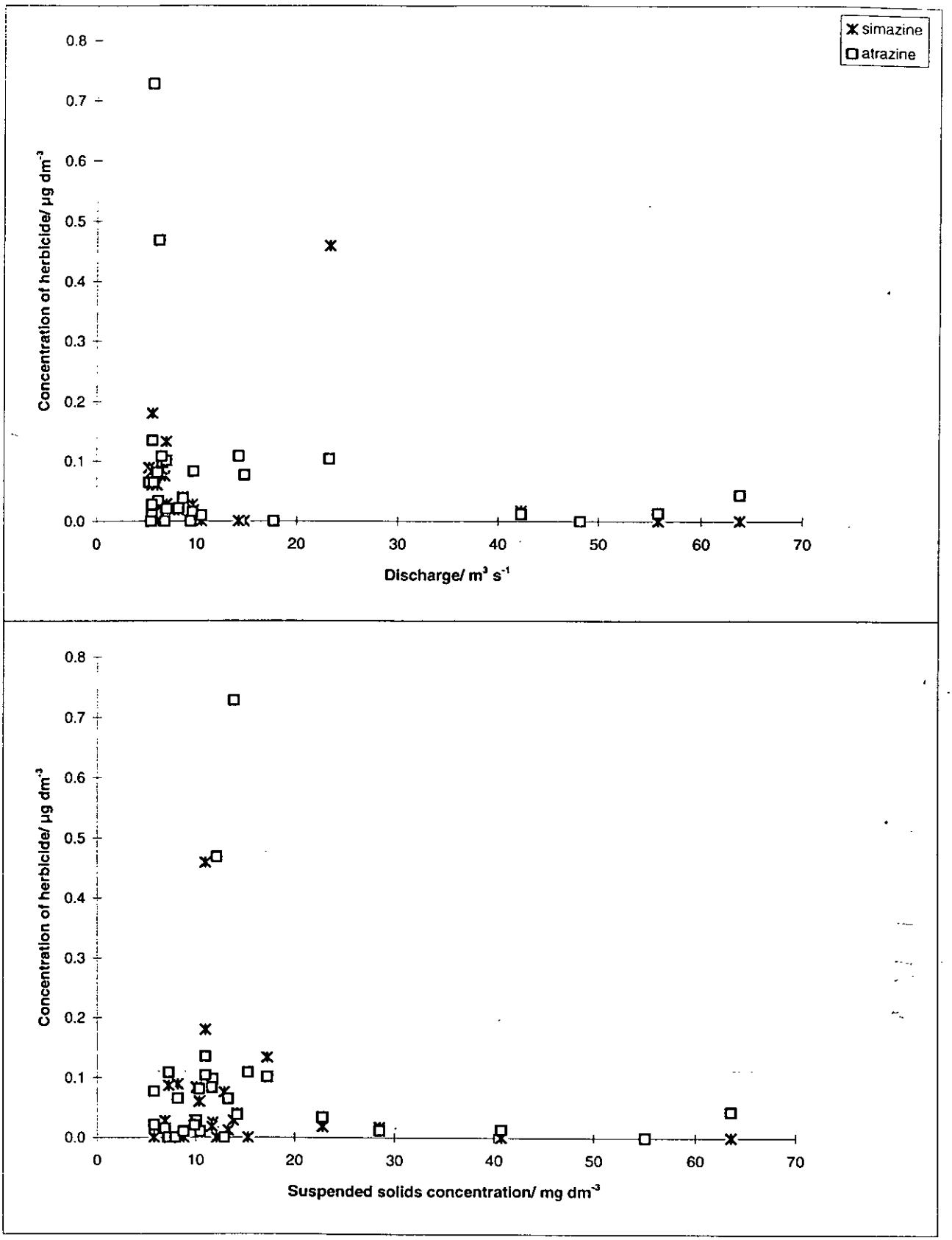


Figure 8.19. Relationship between river discharge, suspendid solids concentration and concentrations of simazine and atrazine in the R. Aire at Allerton Bywater.

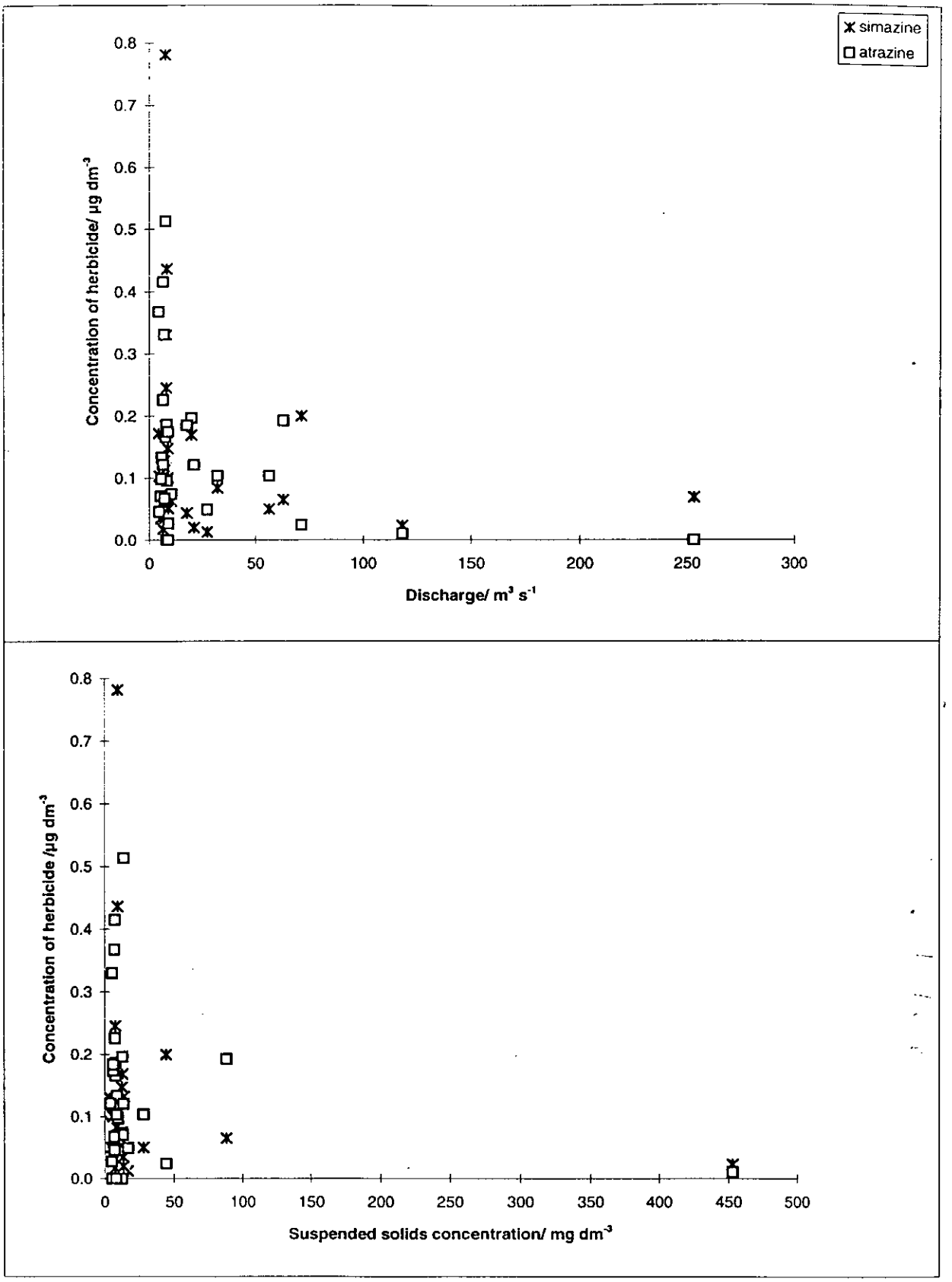


Figure 8.20. Relationship between river discharge, suspended solids concentration and concentrations of simazine and atrazine in the R. Calder at Methley Bridge.

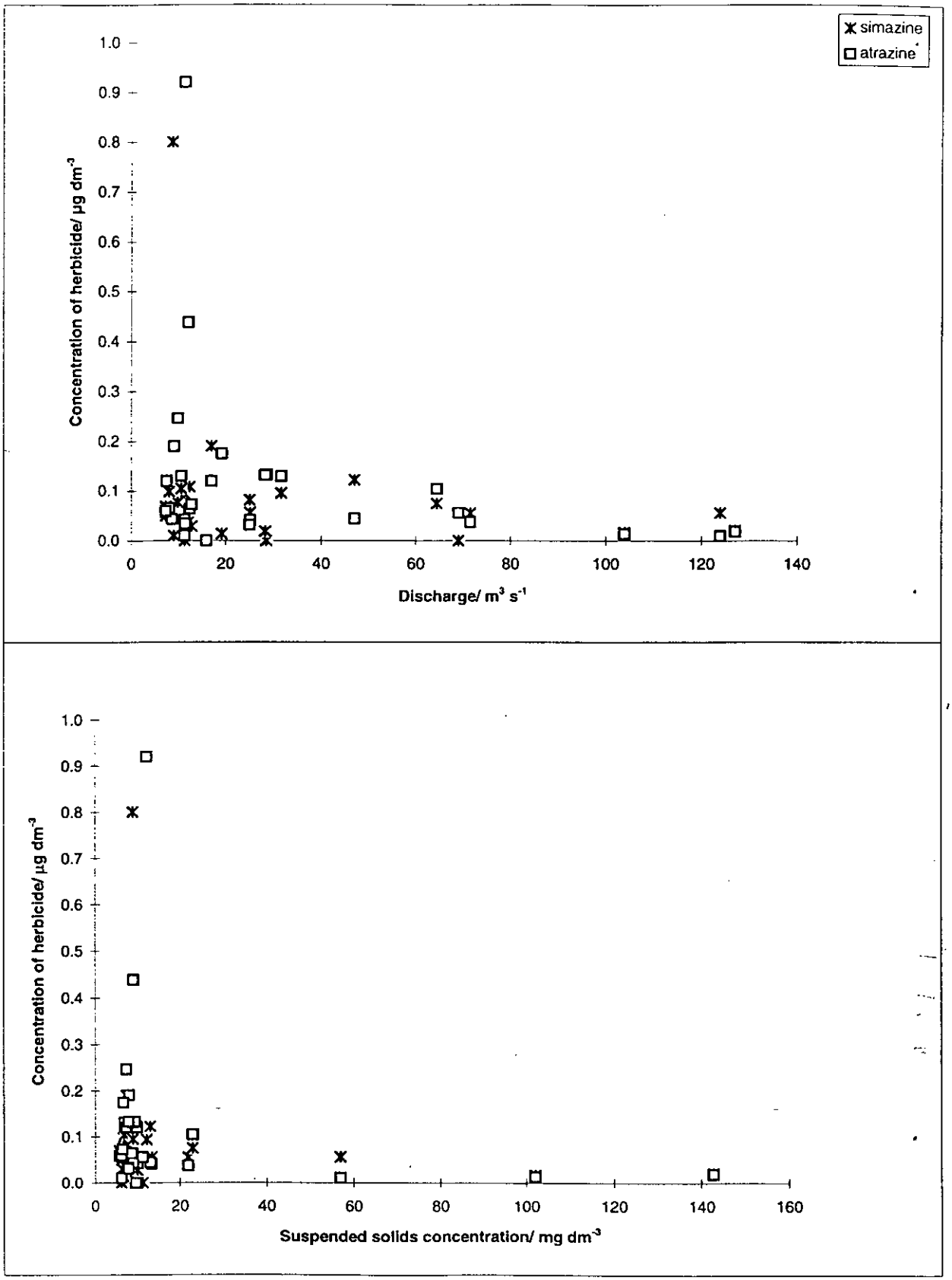


Figure 8.21. Relationship between river discharge, suspended solids concentration and concentrations of simazine and atrazine in the R. Aire at Beal Bridge.

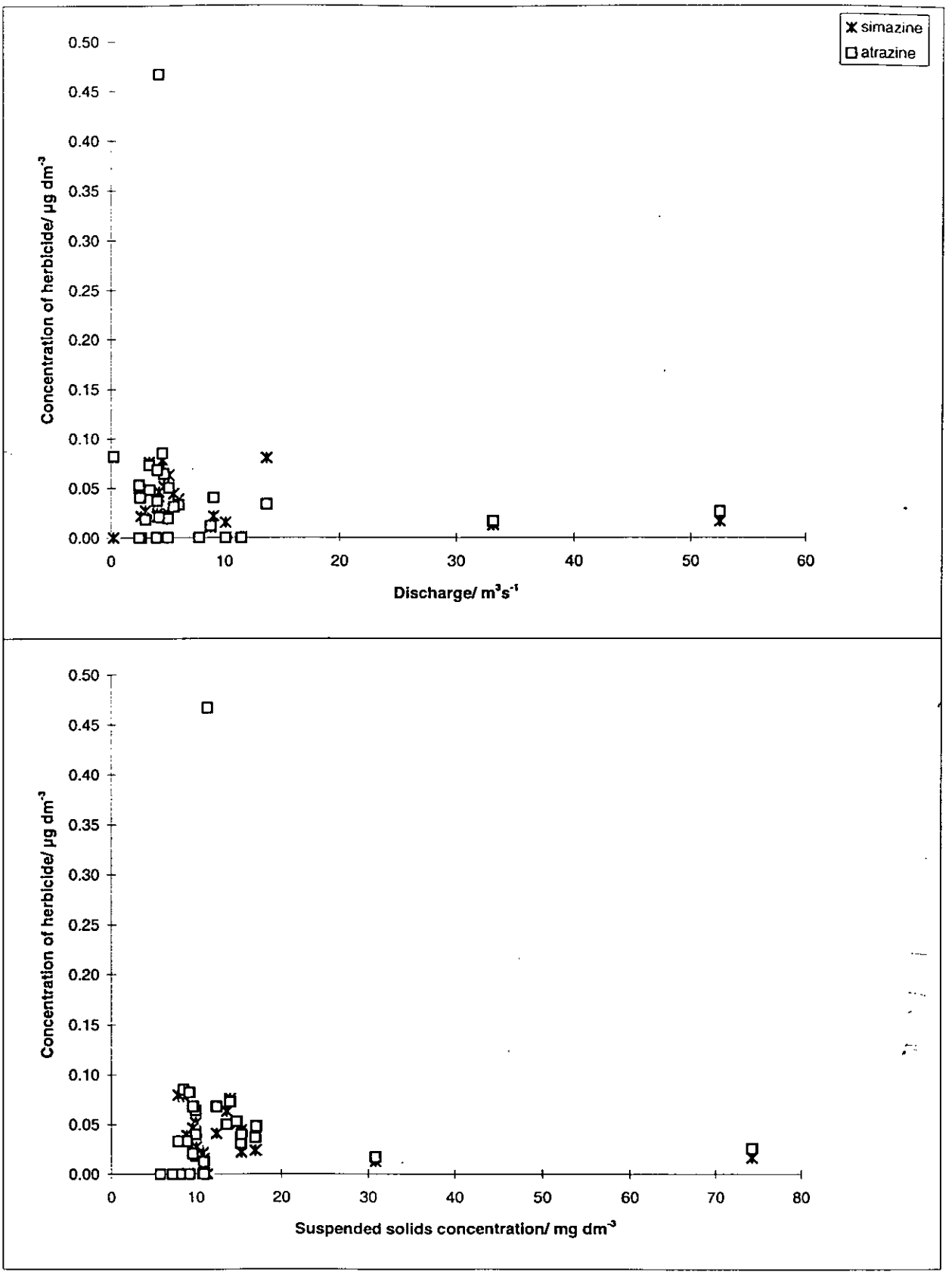


Figure 8.22. Relationship between river discharge, suspended solids concentration and concentrations of simazine and atrazine in the R. Don at Sprotbrough Bridge.

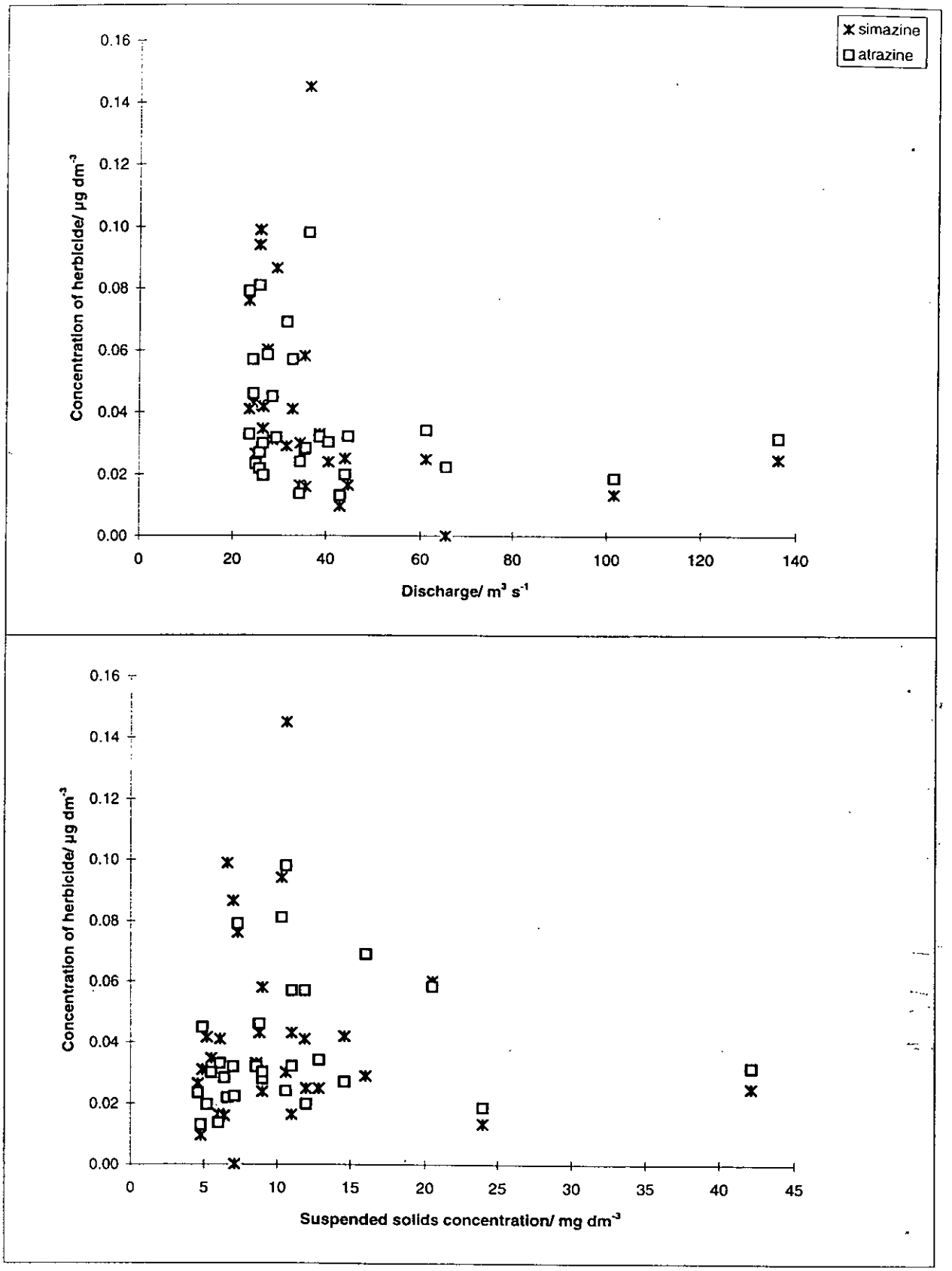


Figure 8.23. Relationship between river discharge, suspended solids concentration and concentrations of simazine and atrazine in the R. Trent at Cromwell Lock.

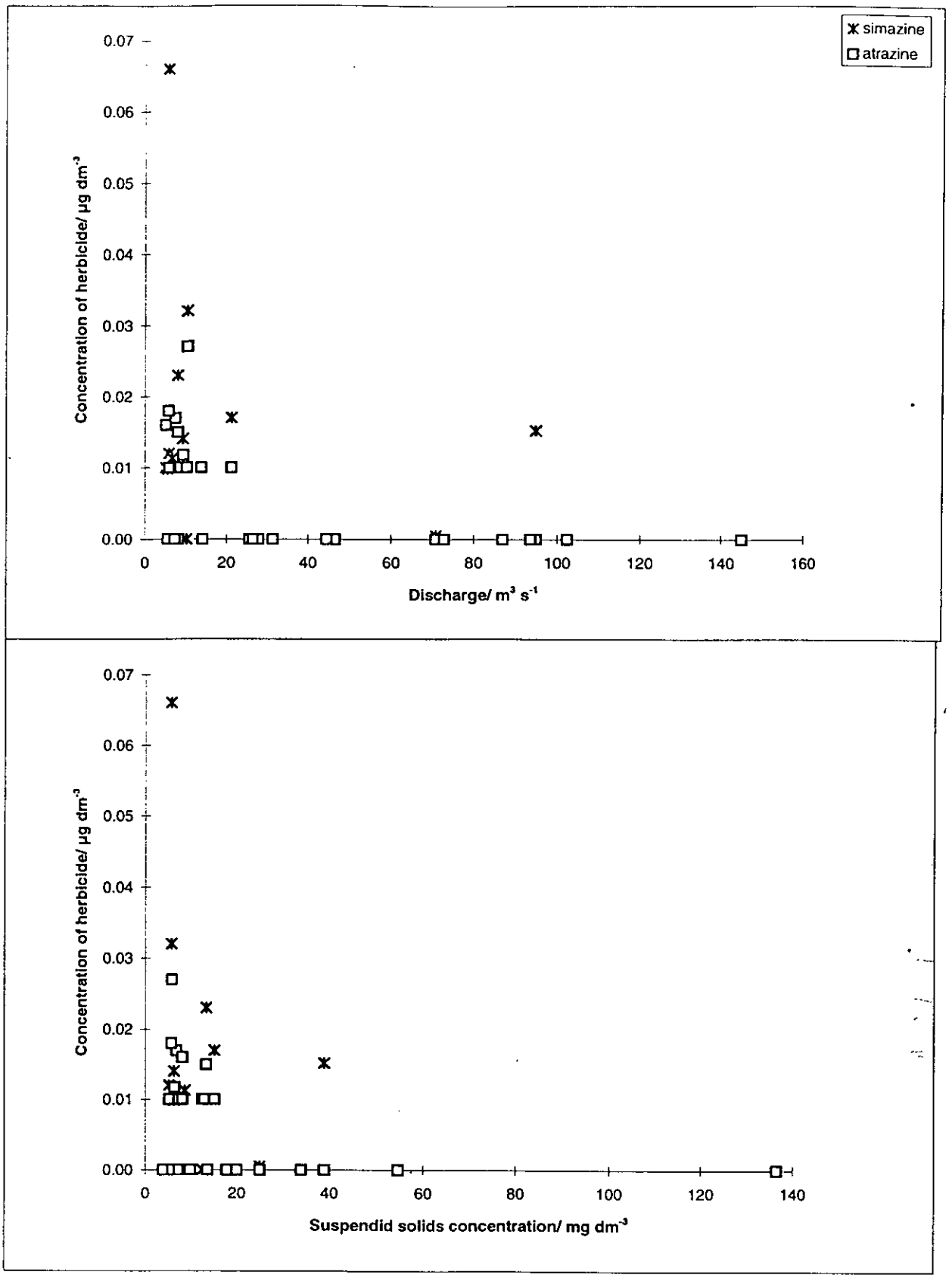


Figure 8.24. Relationship between river discharge, suspended solids concentration and concentrations of simazine and atrazine in the R. Ouse at Acaster (Naburn Lock).

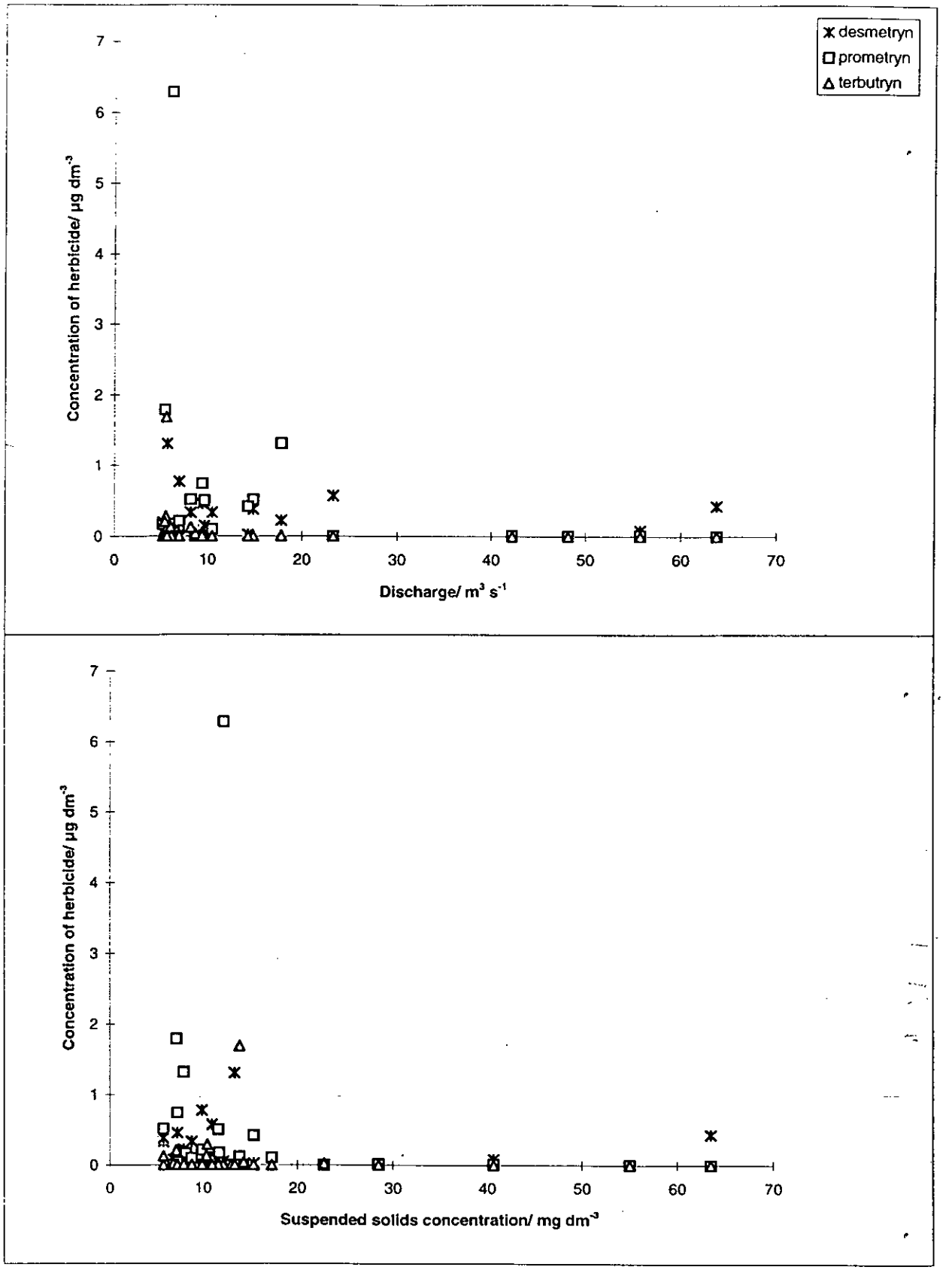


Figure 8.25. Relationship between river discharge, suspendid solids concentration and concentrations of desmetryn, prometryn and terbutryn in the R. Aire at Allerton Bywater.

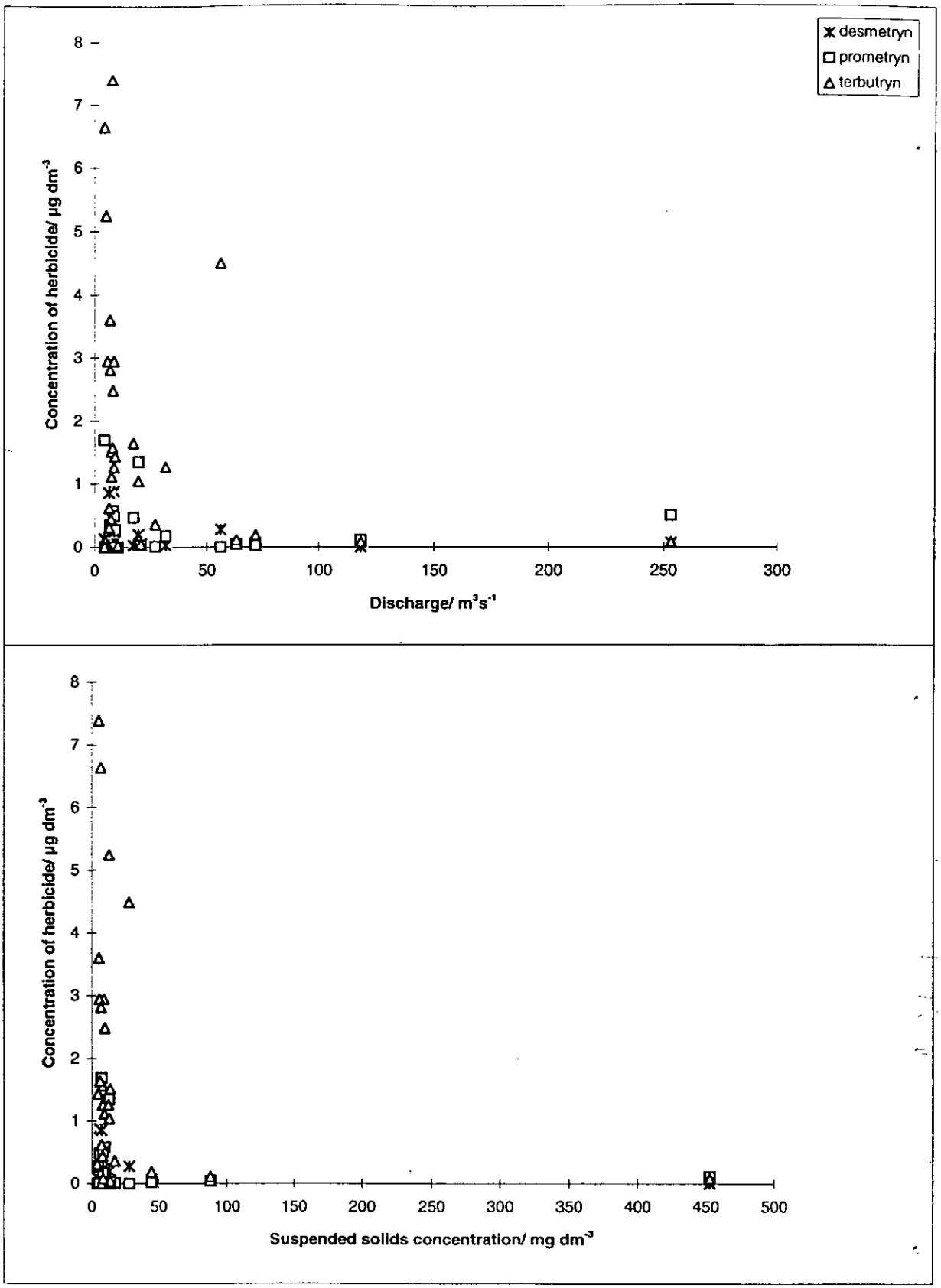


Figure 8.26. Relationship between river discharge, suspended solids concentration and concentrations of desmetryn, prometryn and terbutryn in the R. Calder at Methley Bridge.

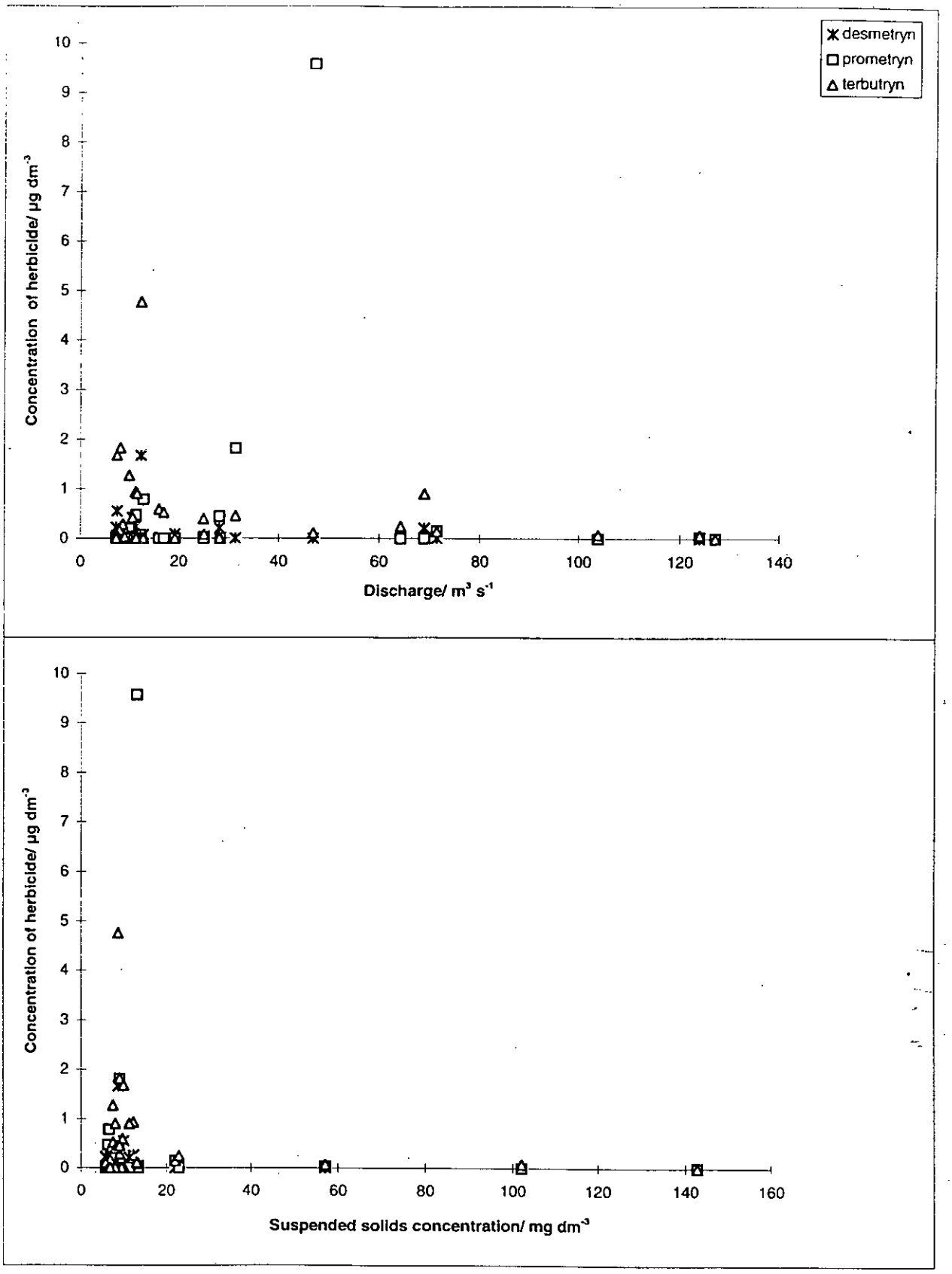


Figure 8.27. Relationship between river discharge, suspended solids concentration and concentrations of desmetryn, prometryn and terbutryn in the R. Aire at Beal Bridge.

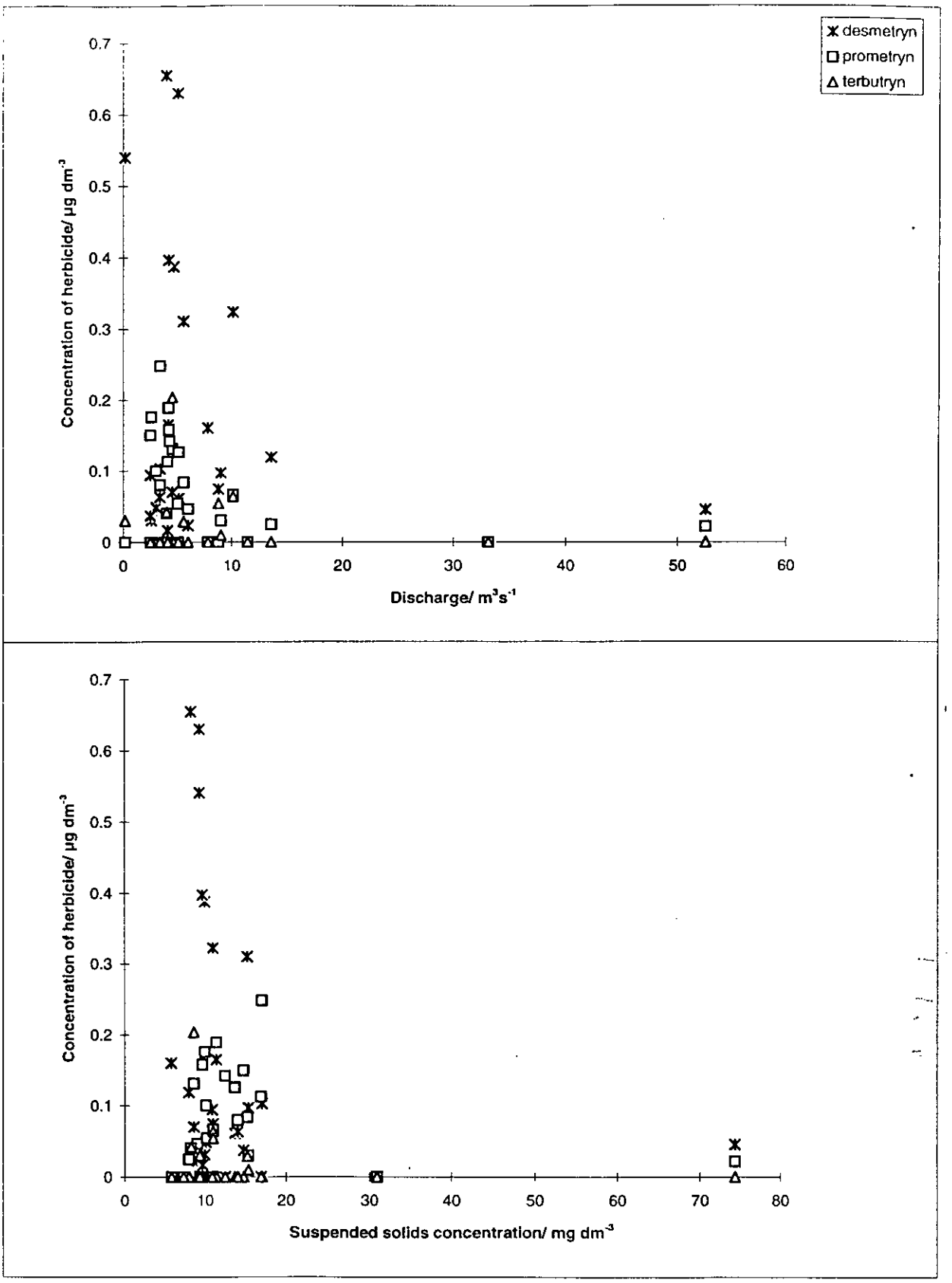


Figure 8.28. Relationship between river discharge, suspended solids concentration and concentrations of desmetryn, prometryn and terbutryn in the R. Don at Sprotbrough Bridge.

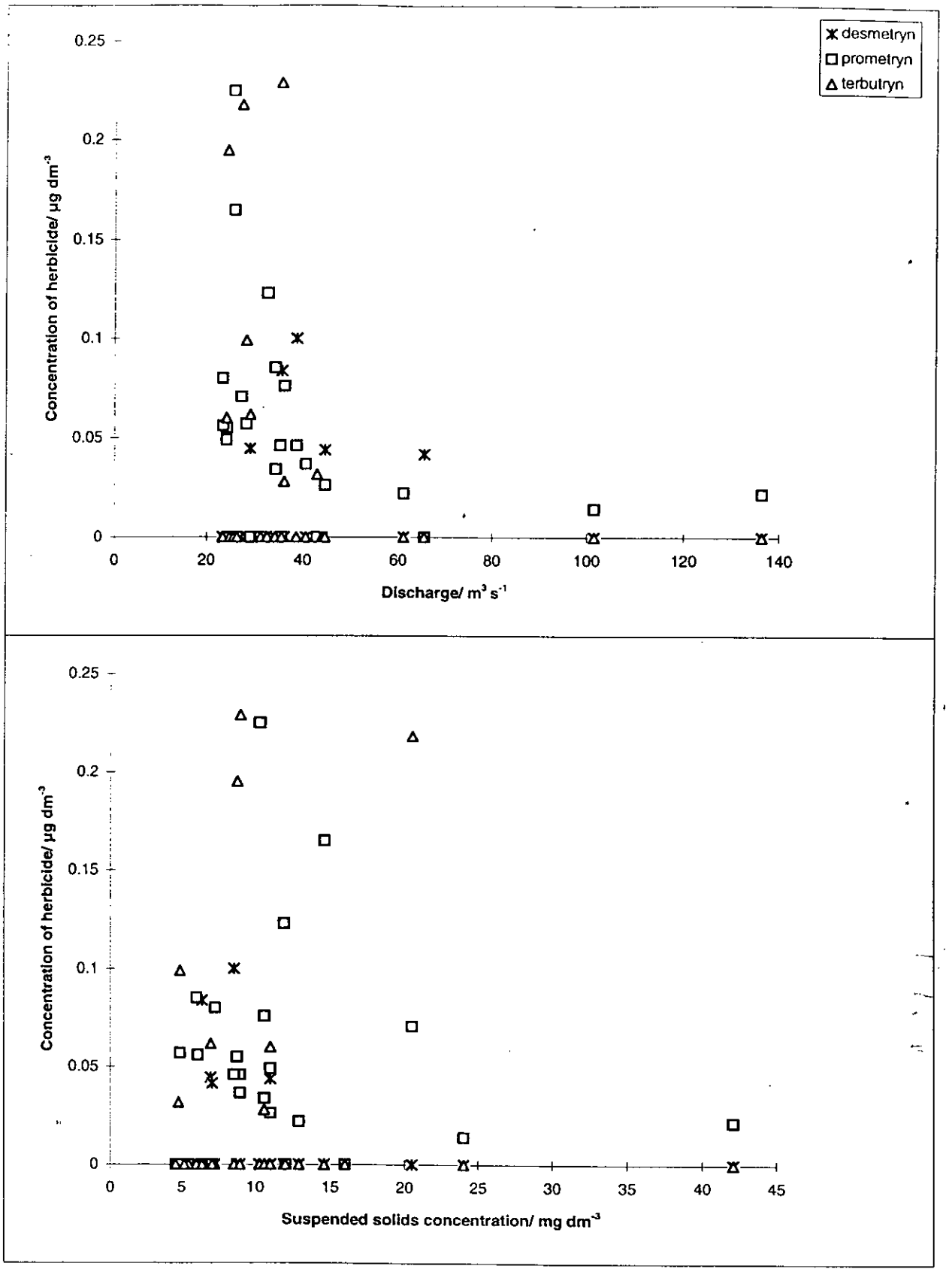


Figure 8.29. Relationship between river discharge, suspended solids concentration and concentrations of desmetryn, prometryn and terbutryn in the R. Trent at Cromwell Lock.

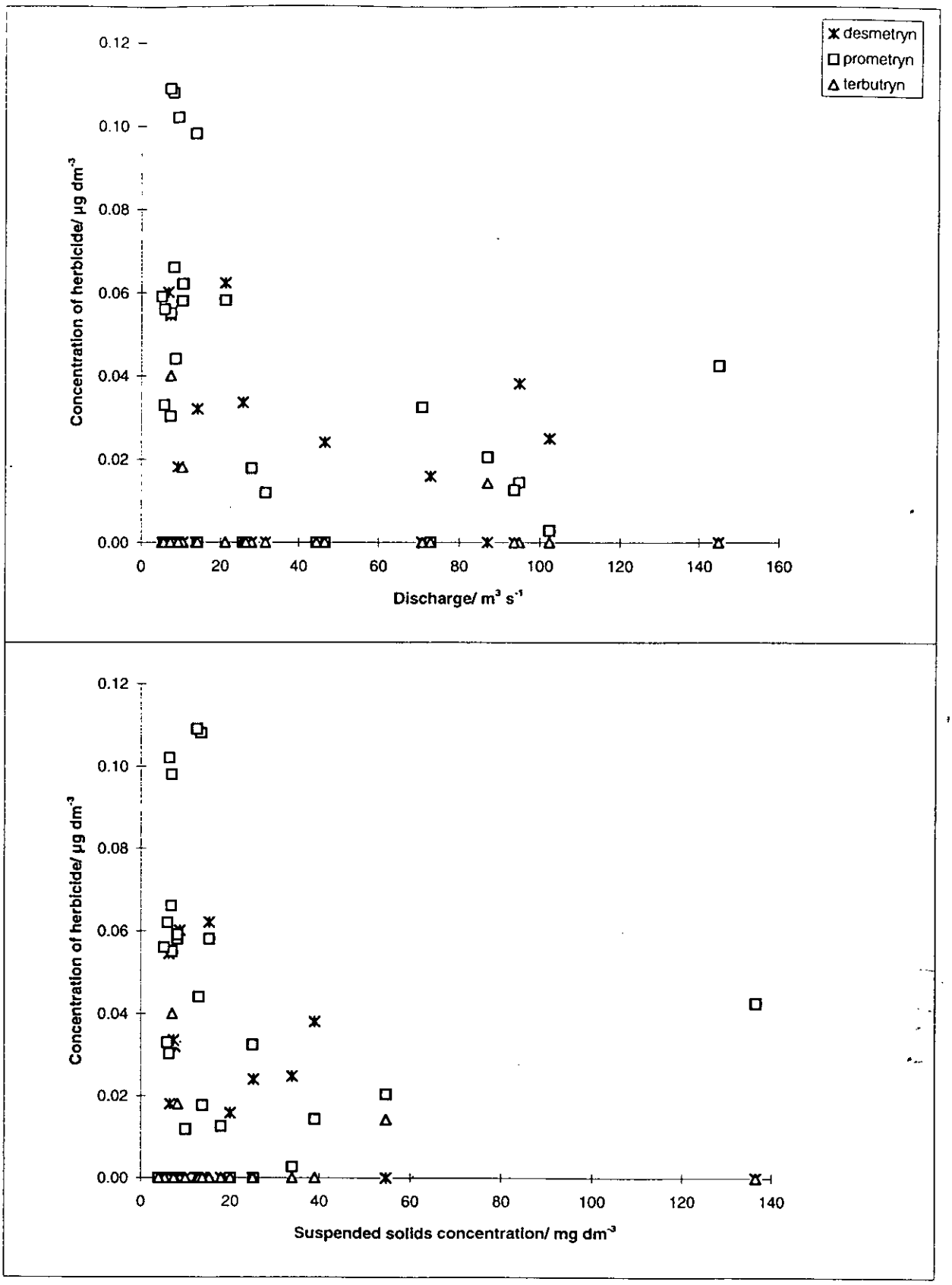


Figure 8.30. Relationship between river discharge, suspended solids concentration and concentrations of desmetryn, prometryn and terbutryn in the R. Ouse at Acaster (Naburn Lock).

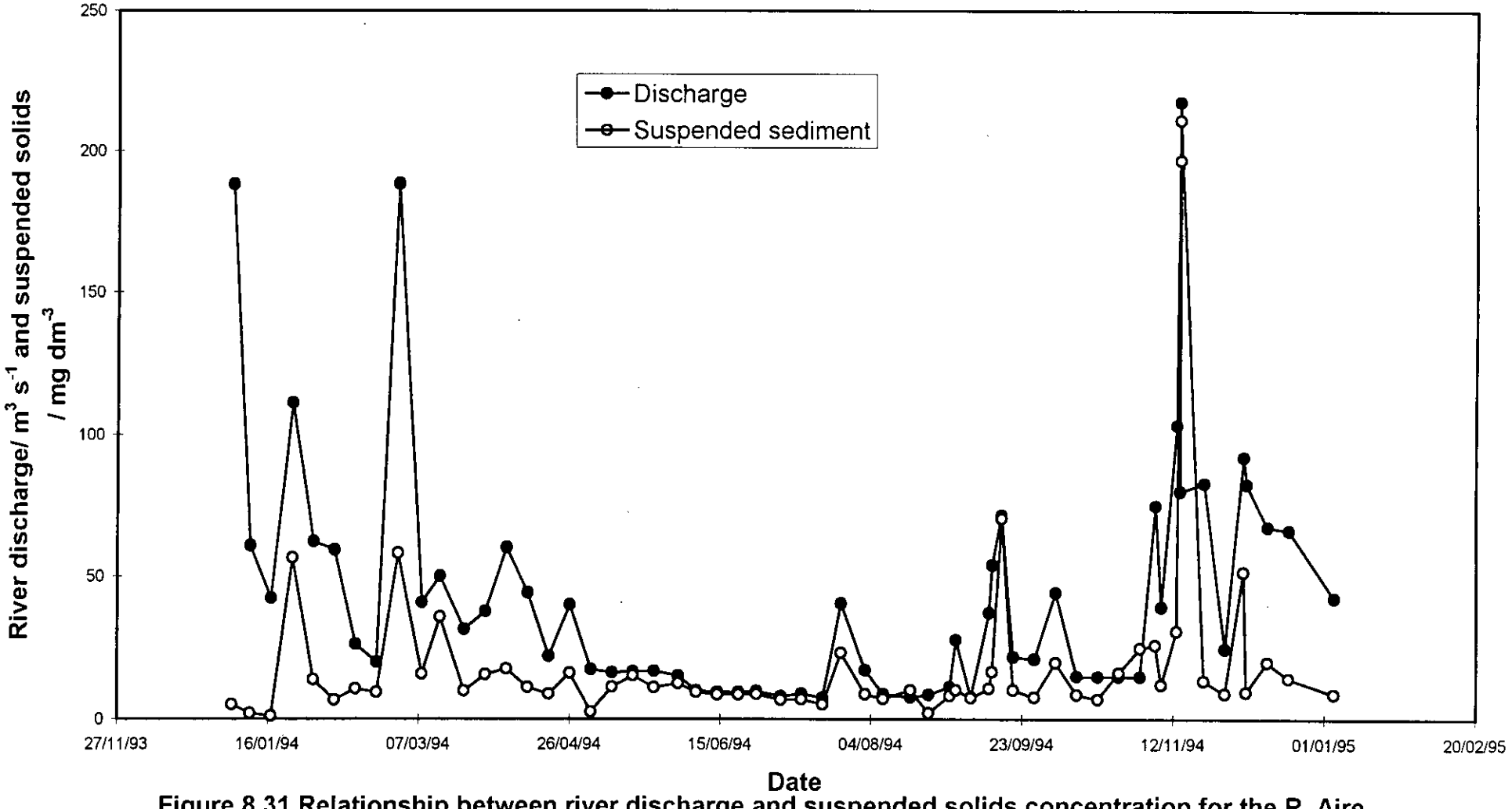


Figure 8.31 Relationship between river discharge and suspended solids concentration for the R. Aire at Beale Bridge

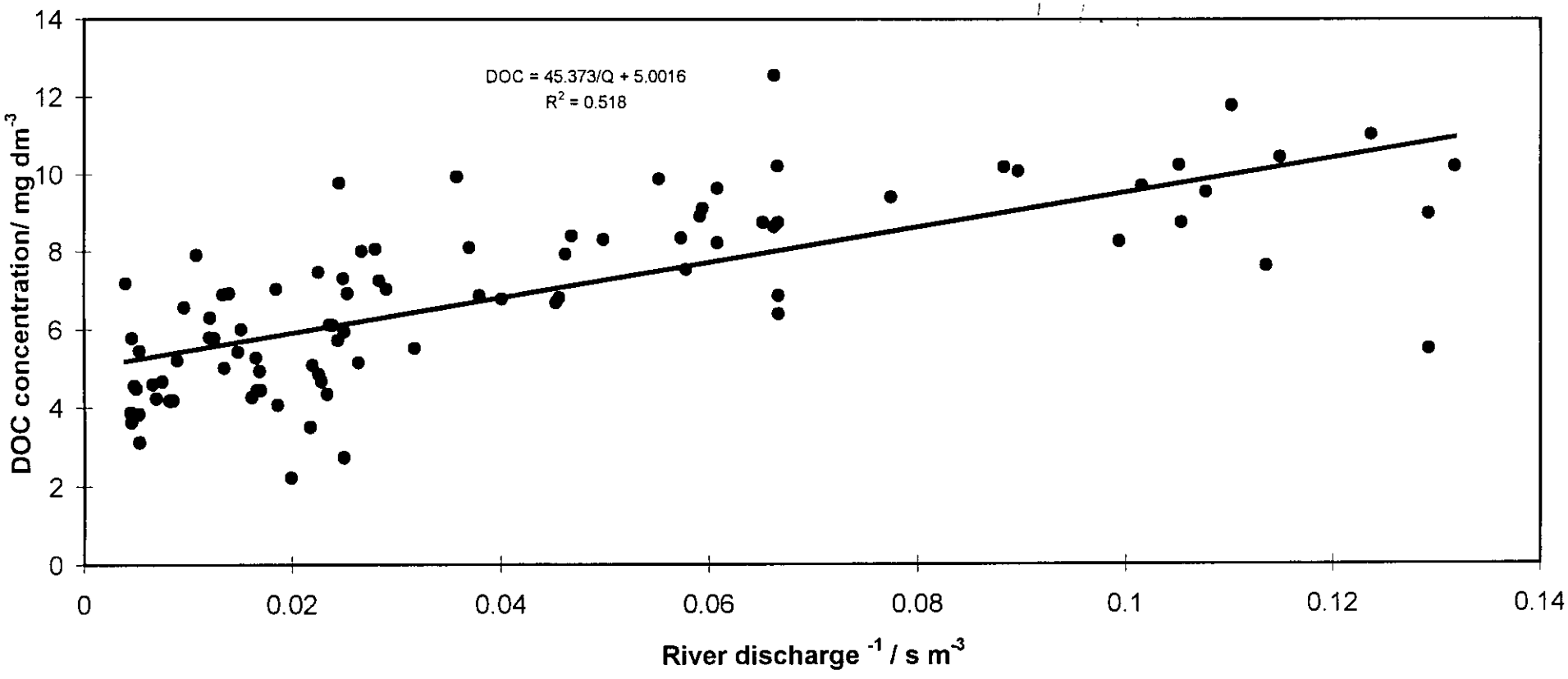


Figure 8.32 Inverse relationship between river discharge and DOC concentration for the R. Aire at Beale

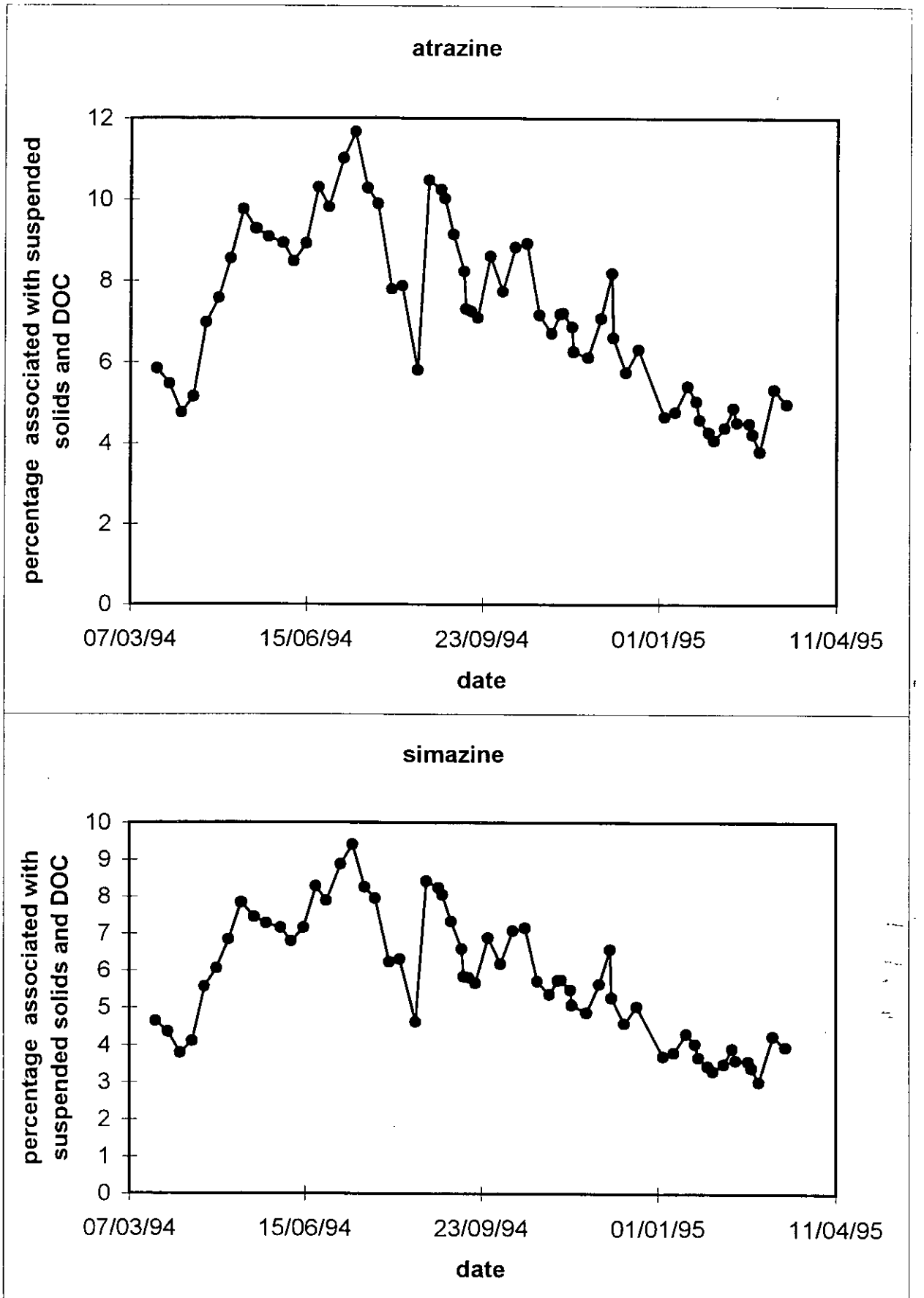


Figure 8.33 Estimate of the distribution of pesticides from DOC and suspended solids measurements in the R. Aire

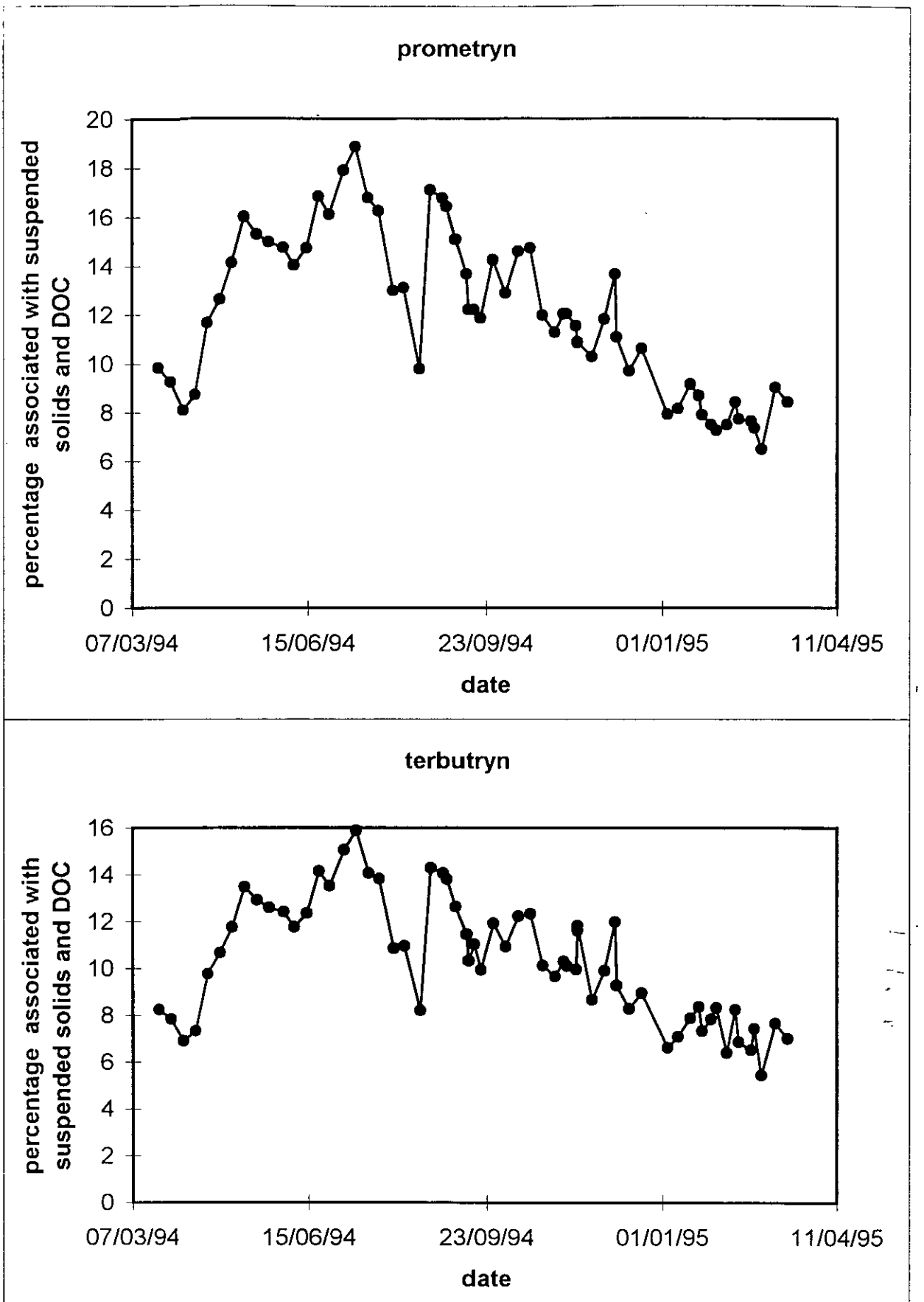


Figure 8.34 Estimate of the distribution of pesticides from DOC and suspended solids measurements in the R. Aire

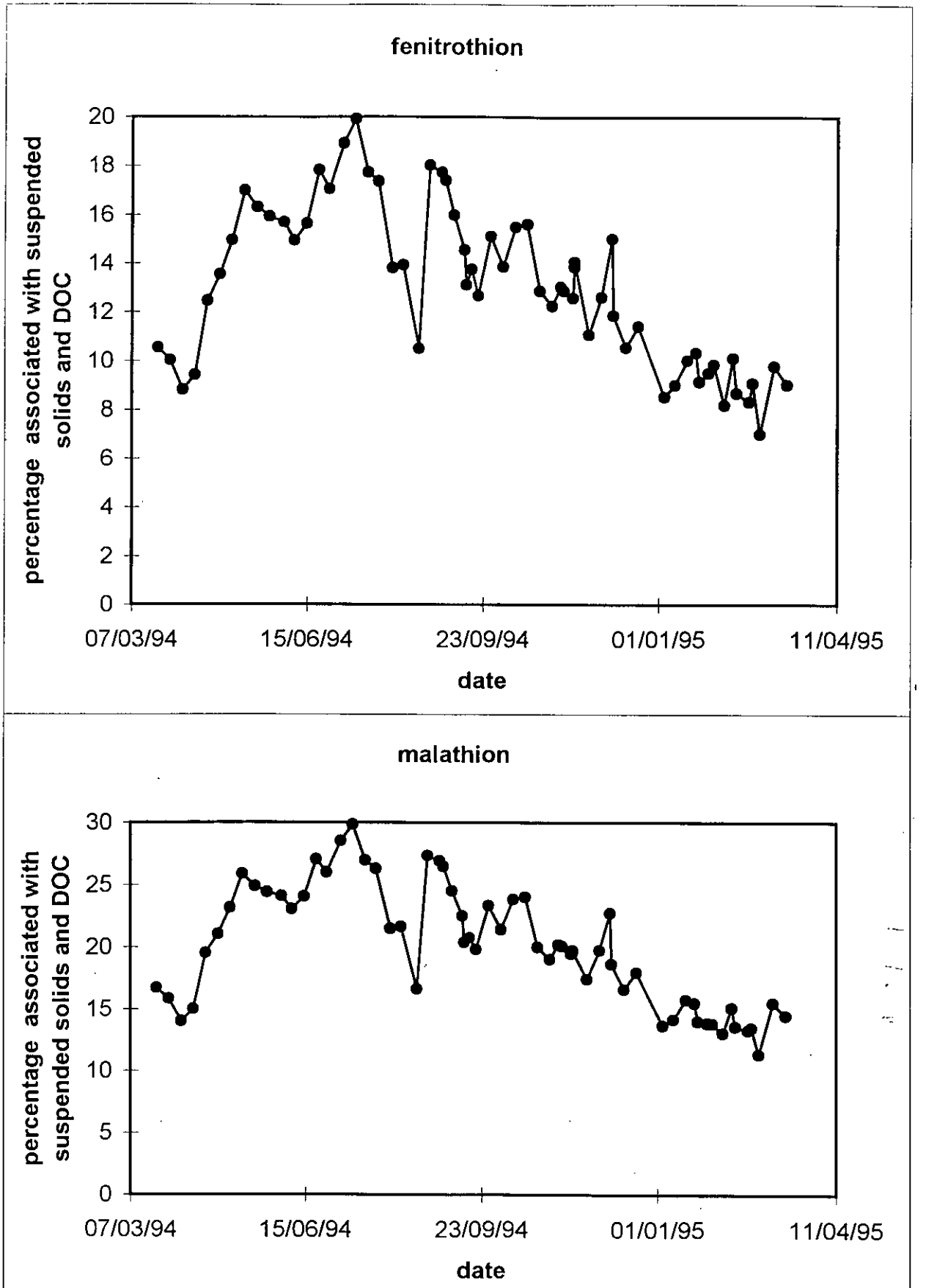


Figure 8.35 Estimate of the distribution of pesticides from DOC and suspended solids measurements in the R. Aire

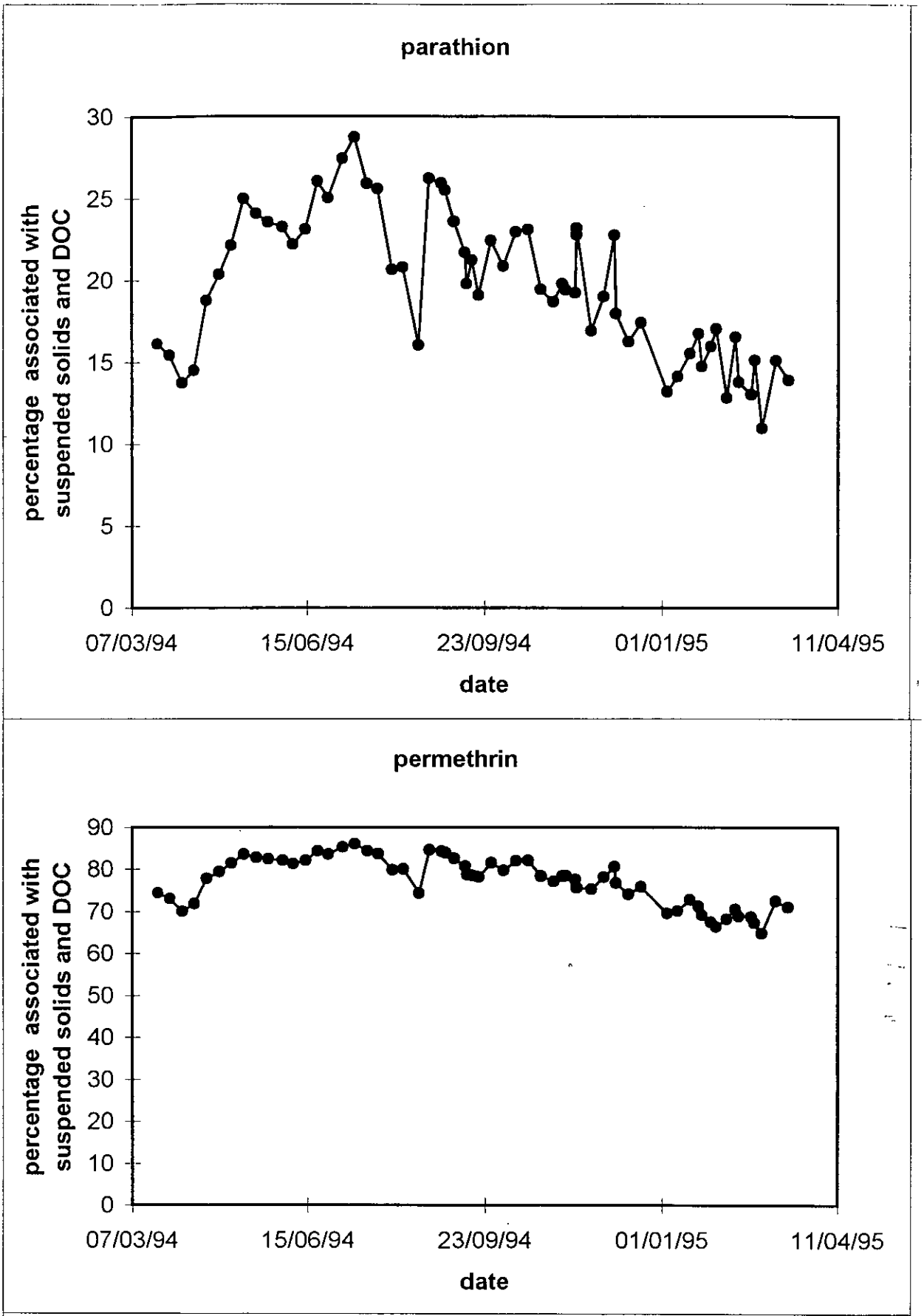
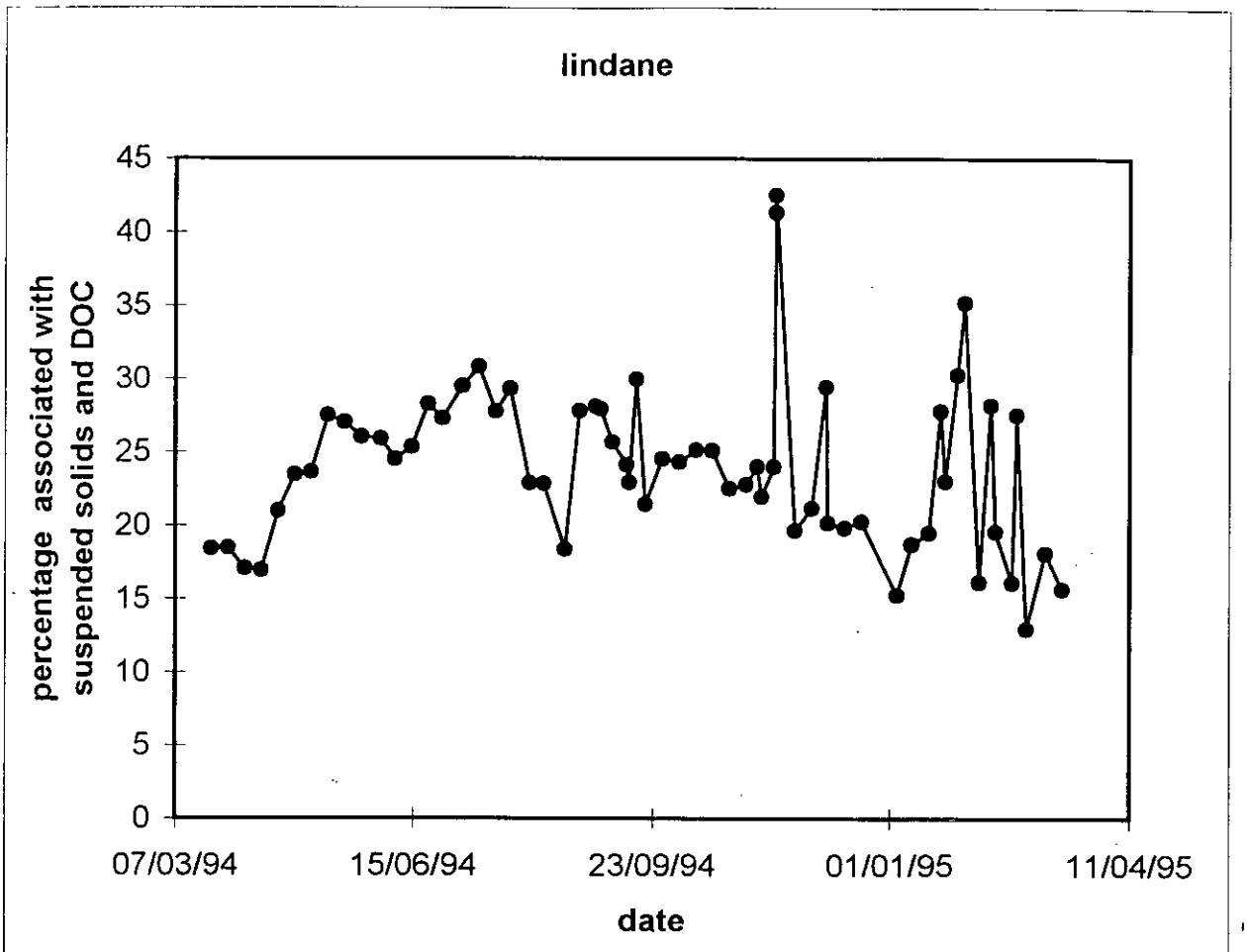


Figure 8.36 Estimate of the distribution of pesticides from DOC and suspended solids measurements in the R. Aire



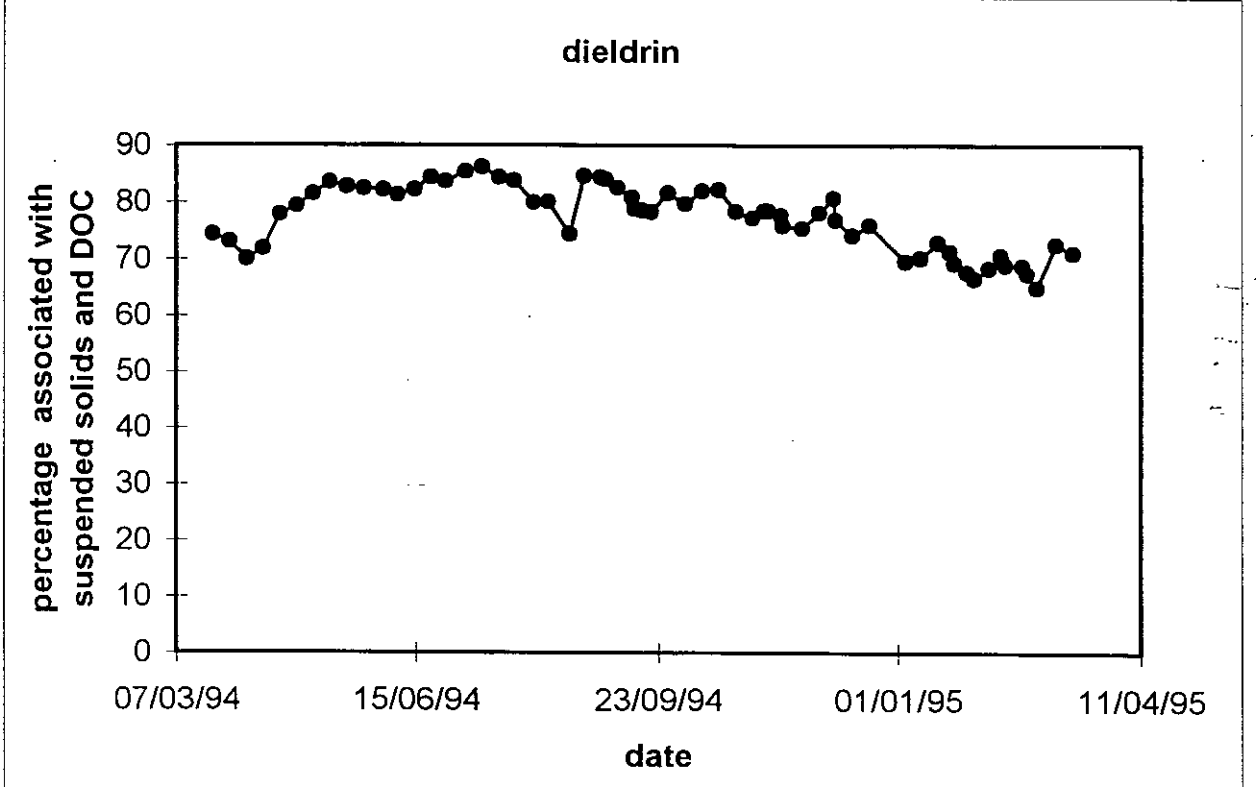


Figure 8.37 Estimate of the distribution of pesticides from DOC and suspended solids measurements in the R. Aire

9.0 ADSORPTION STUDIES

The purpose of this work was to obtain a better understanding of the role of colloidal clay - pesticide interactions and in particular the effects of temperature and ionic strength (related to salinity). This relates to changes in salinity on passage of water from rivers to the tidal zones and into estuaries. Changes in ionic strength change the adsorption interaction and also affect the stability of colloid material. Humic acids and clay colloids aggregate at high ionic strength to form larger particles which deposit into bottom-sediments in estuaries. Major clay components found in the R. Aire sediments were studied (kaolinite and montmorillonite) together with amorphous silica (as silica gel) found in diatom frustules.

9.1 Experimental

The initial concentration of pesticides in all the experiments described below was prepared by diluting the corresponding ≈1 mg dm^{-3} aqueous stock solutions. To prepare the latter, 8 ml of 200 mg dm^{-3} EtAc stock solutions was placed in 1000 ml volumetric flask, evaporated by the flow of dry nitrogen, and the residue dissolved in 1000 ml of aqueous electrolytic solution ($KHCO_3$ or KCl) by stirring overnight, followed by filtration through a 0.45 μm cellulose nitrate membrane.

To determine the concentration of pesticides in a solution, the pesticides were extracted on a C_{18} chromatographic column (*Bakerbond SPE, IST*), eluted by ethylacetate, the eluate dried with Na_2SO_4 (granular, AR grade, cured at 160 °C) and analysed with an automated GC/MS instrument (*Hewlett Packard G1034C MS ChemStation*) equipped with a *Hewlett Packard 5890 Series II Gas Chromatograph*. The sample was introduced via a split/splitless injector to a 5% phenyl methylpolysiloxane capillary column (25 m, 0.2 mm, 0.33 μm film thickness) with He as the carrier gas. The oven program was 15 °C min^{-1} to 170 °C, 5 °C min^{-1} to 240 °C, 2 °C min^{-1} to 270 °C and held at this temperature for 10 min. The analysis was based on detection of peaks of a target ion and a qualifier ion, the list of which is given below together with the corresponding retention times:

Table 9.1 Characteristic peaks in the mass-spectrum of the pesticides

Compound	Retention Time /min	Qualifier m/z	Target ion m/z
DecaChloroBiPhenyl (DCBP), reference compound.	38.9	178	214
flutriafol	22.3	164	123
isoproturon	8.43	161	146
trifluralin	13.88	306	264
propiconazol 1	25.89	259	173
propiconazol 2	26.17	259	173

The instrument was re-calibrated before each measurement using at least three standard solutions with decachlorobiphenyl internal standard. To avoid errors caused by possible

hydrolysis or photolysis of pesticides, their concentration in the aqueous stock solutions was re-determined each time they were used.

Clay colloids, kaolinite, montmorillonite and silica gel, were chosen for study as these are the main components of sediments and inorganic colloids. Kaolinite (*Cornish clay*) and montmorillonite (*Wyoming bentonite*) were first treated with 30% hydrogen peroxide to remove traces of organic substances, then washed several times with distilled water, and transformed to the K^+-form by treatment with 1M solution of potassium chloride as described elsewhere (Zhmud *et al.*, 1997). After final washing, the clay was dried at 120 °C and powdered in a mortar. Silica gel (surface area 300 $m^2 g^{-1}$, pore volume 1.6 $cm^3 g^{-1}$; *Johnson Matthey GmbH*) was used as received.

The specific surface area of kaolinite was 9.5 $m^2 g^{-1}$ by multi-point BET analysis. The total surface area of delamellarized montmorillonite was 462 $m^2 g^{-1}$ by the adsorption of water. The mineral percentage of the clays determined by X-ray diffraction was as follows: kaolinite sample (kaolinite 92.2%, illite/mica 4.3%, and quartz 3.5%); montmorillonite sample (montmorillonite 66.5%, quartz 13.8%, feldspar 17.8%, and sylvite 1.8%).

9.2 Adsorption and kinetic experiments

Weighed amounts of adsorbents (mesoporous silica gel, K^+-kaolinite, and K^+-montmorillonite) were placed in glass bottles containing known amounts of pesticides (isoproturon, flutriafol, and propiconazol) in 0.01M aqueous $KHCO_3$ solution. The initial pH of the solutions was adjusted to pH 7 by bubbling a CO_2/N_2 gas mixture. The bottles were immediately closed and shaken overnight at 20 °C. Separation of sediments from the dispersion was performed either by filtration on a 0.45 μm filter (kaolinite and silica gel) or by centrifugation at 6000 r.p.m. (montmorillonite). The concentration of pesticides in the initial solution and in the filtrate was determined as described before. The adsorption was calculated using the following sequence of operations easily programmed in Excel, Quattro-Pro, SigmaPlot, or other worksheet-processing software:

$$V_{EtAc} = m_{EtAc} / 0.9245$$

$$c_{aq}^{equil} = \frac{c_{EtAc} V_{EtAc}}{V_{sampled}}$$

$$c_{aq}^{init} = \frac{c' V_{add}}{V'}$$

$$Ads = \frac{(c_{aq}^{init} - c_{aq}^{equil}) V_{tot}}{m_{ads}}$$

where m_{EtAc} and V_{EtAc} are the mass and the volume of the EtAc eluate, c_{aq}^{equil} is the equilibrium, and c_{aq}^{init} the initial, concentration of pesticide in the aqueous solution, $V_{sampled}$ is the volume of aqueous solution sampled, V_{add} is the volume of the aqueous stock solution added to the bottles, whereas c' and V' are, respectively, the concentration of pesticide in, and the volume of the aqueous stock solution added to, a reference bottle used for determination of the concentration of the stock solution itself, V_{tot} is the volume of the solution in the bottles, and m_{sample} is the mass of the adsorbent. The density of EtAc was taken as 0.9245. The results are shown in Figures 9.1-9.4.

9.3 Temperature dependence of adsorption affinity of isoproturon to silica gel

The choice of adsorbate and adsorbent was determined by a desire to obtain the most reliable isotherm so that small difference caused by temperature or ionic strength could be resolved. First, the calibration curve for isoproturon is nearly linear, and therefore, the local interpolation error is minimal. Second, the surface of precipitated silica gel, unlike the surface of clays, is relatively homogeneous and stable in aqueous solutions. Thus, the Henry law constants measured for this adsorption system are expected to be the most reliable.
The conditions in the experiments were as follows: temperatures: 5, 20 and 35 °C, m_{sample} = 8 g, V_{tot} = 150 ml, background electrolyte: 0.01 M KCl at pH: 6.6 - 6.7. Use of KCl instead of $KHCO_3$ is desirable since this eliminates any difficulties with maintaining a constant pH (the partial pressure of CO_2 is strongly dependent on temperature).

Plastic bottles (for centrifugation) with samples were equilibrated for 2 days in a water bath. During the first day, they were periodically shaken vigorously. During the second day, particulates were settled, and 10 ml aliquots sampled immediately from the overlying solution. The results are shown in Fig. 9.5.

9.4 Dependence of adsorption affinity of isoproturon to silica gel on salinity.

The experimental conditions were as follows: temperature: 20 °C, m_{sample} = 8 g, V_{tot} = 150 ml and background electrolytes of : 0.001, 0.01, 0.1 and 1M KCl at pH: 6.6 - 6.7.

Plastic bottles (for centrifugation) with samples were equilibrated for 2 days in a incubator. During the first day, they were kept shaken. During the second day, particulates were allowed to settle down, and then 10 ml aliquots were sampled immediately from the overlying solution.

9.4.1 Techniques

Adsorption amounts are extremely low, so a proper choice of the initial concentration of pesticides is crucial for the final isotherm accuracy. In particular, if c_{aq}^{init} is too large, so that $c_{aq}^{init} \approx c_{aq}^{equil}$, or too small, so that $c_{aq}^{equil} \approx 0$, the difference $c_{aq}^{init} - c_{aq}^{equil}$ cannot be adequately quantified (that the standard error of GC/MS determinations is approximately ±10-20%). The following numbers proved to give satisfactory results:
Given V_{tot} = 150 ml, aqueous stock concentration ≈ 1 mg/l, then:

N	V_{added}, ml	m_{sample}, g	$V_{sampled}$, ml
0	20	0	10
1	10	10	10
.	.	.	.
.	.	.	.
.	.	.	.
N	50	10	10
0'	20	0	10

where No. 0 and 0' are the reference bottles needed for independent determination of the concentration of the aqueous stock solution at the time of experiment. In this case, the corresponding concentrations of pesticides in EtAc eluate fall into the range 0.1 to 2.0 mg/l and can be easily quantified by a 3-point calibration curve using 0.2, 1.0, and 2.0 mg/l multi-standards. It is preferable to take two samples from each bottle and to run the GC/MS determination placing the samples, bracketed by the standards, in the sequence:

(EtAc, 0.2, 1.0, 2.0), 0, 1, 2,...,N-1, N, N, N-1,...,2, 1, 0, (EtAc, 0.2, 1.0, 2.0)

In general, this permits more accurate results and shows the inherent errors of the method.

The results of the isotherm measurements in saline conditions are shown in Fig. 9.6.

9.5 Discussion of the results

9.5.1 Comparison of the isotherms

The isotherms at 20 °C are shown in Figures 9.1 to 9.4. The Henry constant was calculated from:

$n_a = m_{sample} \Sigma \Gamma c_{aq}^{equil}$ where Σ is the specific surface area of the material, Γ is the Henry constant, m_{sample} is the mass of the adsorbent and c_{aq}^{equil} the equilibrium concentration of pesticide in contact with the adsorbent. The distribution coefficient, k_d, is related to the Henry constant by: $k_d = \Gamma \Sigma$. Adsorption in the linear region of the isotherm is best quantified in terms of the adsorption normalised with respect to the surface area of the adsorbent rather than the mass, i.e. as with k_d. This is because the pesticides in solution usually only interact the exposed surface area of the particles and not their total bulk mass.

The isotherms were all found to be linear (Figures 9.1-9.4) and intercept the origin with no indication of an initial "knee" which is usually indicative of adsorption to high energy sites on the surface. A regression analysis of the isotherms, with appropriate corrections for the units of adsorption amount and concentration, produced the constants shown in Table 9.2. The highest k_ds were obtained for montmorillonite - a colloidal clay material common in freshwaters. However, the corresponding Henry constants are similar in magnitude to the other adsorbents showing that it is the relatively high specific surface area of the montmorillonite which leads to the larger adsorption amount. A comparison of the Henry constants shows that, apart from on kaolinite, propiconazole has the highest adsorption affinity to the surfaces.

There is little information available from the literature on the adsorption of these compounds to natural sediments or clays. Information which is available for isoproturón for soils (1.36 % organic carbon) gives a k_d of 1.27 $dm^3\ kg^{-1}$ which is lower than the values measured for the clays and silica gel. Unfortunately the specific surface areas of soils and sediments used in sorption studies are often not reported and so it is difficult to compare the Henry constants. No information is available in the literature on the sorption of propiconazol and flutriafol to soils or sediments - a summary for some other herbicides is given in Appendix 3.

Table 9.2 Comparison of the Henry constant and distribution coefficients (k_d) for adsorption of selected herbicides on minerals at 20 °C.

Material	pesticide	Henry constant / 10^{-7} m	k_d/ dm^3 kg^{-1}
silica gel ($300\ m^2\ g^{-1}$)	isoproturon	0.91	27.3
	propiconazol	2.3	69.0
	flutriafol	0.29	8.7
kaolinite ($9.5\ m^2\ g^{-1}$)	isoproturon	2.6	2.5
	propiconazol	1.3	1.2
	flutriafol	0.87	0.8
montmorillonite ($462\ m^2\ g^{-1}$)	isoproturon	1.4	64.7
	propiconazol	6.6	304.9
	flutriafol	1.4	64.7

The results in Table 9.2 permit an estimate of the interaction of the compounds with mineral colloids of different size. The specific surface area may be estimated by assuming spherical particles of density of 2.6 g ml^{-1} so that $\Sigma\ (m^2g^{-1})=3000/(r\ \rho)$ where r is the particle radius in nm and ρ is the density in g ml^{-1}. The results for a range of particle sizes from 1 to 5000 nm are shown in Table 9.3.

The k_ds for the highest Henry constant ($6.6\ 10^{-7}$ m), even for the smallest particle size (2 nm diameter) is less than 1000 dm^3 kg^{-1} which is approximately the smallest value measured using the UFC cell (normalised with respect to the organic carbon content; see Table 5.5).

Table 9.3 Calculated values of the distribution coefficient, k_d (ml g^{-1}) for different particle sizes (r: radius of equivalent sphere) and Henry constants (Γ/m)

Henry constant/m	1.4E-07	6.6E-07	5.0E-06	1.0E-05
r/nm				
1	161.54	761.54	5769.23	11538.5
10	16.15	76.15	576.92	1153.8
100	1.62	7.62	57.69	115.38
500	0.32	1.52	11.54	23.08
1000	0.16	0.76	5.77	11.54
2000	0.08	0.38	2.88	5.77
3000	0.05	0.25	1.92	3.85
4000	0.04	0.19	1.44	2.88
5000	0.03	0.15	1.15	2.31

9.5.2 Temperature dependence

The results for 5, 20 and 35 ^{0} C, in Figure 9.5, show there is an increase in sorption with decrease in temperature. This is indicative of an exothermic interaction between the pesticide

and the surface. All the isotherms for isoproturon adsorption are linear. Similar results were obtained for simazine adsorption to natural materials collected from the Millstream (R. Frome, Dorset) and Rosemaund farm (ADAS), Herefordshire. The free energies of adsorption were calculated as -21.4, -56.2 and -8.4 kJ mol^{-1} for silica gel, Millstream pond and Rosemaund drainage channel respectively, i.e. all exothermic reactions. The temperature dependence is less on the silica gel compared with the relatively high dependence shown for the organic rich Millstream pond material. There is little data in the literature on the temperature dependence; the isotherm data supplied by Talbert and Fletcher (1965) for simazine sorption to soils (Marshall silty clay) permit an estimate of the free-energy as -14.9 kJ mol^{-1} .

For some compounds and sediments/colloids, the increasing sorption with decreasing temperature may be important as the drainage waters cool on transport from terrestrial to aquatic environments.

Table 9.4 Comparison of k_ds (ml g^{-1}) for three sorbents

System	5 °C	25 °C	35°C
Millstream pond (simazine)	9.56	1.88	-
Drainage channel (simazine)	4.84	3.76	-
Silica gel (isoproturon	8.6	6.6 (at 20 °C)	3.5

9.5.3 Effects of salinity

The results (Figure 9.6) show that effects of increasing salinity on the sorption behaviour is not marked. The isotherm measured at 1M NaCl (seawater is approximately 0.6 M) is similar to that for 0.01M NaCl - the lowest adsorption was measured at 0.001 M. Therefore, although the effect is relatively weak, adsorption is most changed between 0.001 and 0.01 M NaCl. In fresh waters, the range of ionic strength is typically from 0.001 (soft water- distilled water is zero) to hard waters at 0.01 M. Hence the transport in surface run-off during rainfall - (low ionic strength) to streams is likely to favour increased sorption to clays. Subsequent increases in ionic strength in the inter-tidal zone are less likely to produce changes in adsorption but will lead to aggregation of suspended and colloidal material.

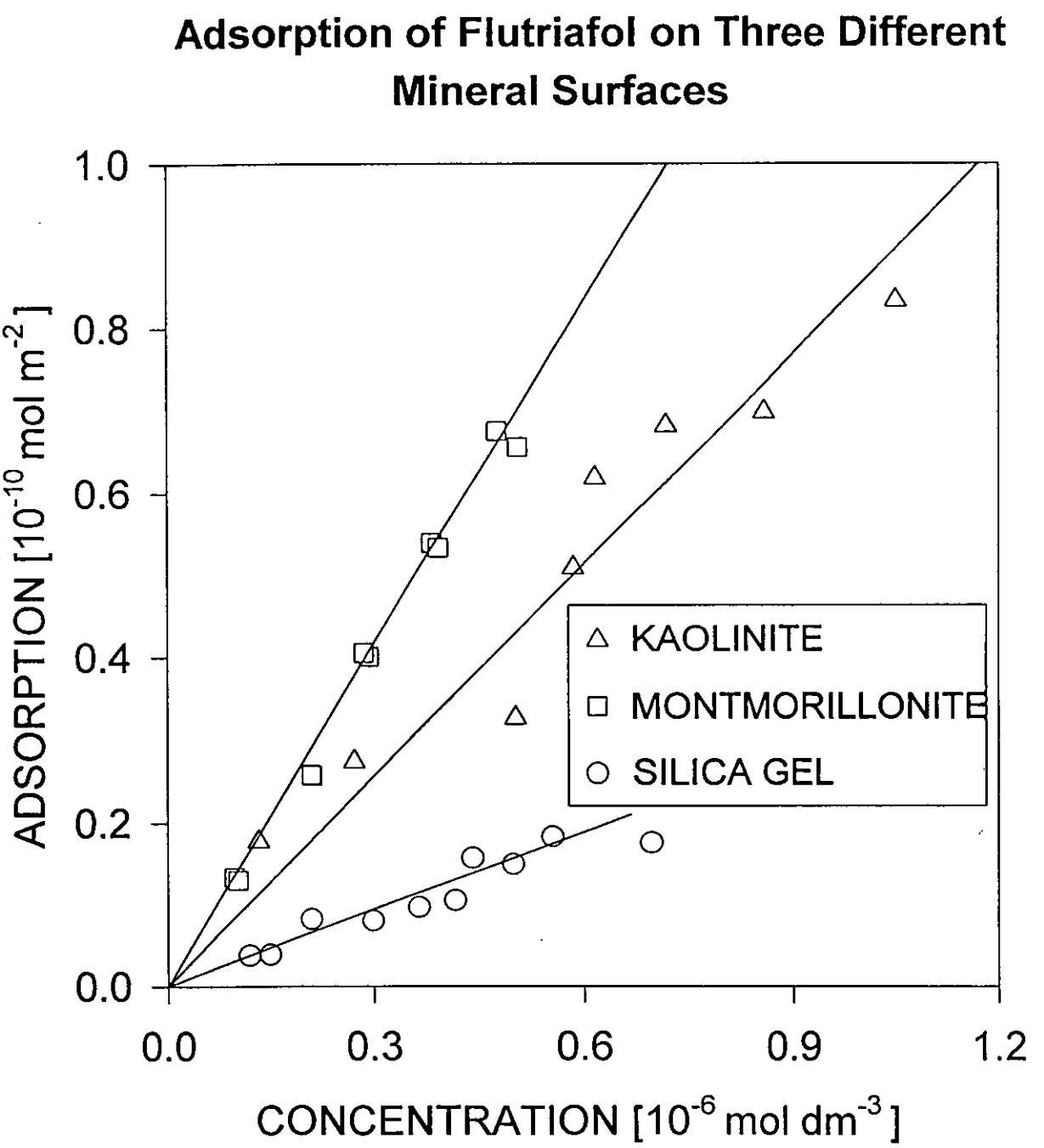

Adsorption of Flutriafol on Three Different Mineral Surfaces
ADSORPTION [10-10 mol m-2]
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.3
0.6
0.9
1.2
CONCENTRATION [10-6 mol dm-3]
KAOLINITE
MONTMORILLONITE
SILICA GEL

Figure 9.1

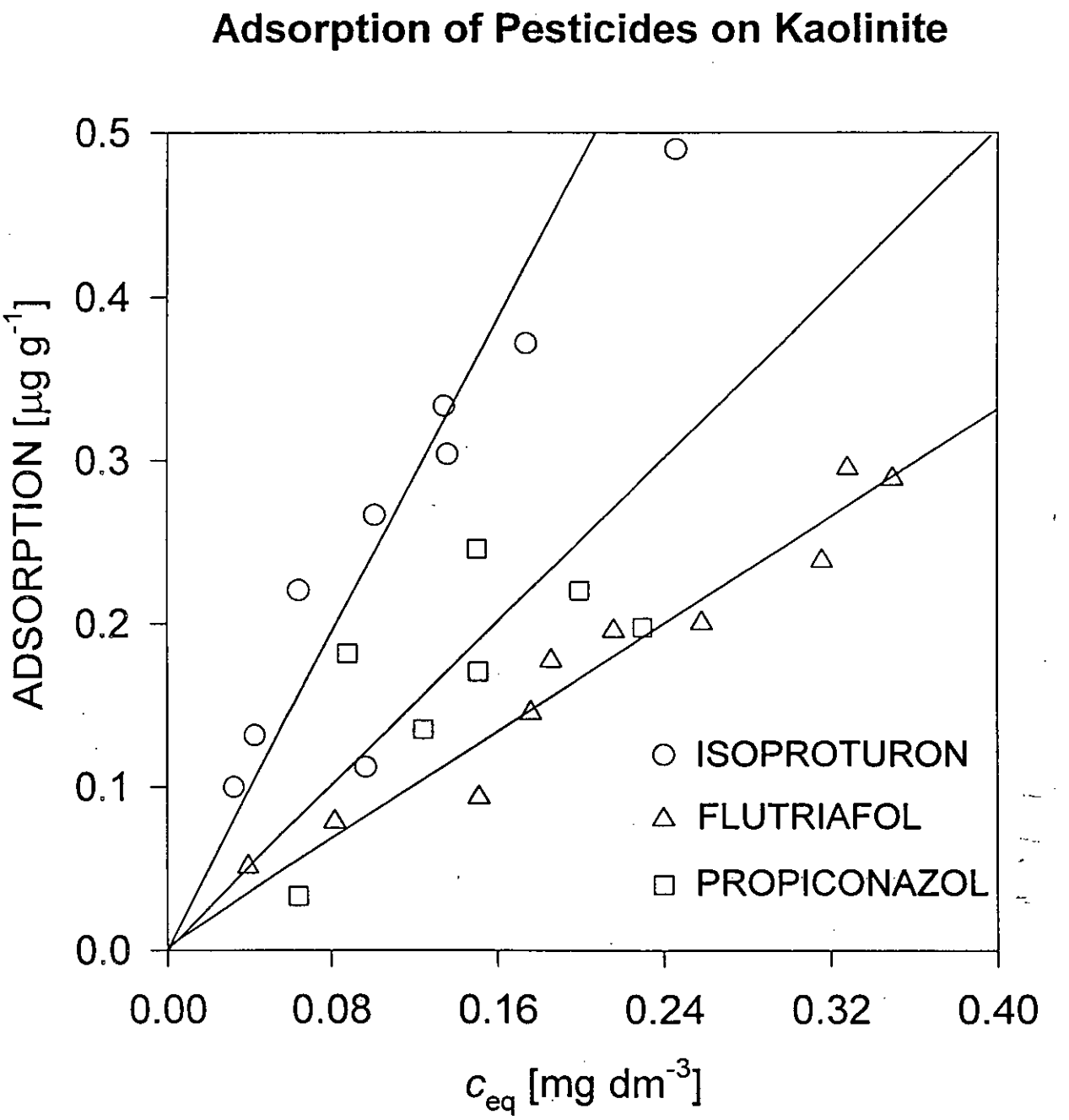

Adsorption of Pesticides on Kaolinite
ADSORPTION [μg g-1]
0.5
0.4
0.3
0.2
0.1
0.0
0.00
0.08
0.16
0.24
0.32
0.40
ceq [mg dm-3]
ISOPROTURON
FLUTRIAFOL
PROPICONAZOL

Figure 9.2

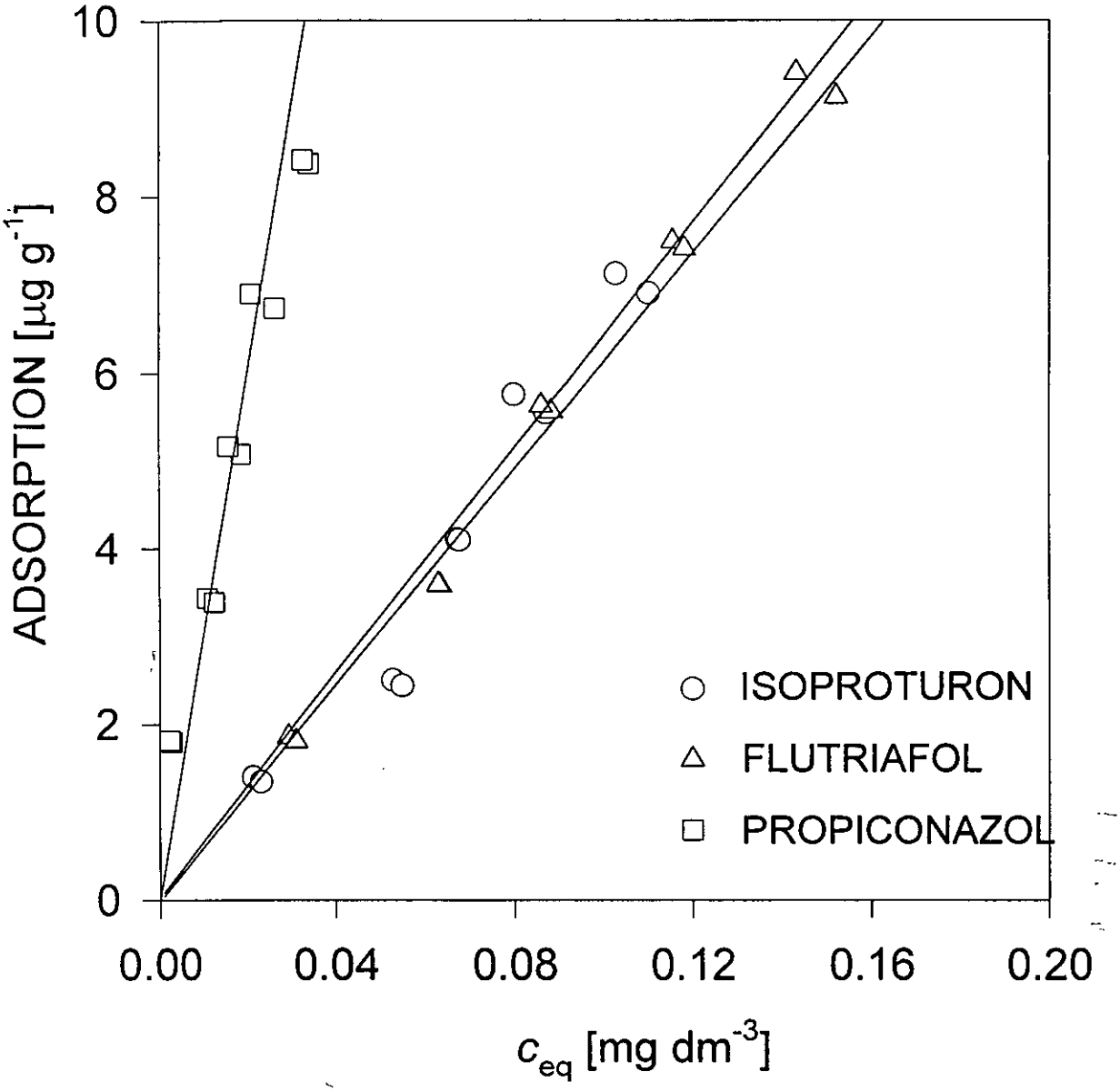

Adsorption of Pesticides on Montmorillonite
ADSORPTION [µg g-1]
10
8
6
4
2
0
0.00
0.04
0.08
0.12
0.16
0.20
ceq [mg dm-3]
ISOPROTURON
FLUTRIAFOL
PROPICONAZOL

Figure 9.3

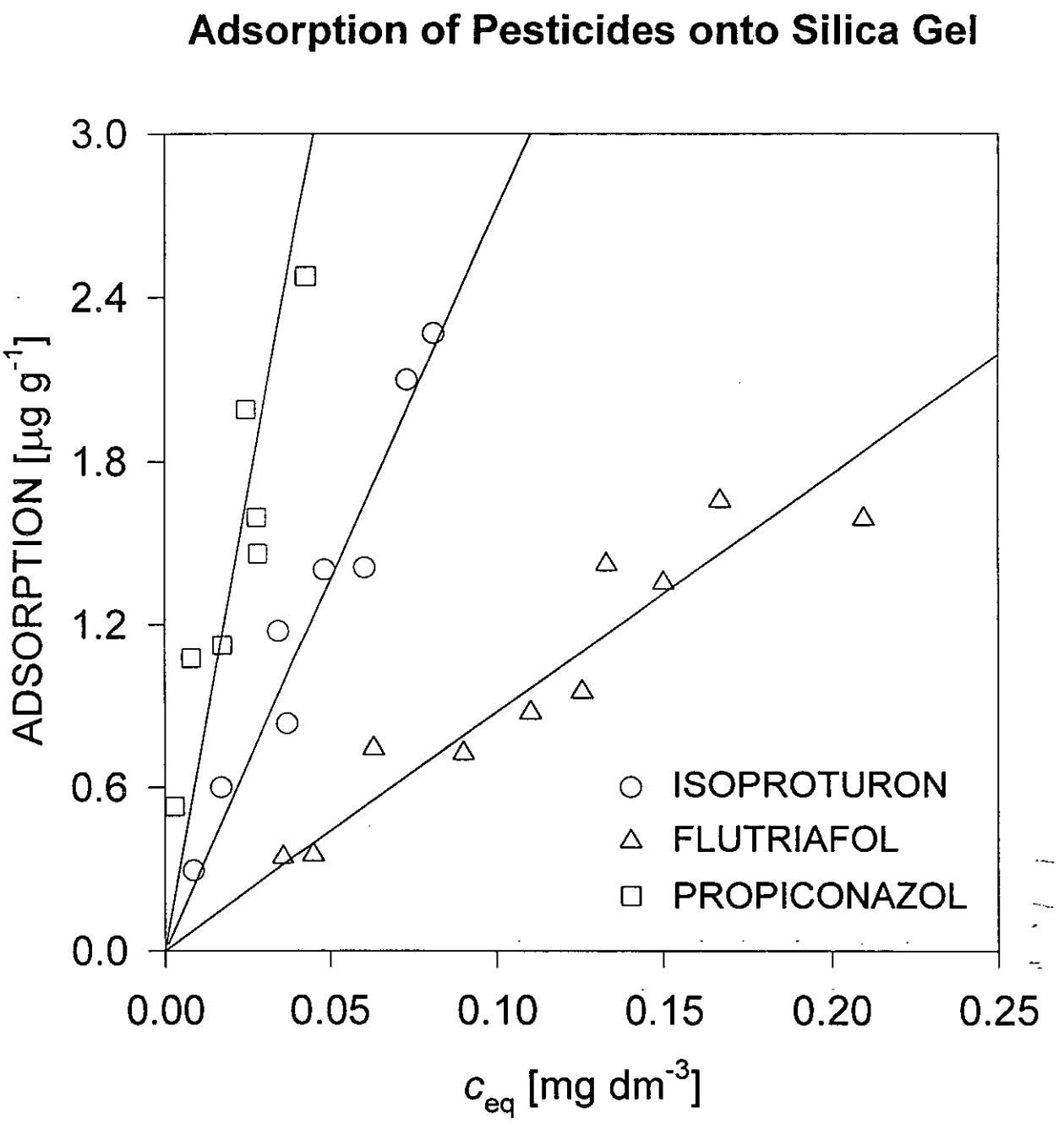
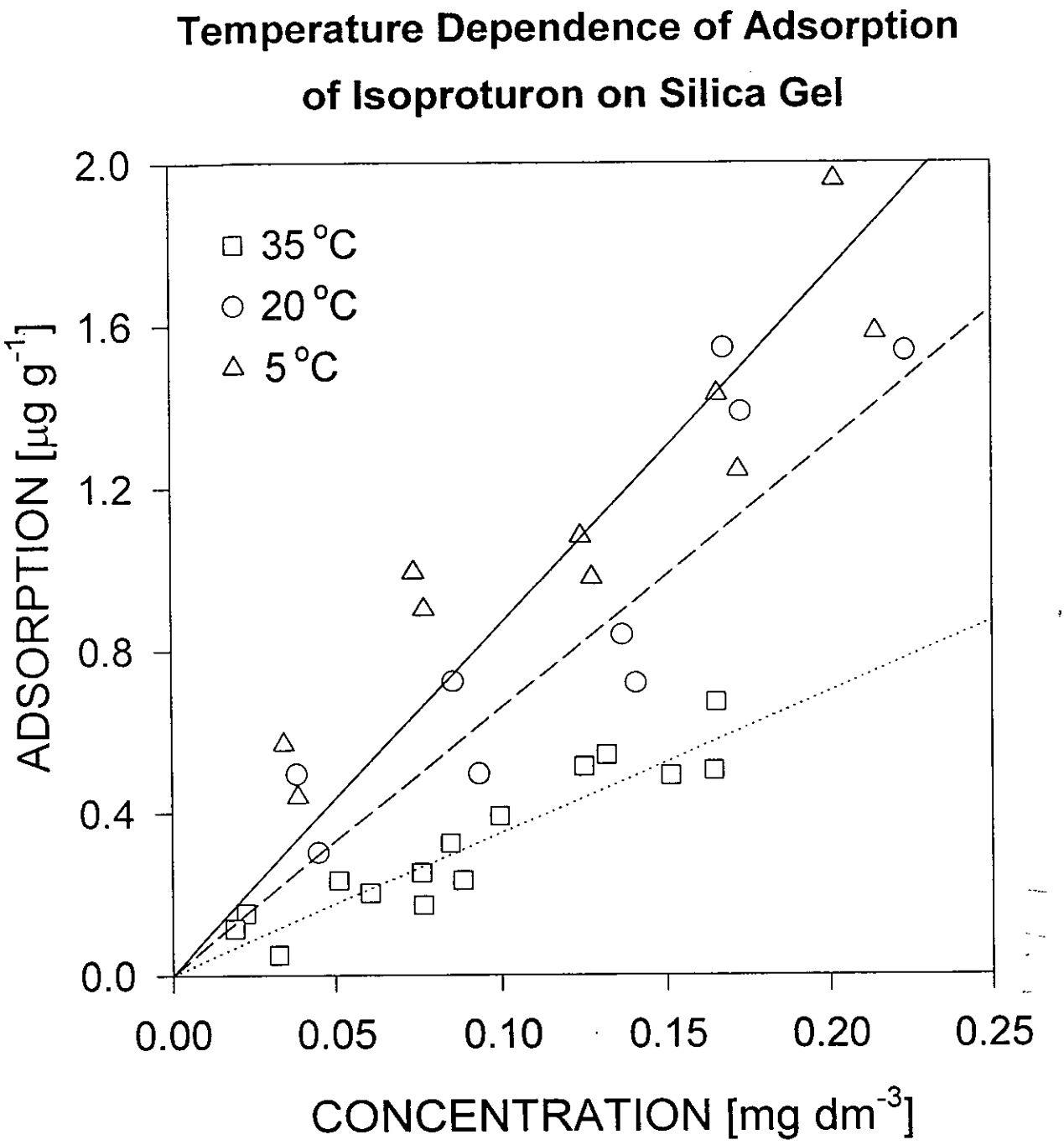

Adsorption of Pesticides onto Silica Gel
ADSORPTION [µg g-1]
3.0
2.4
1.8
1.2
0.6
0.0
0.00
0.05
0.10
0.15
0.20
0.25
ceq [mg dm-3]
ISOPROTURON
FLUTRIAFOL
PROPICONAZOL

Figure 9.4



$K_5 = 8.6\ 10^{-3}$, $K_{20} = 6.6\ 10^{-3}$ and $K_{35} = 3.5\ 10^{-3}\ dm^3\ g^{-1}$

Figure 9.5

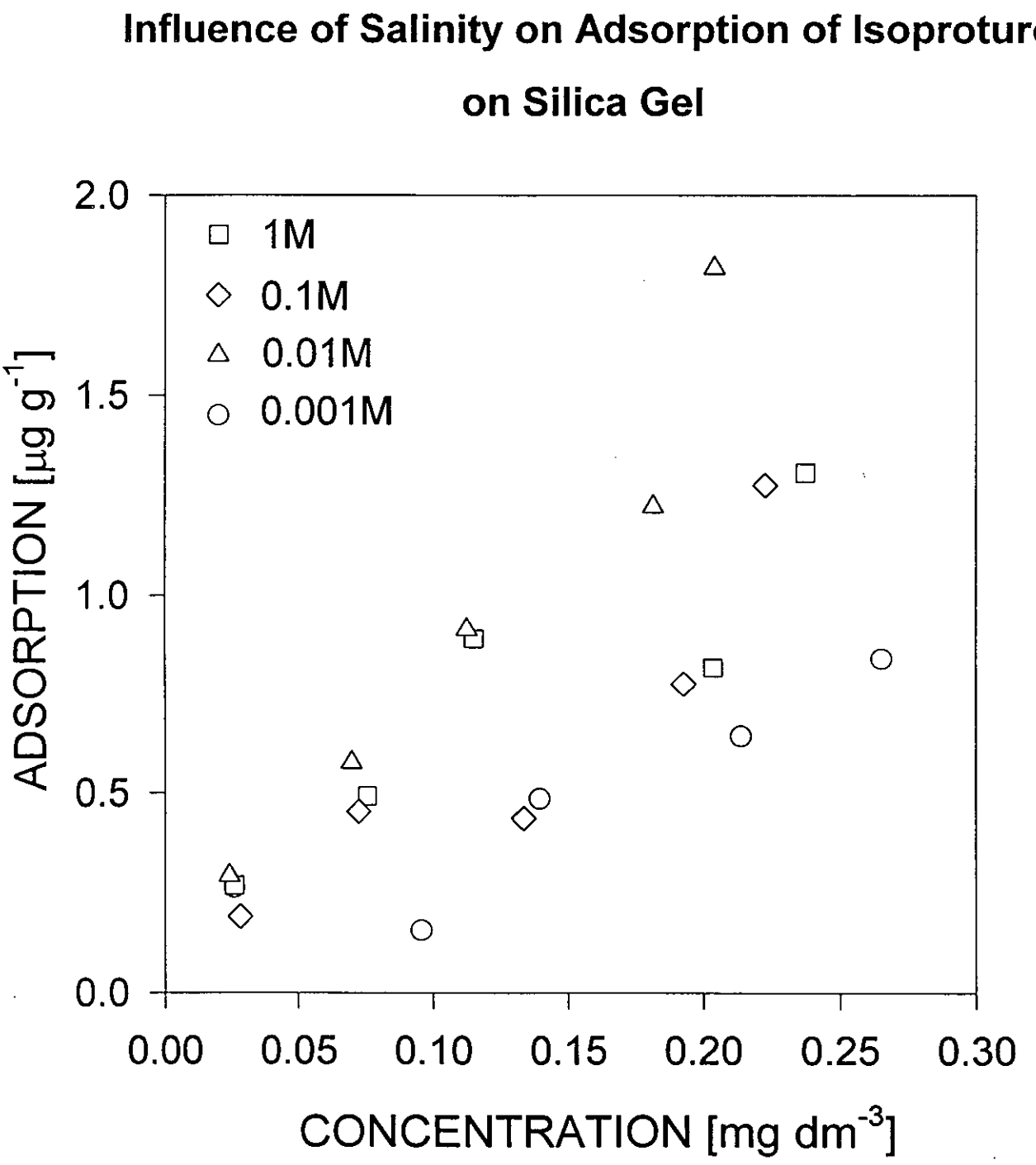

Influence of Salinity on Adsorption of Isoproturon on Silica Gel
1M
0.1M
0.01M
0.001M
ADSORPTION [µg g-1]
CONCENTRATION [mg dm-3]
2.0
1.5
1.0
0.5
0.0
0.00
0.05
0.10
0.15
0.20
0.25
0.30

Figure 9.6

10. CONCLUSIONS

This study shows that natural colloids provide very active sorption sites for a range of pesticides. Although colloids are very heterogeneous in composition, the classification used in this study allows some broad conclusions to be drawn which have important implications when considering the fate of compounds released to the environment. The results indicate that organic colloids have a great affinity for a range of pesticides with distribution coefficients much greater than expected from organic carbon normalised coefficients measurements on soils. Clay and mineral colloids are generally retained with sediments during filtration and centrifugation and may be considered together with the suspended sediment fraction. Hence distribution coefficients for sediments are essential for assessing the fate and behaviour of this fraction of the colloids. The distribution coefficients may be very different from values determined for soils because of the greater organic carbon content and finer particle-size distribution of the components in sediments. The results for the compounds considered here, and other information from the literature, also show that the partition of pesticides with organic colloids may be evaluated from the relationship with the appropriate octanol-water partition coefficients. Hence given two distribution coefficients: sediment distribution coefficient and the organic colloid distribution coefficient (normalised with respect to organic carbon), it is possible to estimate the concentration of sediment and colloid bound pesticides given the aqueous concentration of the pesticide. This estimate depends on environmental measurements of dissolved organic carbon and suspended solids concentration; the measurement of the organic matter content of the sediment will improve the prediction but is not essential. This method could be used to develop a criteria for assessing the risk of movement of new compounds with natural colloids and sediments. Most of the existing assessment of pesticide association with solids is through the determination of soil distribution coefficients which are not generally applicable to sediments. Therefore it is recommended that more appropriate methods involving activity - structure relationships are developed from this work. These should incorporate a consideration of both the sediment and organic colloid distribution coefficients and so more closely reflect the fate and behaviour of pesticides in water bodies.

10.1 Comparisons with other work

There are few studies of the interactions of pesticides with colloid or natural organic matter (NOM) in fresh waters. A selection of those found in the literature are listed below:

1. The interactions of a synthetic pyrethroid, fenvalerate, with NOM have been examined using two techniques - (a) " bottle method" whereby the solution containing the NOM and fenvalerate was passed through a C18 spe column and, (b) the " generator column method" in which the NOM was passed through a column of glass beads onto which fenvalerate was coated (Fan *et al.*, 1998). Values of k_{doc} were of the order of 10^5 dm^3 kg^{-1} which is similar to the values determined for the R. Ouse in March 1995 for a range of compounds (Table 5.5), but much higher than the values measured using samples from other rivers in the Humber catchment. Fenvalerate is similar in chemical structure to permethrin (Table 4.1), with a low solubility in water and lipophilic character leading to a high k_{oc} (10^5 dm^3 kg^{-1} , in

Table 4.1). There was some evidence from this study that the k_{oc} for the higher molecular weight fraction, i.e. > 10K, were higher than the lower molecular weight component (1K - 10K).

2. The interactions of atrazine and a phenylurea herbicide, linuron, with estuarine colloids (passing through a 0.45 μm membrane filter) have been reported by Means and Wijayaratne (1982). The estuarine samples from the Choptank and Patuxent rivers in Maryland, USA, were concentrated using hollow-fibre membranes and ultra-filtration (5000 Dalton), and the adsorption of the compounds on the colloids was expressed in terms of the organic carbon content of the colloid. This is similar to the method employed in the present study. The distribution coefficients were of the order of 1690-13,600 $dm^3\ kg^{-1}$ expressed as k_{oc} for atrazine, and approximately 6500 $dm^3\ kg^{-1}$ for linuron. The values measured for atrazine in this work range between 3000 and 122,000 $dm^3\ kg^{-1}$ and for simazine between 1100 and 19,000 $dm^3\ kg^{-1}$ (measured with respect to the organic carbon content). Sorption coefficients on soil (k_{oc}) are generally much lower, and as shown in Table 4.1, have a range of 57-174 $dm^3\ kg^{-1}$ for atrazine. Therefore, as found by Means and Wijayaratne (1982), the organic material in these natural estuarine and river colloids is far more adsorptive than soil organic matter expressed on a carbon basis.

3. The gas purging method has been used by Hassett and Milicic (1985) to determine the interaction between tetrachlorobiphenyl and sodium humate (Aldrich humic acid, AHA). This method is useful for compounds which are measurable volatile in water but suffers from problems associated with the adsorption to container walls of tubes and vessels. However, this may be overcome by examining the DOC concentration dependence of the sorption isotherm and extrapolating to infinite concentration, i.e. 1/[DOC]=0. This procedure gave a k_{oc} of 71,000 $dm^3\ kg^{-1}$ (standard deviation 24,000 $dm^3\ kg^{-1}$). The value of k_{oc} is theoretically independent of the DOC, so that any measured dependence must be an artefact of the method used in the measurement - in this instance the sorption to container materials. The distribution coefficient is approaching the value obtained for fenvalerate, another very hydrophobic compound.

4. Some studies have examined the interaction of compounds with solid humic acid to measure the distribution coefficient. However, the results from such experiments are difficult to compare with those measuring the interactions with the humic or fulvic acid in colloidal form. This is because of the large difference in the configuration and solvation of humic and fulvic acids in the particulate and colloid materials. Spark and Swift (1994) have attempted to compare these interactions for atrazine, 2,4-dichlorophenoxy acetic acid, isoproturon and paraquat using conventional sorption measurements and fluorescence spectroscopy. They found that the order of sorption to the solid was 2,4-D > atrazine > isoproturon although it is not possible to calculate distribution coefficients from the isotherms which are comparable with other studies because of the units used to measure the adsorption isotherms.

5. Polyaromatic hydrocarbons (PAHs), pyrene and phenanthrene have been investigated using colloids from marine porewaters in Boston Harbour (Chin and Gschwend, 1992). The measured k_{oc}s are in the range of 51,700 to 111,000 $dm^3\ kg^{-1}$ for pyrene and 26,700 dm^3

kg^{-1} for phenanthrene. This association infers that approximately 40-50 % and 25 % of pyrene and phenanthrene respectively in the porewater is bound to colloid material. Other studies with estuarine colloids have also produced high k_{oc}s for PAHs, e.g. Wijayaratne and Means (1984) measured a k_{oc}=510,000 dm^3 kg^{-1} for anthracene.

6. Results of k_{oc} measurements for aldicarb, lindane and pentachlorophenol for samples of fulvic and humic acids (Lafrance *et al.*, 1991), indicated lower values for the fulvic acid sample. The distribution coefficients (unitless) were: 11,480 and 25,700 for lindane ; 11,700 and 42,700 for pentachlorophenol - with the lower values quoted for the fulvic acid sample. The values of k_{oc} for aldicarb were < 20. This again indicates that the molecular composition of the organic colloid is important in determining the adsorption affinity and hence distribution coefficient, i.e the carbon content of the organic colloid is not the sole variable describing the sorption interaction but a more detailed knowledge of the molecular composition is needed.

7. The high affinity of PAHs to DOC has been verified in studies by Rav-Acha and Rebhun (1992). They measured k_{doc} values for a commercial product, Aldrich humic acid, and fluoranthene of 184,000 and 210,000 ml g^{-1} by independent methods. These results are consistent with reports of 170,000, 53,700 and 85,100 for pyrene, phenanthrene and anthracene respectively (Gauthler *et al.*, 1987). These results for PAHs, when combined with a value published for DDT, show a good correlation (r^2=0.98) with log K_{ow}, i.e. Log k_{doc}=0.66 log K_{ow}+1.88 (Rav-Ach and Rebhun, 1992). The values of k_{doc} were on average 1.4 fold greater than the corresponding K_{ow}.

10.2 Role of colloids in pesticide transport

Specific Points:

- Colloids have been divided into either clay-based particles or DOC macromolecules. The results from particle-size measurements on suspended sediments separated by continuous - flow-centrifugation indicate that the clays are not an important component of the centrifugate and their contribution to sorption may be conveniently included in the suspended sediment fraction for most rivers. The results from the R. Aire do however indicate there may be some exceptions to this generalisation when colloidal clay is an important component of the colloidal material. Most research on colloids has examined interactions of micro-organic contaminants with the organic fraction dominated by DOC. The results from this study indicate that organic colloids have a great affinity for a range of pesticides with distribution coefficients much greater than expected from organic carbon normalised coefficients measurements on soils. The results for a range of triazine and organophosphorus pesticides are consistent with the trends demonstrated for PAHs and DDT producing a relationship between log k_{doc} and log K_{ow} shown in Figure 10.1. Although this trend is limited by the variability in k_{doc} values found for the river waters, it does permit an estimate of the contributions of organic colloids to the transport of pesticides.

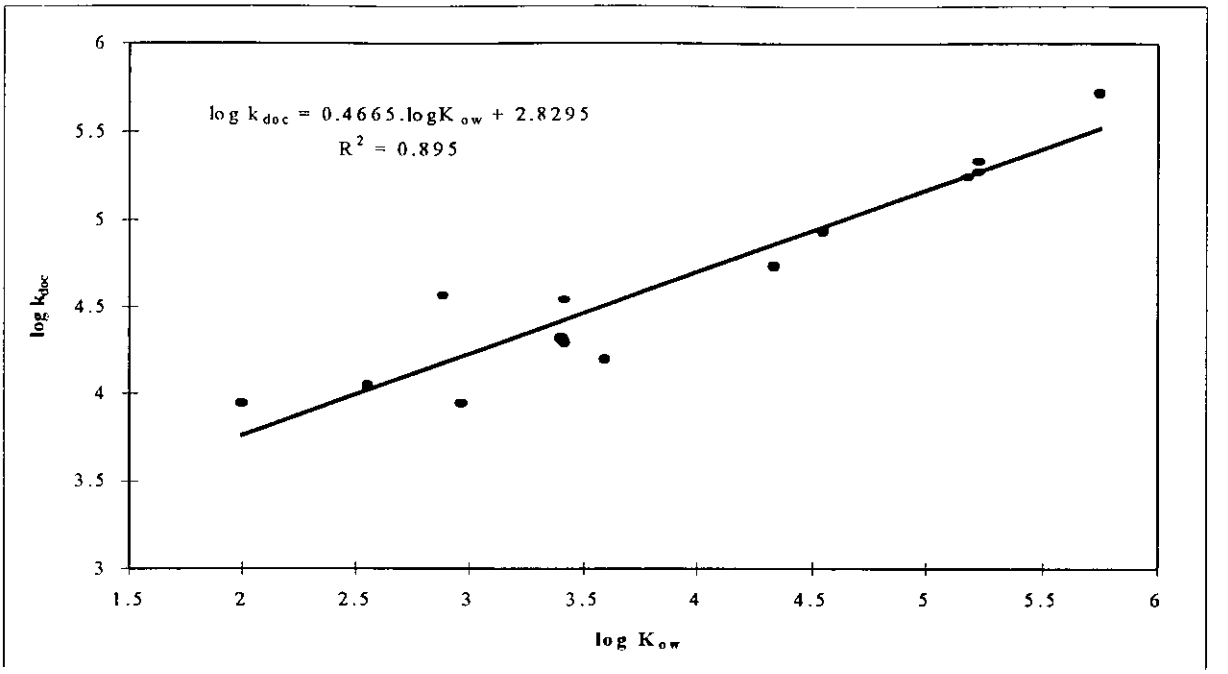


Figure 10.1 Relationship between octanol - water partition coefficient and distribution coefficients for DOC for the compounds investigated here and PAHs and DDT (Rav-Ach and Rebhun, 1992).

- A range of compounds were detected in "whole water" samples collected at weekly intervals and during storm periods in the main Humber rivers - Aire (2 sites), Calder, Trent, Don and Ouse and the R. Swale. These included simazine, atrazine, prometryn, terbutryn, desmetryn, parathion, malathion, fenitrothion, *cis* and *trans* permethrin, dieldrin and lindane. The most frequent occurrence was in the rivers Aire and Calder, particularly for the triazines, permethrin and dieldrin. The more water soluble compounds such as the triazines, were essentially diluted with storm-flow whereas the more hydrophobic compounds, such as permethrin, were mobilised with suspended material during storms. DOC concentrations decreased during high-flow and was greatest in base-flow conditions. A reasonable correlation was found between the inverse of the river discharge and DOC concentration.

- The k_{doc} values for the triazines and organophosphorus compounds were measured using a ultra-filtration system and these results have been combined with k_d values for suspended sediments and weekly measurements of DOC and suspended solids in the R. Aire at Beale (the tidal limit of the river), to predict the relative amount of colloid and sediment bound pesticide. The triazines are most weakly bound with < 20 % adsorbed to sediments or colloids. The organophosphorus pesticides, fenitrothion, malathion and parathion are more strongly bound with < 30 % adsorbed

- Values of k_{doc} have not been measured for the other compounds found in the R. Aire - permethrin, dieldrin and lindane. The k_{doc} values have however been estimated from the relationship between k_{doc} and K_{ow} obtained using the data measured here for the triazines

and organophosphates, and literature data on DDT and PAHs, i.e. more hydrophobic compounds similar in chemical properties to permethrin and dieldrin. The results predict that both dieldrin and permethrin are mainly bound to colloids with up to approximately 90 % adsorbed, and with little variation in the distribution throughout the year.

- Adsorption studies to clay colloids indicate there is a increase in sorption with decrease in temperature which is indicative of an exothermic interactions between pesticides and clays. The isotherms were also found to be linear over a concentration range typical of concentrations found in the British rivers and supports the use of distribution coefficient to characterise the adsorption interaction of pesticides at low concentrations. The effects of increasing salinity on adsorption were found to be small with the weakest sorption at the lowest salinity. The sorption was found to be most changes between 0.001 and 0.01 M NaCl, i.e. salt concentrations between rainwater and hard water rivers. Increases in ionic strength in the inter-tidal zone are less likely to produce changes in sorption but will lead to aggregation of suspended and colloid material in the water.

- Measurements of the Henry's constant for montmorillonite and kaolinite (important components of the clay fraction in the R. Aire), suggest that flutriafol does not enter the expandable clay but bonds to surface edge sites of the clay. The adsorption affinity of the edge sites is similar for kaolinite and montmorillonite. Molecular modelling using molecular mechanics and dynamics indicates that the weak interactions with clays is dominated by hydration and hydrogen bonding. Triazoles may also interact with surface hydroxyls of the clay by an acid-base mechanism. Modelling sorption interactions using modern molecular modelling provides a powerful insight into possible bonding mechanisms and information on the possibility of pesticide molecules penetrating the interlayer spacing of expandable clays such as the smectites, e.g. montmorillonite.

10.3 Future work

There is a need develop better methodology to predict the role of colloids and suspended sediments on the transport of pesticides, including new compounds. Although the work in this study has concentrated on the Humber catchment in Yorkshire, the transport of pesticides in other catchments is likely to be influenced by colloids and sediments. A major concern arising from this work is the expected high affinity of the more hydrophobic compounds which are less water soluble but have a great affinity for organic colloids. This effectively increases their concentration in the water and leads to mobilisation in the environment.

Considerations of the fate of pesticides in water bodies should utilise parameters which are appropriate to rivers, lakes and estuaries rather than soils. There is currently an over-emphasis on the use of information derived from field studies and laboratory adsorption experiments using soils. Much of this is not appropriate to the conditions found in large rivers and generally underestimates the effects of suspended sediments and colloids. Hence when compounds are likely to enter the aquatic environment, the distribution of the compounds with suspended sediments and colloids must be considered and given the same priority as parameters such as water solubility and volatility, in considerations for registration

Particular Points:

There is a need to develop analytical methods to measure pesticides in "whole" water samples. Such techniques should permit the determination of pesticides associated with suspended matter and colloid material and provide more precise concentrations of pesticides in natural water. Current methods which filter samples prior to processing provide only a partial picture of the fate of pesticides in natural waters.

- Further research is needed to measure the sorption interaction of extremely hydrophobic molecules to organic colloids. The present results and predictions indicate that the interaction with DOC will be strong. For rivers such as the R. Aire, this means that between 70-90 % of the amount of hydrophobic compounds, like permethrin, are transported into the estuary in association with colloid material. The task of measuring distribution coefficients for the synthetic pyrethroids is technically difficult because of the strong interactions with container materials, filters and membranes. Methods need to be developed to address this problem for this and similar groups of hydrophobic compounds.

- The interaction of some polar pesticides with clay colloids may be partly through penetration into the interlayer spacing of smectite clays. This will lead to the immobilisation of the compounds as they are effectively removed from the dissolved phase and stored within the clay. Such compounds may be subsequently released from sediments once the concentrations in the overlying water are reduced. The present research has shown that modern molecular modelling can provide a powerful means to investigate such interactions for specific clay- pesticide systems.

- The results from this work show that for even weakly adsorbed compounds, transport in association with organic colloids is important. However, there is a lot of variability in the measured distribution coefficients for organic colloids for samples from different rivers. Further research is needed to measure the extent of the variability in a range of contaminated rivers at different times of the year.

- The resin exchange method for measuring colloid-pesticide interactions has further scope for development using different resins from those studied here. The method needs refining to enable studies with more hydrophobic compounds.

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APPENDIX 1. DESIGN AND OPERATIONAL SOFTWARE

Control software for the ultra-filtration unit.

The following support functions were written to simplify the process of writing the software to control the system.

Sub routine SetValves (ValveState%) this routine accepts an integer as a parameter and sends the lower byte of this to the output port which the valves are connected to.

Sub routine DispVState (ValveState%) this is a utility routine to assist in the debugging of programs; it displays the contents of the integer parameter ValveState% as a binary number on screen.

Function Pow% (X%, Y%) returns X% to the power Y% as a integer. For controlling up to 8 valves this should be a value between 1 and 128.

Function Set% (valve%, State%) this function defines and uses a static local variable to retain the status of the valves between function calls. It expects two parameters which are normally constants defined at the start of the program representing valves, and states. The function returns the predefined constant true% unless an error is detected in which case the constant false% is returned.
It uses Pow% to perform some calculations, SetValves to send an appropriate set of value to the hardware controlling the valves, and DispVState to display a binary number representing the current status of the valves.

Sub routine InitV this subroutine is called at the start of the program and again at the start of a run, to ensure that the system starts in a known state (with all the valves unpowered)
The main software for controlling the system was created by modifying the existing control software for the automated adsorption cell. It required the following modifications.

1. The following constant definitions added at the start of the main program

CONST true% = 0, false% = NOT true, Powered% = true, NoPower% = false

CONST ValvePortAddr% = &H2A0 + 3

CONST Valve1% = 6, Valve2% = 7, Valve3% = 1, Valve4% = 0

2. The addition of the subroutines and function described above

3. The addition of the line:

Set (Valve1%, Powered%) at the start of the routine responsible for adding spike solution to the cell, and the line:

Set (Valve1%, NoPower%)

at the end of this routine

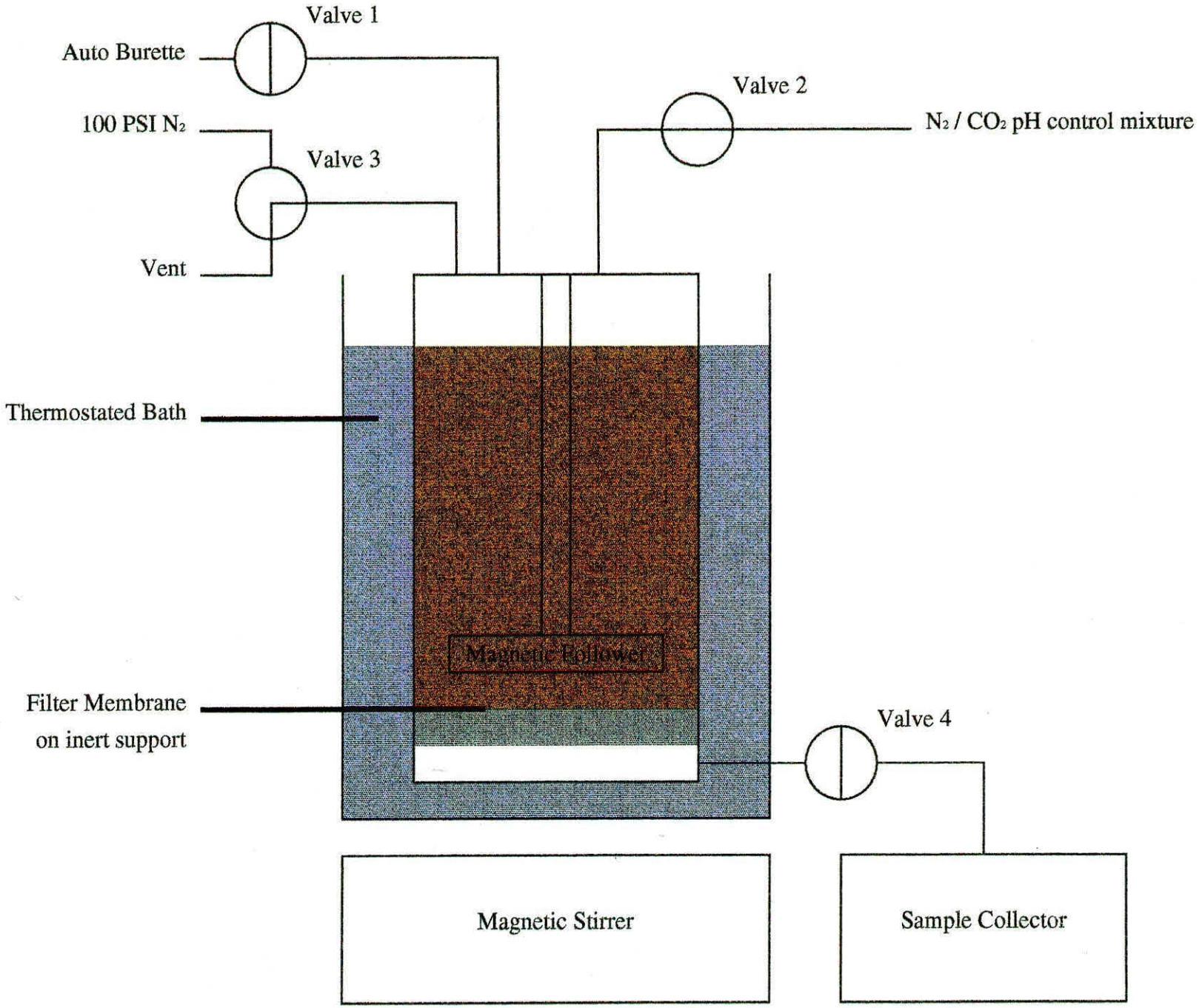
4. The sampling procedure was changed to:

```
IF Set(Valve2%, Powered%) = false% THEN PRINT "IN SAMPLE SUBROUTINE"
        Pause (1)
        PRINT "pH purge shut off"
        IF Set(Valve3%, Powered%) = false% THEN PRINT "IN SAMPLE SUBROUTINE"
        Pause (1)
        PRINT "Cell Pressurised"
        IF Set(Valve4%, Powered%) = false% THEN PRINT "IN SAMPLE SUBROUTINE"
        PRINT "Collecting Sample for "; sampletime; "seconds";
        Pause (sampletime)
        IF Set(Valve4%, NoPower%) = false% THEN PRINT "IN SAMPLE SUBROUTINE"
        PRINT "Sample collected"
        Pause (1)
        IF Set(Valve3%, NoPower%) = false% THEN PRINT "IN SAMPLE SUBROUTINE"
        PRINT "Pressure Dropping"
        Pause (purgedelay)
        IF Set(Valve2%, NoPower%) = false% THEN PRINT "IN SAMPLE SUBROUTINE"
        PRINT "Restarting pH purge"
```

This applies power to the valves in order 2, 3, 4 with delays to allow valves to fully shut and the system to settle, sample is allowed to flow out of the ultra-filtration cell through the membrane for a user specified time before valve 4 is shut and the cell depressurised. The IF...THEN statements were designed to aid debugging - allowing messages to be printed indicating the source of any possible errors.

PROGRAMS AVAILABLE

AUTOUFC: performs an auto-adsorption experiment
MSPIKE: adds a single user defined spike
MSAMPLE: takes sample for a user defined period
MANUAL: combines the functions of MSPIKE and MSAMPLE in one program



Ultra-filtration cell

APPENDIX 2. DEFINITION OF DISTRIBUTION COEFFICIENTS

The distribution coefficient, k_d, is defined:

$$k_d = \frac{concentration\ of\ pesticide, solid, ng\ g^{-1}}{concentration\ of\ pesticide, solution, ng\ ml^{-1}} \quad 1$$

This may be normalised with respect to organic carbon, OC, i.e.

$$k_{oc} = k_d * 100\ /\ OC \quad 2$$

where OC is the percentage organic carbon in the solid phase. A similar expression may be written for k_{doc} the distribution coefficient normalised with respect to dissolved organic carbon, DOC.
The distribution coefficient describing the interaction with colloidal material, k_{coll}, may be defined:

$$k_{coll} = \frac{concentration\ of\ pesticide\ with\ colloids, ng\ g^{-1}}{concentration\ of\ dissolved\ pesticide, ng\ ml^{-1}} \quad 3$$

in units of ml g^{-1} or $dm^3\ kg^{-1}$. If C_f and C_s are the concentrations of pesticide in the filtrate and supernatant of the ultra-filtration cell and C_{coll} is the concentration of organic colloid (here expressed as dissolved organic carbon, DOC, in mg dm^{-3}), the distribution coefficient for colloidal material is:

$$k_{coll} = \frac{(C_s - C_f) * 10^6}{C_{coll} * C_f} \quad 4$$

or

$$k_{coll} = \frac{10^6}{C_{coll}} * [(C_s / C_f) - 1] \quad 5$$

Hence if k_{coll} is constant, the ratio of the concentrations in the filtrate and supernatant of the ultra-filtration cell should be constant and independent of the pesticide concentration.

Reference for further details: House, W.A. (1994) The role of sediment-water interaction in the riverine transport of pesticides. In: *Proceedings of the Environmental Sedimentology. The interaction of water, sediment and waste, University of Reading, 7-8 April 1994*, pp. 8.

APPENDIX 3. *Comparison of partition and distribution coefficients for compounds in the chemical groups considered in this work. k_d in $dm^3\ kg^{-1}$; k_{oc} distribution coefficient normalised with respect to organic carbon; k_{om} distribution coefficient normalised with respect to organic matter and K_{ow} octanol-water partition coefficient.*

Pesticide	Constant	Value	Ref
atrazine	log(k_{OC})	2.65	1
atrazine	k_d (soil)	1-10	2
atrazine	k_{om}	125-232	3
atrazine	non equilibrium distribuion coefficient 30-45 min	560	3
atrazine	k_d (3.5 day)	875	3
chlortoluron	log(k_{OC})	3.14	1
fonfos	non equilibrium distribuion coefficient 30-45 min	2300	3
fonfos	k_d (3.5 day)	2720	3
isoproturon	log(k_{OC})	2.61	1
isoproturon	log (K_{ow}) (octanol water partiton)	2.48	4
isoproturon	k_d to soil (1.36 % organic carbon)	1.27	5
linuron	k_d (soil)	31-40	2
linuron	k_{om}	813-5000	2
paraquat	k_d (soil)	2.5-243	2
paraquat	k_{om}	58-16200	2
simazine	log(k_{OC})	2.93	1
simazine	k_d (soil)	0.9-5.6	2
simazine	k_{om}	112-234	2
terbuthylazine	log(k_{OC})	2.92	1
trifluralin	k_d (soil)	51-416	2
trifluralin	k_{om}	1186-24733	2
trifluralin	non equilibrium distribuion coefficient 30-45 min	11570	3
trifluralin	k_d (3.5 day)	4320	3
trifluralin	K_{ow}	15384	6
trifluralin	k_{om}(soil)	6423	6
trifluralin	k_{om}(lake sediment) - paper suggests river sediments more like soils	16581	6

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APPENDIX 4. *Adsorption interactions with colloidal silicates and clays*

INTERACTION OF FLUTRIAFOL WITH THE SURFACE OF SILICA AND LAYER SILICATES

Summary The mechanism of adsorption of flutriafol (CAS #76674-21-0), a large polyfunctional molecule used in fungicide formulation, from aqueous solution on the surface of kaolinite, montmorillonite, and silica gel has been studied combining the use of classical adsorption and kinetic experiments with modern computational methods of chemistry, such as AM1, MNDO-PM3, molecular mechanics, and molecular dynamics. Measurements are reported of the of the adsorption isotherms at 20 °C and diffusion kinetics of flutriafol in consolidated adsorbents. The contribution of different interactions to the total bonding energy has been compared. Hydration effects and hydrogen bonding dominate the adsorption from aqueous solutions; the characteristics of the most important hydrogen bonds and heats of hydration are reported. Possible influences on the adsorption isotherm of the acid-base reactions involving the adsorbate are discussed. The results suggest that flutriafol does not likely penetrate the interlayer spacing of K^+-montmorillonite in the conditions studied, but interacts only with the edge sites with an affinity similar to that measured for K^+-kaolinite.

1.0 INTRODUCTION

The mechanism of sorption of organic molecules by silica and layer silicates is not yet fully understood, mainly because the factors controlling the interactions vary from system to system. It is usually supposed that the bonding of microorganic compounds occurs by one of the following mechanisms:

(i) replacement of exchangable inorganic cations by organic cations;

(ii) hydrogen bonding of the type NH...O, OH...O, CH...O, etc.;

(iii) van der Waals attraction, which can dominate adsorption of large molecules and ions;

(iv) electrostatic interaction;

(v) coordination to interlayer cations.

Comprehensive reviews of the subject are available [1,2].

Most studies of the interaction mechanism utilize infrared spectroscopy [3-6] to probe changes in the adsorbate environment. However, the applicability of this technique is limited to reactions on dry surfaces or use in non-aqueous solution, whereas many effects of practical importance are related to the solid/aqueous solution interface.

The 8th edition of *The Pesticide Manual* [7] lists more than one thousand formulations of commercial pesticides, and considering the number of known minerals, it does not seem practicable to investigate all possible adsorbate/adsorbent combinations. However the underlying physicochemical principles governing adsorption are common to many of these systems and are worthy of investigation.

This study, combining classical adsorption and kinetic experiments and modern chemical computational methods, examines the adsorption of a relatively complex pesticide molecule, (RS)-2,4'-difluoro-α-(1H-1,2,4-triazol-1-ylmethyl)-benzhydryl alcohol, more often known under the trivial name, flutriafol [7], on the surface of kaolinite, montmorillonite and silica gel.

2.0 EXPERIMENTAL

Preparation of Aqueous Solutions of Flutriafol. The desired initial concentration of flutriafol in the solutions used in the kinetics and adsorption experiments was prepared by diluting the 1.0 mg dm^{-3} aqueous stock solution of the pesticide. To prepare the latter, 8 ml of 200 mg dm^{-3} stock solution, which had in turn been prepared by dissolution of a weighted amount of flutriafol (*Analytical Standard, IOIC*) in ethylacetate (*Fisher*), were placed in 1000 ml volumetric flack and ethylacetate was evaporated by the flow of dry nitrogen. The residue was dissolved in 1000 ml of 0.01M aqueous solution of potassium hydrogen carbonate (AR grade, *BDH*) by stirring overnight and the solution filtered through a 0.45 μm cellulose nitrate membrane.

Determination of the Concentration of Flutriafol. To determine the concentration of flutriafol in a solution, the pesticide was extracted on a C_{18} chromatographic column (*Bakerbond SPE, IST*), eluted by ethylacetate, the eluate dried with Na_2SO_4 (granular, AR grade, cured at 160 °C) and analysed with an automated GC/MS instrument (*Hewlett Packard G1034C MS ChemStation*) equipped with a *Hewlett Packard 5890 Series II Gas*

Chromatograph. The sample was introduced via a split/splitless injector to a 5% phenyl methylpolysiloxane capillary column (25 m, 0.2 mm, 0.33 μm film thickness) with He as the carrier gas. The oven program was 15 °C min^{-1} to 170 °C, 5 °C min^{-1} to 240 °C, 2 °C min^{-1} to 270 °C and held at this temperature for 10 min. The analysis was based on detection of peaks of a target ion (*m/z* 123) and a qualifier ion (*m/z* 164), the retention time being 22.3 min. The instrument was recalibrated before each measurement using at least three standard solutions with decachlorobiphenyl internal standard (*m/z* 178 and 240). In order to avoid any errors caused by possible hydrolysis or photolysis of flutriafol, its concentration in the aqueous stock solution was redetermined each time it was used.

Pretreatment of Adsorbents. Kaolinite (*Cornish clay*) and montmorillonite (*Wyoming bentonite*) were first treated with 30% hydrogen peroxide to remove traces of organic substances, then washed several times with distilled water, and transformed to the K^+-form by treatment with 1M solution of potassium chloride as described elsewhere [8]. After final washing, the clay was dried at 120 °C and powdered in a mortar. Silica gel (surface area 300 $m^2 g^{-1}$, pore volume 1.6 $cm^3 g^{-1}$; *Johnson Matthey GmbH*) was used as received.

The specific surface area of kaolinite was 9.5 $m^2 g^{-1}$ by multipoint BET analysis. The total surface area of delamellarized montmorillonite was 462 $m^2 g^{-1}$ by the adsorption of water.

The mineral percentage of the clays determined by X-ray difraction was as follows: kaolinite samples (kaolinite 92.2%, illite/mica 4.3%, and quartz 3.5%); montmorillonite samples (montmorillonite 66.5%, quartz 13.8%, feldspar 17.8%, and sylvite 1.8%).

Adsorption Experiment. Weighed amounts of adsorbent were placed in glass bottles containing known amounts of flutriafol in 0.01M aqueous $KHCO_3$ solution. The initial pH of the solutions was adjusted to pH 7 by bubbling a CO_2/N_2 gas mixture. The bottles were immediately closed and shaken overnight at 20 °C. Separation of sediments from the dispersion was performed either by filtration on a 0.45 μm filter (kaolinite and silica gel) or by centrifugation at 6000 r.p.m. (montmorillonite). The concentration of flutriafol in the initial solution and in the filtrate was determined as described before. The experimental technique and precautions necessary in adsorption measurements are discussed more fully elsewhere [8-10].

Kinetic experiment. Adsorption to a packed bed of adsorbent was measured at room temperature using a pyrex glass apparatus consisting of a 200 ml reservoir of aqueous

flutriafol (initial concentration 0.2 μmol dm^{-3}) mounted on the top of a 4 cm cylindrical pot containing adsorbent. The adsorbent was separated from the overlying solution by a 1 mm metal grid to minimize any disturbance of the adsorbent phase. The change in the concentration of flutriafol was measured over a period of one month by sampling 10 mls at intervals. The apparent porosity of sorbents was estimated using the water pycnometry [11].

3.0 ADSORPTION ISOTHERMS AND ADSORPTION KINETICS

In the concentration range studied, adsorption of flutriafol on all three adsorbents follows the Henry law (Fig. 1). Adsorption equilibrium was established in less than 1 hour when the adsorbent was in suspension, and so, the adsorbent/solution contact area was at a maximum. When the adsorption rate is limited by diffusion, the equilibrium time increases by many orders of magnitude.

Often with natural minerals the specific surface area is difficult to determine or is uncertain because of the changes in particulate structure which occurs during drying. In such situations, the adsorption is conventionally expressed by a distribution coefficient, K_d, defined as the ratio of the weight concentration of adsorbate on the surface to its equilibrium concentration in the solution, so that $K_d = \Gamma S_{sp} \cdot 10^6$ $dm^3\,g^{-1}$, where S_{sp} is the specific surface area. So determined, K_d's for kaolinite, montmorillonite and silica gel are 0.8, 64.7 and 8.7 $dm^3\,kg^{-1}$, respectively, and well in the range found for natural sediments.

When flutriafol is adsorbed by a sufficiently thick undisturbed layer of adsorbent, the adsorption kinetics are described by a one-dimensional semi-infinite diffusion model with adsorbate binding [12]. The latter can be thought of as a modification of the classical model due to Ward and Tordai [13]. In summary: let the adsorption equilibrium become settled at each point of the adsorbent phase for a so short time that the overall concentration profile remains almost unaltered. The adsorption, $a(x,t)$, which here is measured in moles per unit volume of the adsorbent phase, in the point x at the time t is then related to the concentration, $c(x,t)$, of adsorbate in the neighbourhood of this point by a local isotherm equation, the simplest of which is due to Henry,

$$a(x,t) = \iota S_{sp} \Gamma c(x,t) \qquad (1)$$

where ι is the pycnometric density, and Γ is the Henry constant.

Except for the case of strong localized adsorption, both the dissolved and adsorbed molecules can be involved in the diffusion motion. Let D_s and D_a be the corresponding diffusion coefficients. The governing equations are

$$\lambda \frac{\partial c}{\partial t} = D_s \frac{\partial^2 c}{\partial x^2}; \quad (1-\lambda)\frac{\partial a}{\partial t} = D_a \frac{\partial^2 a}{\partial x^2} \tag{2}$$

where λ is the porosity. After substitution of eqn.(1) for a and adding the above two equations, one gets

$$\frac{\partial c}{\partial t} = \delta^2 \frac{\partial^2 c}{\partial x^2}; \quad \delta^2 = \frac{D'}{\lambda + \Gamma'(1-\lambda)}; \quad \Gamma' = tS_{sp}\Gamma; \quad D' = D_s + \Gamma' D_a \tag{3}$$

where D' is termed the effective diffusion coefficient.

Finally, imposition of the boundary conditions,

$$c(0,t) = c(t); \quad c(x,0) = 0, \tag{4}$$

$c(t)$ being the concentration of the adsorbate in the outer solution, and the mass balance requirement,

$$\{\lambda + \Gamma'(1-\lambda)\}\int_0^\infty c(x,t)\mathrm{d}x = L\{c(0) - c(t)\}, \tag{5}$$

where L is the effective depth of the overlying solution, and the upper bound of integration has been extended to infinity in view of the assumtion that $x >> (D't)^{1/2}$, leads to

$$c(t) = c(0)\exp(\pi A^2 t)\mathrm{erfc}(A\sqrt{\pi t}); \quad A^2 = \frac{D'(\lambda + \Gamma'(1-\lambda))}{\pi L^2} \tag{6}$$

As $t \to 0$, this reduces to

$$c(t) \cong c(0)\left[1 - 2At^{1/2}\right] \tag{7}$$

Proportionality of the concentration to the square root of time is a characteristic of diffusion-controlled processes [13-15]. Eqs.(6) and (7) were obtained in an earlier work [12], but the coefficient A was unfortunately determined incorrectly.

The corresponding kinetic curves for flutriafol adsorption on the sorbents under study are represented in Fig. 2. It should be noted that the diffusion coefficient of flutriafol proves to be of the same order of magnitude as the coefficients of self-diffusion of alkylammonium ions in wet montmorillonite [16].

4.0 THE MECHANISM OF BONDING

4.1 Chemical Interactions

4.1.1 Description of Molecular Models.

The surface of colloidal particles of montmorillonite and kaolinite was simulated using clusters composed of one to three disc-shaped fragments having the formulas $Si_{102}O_{318}Al_{57}H_{83}$ (M = 9574.1) and $Si_{54}O_{235}Al_{57}H_{109}$ (M = 6924.3), respectively, and radius of approximately 14 A. An example of such a model is shown in Fig. 3. Taking into account the globular structure of silica gel [17], its surface was simulated by a spherical cluster $Si_{51}O_{131}H_{58}$ (M = 3586.7) having radius of approximately 8.5 A and lattice of β-crystoballite. All the clusters were constructed on the basis of the crystallographic data [18] and optimised using the extended MM2 force field [19]. To avoid the undesirable distortion of the kaolinite and montmorillonite clusters during optimisation, all the octahedral positions were filled with Al atoms. The resulting trioctahedral structures inevitably possess an excess positive charge, whereas the naturally occurring dioctahedral structures are known to be negatively charged [20,21]. To overcome this difficulty, all the Al atoms were assigned an effective charge lower than the charge of Al^{3+} ions. This can be imagined as uniform isomorphous substitution of a part of the Al^{3+} by Mg^{2+} ions as occurs in nature.

For semiempirical calculations, clusters of smaller size, containing the functionality of interest, were isolated from the large clusters and the broken bonds saturated with pseudoatoms [22].

Information concerning the hydration energy, sorption capacity, and other similar characteristics of the surface may be obtained by counting the different functional groups at the cluster surface and assessment of the cluster size. Thus, on the basis of the described models, the density of siloxane bridges, SiOSi, at the basal plane of layer silicates is estimated to be 15.5 nm^{-2}, whereas the density of the bridge hydroxyl groups coordinated to Al ions is only 3.2 nm^{-2}. The density of surface silanols, SiOH, at the edge surface is found to be 3.8 nm^{-2}. It is also evident that the ratio of the amount of groups situated at the basal plane to the amount situated at the edge is proportional to the radius of the cluster.

The density of surface silanols at the completely hydroxylated surface of silica is estimated as 6.4 nm^{-2}, almost six times the value commonly accepted for the density of

isolated silanols at the surface of *dry* silica gel [23-25]. A possible explanation is that the geminal silanol groups representing the majority at the surface of the model cluster, are unstable and easily eliminate water while drying.

4.1.2 Theoretical Assessment of the Hydration Energy of the Surface

To calculate the hydration energy of a mineral surface, it is necessary to estimate (i) the energy of association of water molecules with different polar groups resident at the surface and (ii) the density of these groups. The latter has just been done in the previous section. The energy of association, in this context termed usually as hydrogen bonding, in the structures shown in Fig. 4-a has been calculated using the semiempirical methods AM1 [26-29] and MNDO-PM3 [30]. Fig. 4-b shows the cluster $Si_{12}O_{34}Al_4H_{14}$ used in the calculation. The use of pseudoatoms was made whenever it seemed to be justified. The choice of the structures to be considered is not unique and has been made on the basis of chemical intuition. The possibility of the direct coordination of water molecules to silicon atoms was examined elsewhere [24] and is not discussed here. The characteristics of the calculated H-bonds are summarised in Table 1.

It is rather unexpected that the most acidic bridged hydroxyl groups fail to bond water. A possible explanation is as follows: In order for a water molecule to satisfy the geometrical criteria enabling hydrogen bonding, it has to be orientated over the SiOSi plane, leading to strong repulsion between the non-bonding electron pairs of the oxygen atoms (Fig. 4-c). This causes the water molecule to realign, so that it forms a hydrogen bond of the type 2 instead.

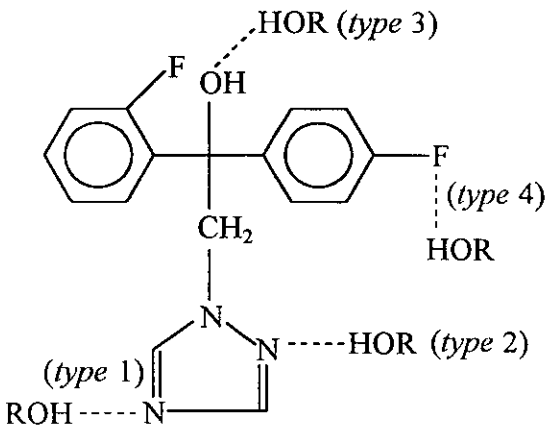
Both hydrogen bonding and orientation of water molecules in the potential field of the surface contribute to the hydration energy. However, once the use of the above-mentioned parametrical methods is made, there is little point in trying to assess the role of the orientation effect separately (although it is possible on the basis of existing macroscopic theories [31]), since these methods have been parametrized to describe, with the best possible precision, a large number of molecular properties including intermolecular interactions. However, if these methods predict attraction between two molecules, it is not always possible to say definitely whether this is a hydrogen bond or just the dispersion interaction. This is why some additional geometrical criteria concerning the bond length and angle are used [32,33]. Nevertheless, without exact stipulation of the meaning of "hydrogen bond", the hydration energy of a

surface can be estimated by summing the calculated heats of formation of the hydrogen bonds between water and polar groups situated at that surface. This yields 0.088 - 0.098 cal m^{-2} of the basal plane, and 0.015 - 0.041 cal m^{-2} of the edge surface.

An independent estimate of the hydration energy has been gained from a molecular dynamic simulation of a periodic box with a cluster of interest surrounded by up to 500 water molecules (MM2 force field, HyperChem software). This gives approximately 0.015 kcal m^{-2} for $T = 298$ K, and, as expected taking into view the underlying approximations of the method, the result is almost independent of the chemical speciation of the surface. Multiplying this result by the surface area of the clusters and dividing by their molecular mass yields an estimate of 26 - 38 cal g^{-1} of dry substance. The available literature data on heats of immersion vary in the range 16 - 35 cal g^{-1} [34-36], and are in essential agreement with the theoretical predictions.

4.1.3 Theoretical Assessment of the Hydration Energy of Flutriafol

Following the above considerations, the energies of the most realistic hydrogen bonds arising between water and the polar functional groups of flutriafol have been calculated. The results are summarised in Table 2. The following sketch explains the bond notation used in this paper.



R = H; $Si(OH)_3$; $Si_{10}O_{27}H_{15}$; $Si_{12}O_{33}Al_4H_{13}$

There also exists the probability of weak hydrogen bonds ($-\Delta H_f \cong 1.0$ kcal mol^{-1}) with the methylene group. The characteristics of the hydrogen bonds with the fluorine atoms in *ortho* and *para* positions are nearly identical. The total hydration energy of flutriafol is thus

estimated to be 22.6 kcal mol^{-1} by AM1 and 13.8 kcal mol^{-1} by MNDO-PM3. Molecular dynamics simulation (MM2 force field) of a periodic box containing 244 water molecules surrounding a flutriafol molecule yields 21.6 kcal mol^{-1} at 298 °K.

It is commonly assumed that the protonated or cationic form of most pesticide molecules should be considered as weakly hydrated. This belief most likely stems from a misinterpretation of the fact that the hydration of cations weakens with their increasing size, as occurs, for example, in the series $Li^+ > K^+ > NMe_4^+ > NBu_4^+$. Most pesticide molecules, including flutriafol, are polyfunctional, and deactivation of a given functional group by protonation does not preclude hydration of the whole molecule if there are other functional groups capable of bonding with water.

4.1.4 Interaction of Flutriafol with the Surface

Flutriafol can form stable hydrogen bonds with the surface of montmorillonite, kaolinite, and silica. With the silica gel surface and the edge surface of kaolinite and montmorillonite, hydrogen bonding is primarily effected through the free silanol groups [37-40]. The characteristics of the most probable bonds of this type are given in Table 3. The bond notation is the same as before. For comparison, heats of adsorption of alcohol on silica glasses fall into the range of 5.7 to 10.0 kcal mol^{-1} [41].

The only stable hydrogen bond with the basal plane is through the alcohol hydroxyl group of flutriafol to a bridge siloxane oxygen. Its characteristics are as follows: (AM1) $-\Delta H_f$ = 2.9 kcal mol^{-1}, d(H...O) = 2.73 A, ∠(O-H...O) = 169.0°; (MNDO-PM3) $-\Delta H_f$ = 0.2 kcal mol^{-1}, d(H...O) = 1.87 A, ∠(O-H...O) = 168.0°. The relatively low energy of this bond conforms to the fact that the siloxane oxygen is a weak donor of electrons [24,38].

Hydrogen bonding through the bridge hydroxyl groups situated at the apices of AlO_6 octahedra is sterically hindered by a crown of six SiO_4 tetrahedra making these groups inaccessible to large molecules. If this crown is removed by displacement of the SiO_4 tetrahedra by hydrogen atoms, this type of hydrogen bonding is enabled. Such displacement may occur in the vicinity of the lattice edge due to preferential dissolution. Because of participation of the π-electron aromatic system of the triazole group in the bonding, the formed adduct may be expected to have some properties of a π-complex. However, because

of high acidity of the bridge hydroxyl groups [42], complete transfer of proton to flutriafol seems more probable.

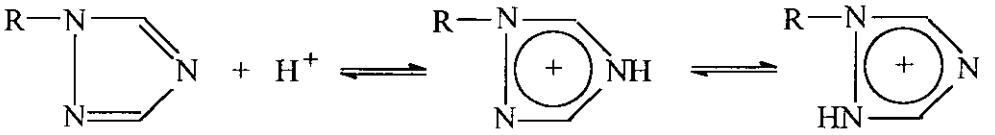
In the case of montmorillonite, an expandable clay, there is also the possibility for fixation of flutriafol by coordination to the interlayer exchangable cations [43-45], as, for example, shown in Fig. 3. Such coordination can be through any electron-donating groups, such as triazole, hydroxyl, and to a smaller extent, fluorine and aromatic rings. Bonding through the triazole group is the strongest, with the bond energy for univalent cations calculated by AM1 and MNDO-PM3 as 9.8 - 9.9 kcal mol^{-1}, rising to 27.4 - 29.1 kcal mol^{-1} for divalent cations. When coordinated to certain transition metal ions, the bonding is expected to be even stronger because of the presence of *d*-orbitals. However, as shown by comparison of the adsorption to montmorillonite and kaolinite, no appreciable adsorption to the interlayer of montmorillonite occurs. One reason for this behaviour is as follows. In the case of small and therefore strongly hydrated cations, such as Li^+ and Mg^{2+}, where the interlayer spacing is large enough to allow accommodation of a flutriafol molecule, water is a better candidate for a place in the coordination sphere and displaces flutriafol. Coordination of water also reduces the polarising power the ions. In contract, for large cations, such as K^+ and Ba^{2+}, with weaker hydration, there is nothing to prevent flutriafol from the coordinating, however the interlayer spacing is reduced leaving insufficient room for a bulky flutriafol molecule to penetrate. This means that flutriafol is mainly adsorbed at the edge surface and explains why the observed adsorption of flutriafol on K^+-montmorillonite is similar to K^+-kaolinite. Another reason for the discrepancy is that the penetration of a flutriafol molecule to the interlayer space inevitably results in displacement of several water molecules from the relatively highly ordered hydration shell of the surface, thereby increasing the free energy of the system.

It is of interest to examine, at least at a qualitative level, how the probability of entrance of flutriafol to the interlayer space depends onto the interlayer separation. A system similar to that shown in Fig. 3 has been modelled. A flutriafol molecule was placed in the plane lying between the two halves of a two-disc montmorillonite cluster parallel to their basal surface at a distance of approximately 20 A from the edge. Then it was given an initial impetus to cause its movement toward the cluster. Its further trajectory was calculated according to the principles of molecular dynamics (HyperChem Software). The cluster was fixed, thus no dissipation of energy was allowed. Fig. 5 represents the result of molecular dynamic simulation

of this process. It has been found that the activation energy increases rapidly as the interlayer separation becomes less than 12.6 A. On the contrary, if it is greater than approximately 16 A, the process can carry out without activation.

4.1.5 Protolytic Transformations and Adsorption

Bearing a base triazole functionality, flutriafol is involved in the acid-base reaction



(I) (II)

with the conjugated acid existing in two tautomeric forms. The results of AM1 and MNDO-PM3 calculation show that the cation I should be more stable than the cation II; the corresponding difference in the energy of formation is 7.9 - 12.7 kcal mol^{-1} in favour of the first ion. The polarizability of flutriafol (22.0 - 23.3 A^3) is almost unaffected by protonation, whereas the dipole moment increases from 3.7 Debye for the deprotonated molecule to 9.7 - 13.3 Debye for the cation I, and to 8.3 - 8.9 Debye for the cation II. Both cations can form stable hydrogen bonds with water and surface silanols, and owing to their high dipole momenta and polarizabilities, undergo strong electrostatic attraction to the surface.

The relative affinity of the neutral and cationic forms of the adsorbate can affect the adsorption isotherm [46-48]. The adsorption of flutriafol is governed by the following system of stoichiometric equations,

$$\begin{aligned} Fl + H^+ &\xleftrightarrow{K_p} FlH^+ \\ S + Fl &\xleftrightarrow{K_1} SFl \\ S + FlH^+ &\xleftrightarrow{K_2} SFlH^+ \end{aligned} \qquad (8)$$

each reaction being characterised by its equilibrium constant. Here Fl and FlH^+ designate the deprotonated and the protonated form of flutriafol, respectively, and S an adsorption site. The above equations describe what is generally called localised adsorption. However, without exact stipulation of the term "adsorption site", they remain valid for non-localised adsorption too. Under the conditions which Henry's law applies, i.e. [S] >> [SFl] + [$SFlH^+$], the amount of free adsorption sites is unaltered during adsorption. The system (8) can then be closed by adding a single mass balance equation,

$$V[\mathrm{Fl}]\left(1 + K_p[\mathrm{H}^+]\right) + mS_{sp}c_s[\mathrm{Fl}]\left(K_1 + K_2K_p[\mathrm{H}^+]\right) = c_{\mathrm{Fl}}^0 V \qquad (9)$$

where V is the volume of the solution, m and S_{sp} are the weight and the specific surface area of the adsorbent, c_s is the density of the adsorption sites (mol m^{-2}), and c_{Fl}^0 is the initial concentration of flutriafol in the solution. Now, the amount of flutriafol adsorbed per unit surface is given by

$$n_{\mathrm{Fl}}^{\mathrm{ads}} = \frac{c_s c_{\mathrm{Fl}}^0 V\left(K_1 + K_2K_p[\mathrm{H}^+]\right)}{V\left(1 + K_p[\mathrm{H}^+]\right) + mS_{sp}c_s\left(K_1 + K_2K_p[\mathrm{H}^+]\right)} \qquad (10)$$

If only the cationic form of flutriafol is capable of adsorption, eqn.(10) can be simplified by putting $K_1 = 0$. The adsorption then becomes independent of pH when $K_p[H^+] >> 1$. If only the neutral form is capable of adsorption, the adsorption becomes independent of pH when $K_p[H^+] << 1$. Finally, if the protonated and deprotonated forms have similar adsorption affinities, i.e. $K_1 \cong K_2 \cong K$, the adsorption is always independent of pH,

$$n_{\mathrm{Fl}}^{\mathrm{ads}} = \frac{c_s c_{\mathrm{Fl}}^0 VK}{V + mS_{sp}c_s K} = \Gamma c_{\mathrm{Fl}}^0 \qquad (11)$$

where Γ is the Henry's law constant.

The protonation constant, K_p, of the triazole group of flutriafol is not likely to differ much from that of imidazole (pK = 6.95). Therefore, the protonated and deprotonated forms coexist at similar concentrations at pH close to 7. Nevertheless, the adsorbed state flutriafol is expected to be entirely protonated, irrespectively of which form predominates in the solution. This hypothesis is based on the fact that the surface of silica and clays possess a negative charge in the pH range of interest [12]. Let $-\psi_s$ be its electrostatic potential, which attains a value of 80 - 100 mV at pH $\cong$ 7. Then, in accordance with the generalised mass action law [11], the effective protonation constant of adsorbed molecules increases by a factor of $\exp(e\psi_s / kT)$ relative to the protonation constant, K_p, characteristic of molecules in the bulk solution. Hence, with high acidity of surface silanols and bridge hydroxyl groups, protonation of adsorbed flutriafol is highly probable.

The possibility of protonation of a given compound depends upon its pK, and also upon pH of the surrounding solution. Thus, many amines and amides are known to be protonated when adsorbed onto clays [49-51], whereas atrazine not [52]. However, the

possibility of protonation of some very basic amines, such as propylamine and ethylendiamine, has been questioned by the authors of paper [53].

4.2 Physical Interactions

A study of the physical interactions of flutriafol to a mineral surface has been performed on the basis of a computer simulation of interactions between a flutriafol molecule and a montmorillonite cluster composed of two disc-shaped fragments $Si_{102}O_{318}Al_{57}H_{83}$ with the interlayer spacing of 12.6 A. A similar system is shown in Fig. 3. The potential energy function used was as follows

$$U = \sum_i \sum_j \varsigma\left[(\kappa / R_{ij})^{12} - 2(\kappa / R_{ij})^6\right] - \mathbf{p}\cdot\mathbf{E} - \frac{1}{2}(\alpha\mathbf{E})\cdot\mathbf{E} \qquad (12)$$

where the first term represents the well-known Lennard-Jones 6-12 potential to allow for the van der Waals interactions between atoms. The last two terms describe, in a highly approximative manner, the long-range electrostatic interactions, such as the interaction of the permanent dipole, $\mathbf{p}$, and the induced dipole, $\alpha\mathbf{E}$, of the adsorbate molecule, which is considered as a rigid anisotropic spheroid with a polarizability tensor α, with the electric field, $\mathbf{E}$, produced by the cluster. An important role of the electrostatic interaction in adsorption on polar surfaces has also been emphasised in papers [54,55]. In eqn.(12), R_{ij} is the distance between the i th atom of the cluster and the j th atom of the molecule, and ζ and κ are, correspondingly, the intensity and the width parameters characterising the shape of the atom-atom potential [56]. For the sake of simplicity, the latter have been taken the same for all atoms. A constant term corresponding to the interactions within the groups of atoms belonging separately to the cluster and the flutriafol molecule has been omitted since it does not affect the further results.

It is convenient to use the principal axes of inertia of the cluster and of the adsorbate molecule as the axes of the local coordinate systems bound to the cluster and to the molecule, respectively. Then

$$\mathbf{E}(\mathbf{R}) = \sum \frac{\rho_i e(\mathbf{R} - \mathbf{r}_i)}{\varepsilon|\mathbf{R} - \mathbf{r}_i|^3}; \quad R_{ij} = |\mathbf{R} - \mathbf{r}_i + \mathbf{r}_j'| \qquad (13)$$

where ρ_i is the charge number of the i th ion of the cluster, ε is the dielectric constant of the medium, $\mathbf{r}_i$ is the position of the i th ion of the cluster and $\mathbf{r}_j'$ is the position of the j th ion of the molecule in their local coordinate systems, and $\mathbf{R}$ joins the origin of the first coordinate system to the origin of the second. It is not yet clear how to determine the distance between the cluster and the molecule, unless they are point-wise. If it is intended to analyse the interaction with the basal plane and the edge surface only, it is convenient to direct the z-axis of the first coordinate system towards the adsorbate molecule and to place the latter so that its centre of gravity is on this axis. Then the separation, s, between the basal plane and the molecule can be determined as

$$s = |\mathbf{R}| - \max_i\left(\frac{\mathbf{r}_i \cdot \mathbf{R}}{|\mathbf{R}|}\right) - \min_j\left(\frac{\mathbf{r}_j' \cdot \mathbf{R}}{|\mathbf{R}|}\right), \quad \mathbf{E}(s) \cong \frac{(\mathbf{E}\cdot\mathbf{R})}{\mathbf{R}^2}\mathbf{R}, \quad \text{and} \quad |\mathbf{R}| \cong z \qquad (14)$$

In view of the made assumptions, U is also dependent on the three Euler angles, η, θ, and ϕ, necessary to define the orientation of the adsorbate molecule with respect to the cluster. Hence, U must be averaged over these angles with the Boltzmann weighting factor to allow for the contribution of different orientations [56],

$$\overline{U} = N\int U \exp(-U / kT)\mathrm{d}\eta\mathrm{d}\theta\mathrm{d}\phi \qquad (15)$$

N being the normalising factor.

The integration in eqn.(15) was performed numerically, leading to the results shown in Fig. 6. The parameters used in the computations are given in Table 4. The dipole moment and polarizability of the ground state of a flutriafol molecule have been calculated using the AM1 method [25,27]. The effective charges on the atoms of Si, O, and H have been taken the same as those calculated for the cluster $Si_{10}O_{28}H_{16}$ [57]. The effective charge of the Al atoms has been assigned to ensure electroneutrality of the whole cluster. The dielectric constant, ε, has arbitrarily been assigned a value of 10, to account for a reduction in the dielectric constant of water close to the surface.

As can be seen in Fig. 6, the interaction of flutriafol with the flat basal surface is much stronger that with the rough edge surface. Conversely, in the preceding discussion it has been emphasised that specific interactions, such as hydrogen bonding, may change the entire energy balance. In the absence of the latter, the Henry constant is determined by the relation [58]

$$\Gamma = \int_0^{\infty} \left[\exp(-\overline{U} / kT) - 1 \right] ds \qquad (16)$$

and hence should be equal to $2.6 \cdot 10^{12}$ m for the basal plane, and only $3.9 \cdot 10^{-5}$ m, that is seventeen orders of magnitude less, for the edge. The latter value depends considerably upon the cluster size and the interlayer spacing, and can be much higher for a concave surface. Consequently, if physical interactions dominated adsorption, a very strong dependence of the Henry constant on the dispersity of adsorbent would be expected. Although such a dependence does take place, it is minimal, suggesting that the role of the physical interactions is relatively small, at least for the adsorption from aqueous solutions, in comparison with the role of the chemical interactions discussed before.

The experimentally determined value of the Henry constant can be related to the quantities introduced in the previous sections in the following way. Writing

$$\Gamma = \gamma \exp(-\Delta H / kT) \qquad (17)$$

where γ depends only on the entropy change during adsorption. The total heat of adsorption, ΔH, is in a very crude approximation given by

$$\Delta H = \Delta H^{a}_{bond} + \overline{U}^{a} - n(\Delta H^{s}_{bond} + \overline{U}^{s}) \qquad (18)$$

where the superscripts a and s refer to the adsorbate and solvent, respectively, and n is the mean number of solvent molecules replaced by one adsorbate molecule during adsorption. Each molecule is assumed to be bonded with the surface, the heat of bonding being ΔH_{bond}, and is subject to the action of the potential field of the surface. An additional term must be added to eqn. (18) if the adsorbate is known to lose a part of its hydration shell while being adsorbed.

The number of the solvent molecules being replaced during adsorption can be estimated as the ratio of molecular volumes of adsorbate and solvent; for the flutriafol/water pair $n \cong 22$. In a hypothetical case of the absence of solvent (a gas-phase process) $n = 0$, so the Henry constant can be expected to be very high. To some extent, this should hold for adsorption from non-polar solvents, in which case ΔH^{s}_{bond} and $\overline{U}^{s}$ are relatively small. On the contrary, for the adsorption from aqueous solutions, the bonding energy of water, ΔH^{s}_{bond}, is close to that of flutriafol, ΔH^{a}_{bond}, leading to the low values of the Henry constant observed.

5.0 CONCLUSIONS

The adsorption of flutriafol from aqueous solution at 20 °C on kaolinite, montmorillonite and silica gel follows the Henry law for equilibrium concentrations of the order of 1 μmol dm^{-3} with the adsorption affinity changing in the sequence: kaolinite ≈ montmorillonite > silica gel. The similar affinities of flutriafol to montmorillonite (expandable clay) and kaolinite (non-expandable clay) suggest that flutriafol does not enter the interlayer space of the expandable clay but bonds to the edge sites.

Estimates of the physical interaction energy indicate that the degree of dispersity of clay should have a very strong effect on the adsorption. However, this is not observed experimentally, suggesting physical interactions are not dominant for the systems in question. Molecular calculations indicate a weak interaction dominated by the hydration and hydrogen bonding effects. It is also possible that the triazole base interacts with the acidic bridged hydroxyl groups by the acid-base mechanism.

The results of adsorption and kinetic measurements have been applied to estimate the effective diffusion coefficients of flutriafol in consolidate adsorbents using the model of semi-infinite diffusion with adsorbate binding. The obtained diffusion coefficients are of magnitude typical of molecular diffusion in gels.

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Table 1. Characteristics of the Hydrogen Bonds between Water and Polar Groups at the Surface of Silica and Layer Silicates

Bond Type	1	2	3
$-\Delta H_f$, kcal mol^{-1}	unstable	3.4/3.8[a]	6.4/2.3
d(X...H), A	-	2.57/1.84	2.20/1.84
∠(X...H-O), deg	-	141.9/162.6	144.3/167.0

[a] The first result is obtained by AM1 method, and the second by MNDO-PM3.

Table 2. Characteristics of the Hydrogen Bonds between Water and Polar Groups of Flutriafol

Bond Type	1	2	3	4
$-\Delta H_f$, kcal mol^{-1}	2.7/2.5[a]	3.8[b]/1.3	8.5/4.1	3.3/2.7
d(X...H), A	2.72/1.84	3.08[b]/1.87	2.13/1.82	2.33/1.78
∠(X...H-O), deg	112.0/177.4	87.2[b]/172.1	144.6/167.2	101.6/165.2

[a] The first result is obtained by AM1 method, and the second by MNDO-PM3.

(b) In this case, the position of water molecule is geometrically more appropriate for hydrogen bonding through the oxygen atom of the adjacent hydroxyl group of flutriafol (d(O...H) = 2.19 A, ∠(O...H-O) = 106.8°) than for bonding through the 2-nitrogen atom of the triazole group.

Table 3. Characteristics of the Hydrogen Bonds between Surface Silanols and Polar Groups of Flutriafol

Bond Type	1	2	3	4
$-\Delta H_f$, kcal mol^{-1}	3.2/0.9[(a)]	3.9/2.5	3.7/2.4	4.9/1.0
d(X...H), A	2.59/1.85	2.68/1.87	2.19/1.85	2.30/1.79
∠(X...H-O), deg	151.7/177.3	110.0/160.1	110.6/134.9	141.1/165.8

(a) The first result is obtained by AM1 method, and the second by MNDO-PM3.

Table 4. Parameters Used in Calculation of the Potential Energy Curves in Fig. 6.

Charge on the atoms, a.u.	Si	+1.85
	O	- 0.99
	Al	+1.95
	H	+0.24
Polarizability tensor, A^3	α_{xx}	16.2
	α_{yy}	24.1
	α_{zz}	29.8
Dipole moment, Debye	p	3.68
Intensity parameter, kcal mol^{-1}	ζ	0.05
Width parameter, A	κ	3.80

FIGURE CAPTIONS

Fig. 1. Isotherms of adsorption of flutriafol. The corresponding Henry constants, Γ, are as follows: $8.6 \cdot 10^{-8}$ m (kaolinite), $1.4 \cdot 10^{-7}$ m (montmorillonite), and $2.9 \cdot 10^{-8}$ m (silica gel).

Fig. 2. Diffusion-controlled kinetics of adsorption of flutriafol. The effective diffusion coefficients are as follows: $6.5 \cdot 10^{-11}$ m^2 s^{-1} (kaolinite, $\lambda = 0.75$), $3.2 \cdot 10^{-12}$ m^2 s^{-1} (montmorillonite, $\lambda = 0.86$), and $5.5 \cdot 10^{-12}$ $m^2 s^{-1}$ (silica gel, $\lambda = 0.81$).

Fig. 3. Molecular mechanic model of the flutriafol-montmorillonite intercalate with the interlayer spacing of 17 A. Here, flutriafol is coordinated (dotted line) to a hydrated exchangable cation of magnesium.

Fig. 4. (a) Possible types of hydrogen bonds responsible for hydration of the surface; (b) the montmorillonite cluster used for simulation of the surface in semiempirical calculations; (c) to the explanation of instability of the type 1 hydrogen bonds.

Fig. 5. Molecular dynamics simulation of entrance of a flutriafol molecule to the interlayer space of the montmorillonite cluster. The interlayer spacing is (°) 15 A; (•) 17 A. In each case, approximately 6000 points have been generated.

Fig. 6. Physical interaction of flutriafol with the basal plane and the edge of the montmorillonite cluster (interlayer spacing 15 A): (———) and (- - - -) the van der Waals interaction, and (- · - · -) and (· · · · · ·) the electrostatic interaction.

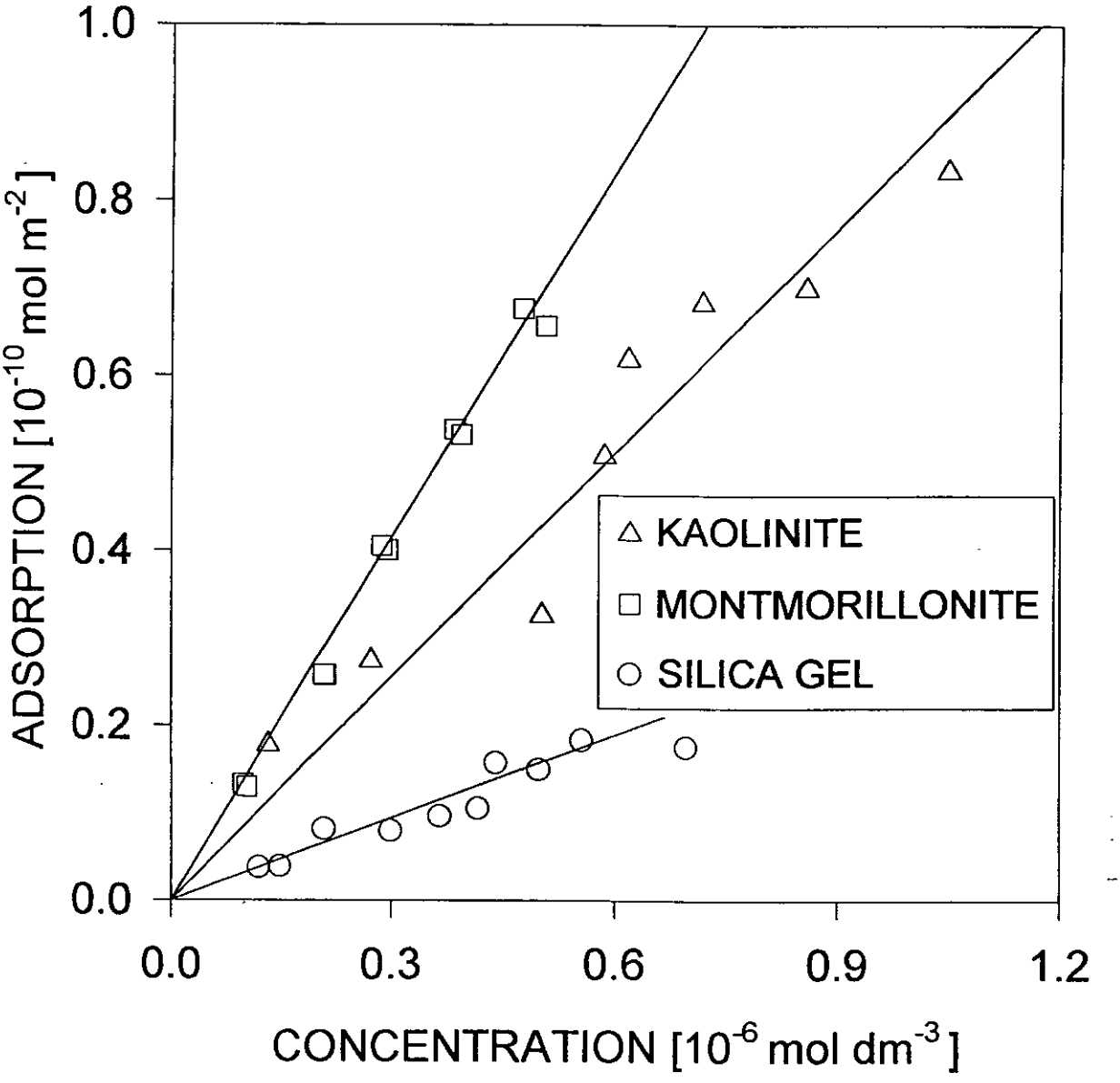
1.0
0.8
0.6
0.4
0.2
0.0
ADSORPTION [10-10 mol m-2]
0.0
0.3
0.6
0.9
1.2
CONCENTRATION [10-6 mol dm-3]
KAOLINITE
MONTMORILLONITE
SILICA GEL

Fig. 1

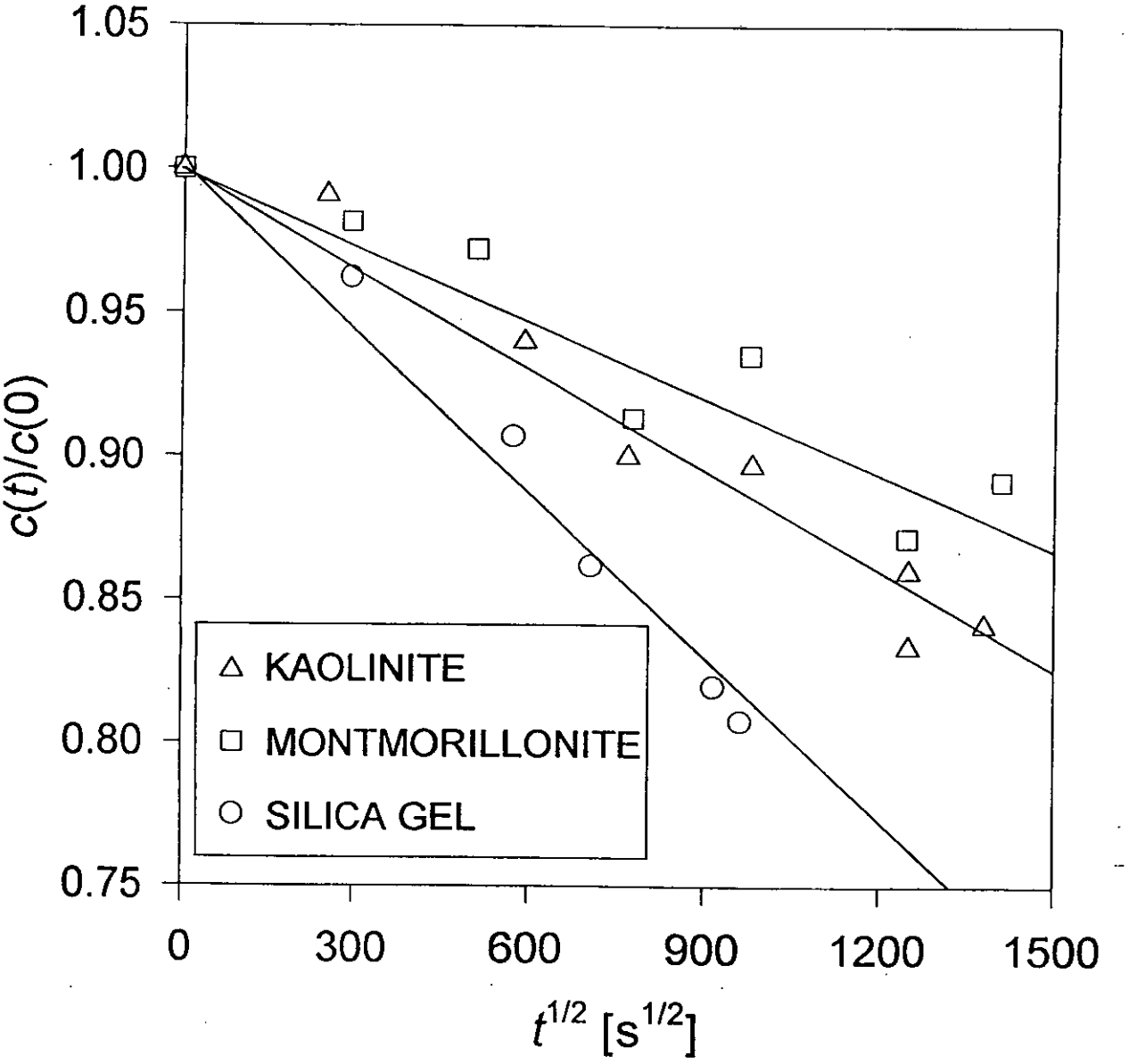
1.05
1.00
0.95
0.90
0.85
0.80
0.75
c(t)/c(0)
KAOLINITE
MONTMORILLONITE
SILICA GEL
0
300
600
900
1200
1500
t^1/2 [s^1/2]

Fig. 2

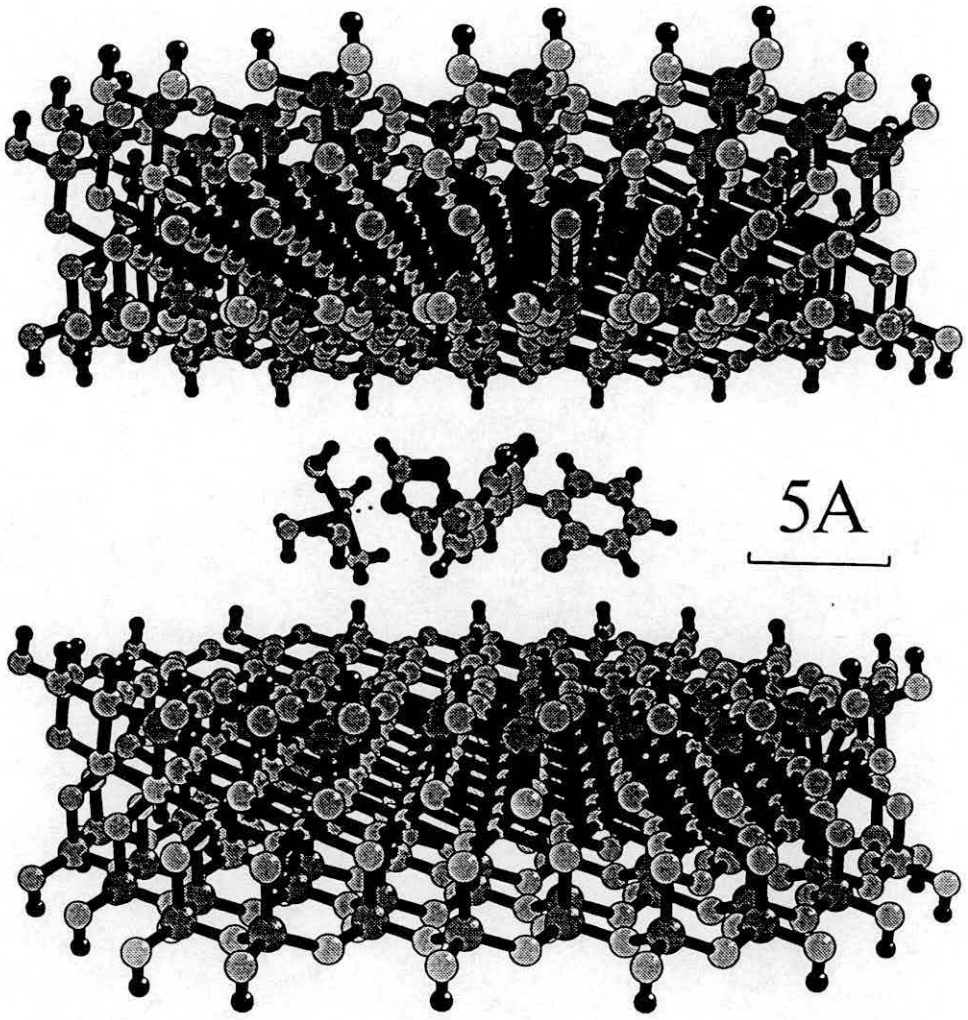

Fig. 3

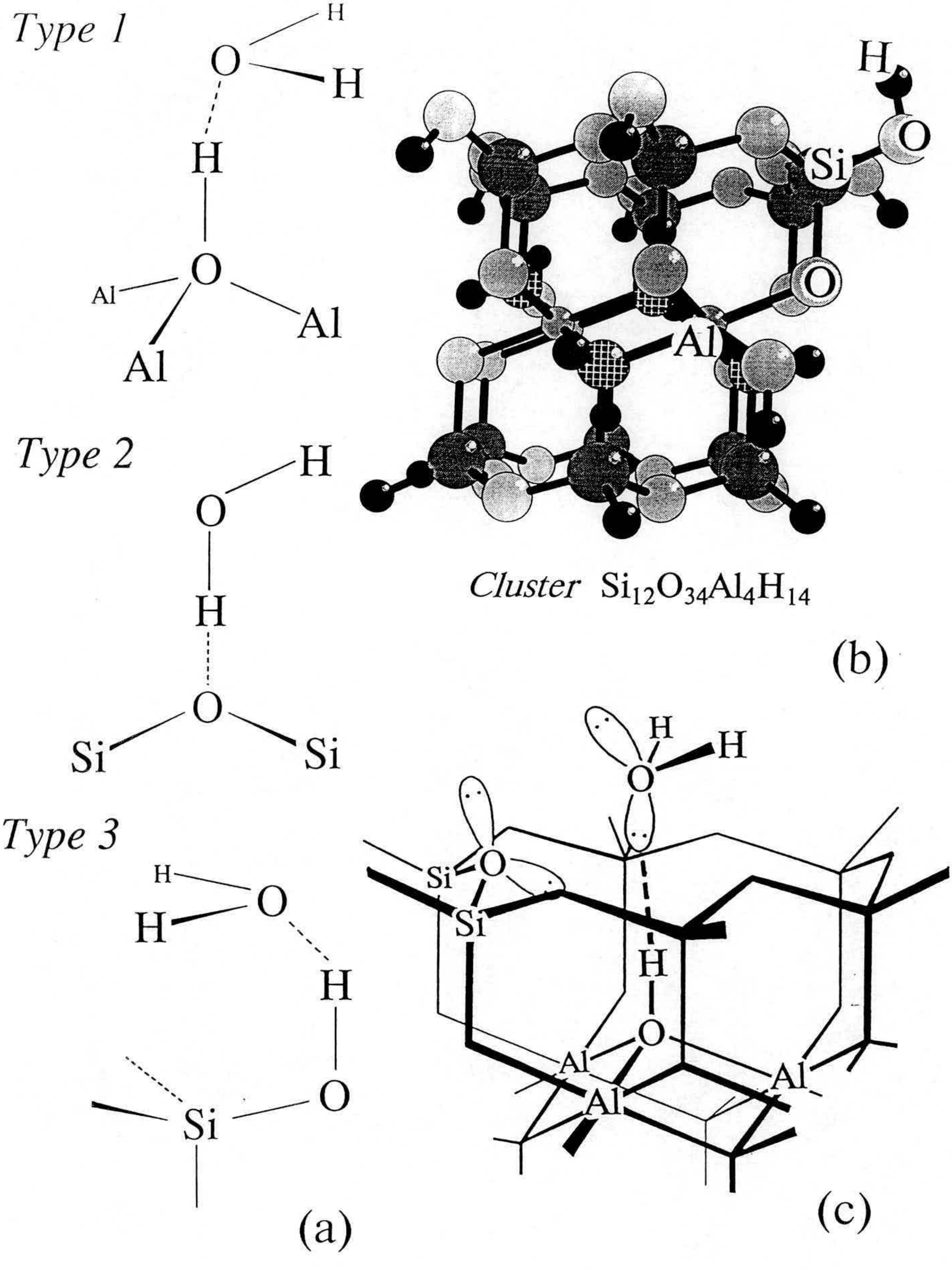
Type 1
H
O
H
H
O
Al
Al
Al
Type 2
H
O
H
O
Si
Si
Type 3
H
O
H
H
O
Si
(a)
H
O
Si
O
O
Al
Cluster Si12O34Al4H14
(b)
H
H
O
Si
O
Si
H
O
Al
Al
Al
(c)

Fig. 4

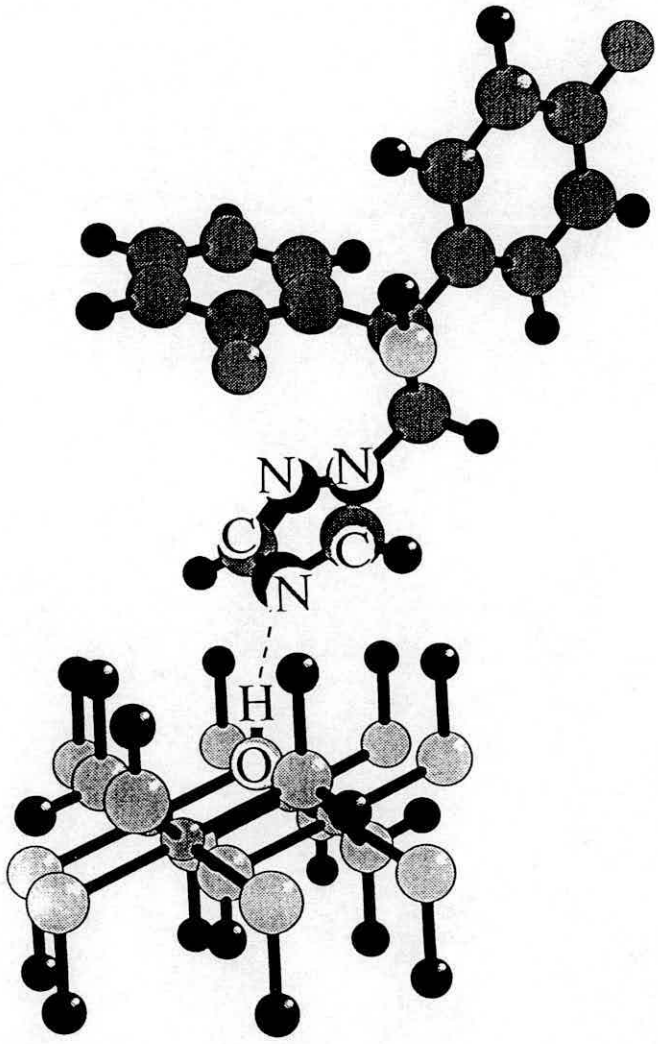

Fig. 5

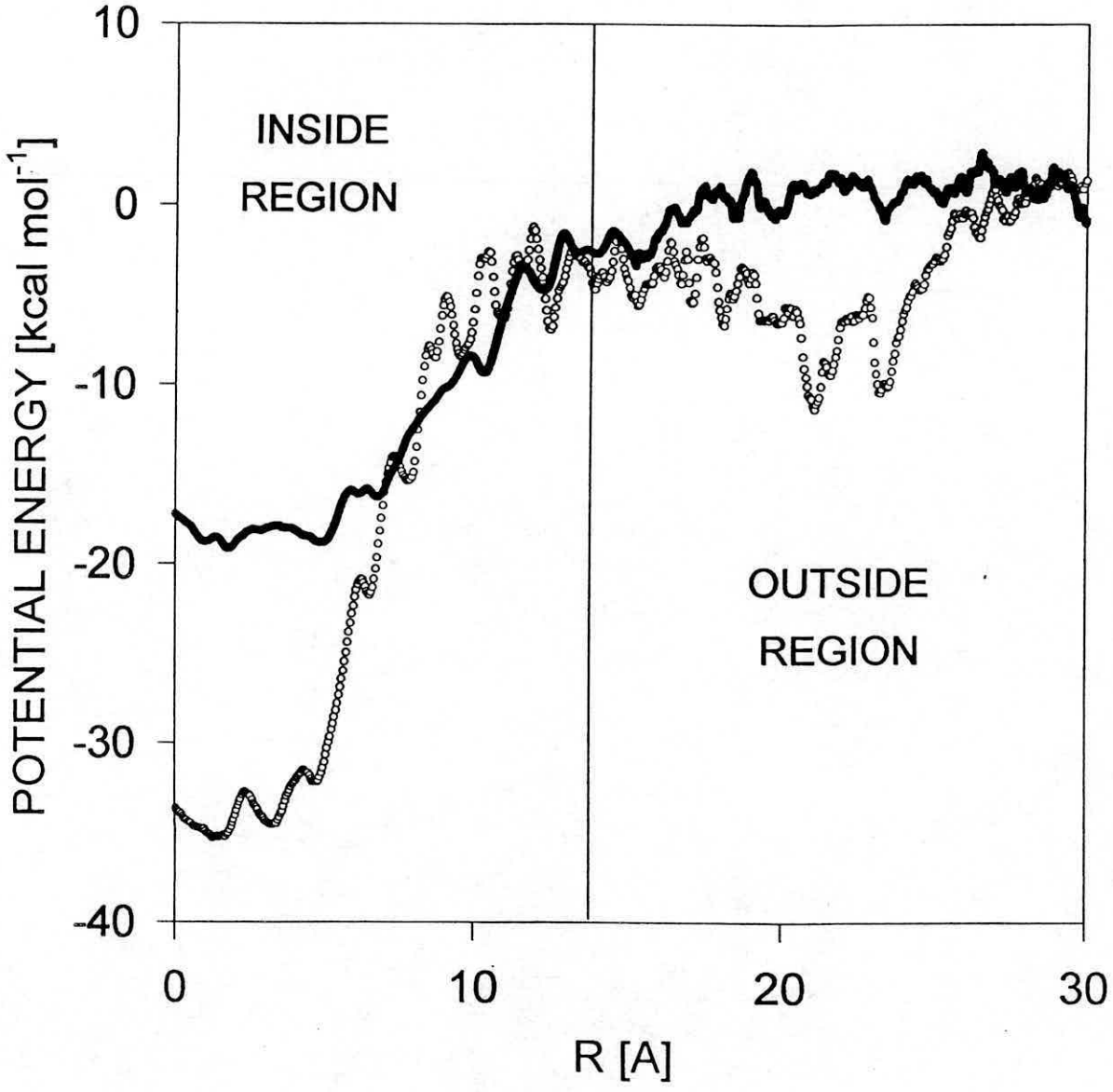
10
0
-10
-20
-30
-40
POTENTIAL ENERGY [kcal mol-1]
INSIDE
REGION
OUTSIDE
REGION
0
10
20
30
R [A]

Fig. 6

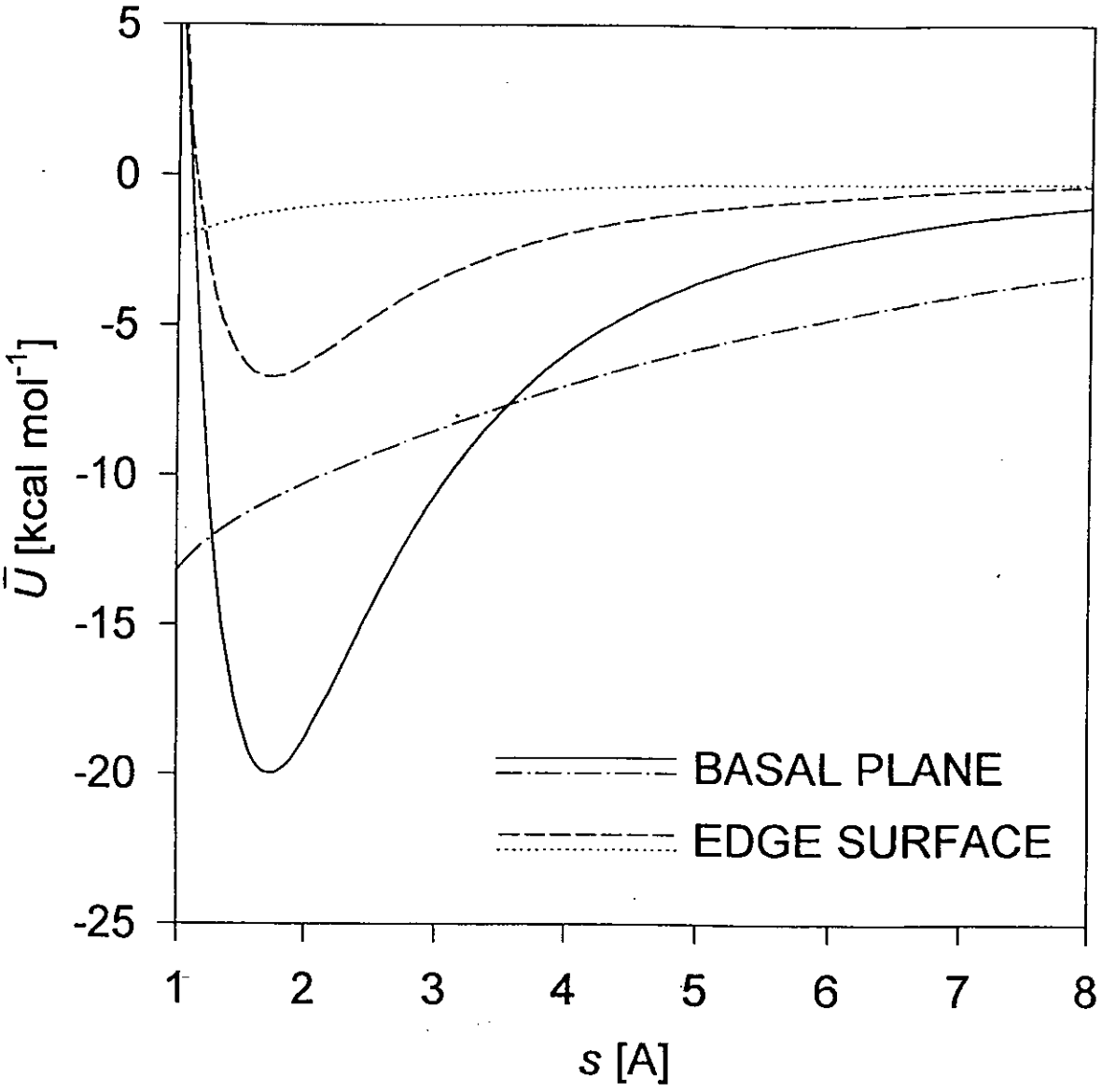
5
0
-5
-10
-15
-20
-25
$\bar{U}$ [kcal mol^{-1}]
1
2
3
4
5
6
7
8
s [A]
BASAL PLANE
EDGE SURFACE

Fig. 7

Centre for Ecology & Hydrology

Institute of Freshwater Ecology
Institute of Hydrology
Institute of Terrestrial Ecology
Institute of Virology & Environmental Microbiology

Natural Environment Research Council